Werner Centennial

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N. Y., Sept. 12–16, 1966.

George B. Kauffman, *Symposium Chairman*

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FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

This book is dedicated to the memory of
Alfred Werner

Born: Mulhouse (Haut-Rhin), France, December 12, 1866
Died: Zürich, Switzerland, November 15, 1919

Doktor der Philosophie, Eidgenössisches Polytechnikum, Zürich, October 13, 1890
Privat-Dozent, Eidgenössisches Polytechnikum, January 4, 1892–September 29, 1893
Ausserordentlicher Professor, Universität Zürich, August 31, 1893–June 7, 1895
Ordentlicher Professor, June 8, 1895–October 15, 1919

Nobel Prize in Chemistry, December 11, 1913

Alfred Werner, the undisputed founder and systematizer of coordination chemistry, played such a central role in this particular field of science that his name is virtually synonymous with the field. Werner devoted his entire scientific career to amassing the experimental evidence required to prove the validity of his coordination theory, which he proposed in 1893 at the age of 26. Beginning with a study of the hitherto unexplained "molecular compounds" (metal-ammines, hydrates, and double salts), his ideas soon encompassed almost the whole of systematic inorganic chemistry and even found application in the organic realm. He was the first to demonstrate that stereochemistry is a general phenomenon not limited to carbon compounds, and even today his experimental and theoretical papers remain a foundation and guide for investigations in coordination chemistry. In 1913 he was awarded the Nobel Prize in chemistry in recognition of "his work on the linkage of atoms in molecules, by which he has thrown fresh light on old problems and opened new fields of research, particularly in inorganic chemistry." Today, when the practical and theoretical significance of modern structural inorganic chemistry is unquestioned, it is clear that the foundations of this field were erected largely by Alfred Werner, the man sometimes honored by the epithet of "the inorganic Kekulé."

George B. Kauffman

Fresno, Calif.
September 1966

Some Personal Recollections of Alfred Werner

YUJI SHIBATA

Japan Academy, Ueno Park, Tokyo

About two years ago, I asked a friend going abroad to search for the first edition of Alfred Werner's "Neuere Anschauungen auf dem Gebiete der inorganischen Chemie" which I had lost somewhere unnoticed. Unfortunately, he failed to find my original copy but presented me with a second edition purchased in Vienna.

This volume must have belonged to a student of Werner because I found a yellowish newspaper cutting pasted inside the cover. It was an obituary of Alfred Werner. So lucid and accurate were the facts about Werner's scientific career that I guessed that the author must have been a close friend of the great chemist. I thought P. Karrer must have written this. And his was the name I found printed at the end. This experience awakened many memories of Alfred Werner.

I had recently graduated from the University of Tokyo when I first read "Neuere Anschauungen." In those days I was interested in organic chemistry and published two papers on Grignard reactions; therefore, I had a poor understanding of the book at first. When I read the chapter on isomeric phenomena in inorganic chemistry, however, I was strongly tempted to enter the enchanting domain of coordination chemistry.

I decided to go to Zürich to study under Werner. When I arrived I heard that the great professor was leaving in a few days for the University of Würzburg. So I changed my plans and went to Leipzig to study under Werner's teacher and lifelong friend, Arthur Hantzsch. Later I learned that Werner had not left Zürich after all.

After finishing my research on cobalt thiocyanate in Leipzig I wrote to Werner, asking for a place in his laboratory. In his own hand he replied, "I should like to inform you that I would be happy to have you work with me. At present there is so much of interest to investigate here that a topic will certainly be found that will give you special pleasure."

In August 1911 I visited Werner for the first time. On the spot he suggested that I study the synthesis and resolution of diaminediethylenediamine cobaltic salts $(Co(NH_3)_2en_2)X_3$. Such assymetric molecular complexes had not yet been studied. I solved this problem after one year, and it was published jointly with Werner in *Berichte der Deutschen*

Chemischen Gesellschaft. After finishing the project, I gave him a carton containing bottles of all the substances used, from starting compounds to end products. This was the custom in Werner's lab—often called a little present to the teacher.

Although Werner published many papers, he wrote only two books. One, "Lehrbuch der Stereochemie" (1904), contains many of his original works—notably those concerning the stereochemistry of oximes and nitrogen compounds in general. The second book, "Neuere Anschauungen" (1905), is the bible of coordination chemistry. In the preface of this work he states modestly, "We are quite conscious that our new concepts are only summarizing pictures . . . that they, as Mach expressed it, provide us with a certain economy of thought and description . . . It is in this spirit that I submit the following comprehensive presentation of hypotheses which are decisive for inorganic chemistry."

To systematize the structural problems of the so-called compounds of higher order he reconsidered valency. Thus, he advanced the idea of "Hauptvalenz" and "Nebenvalenz," which could be said to contain the image of modern ionic and covalent bonding theory. Furthermore, he visualized the valence bond not as small sticks existing around atoms in a plane, as conceived by Kekulé, but as positions taken by bond arms on the surfaces of spherical atoms in three dimensions. Could this idea not be a precursor to the modern conception of bond orbitals?

His concepts were not easily accepted by his contemporaries, and authors of inorganic chemistry books often ignored his descriptions of isomeric behavior. His admirers were greatly augmented after he received the Nobel Prize. The one man who always stood by him and encouraged him was Arthur Hantzsch.

Although the two great masters of chemistry held each other in great esteem and confidence, they gave very different impressions. Hantzsch was of slender build and spoke rapidly in a high-pitched tone. Werner, on the other hand, and only about 45 years old when I knew him, was already quite gray-haired and very fat. The arteriosclerosis which was to kill him seven years later was making inroads even then. Also, in contrast to Hantzsch, Werner always spoke slowly with a smile on his lips.

Alfred Werner

SAMUEL SOLOVEICHIK and HENRY KRAKAUER

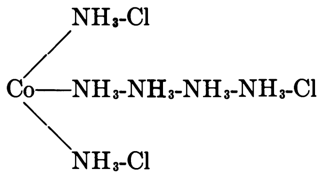
Yeshiva University, New York, N. Y. and Yale University, New Haven, Conn.

Alfred Werner was born in 1866 and died from arteriosclerosis in 1919. He started as an organic chemist and finished his chemical career in 1915 as one of the foremost inorganic chemists.. He won the Nobel Prize in 1913. During a period of two and a half decades he published 174 papers and supervised the work covered by 200 doctoral dissertations. Werner was the founder of coordination chemistry. He rejected the then prevailing concept (formulated by Kekulé) that the valence of an element is invariable and introduced instead the notion of principal and auxiliary valence. He also formulated the concept of coordination number. Werner used both the inductive and the deductive methods of reasoning. Most of his predictions on geometrical and optical isomerism were verified by experiment.

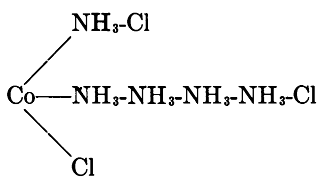
The concept of valence and the principle of constancy of valence permitted the formulation of the structural theory which led to the rapid and brilliant development of organic chemistry. The same concepts applied to inorganic chemistry were not fruitful but rather stultifying. In fact, only three names stand out in the field of inorganic chemistry during the turn of the past century — those of Ramsay, Moissan, and Alfred Werner.

Werner was born into a family of modest means in the Alsatian town of Mulhouse four years before the Franco-Prussian war. From his early years he showed a keen affinity for chemistry. With money earned by doing menial tasks for the local people, he equipped a laboratory in his father's barn with books, apparatus, and chemicals. At 18 he submitted a report of his research to E. Noelting, director of the school of chemistry in Mulhouse, with a curious and innocent inquiry as to how long it would take to become a professor. "A sympathetic appreciation of the work, with a guarded reply to his question, confirmed Werner in his enthusiasm for chemistry" (4). Thus, a year later, when in the German army stationed in Karlsruhe, he took the opportunity to attend lectures on chemistry at the technical "Hochschule." The following year (1886) he moved to Zurich to begin his studies at the Federal Polytechnic School. Born French and raised a German, Werner took to his new country with enthusiasm, adopting the Swiss-German accent and taking pride in his knowledge of the local patois. He became a citizen of the Swiss Confederation in 1894, the year of his marriage to a lady of Zurich. A year later he was promoted to a full professorship at the University of Zurich. Three of his teachers at the Polytechnic School were the eminent chemists Georg Lunge, Arthur Hantzsch, and Frederic P. Treadwell. Alfred Werner was awarded the doctorate by the University of Zurich for work done under Hantzsch on the structure and stereochemistry of organic nitrogen compounds. Within five years he was a full professor. Throughout his early university years Werner vacillated between organic and inorganic chemistry, though he was swayed toward the latter by a former colleague. Even until about 1900, however, there was considerable organic content in his work (3).

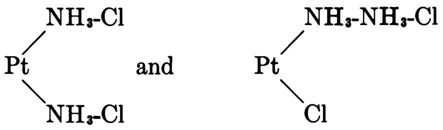
In 1891 Werner began to apply himself to the problem of valence with his "Contributions to Theory of Affinity and Valence." At that time Kekulé's principle of fixed valence, so useful in organic chemistry, was being applied by chemists such as Blomstrand and Jørgensen to complex metal salts resulting in formulations of, for example, hexammine cobaltic chloride as:



and the salt obtained by heating of the above and containing only two chlorine atoms precipitable by $AgNO_3$ as:



Such formulas accounted for the masking of one of the chloride atoms by its direct attachment to the metal. Other Blomstrand formulas (2), such as shown below (respectively known as Reiset's chloride and Peyrone's yellow chloride), accounted for isomerism and change of color. But they "could not give lasting satisfaction for they aroused no incentive to a further development of chemistry" (*6*).



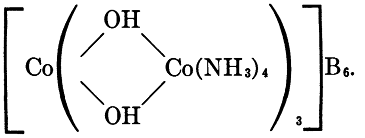
In his papers of 1891, 1892, and 1893, Werner discarded the concept of valence as a fixed directed force with a fixed number of units of definite spatial distribution which attributes a definite integral valence number to each atom. For him it was a force which acted symmetrically but could be divided into units of varying number and intensity.

In 1902 Werner formulated the concept of principal and auxiliary valence. According to this, an atom could have a principal and an auxiliary valence. The latter coordinates atoms or groups to the central ion in a firm and relatively nondissociating combination. The maximum number of entities that can be so associated is the coordination number, usually four or six, but in some cases two, three, five, seven, or eight. Beyond these are the dissociated ions which satisfy the principal valence of the central atom. The principal valence, however, may be also satisfied by coordinated groups of opposite charge to the coordinating ion. Thus, $[Co(NH_3)_6]Cl_3$ has three dissociable chlorine atoms, while $[Co(NH_3)_5Cl]Cl_2$ has only two, one chlorine atom having been taken into the coordination sphere of six, reducing simultaneously the principal valence. Though Werner at first clearly distinguished between the two types of valence, he later came to realize their essential equivalence.

Though the conception of the coordination theory was sudden and intuitive (by his own account he awoke with a start at 2 A.M. with its key lodged in his mind) (*6*), he verified and exploited it very thoroughly and systematically. In a Baconian manner he tabulated the known compounds in a series such as $[Co(NH_3)_6](NO_2)_3$ to $K_3[Co(NO_2)_6]$ or $[Pt(NH_3)_6]Cl_4$ to $K_2[Pt\ Cl_6]$, according to the number and type of the coordinated groups in which the metal atom was surrounded. Werner's original tables did not include $K_2[Co(NH_3)(NO_2)_5]$, which is unknown, and also $[Pt(NH_3)_5Cl]Cl_3$, which was not discovered until 1915 by Chugaev. It was then seen that the conductivities of these compounds fell into the same pattern as the postulated number of dissociating groups. From such an inductive base, Werner proceeded to investigate the consequences of his theory, particularly the deductions concerning geometric isomerism (*1*). His efforts in this area over a span of two decades were prodigious. At first his facilities were meager indeed. His laboratories were located in the cellars of the university and were poorly lit and ventilated. They richly deserved their popular designation, "the Catacombs." In 1909 the frugal authorities finally acceded to the persistent requests of the now famous professor and provided him with laboratories to his specifications. Werner, though reputed to be of modest habits and jovial disposition, possessed extraordinary drive and capacity for work. Always the first to work at eight, he was frequently the last to leave in the evening. In all, 173 or 174 papers bear his name, and his students produced 200 doctoral dissertations. Assistants and students were driven hard, but their rigorous training served them well. Werner was also a masterful teacher, his lectures on inorganic chemistry being described by an English pupil as "a perfect joy" (*4*).

Alfred Werner was endowed with a remarkable facility for handling geometric and configurational problems. He thus felt great assurance in his predictions on optical isomerism and indeed they were, in the majority of cases, verified by experiment. It is in this area that his research reached its culmination.

In complexes with coordination number six, the existence of two differently colored isomers of, for example, $[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl}$ (en = ethylene-diamine), was explained by Werner by postulating octahedral symmetry in the disposition of the coordinated groups. In that case the 2Cl may occupy either cis or trans positions. If octahedral symmetry results, similar isomers containing four ammonia molecules in place of the two ethylene-diamine molecules should exist, and indeed in 1907 Werner succeeded in preparing the two forms of $[\mathrm{Co(NH_3)_4Cl_2}]^+$. Moreover, it also follows that the cis isomers containing two bidentate ligands should exist as enantiomorphs. Demonstration of this took many years because of the difficulties in preparing and resolving these compounds. It was not until 1911 that the optically active forms of *cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{Cl}$ were found. For the few years remaining to him, Werner continued his investigations of optically active complexes. In 1914, he accomplished his greatest achievement by removing the last lingering doubts that optical activity of his complexes was due to their geometry and not in some way to the presence of carbon. This was proved by synthesizing the completely inorganic but active complex (*5*):



$$\left[\mathrm{Co}\left(\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\mathrm{Co(NH_3)_4}\right)_3\right]\mathrm{B_6}.$$

Alfred Werner's brilliant researches earned him recognition and honors from learned societies throughout the world. He was awarded the Nobel Prize in 1913. But even then the manifestations of arteriosclerosis were appearing. For two more years, new and exciting papers continued to come from his laboratories. He continued to lecture as usual, even though he became more and more eccentric in his demonstrations. In 1915 on medical advice, he retired from his research and teaching positions. Although he attempted to resume his duties twice, his growing infirmity would not permit. His final years were filled with tragedy and suffering. Finally, in November 1919, "death brought [Alfred Werner] respite and release" (*4*).

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RECEIVED July 6, 1966.

3

Effect of the Fixity of Ideas on the Werner-Jørgensen Controversy

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The Werner-Jørgensen controversy is viewed through graphics and models to represent molecular structures. Werner's development of the coordination sphere concept and his synthesis of an inorganic coordination isomer was not traditional in approach. He was not hesitant to express his theories even though he did not have "absolute" proof; his analysis was qualitative and relied on a bubbling of gas or a rapid color change. Jørgensen, the traditionalist, could not accept such hastily conceived notions. He insisted on complete, exacting studies of each reaction. The "fixity of ideas" prevented the needed breakthrough in chemistry. A man who did not play by the rules, who was impulsive, yet sharp of mind, was needed for the next step. Alfred Werner was such a man.

This paper attempts to explore one of the basic problems that has plagued the sciences since their very inception and perhaps delayed their growth as well. This is the problem of "fixity of ideas." I will attempt to show that while model building has helped the scientist, it has hindered him just as much if not more. Two recent, separate, and totally unrelated papers (*32*, *45*) have indicated the severity of this situation. By using the Werner-Jørgensen coordination bonding controversy in chemistry as the example, we will see through the historical sequence of events that chemists had worked themselves into a blind alley by using only established principles and methods. The genius of the Nobel prize winner, Alfred Werner, was needed to get them out of this predicament.

Since the days of earliest man there has been a desire to represent objects and concepts in a graphical manner. Cave drawings, idols, and statues have all been used by the most primitive and the most sophisticated cultures to represent events and folklore. As a logical outgrowth, we find graphical representation in the sciences. Such graphics can, indeed, help the mind to perceive the abstract thought in terms that activate the senses and allow earlier conceptualization. One should note that graphics and model building have helped to clarify and elucidate the theories and hypotheses of the science of chemistry. But have they always done this?

Man often gets himself trapped in a "fixity of ideas." His ability to perceive ideas in a new and different light is often limited by his inability to reperceive ideas, to modify the previous model, or conceive a totally different model. "The direct availability of a habitual mode of response may make it much harder to break with habit and approach a problem afresh" (*45*). "Insight is the essential element in intelligent problem solving; fixation is its archenemy" (*45*). This was, and is, one of the basic problems scientists face. Such a problem is the basis for one of the best-known controversies in chemistry—the Werner-Jørgensen coordination bonding argument. How did such a dispute develop?

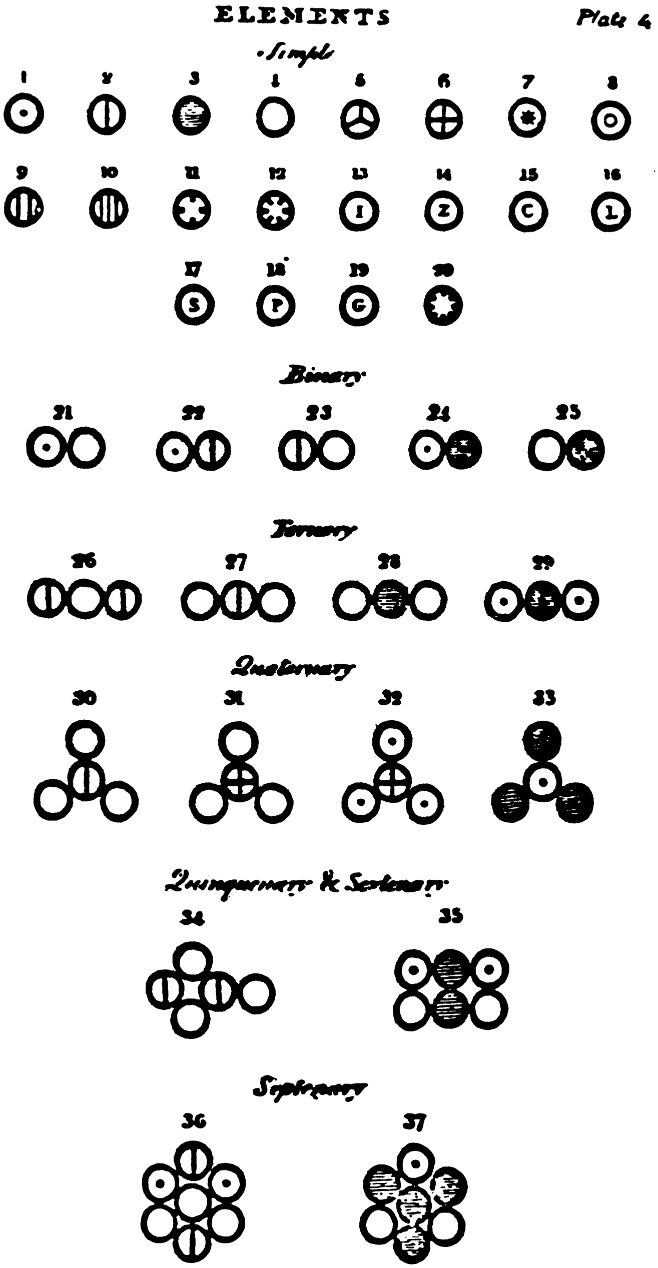
To study the problem in a meaningful manner one must follow several developmental trends, graphical representations, chemical data, and interpretations of the data. To avoid excess confusion we will attempt herein to avoid notation of the side arguments of various theories that developed along with the graphics. This may lead one to wonder why certain pictures and models developed. However, such will be necessary to keep this paper reasonable in length.

Let us begin many years before the actual controversy appeared. In 1798, Tassaert, in his "Analyse du Cobalt de Tunaberg," describes this compound of which he claims "ses proprietes les plus remarquables" (*47*). He describes an analysis of its components and discusses its magnetic properties and its combining and reacting powers with ammonia. Little other work was initiated with ammonia compounds for some 39 years. During this time, however, other trends of thought appeared.

Dalton in 1808 proposed a "New System of Chemical Philosophy" which outlined compound formation in a graphical manner (*13*). This was perhaps the first attempt at graphics since the alchemists.

Dalton, usually given credit for the circle diagram, used these sketches in his works of 1803 and those works which followed. Starting with this primary attempt at formula writing, a whole series of "laws" of the combining power of elements in a quantitative manner evolved as shown in Figure 1.

Berzelius in 1819 presented a system of writing compounds which used letters and symbols as abbreviations (*1*). (*See* Figure 2.) The basics of these two systems (Dalton's and Berzelius') have affected scientific notations since their inception. We shall see them occur and reoccur again and again throughout this paper.


ELEMENTS
Plate 4
Simple
1
2
3
4
5
6
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9
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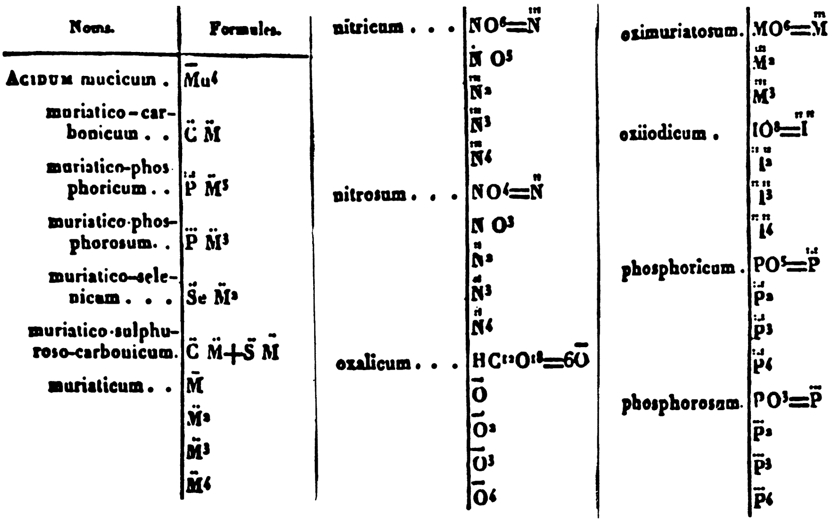
11
12
13
14
15
16
I
Z
C
L
17
18
19
20
S
P
G
Binary
21
22
23
24
25
Ternary
26
27
28
29
Quaternary
30
31
32
33
Quinquenary & Sextenary
34
35
Septenary
36
37

Figure 1

PLATE IV. This plate contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

Fig.			Fig.		
1	Hydrog. its rel. weight	1	11	Strontites - - -	46
2	Azote, - - - - -	5	12	Barytes - - - -	68
3	Carbone or charcoal, -	5	13	Iron - - - - -	38
4	Oxygen, - - - -	7	14	Zinc - - - - -	56
5	Phosphorus, - - -	9	15	Copper - - - -	56
6	Sulphur, - - - -	13	16	Lead - - - - -	95
7	Magnesia, - - - -	20	17	Silver - - - - -	100
8	Lime, - - - - -	23	18	Platina - - - -	100
9	Soda, - - - - -	28	19	Gold - - - - -	140
10	Potash, - - - -	42	20	Mercury - - - -	167

21. An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat; its relative weight = - - - - - 8
22. An atom of ammonia, composed of 1 of azote and 1 of hydrogen - - - - - - - - - - 6
23. An atom of nitrous gas, composed of 1 of azote and 1 of oxygen - - - - - - - - - 12
24. An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen - - - - - - - - - 6
25 An atom of carbonic oxide composed of 1 of carbone and 1 of oxygen - - - - - - - - 12
26. An atom of nitrous oxide, 2 azote + 1 oxygen - 17
27. An atom of nitric acid, 1 azote + 2 oxygen - - 19
28. An atom of carbonic acid, 1 carbone + 2 oxygen 19
29. An atom of carburetted hydrogen, 1 carbone + 2 hydrogen - - - - - - - - - - - - 7
30. An atom of oxynitric acid, 1 azote + 3 oxygen 26
31. An atom of sulphuric acid, 1 sulphur + 3 oxygen 34
32. An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen - - - - - - - - - - - - 16
33. An atom of alcohol, 3 carbone + 1 hydrogen - 16
34. An atom of nitrous acid, 1 nitric acid + 1 nitrous gas - - - - - - - - - - - - - - 31
35. An atom of acetous acid, 2 carbone + 2 water - 26
36. An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water - - - - - - - - - 33
37. An atom of sugar, 1 alcohol + 1 carbonic acid - 35



Noms.	Formules.
Acidum mucicum .	$\bar{M}u^4$
muriatico-carbonicum . .	$\ddot{C}\ \ddot{M}$
muriatico-phosphoricum . .	$\overset{\cdot\cdot\cdot\cdot\cdot}{P}\ \bar{M}^5$
muriatico-phosphorosum. .	$\dddot{P}\ \ddot{M}^3$
muriatico-selenicum . . .	$\ddot{S}e\ \ddot{M}^2$
muriatico-sulphuroso-carbonicum.	$\ddot{C}\ \ddot{M}+\ddot{S}\ \bar{M}$
muriaticum . .	$\bar{M}$ $\ddot{M}^2$ $\ddot{M}^3$ $\ddot{M}^4$
nitricum . . .	$NO^6=\overset{\cdot\cdot\cdot}{N}$ $\dot{N}\ O^5$ $\overset{\cdot\cdot\cdot}{N}^2$ $\overset{\cdot\cdot\cdot}{N}^3$ $\overset{\cdot\cdot\cdot}{N}^4$
nitrosum . . .	$NO^4=\ddot{N}$ $N\ O^3$ $\ddot{N}^2$ $\ddot{N}^3$ $\ddot{N}^4$
oxalicum . . .	$HC^{12}O^{18}=6\bar{O}$ $\bar{O}$ $\bar{O}^2$ $\bar{O}^3$ $\bar{O}^4$
oximuriatosum.	$MO^6=\overset{\cdot\cdot\cdot}{M}$ $\overset{\cdot\cdot\cdot}{M}^2$ $\overset{\cdot\cdot\cdot}{M}^3$
oxiiodicum .	$IO^8=\overset{\cdot\cdot\cdot\cdot}{I}$ $\overset{\cdot\cdot\cdot\cdot}{I}^2$ $\overset{\cdot\cdot\cdot\cdot}{I}^3$ $\overset{\cdot\cdot\cdot\cdot}{I}^4$
phosphoricum .	$PO^5=\overset{\cdot\cdot\cdot\cdot\cdot}{P}$ $\overset{\cdot\cdot\cdot\cdot\cdot}{P}^2$ $\overset{\cdot\cdot\cdot\cdot\cdot}{P}^3$ $\overset{\cdot\cdot\cdot\cdot\cdot}{P}^4$
phosphorosum.	$PO^3=\bar{\dddot{P}}$ $\bar{\dddot{P}}^2$ $\bar{\dddot{P}}^3$ $\bar{\dddot{P}}^4$

Figure 2

Liebig in 1834 proposed that a single letter be used in place of a "Radikal" (*35*) as follows:

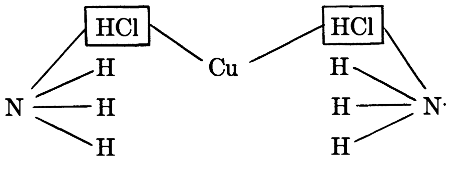
$$E = \text{Radikal des Aethers} = C_4H_{10}$$

$$E + B_2 = \text{Bromur}$$

In his early work (1835–1838) Graham (*21*) used the same notation as was developed by Berzelius, which is:

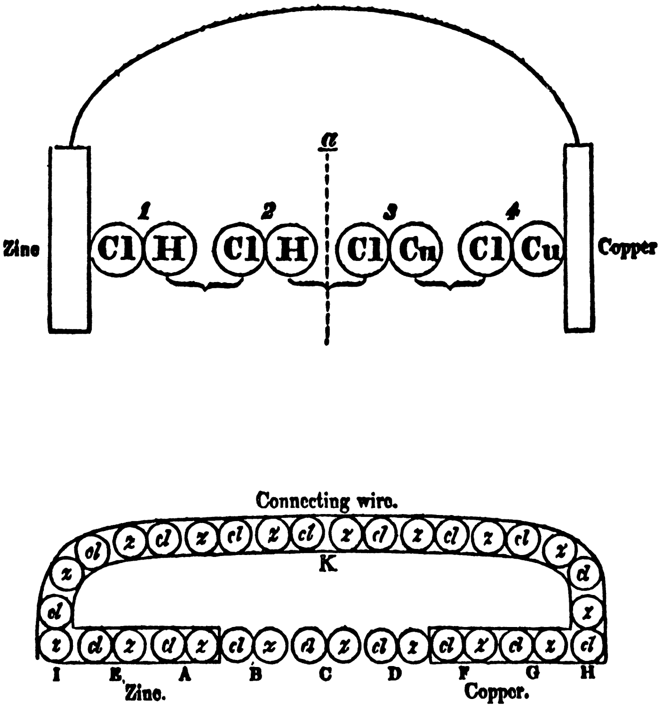
Gypsum.................................. CaSH + H
Gypsum dried at 212°...................... CaSH
Anhydrous gypsum (dried at 270°)............ CaS—
Anhydrite................................ CaS

In his later work (1840) Graham proposed a compound which he represented graphically:



(*2*)

Two years later he considered the metal ammoniates as substituted ammonia compounds (*21*). Here we see the first attempt at a theoretical explanation for the metal ammoniate formation. Note also his use of the two dimensional bonded atoms and molecules in a linear chain. In the very same year, however, he modified his second representation and presented the formula MgO,SO_3(MO) + 6HO. Graham in 1842 used the Dalton circles to explain "inductive affinity" (*22*) and the "voltaic circle" shown in Figure 3. Yet, when he wrote "On the Ammonium Theory" he used the following:



Z = Zn

Figure 3

Fe_2, N_3C_6 + Fe_3, N_3C_6 . . . . . . Prussian blue

Fe_2, N_3C_6 + K_3, N_3C_6 . . . . . . Percyanide of iron and potassium

In 1844 Reiset, building upon the theories and graphics of Graham, claimed of the equation, $3(AzH^3PtCl) = 2(ClH,AzH^3) + ClH + AzPt^3$, that "Elle démontre enfin l'existance ephemere de l'azoture $AzPt_3$ pendant une des phases de cette decomposition" (*42*). This is one of the basic steps that led to the bonding controversy at a later date.

Fownes in 1844 used Dalton's circles and added a new idea to their uses. He used them to explain water electrolysis (*16*) (Figure 4). Note

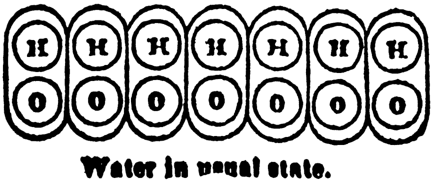


Figure 4

his use of encompassing ovals rather than connecting the circles to indicate molecule formation.

The whole concept of diagraming molecules and compounds spread quickly throughout the chemical world. Almost every chemist of the day had something to say about a particular representation.

In 1850 Wurtz (*52*), in a further attempt to explain and to demonstrate bonding, describes such compounds as shown in Figure 5.

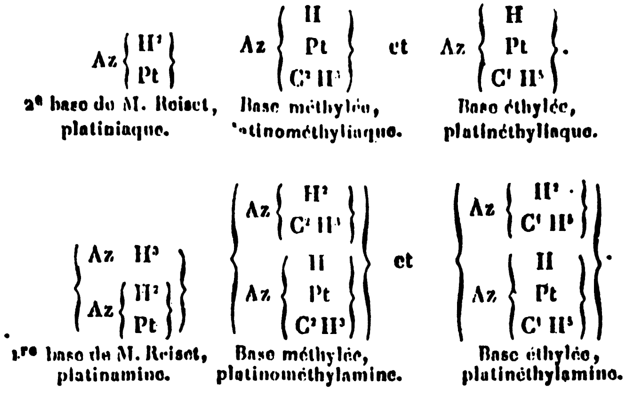
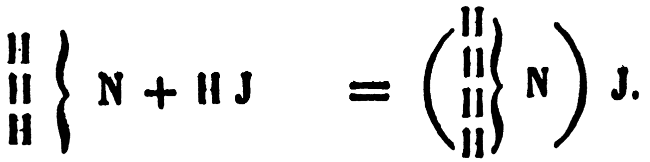


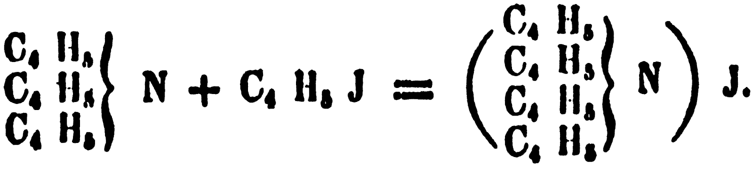
Figure 5

Hofmann (*25*) in 1851 used the stratified formula picture presented below. His addition of the parenthesis allowed him to justify his idea that the ammonium hydrogen was replaceable by both metals and other ammonium groups.

Frankland, just one year later, noted that the "saturation capacity" of an element cannot be exceeded (*17*). We will return to this point in our discussion of the Werner theories.



$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\} N + HJ = \left(\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\} N\right) J.$$



$$\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\} N + C_4H_5J = \left(\left.\begin{matrix}C_4H_5\\C_4H_5\\C_4H_5\\C_4H_5\end{matrix}\right\} N\right) J.$$

Stockhardt in his text book of 1852 uses several modes of graphical presentation. He uses the linear letter form in a slightly modified format and then reverts back to Dalton's circles (*46*). He does discuss, however, the relative position of the "atoms toward each other" and then adds a chessboard grid to explain stereochemical problems (Figure 6). He uses a concept that was considered by Dalton—the relative sizes of various atoms. This concept is indeed an important step forward but, nevertheless, we still see no mention of the solid figure (Figure 7).

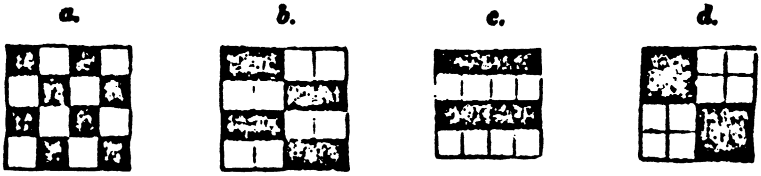


Figure 6

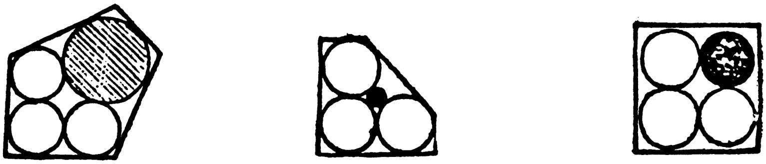


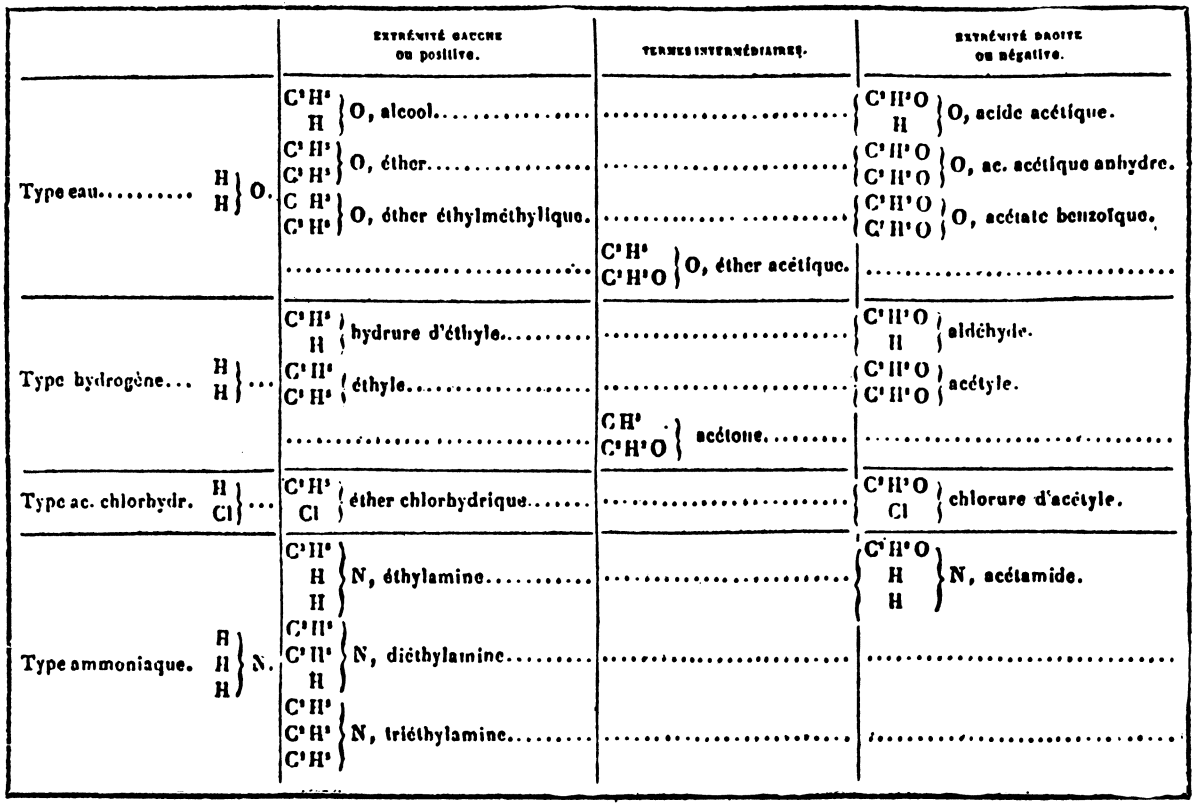
Figure 7

Eighteen fifty-three saw Gerhardt make a further improvement on the standing concept of structure (*20*). He proposed the "hydrogen," "hydrogen chloride," and "ammonia" type of molecule, as shown in Figure 8.

Carl Claus in 1854 wrote a rather succinct study of the transition metals in general and platinum in particular (*8*). In this book he predominantly used the linear notation shown below.

$$Ir_2Cl_3 + NaCl + 24HO$$

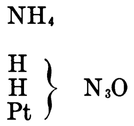
$$Ir_2O_3, 5NH_3 + 3CO_2, 3HO$$



	EXTRÉMITÉ GAUCHE ou positive.	TERMES INTERMÉDIAIRES.	EXTRÉMITÉ DROITE ou négative.
Type eau......... $\left.\begin{matrix}H\\H\end{matrix}\right\}O.$	$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}$O, alcool		$\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}$O, acide acétique.
	$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}$O, éther		$\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}$O, ac. acétique anhydre.
	$\left.\begin{matrix}C\ H^3\\C^2H^5\end{matrix}\right\}$O, éther éthylméthylique.		$\left.\begin{matrix}C^7H^5O\\C^2H^3O\end{matrix}\right\}$O, acétate benzoïque.
		$\left.\begin{matrix}C^2H^5\\C^2H^3O\end{matrix}\right\}$O, éther acétique.	
Type hydrogène... $\left.\begin{matrix}H\\H\end{matrix}\right\}$...	$\left.\begin{matrix}C^2H^5\\H\end{matrix}\right\}$ hydrure d'éthyle		$\left.\begin{matrix}C^2H^3O\\H\end{matrix}\right\}$ aldéhyde.
	$\left.\begin{matrix}C^2H^5\\C^2H^5\end{matrix}\right\}$ éthyle		$\left.\begin{matrix}C^2H^3O\\C^2H^3O\end{matrix}\right\}$ acétyle.
		$\left.\begin{matrix}CH^3\\C^2H^3O\end{matrix}\right\}$ acétone	
Type ac. chlorhydr. $\left.\begin{matrix}H\\Cl\end{matrix}\right\}$...	$\left.\begin{matrix}C^2H^5\\Cl\end{matrix}\right\}$ éther chlorhydrique		$\left.\begin{matrix}C^2H^3O\\Cl\end{matrix}\right\}$ chlorure d'acétyle.
Type ammoniaque. $\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N.$	$\left.\begin{matrix}C^2H^5\\H\\H\end{matrix}\right\}$N, éthylamine		$\left.\begin{matrix}C^2H^3O\\H\\H\end{matrix}\right\}$N, acétamide.
	$\left.\begin{matrix}C^2H^5\\C^2H^5\\H\end{matrix}\right\}$N, diéthylamine		
	$\left.\begin{matrix}C^2H^5\\C^2H^5\\C^2H^5\end{matrix}\right\}$N, triéthylamine		

Figure 8

However, in one section, referring to the work of a Hugo Muller, he returns to the stacked formula type:



$$\begin{matrix} NH_4 \\ \left.\begin{matrix} H \\ H \\ Pt \end{matrix}\right\} N_3O \end{matrix}$$

Claus in 1856 preferred not to indicate exactly how the molecule was joined together. Thus, in order to show connecting influence, he used arched lines (*9*), as follows:

$$NH_3,\frown Hg_2 + Cl \text{ und } NH_3,\frown Fe_2 + Cl_3,$$

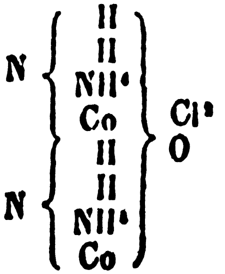
This was a modification of the Gerhardt formulae which were presented as:

$$\begin{matrix} K.Cl\frown Cl \\ K.Cl\frown Cl \end{matrix} Pt, \; .$$

$$\begin{matrix} K.Cy\frown Cy \\ K.Cy\frown Cy \end{matrix} Pt \; .$$

In these we see the true chain formulae which were used by Jørgensen in his arguments with Werner.

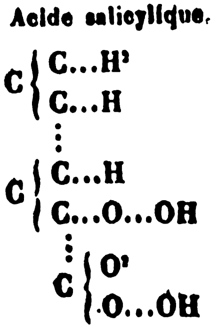
Even with the progress and change already noted, the traditionalists continued to use the bracketed, stacked formulae.

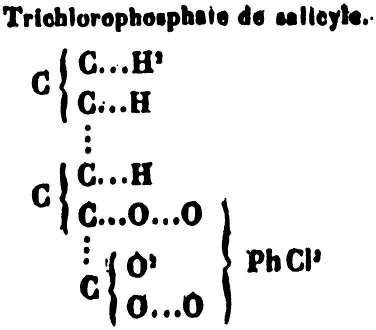


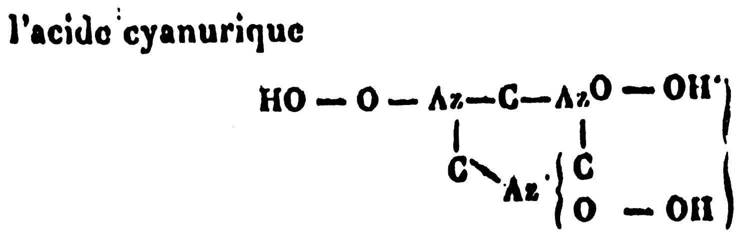
$$\left.\begin{matrix} N\left\{\begin{matrix} H \\ H \\ NH^4 \\ Co \end{matrix}\right. \\ N\left\{\begin{matrix} H \\ H \\ NH^4 \\ Co \end{matrix}\right. \end{matrix}\right\} \begin{matrix} Cl^3 \\ O \end{matrix}$$

Weltzien, in 1856, was such a writer (*49*). In 1858, Couper presented a new form. It was a composite of the Berzelius stick formulation and the A. Crum Brown line formulae (*10, 11*) as shown at the top of the following page. This is considered by most to be the first constitutional formula format.

His third paper on the same subject used dotted lines instead of the







solid ones (*12*). This change may have been no more than a printer's preference, yet a change was made.

In 1858 Odling developed a system which indicated the valence of the metal (*40*), such as:

Pt Cl	analogous to HCl
Pt Cl^2	analogous to H^{2}Cl^2
NH^{2}Pt NH Pt	analogous to NH^3

In a lecture in 1848 Louis Pasteur considered for the first time some of the chemical problems involved with stereochemical compounds (*41*). This was an area of discussion which had deep implications in the Werner theory, yet to come.

Loschmidt in 1861 reverted back to Dalton's graphics of 53 years before (*36*) (Figure 9). Note his formula for benzene (No. 185, Figure 9). This is also remarkably like Kekulé's form, which was presented four years later. It is just this type of building upon established principles which Jørgensen proposed as the soundest method to scientific progress.

A. Crum Brown, writing in the same year, used graphics that corresponded somewhat to Couper (*7*) (Figure 10).

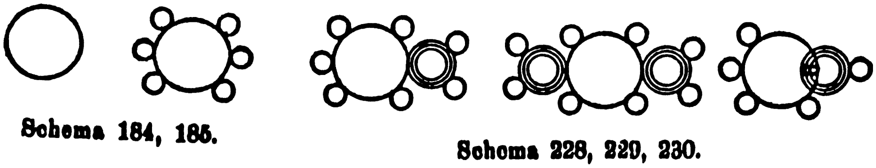
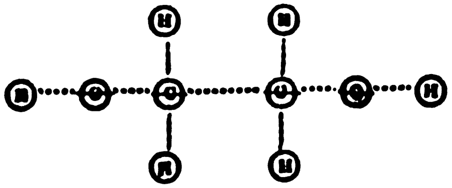


Figure 9



(glycol)

Figure 10

In 1861, Kekulé presented the first of several volumes of his now famous textbook (*33*). In it he used several forms of graphical representation. One is the established bracket form shown in Figure 11, and a second is probably derived from Dalton's circles, as shown in Figure 12.

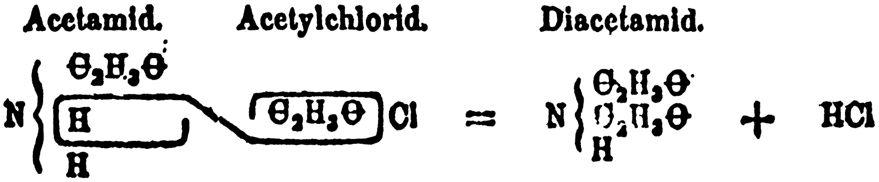


Figure 11

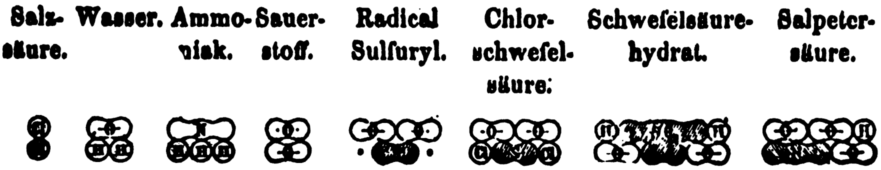


Figure 12

Bodeker in 1862, in an effort to shorten the rather cumbersome linear chain formulae, presented a system of abbreviations (*34*). While the idea of a single symbol representing many atoms was used earlier by Berzelius, Bodeker's format is a much more reasonable approach to the problem in that it permitted concisely written formulae (*5*), such as shown below.

$$R = N\left|\begin{matrix}Co\\H^3\end{matrix}\right. = \text{Kobaltid-Ammonium und}$$

$$Ra = \begin{matrix}\\N\end{matrix}\left|\begin{matrix}N\left|\begin{matrix}Co\\H^3\end{matrix}\right.\\H^3\end{matrix}\right. = \text{Kobaltid-Disammonium.}$$

His formulae were thus written as follows:

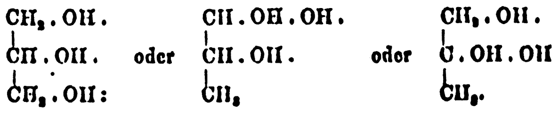
Chlorür $RCl + HO$

Nitrat $\left.\begin{matrix}R\\NO^4\end{matrix}\right|\begin{matrix}O\\O\end{matrix} + H^2O^2$

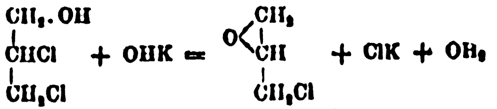
Sulfat $\left.\begin{matrix}R^2\\S^2O^4\end{matrix}\right|\begin{matrix}O^2\\O^2\end{matrix}$

In connection with a lecture given in 1865 before the Royal Institution, Hofmann used croquette balls and sticks to represent his molecular model (*26*). (The ball and stick model is still used today in chemistry classes.) Even though this was a new insight into the problem, he did not have enough creativity to see the stereochemical implications it exposed.

In 1866, E. Erlenmeyer, claiming to be improving upon the work of Kolbe (actually Couper had presented a similar scheme to Erlenmeyer's in 1858), presented the following formulae:



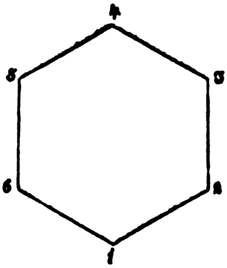
$$\begin{matrix}CH_2.OH.\\|\\CH.OH.\\|\\CH_2.OH:\end{matrix}\quad\text{oder}\quad\begin{matrix}CH.OH.OH.\\|\\CH.OH.\\|\\CH_3\end{matrix}\quad\text{oder}\quad\begin{matrix}CH_2.OH.\\|\\C.OH.OH\\|\\CH_3.\end{matrix}$$



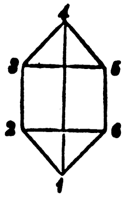
Epichlorhydrin,

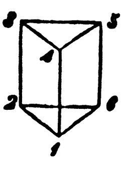
These formulae surely had their effects upon chemistry in general (*37*) and, as we shall see later, Blomstrand in particular. Indeed, Erlenmeyer's use of groups linked into chains, rings, and double bonds in this manner improved the existing systems. Indeed, the suggestion of varied length chains had deep implications in the work of Jørgensen.

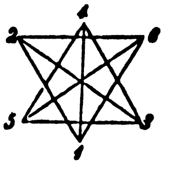
Kekulé, using the Couper bonds and the A. Crum Brown graphic formulae, saw "in a dream" that benzene was composed of a closed chain (1865) (*34*), as shown below:



His students and he (*14*), in an effort to improve upon the hypothesis, suggested other forms as follows:







In an effort to collect a number of graphic models into a meaningful whole he gives us the rather cumbersome diagram shown in Figure 13 (*34*).

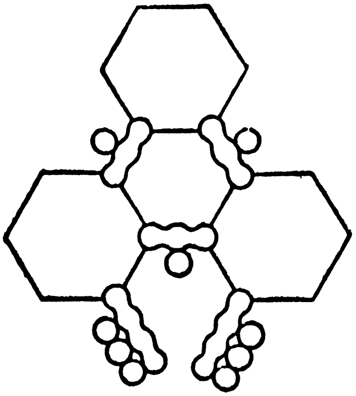


Figure 13

In this same book, Kekulé is careful to note that Havrez presents a solid figure form for the benzene molecule (Figure 14) (*23*).

In this same book Kekulé proposes a series of ovals and spheres as molecular models. Naquet used these a few years hence. (Figure 15 (*34*).) This is a full seven years before Le Bel and van't Hoff presented their presentations as solid figures (Figure 16). In this same eventful year, Dewar, in a lecture prepared for the Royal Society of Edinburgh, presented "working" models of compounds using brass rods and "disc of blackened brass" (*14*). The lecture was actually communicated by Lyon Playfair—the same professor who "communicated" the famous work of geology for Hutton. Couper, working in Lyon Playfair's laboratory at the time, was taken ill and thus the speaker substitution.

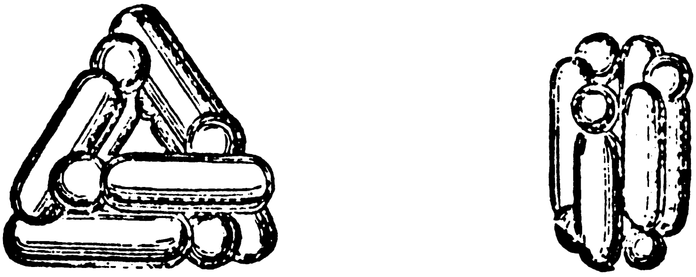


Figure 14

Other men the same year were working with the idea of shortening formulae with abbreviations. Frankland, calling upon Odling's earlier works, suggested the following (*18*):

$Me'' = CH_2$ or Methylene
$Me''' = CH$ or Formyl
$Et'' = C_2H_2$ or Ethylene

In the very next year, however, he expanded his formulae again to that shown in Figure 17 (*19*). We see here a multitude of representations as in Kekulé. This is most indicative of the quandary that chemists were in. No one representation was satisfactory for all the known data, yet there was no other method of representation known. Suggestions were made for a way out, but they offered little promise.

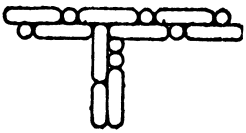
In the year 1868, some 98 years ago, Brodie conceived the idea that both the elements and actions should be placed in a formula (*6*). His formulae therefore contain two types of symbols:

$$2\alpha\xi = 2\alpha + \xi^2,$$
$$\alpha\xi^2 = \alpha + \xi^2.$$

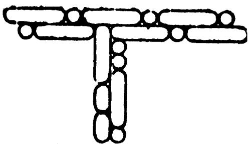
α = unit of hydrogen
ξ = operation in the preparation of oxygen

His article of 100 pages has a review of graphics to that date.

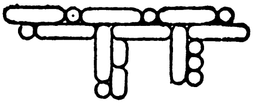
Naquet used a combination of several schemes: stacked chain formulae and modified linked spheres (*39*). (*See* Figure 18.)



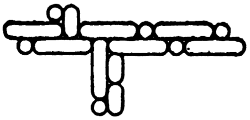
1. Benzylcyanid.



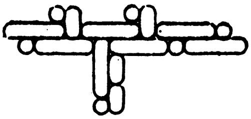
2. a-Toluylsäure



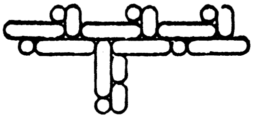
3. Toluylsäure.



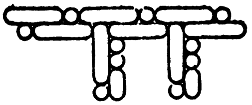
4. Oxybenzoësäure



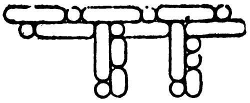
5. Protocatechusäure.



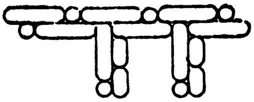
6. Gallussäure.



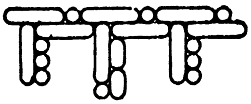
7. Glycol.
(unbekannt)



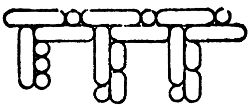
8 Glycolsäure
(unbekannt.)



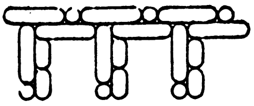
9. Dicarbonsäure
Terephtalsäure.



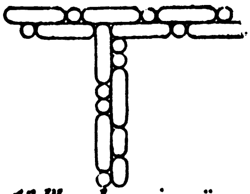
10. Xylylsäure.



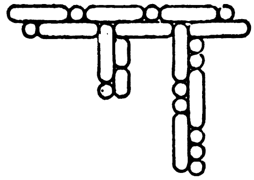
11. homolog mit
Terephtalsäure.
(unbekannt)



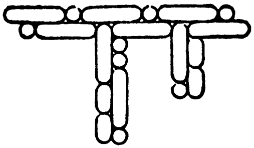
12. Tricarbonsäure



13. Phenylpropionsäure
Homotoluylsäure

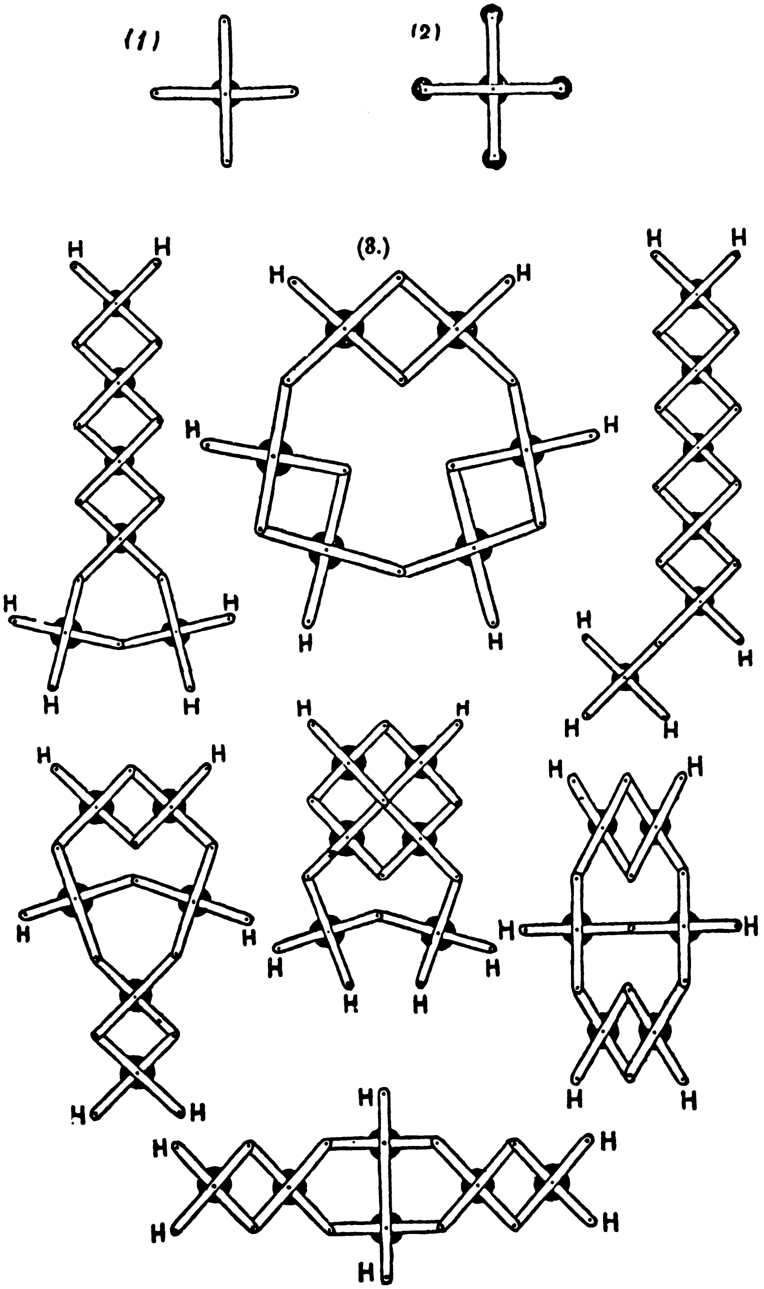


14. Cuminsäure.



15. Homolog mit
Terephtalsäure
(unbekannt)

Figure 15



Formulæ of Benzol.

Figure 16

The critical state of affairs in chemistry was destined to lead to chemical stagnation unless some new, radical innovations were added to existing theories.

Traditionalists were the prime chemists in the late nineteenth century. These are exemplified by Blomstrand and Jørgensen. Both men were professors and devoted chemists who had set out to find a rational explanation to the existing dilemma.

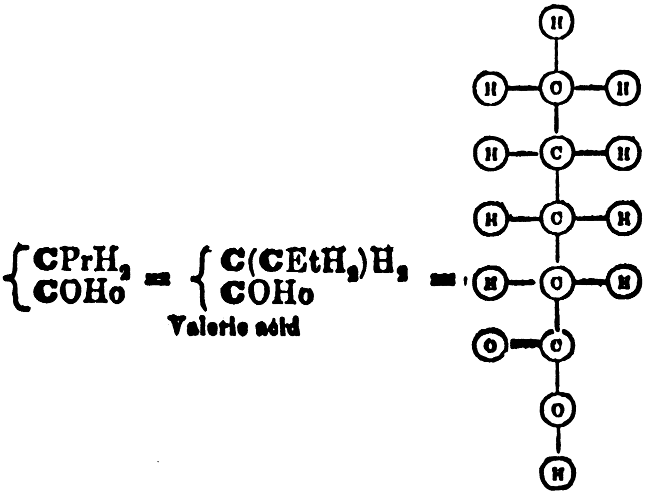


Figure 17

Blomstrand was the first of the two to set his ideas forth. In 1869 he published "Die Chemie der Jetztzeit" (*4*). In this book he hoped to explain chemistry from an "electrochemical standpoint." He proposed not only to present the then current ideas but to "join them with the past." There was no need for him to make a conscious effort to connect the established work with the "current" work. This "new" work was quite solidly based on past principles. He considered the ideas of Berzelius as the foundation of chemistry, and he was most apologetic about having to modify some of the existing Berzelian concepts. Blomstrand claimed that qualitative rather than quantitative explanations were needed to gain new insights. Perhaps he had a vision of the type of work that Werner was to develop for he decries theories that are built on "fantasy." (We shall see shortly exactly how this applied to Werner.) He clearly states that new work must be built on established principles, modified where needed, and justified with experiments.

Graphically speaking, upon which established works did Blomstrand build? We can conjecture that he expanded upon Graham's 1840 representation, Wurtz' stacked formulae, A. Crum Brown's work, Hofmann's

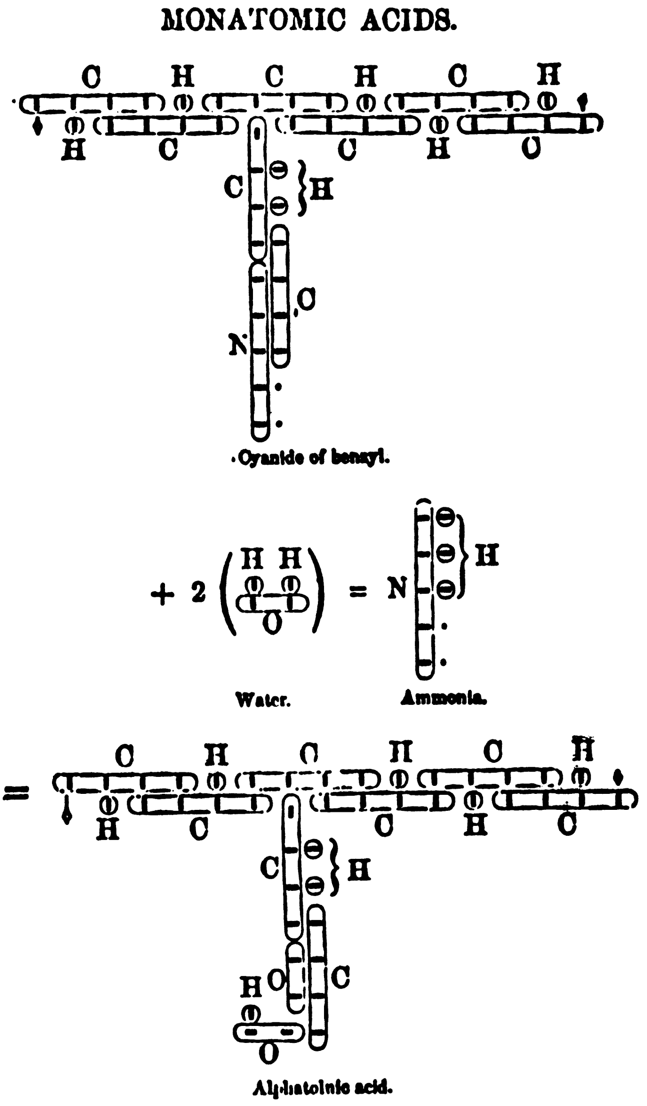
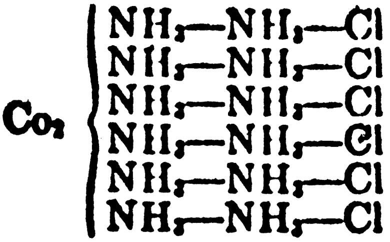


Figure 18

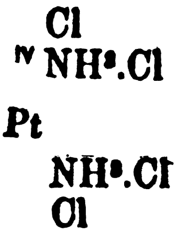
work with the hydrogen in ammonia and its replacability with both metals and other ammonium groups, Gerhardt's hydrogen, hydrogen chloride, and ammonia type of bond and his chain formulae, Kekulé's chains or circles, and Erlenmeyer's chain formulae. Clearly these chemists' ideas are seen in the following work of Blomstrand.

Blomstrand assumed that the ammonia molecule could work as a divalent radical and thus could form chains connecting the central metal atom and the ions. We see herein a modified synthesis of the Erlenmeyer chain and the Hofmann substitution of metal atom on the ammonia.



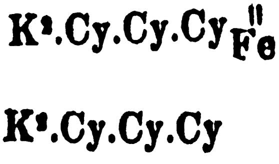
$$\mathrm{Co_2}\left|\begin{array}{l} NH_3—NH_3—Cl \\ NH_3—NH_3—Cl \\ NH_3—NH_3—Cl \\ NH_3—NH_3—Cl \\ NH_3—NH_3—Cl \\ NH_3—NH_3—Cl \end{array}\right.$$

The difference in reactivity of the chlorines was explained by the proximity to the metal atom—the "nearer" halogens being connected directly to the metal and the "farther" halogens being out on the end of an NH_3 chain.



$$\begin{array}{ll} & Cl \\ {}^{IV} & NH^3.Cl \\ Pt & \\ & NH^3.Cl \\ & Cl \end{array}$$

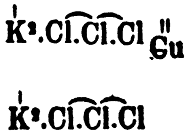
The "farther" and "nearer" halogens would have varied precipitation abilities with $AgNO_3$. He continued the chain concept to include anionic groups such as chloride, cyanide-, and nitro-, as follows:



$$\begin{array}{l} K^3.Cy.Cy.Cy \, \overset{II}{Fe} \\ K^3.Cy.Cy.Cy \end{array}$$

He also expanded the idea of divalency to include chlorine—e.g.,

$2KCl + CuCl$ wird nämlich



$$\begin{array}{l} \overset{I}{K}{}^3.Cl\overset{\frown}{.}Cl\overset{\frown}{.}Cl \, \overset{II}{Cu} \\ \overset{I}{K}{}^3.Cl\overset{\frown}{.}Cl\overset{\frown}{.}Cl \end{array}$$

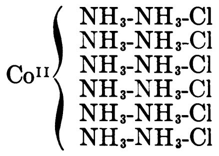
We know today that these concepts leave much to be desired even though Blomstrand was careful to document each as best he could. As we shall see, other chemists, in an effort to test the implications of this work, soon found it lacked much.

Criticizing past work with gained insight is easy, but let us not be too harsh on Blomstrand. His work was most valuable and most profitable for chemistry. His chain theory led to the studies of Jørgensen and the subsequent development of a whole school of chemical thought. We shall see shortly how the "nearer" and "farther" halogens of Blomstrand probably led Werner to his "primary" and "secondary" valencies. Blomstrand's hypothesis could not explain all the known phenomena of that date. Modifications were needed, and the man who made many of these was Sophus Mads Jørgensen. The two chemists came into direct contact when Jørgensen was appointed professor of chemistry at the University of Copenhagen in 1871.

During the next few years Jørgensen studied Blomstrand's concepts. In 1878 he published his first of a series of papers on the subject (*28*). While Jørgensen modified a few points, he basically agreed with the Blomstrand chain theory. Indeed, he became the main protagonist in favor of the theory and often is given credit for much of the work originally suggested by Blomstrand.

A comparison of the work presented by these two men, Blomstrand and Jørgensen, will delineate the differences in their work.

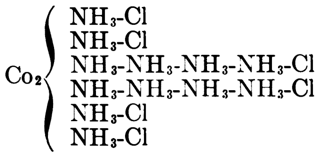
Blomstrand(*4*)



$$\mathrm{Co^{II}}\left\{\begin{array}{l} NH_3\text{-}NH_3\text{-}Cl \\ NH_3\text{-}NH_3\text{-}Cl \\ NH_3\text{-}NH_3\text{-}Cl \\ NH_3\text{-}NH_3\text{-}Cl \\ NH_3\text{-}NH_3\text{-}Cl \\ NH_3\text{-}NH_3\text{-}Cl \end{array}\right.$$

Luteosalze

Jørgensen(*29*)



$$\mathrm{Co_2}\left\{\begin{array}{l} NH_3\text{-}Cl \\ NH_3\text{-}Cl \\ NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}Cl \\ NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}Cl \\ NH_3\text{-}Cl \\ NH_3\text{-}Cl \end{array}\right.$$

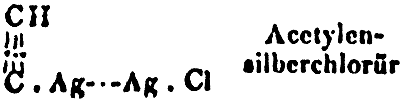
Luteosalze

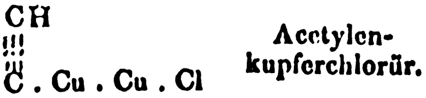
The changes in chain lengths, as proposed by Jørgensen, were intended to account for the varied precipitation rates of the halogens with $AgNO_3$.

Blomstrand, recognizing that Jørgensen was a man who "always preferred facts to bold hypothesis" (*3*), carefully studied the changes and then acknowledged them as correct. "As a research worker, Jørgensen was methodical, deliberate, and careful" (*3*). He tested and retested each of Blomstrand's propositions and then, and only then, suggested the modifications. In his textbook of 1902, "Kemiens Grundbegreber" (*31*), Jørgensen summarized all his modifications to date.

As the Blomstrand-Jørgensen school of thought grew, so grew the amount of research into testing its implications. As each new problem arose, new modifications were suggested. It soon became obvious, however, that certain compounds when finally synthesized did not react as expected. Efforts to build upon established principles were becoming more frustrating and the results seemed less convincing.

Other chemists during this same period were attempting, with equal frustration, to find an alternate working theory. Meister (*38*) in 1871 proposed a triple bond as shown below:

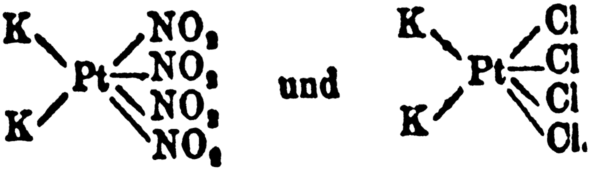




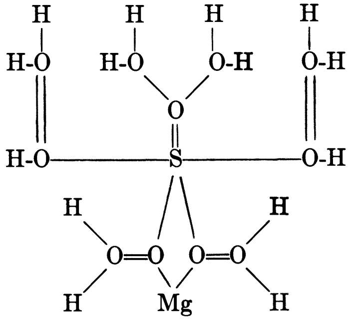
Gerhardt in 1882 was still using the Odling abbreviations (*48*):

$$H'Cl \qquad C'''' \, Cl_4 \qquad Pt'' \, Cl_2 \qquad Pt' \, Cl$$

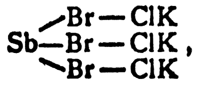
Horstmann in 1885 presented a representation which he hoped would clear up the situation (*27*).



While he failed to achieve his goal, he may very well have had a strong influence on Werner's thinking (as such diagrams were discussed by Werner). McLeod in 1889 diagramed what he saw as a typical hydrated salt (*37*).

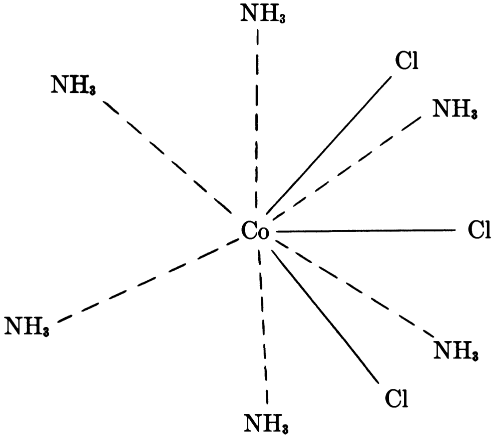


In 1887 Remsen, in an effort to explain double salt formation, represented $SbBr_3 \cdot 3KCl$ as shown below:

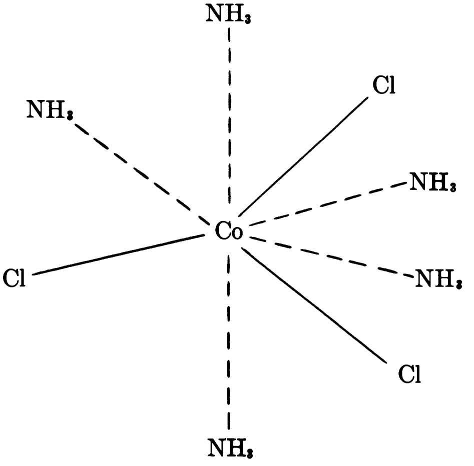


We have seen so far almost all of the representations as lacking depth in space, comprehensiveness, and/or totality of inclusiveness as far as all known data were concerned.

In 1893 Alfred Werner (*50*) conceived his revolutionary hypothesis. He perceived the metal atom as having two types of valencies: "Hauptvalenz" or primary or ionizable and "Nebenvalenz" or secondary or nonionizable. Each metal has a set number of secondary valencies or a set coordination number. He claimed that the primary valence must be satisfied only by negative ions, whereas the secondary valencies may be satisfied by negative ions or neutral groups. These secondary valencies



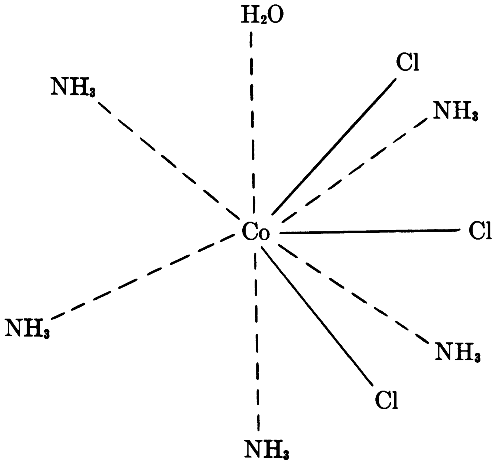
$CoCl_3 \cdot 6NH_3$



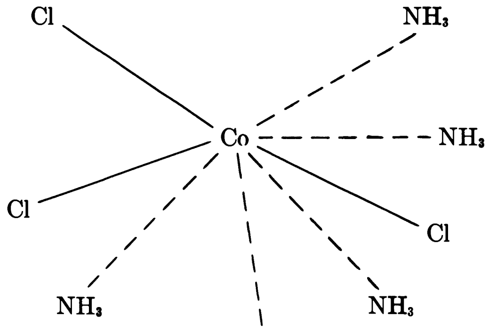
$CoCl_3 \cdot 5NH_3$

Figure 19. Secondary valencies directed in space around

are directed into space around the central metal ion. We can represent these as shown in Figure 19. The similarity to Horstmann's model is most striking. Also note the analogy to Frankland's 1852 "saturation capacity" and the Blomstrand valency concept. Note that the total charge of the complex ions is equal to the central metal charge if the ligands are neutrally charged. We have thus a nonelectrolyte. Jørgensen would have predicted an electrolyte based on his model. Data indicate that Werner's predictions are the correct ones. If we represent the complex as a solid figure, as Werner did, and then compare it to Jørgensen, we can further see this point.

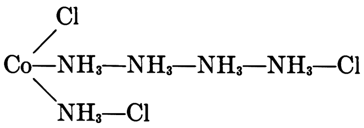


$CoCl_3 \cdot 5NH_3 \cdot H_2O$

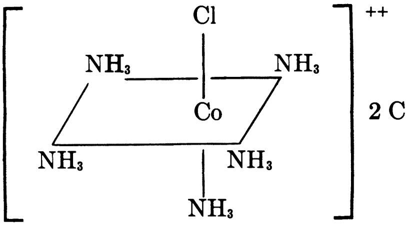


$CoCl_3 \cdot 4NH_3$

central metal atom, as conceived by Werner



Jørgensen

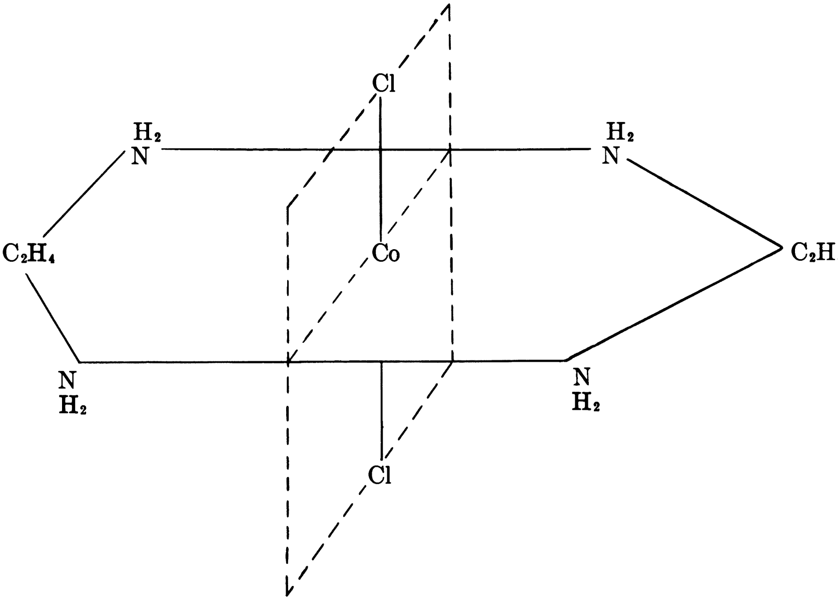


Werner

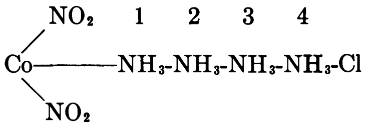
In the Jørgensen representation we note that the Cl is attached to the metal atom through an NH_3 molecule. In the Werner equivalent the Cl^- is ionic or "at large." Other examples of the structural argument are seen below. Examples number 4 and 5 are structural isomers; they differ only in atomic arrangement (i.e., Co attached to N or O of NO_2 group). Both Werner and Jørgensen agreed that this phenomenon exists; only the space arrangement was in contention.

The crux of the argument rested upon a Werner prediction. He predicted that compounds of the type MA_4B_2 that do not contain ethylenediamine (NH_2—C_2H_4—NH_2) should exhibit isomerism. In other words, these compounds should have the same atomic structure but different geometric structure and, therefore, different physical properties. Werner thus predicted a series of violeo (*cis*-dichlorotetramminecobalt(III)) salts, $(Co(NH_3)_4Cl_2)Cl$, with praseo (trans) counterparts. Jørgensen protested that this theory predicted a whole series of unknown salts. To Blomstrand's way of thinking, Werner's statement surely was a totally unscientific statement to make. These compounds were finally synthesized and theoretically explained by Werner. Blomstrand, along in years, but still an active chemist, refused to concede that his chain theory was no longer valid.

Let us look at a few additional examples of Werner and Jørgensen's formulations (pp. 34, 35, 36, and 37) and see where they differed. These formulae were intended to demonstrate the varied physical and chemical properties of two sets of isomers. Jørgensen predicted that the violeo compound would have adjacent NH_2 groups connected or "chelated" (this word was coined many years later), while the praseo isomer had alternate NH_2 groups chelated. He gave, however, no reason why the C_2H_4 bonds would be so much longer in one case than in the other. Werner said that chelation could only take place across adjacent or "cis" positions. It was, then, the relative position of the groups within the complex that determined properties of the compound. The resulting symmetry or dissymmetry of structure was the important point to Werner. In Werner's violeo formula no plane can be placed through the structure that will form two identical halves. It is, therefore, dissymmetrical. In his praseo form we see several such planes, only one of which is represented below:



Jørgensen's formulae would indicate that each of the NH_3 groups should differ in its properties, as follows:

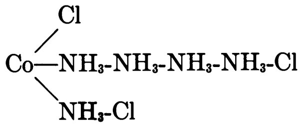


$$\begin{array}{l} \quad NO_2 \quad 1 \quad 2 \quad 3 \quad 4 \\ Co\text{———}NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}Cl \\ \quad NO_2 \end{array}$$

NH_3 No. 1 is connected to a Co and NH_3 group; numbers 2 and 3 are connected to only other NH_3 groups and thus should differ since they are different distances from the central metal atom. The number 4 is connected to the number 3-NH_3 and a Cl atom. Werner pointed out that no data indicated that such differences existed. In his representation of the croceo compound he showed all the NH_3 groups as equal. They all are equidistant from the central metal atom and equally affected by the NO_2 influence.

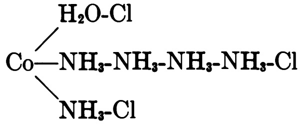
Why then did Jørgensen not accept Werner's ideas? Jørgensen, as a traditionalist, demanded irrefutable proof. Werner's work, as first presented, was only conjecture. His space arrangement lacked experimental evidence, and it was not solidly based on any established principles. Al-

2)



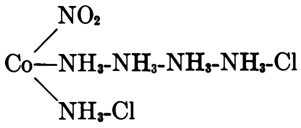
$$\mathrm{Co}\begin{array}{l}\diagup\,\mathrm{Cl}\\ \text{—}\mathrm{NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}Cl}\\ \diagdown\,\mathrm{NH_3\text{-}Cl}\end{array}$$

3)



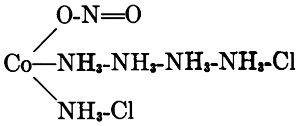
$$\mathrm{Co}\begin{array}{l}\diagup\,\mathrm{H_2O\text{-}Cl}\\ \text{—}\mathrm{NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}Cl}\\ \diagdown\,\mathrm{NH_3\text{-}Cl}\end{array}$$

4)

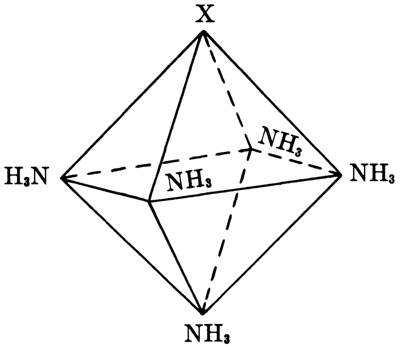


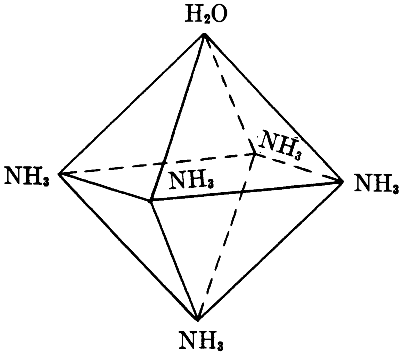
$$\mathrm{Co}\begin{array}{l}\diagup\,\mathrm{NO_2}\\ \text{—}\mathrm{NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}Cl}\\ \diagdown\,\mathrm{NH_3\text{-}Cl}\end{array}$$

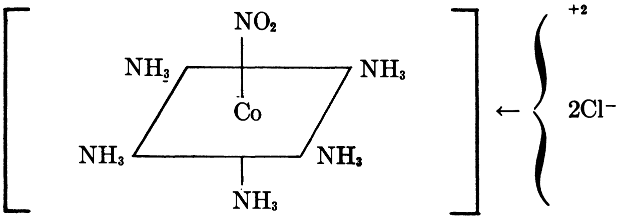
5)

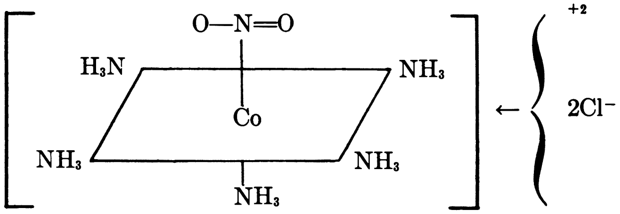


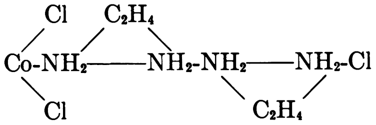
$$\mathrm{Co}\begin{array}{l}\diagup\,\mathrm{O\text{-}N{=}O}\\ \text{—}\mathrm{NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}Cl}\\ \diagdown\,\mathrm{NH_3\text{-}Cl}\end{array}$$


X
H₃N
NH₃
NH₃
NH₃
NH₃


H₂O
NH₃
NH₃
NH₃
NH₃
NH₃

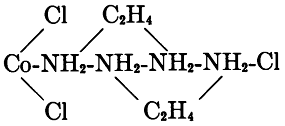

NO₂
NH₃
NH₃
Co
NH₃
NH₃
NH₃
+2
2Cl⁻


O—N=O
H₃N
NH₃
Co
NH₃
NH₃
NH₃
+2
2Cl⁻

6) 

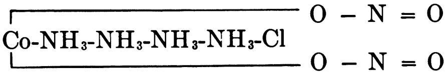
$$\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{Co}}}\text{-}\mathrm{NH_2}\overset{\mathrm{C_2H_4}}{\text{———}}\mathrm{NH_2}\text{-}\mathrm{NH_2}\underset{\mathrm{C_2H_4}}{\text{———}}\mathrm{NH_2}\text{-}\mathrm{Cl}$$

Violeo

7) 

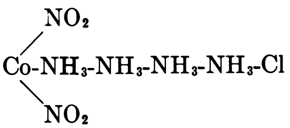
$$\underset{\mathrm{Cl}}{\overset{\mathrm{Cl}}{\mathrm{Co}}}\text{-}\mathrm{NH_2}\text{-}\overset{\mathrm{C_2H_4}}{\mathrm{NH_2}\text{-}\mathrm{NH_2}}\text{-}\mathrm{NH_2}\text{-}\mathrm{Cl}$$

Praseo

8) 

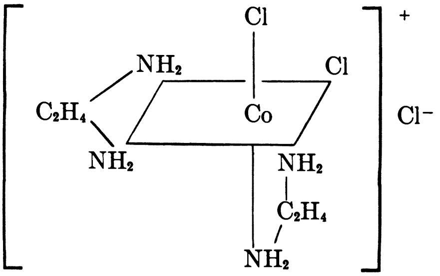
$$\mathrm{Co\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}Cl}\quad \begin{matrix}\mathrm{O-N=O}\\ \mathrm{O-N=O}\end{matrix}$$

Flavo

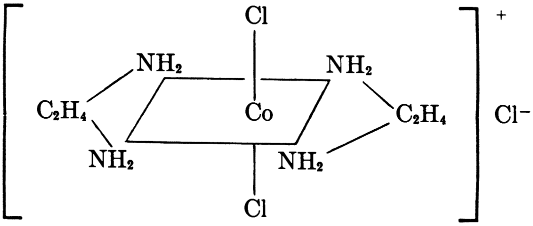
9) 

$$\underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{Co}}}\text{-}\mathrm{NH_3\text{-}NH_3\text{-}NH_3\text{-}NH_3\text{-}Cl}$$

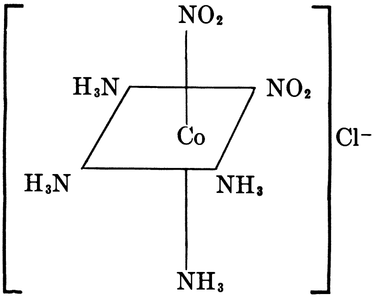
Croceo

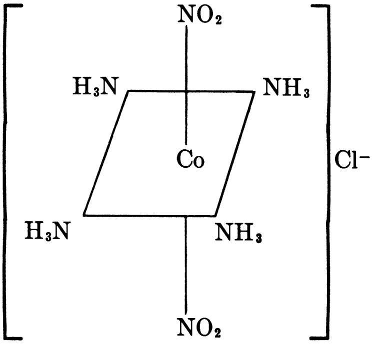


Violeo (*cis;* 1, 2)



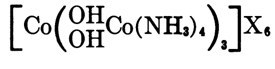
Praseo (*trans;* 1, 6)





though Werner drew upon a few earlier ideas, this dependence upon previous work was only marginal in depth. The bitter attacks upon his work were based primarily upon this point. Werner had no proof. Werner had broken with tradition; he was a revolutionary.

Werner spent the next 20 years in the laboratory trying to satisfy all his critics. He had actually resolved a number of inorganic compounds containing organic ligands during this time, but his critics protested, for some rather vague reasons, that organic compounds would not prove his theory. They would not be satisfied until an optically active inorganic coordination isomer could be furnished. This he finally accomplished in 1914 with the following (*51*):



$$\left[\mathrm{Co}\left(\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}\mathrm{Co(NH_3)_4}\right)_3\right]X_6$$

The Nobel Prize Committee awarded Werner the prize in 1913 (without his inorganic complex). Werner had indeed found a workable solution to the dilemma through the coordination sphere and stereochemistry.

What allowed Werner to break with tradition and to present this new radical hypothesis? He was an impulsive worker. Werner could not be troubled with minute details. His laboratory was noted as being covered with a multitude of unlabeled watch glasses scattered at random across the work areas. Yet he seemed to know exactly what each contained and how it was to be used. His chemical tests were qualitative, quick reacting spot tests which relied on a bubbling, change of color or solubility. He was able to discuss varied subjects at the same time and switch from one to the other easily and with complete continuity. His personality could not fit into the yoke of traditionalism, and his thought patterns were not "fixed" in traditional thinking modes. Werner is best described as a brilliant impulsive, just the thing that chemistry needed. These very properties were the things that caused Jørgensen to be repelled by Werner's ideas. Jørgensen would not accept Werner's thoughts until he was satisfied that they were the product of careful consideration. If Werner's theory predicted a maximum coordination number of six, how could hydrates with more than six molecules of water be explained? Werner assumed double water molecules, H_4O_2. This theory has never been validated. Jørgensen (*30*) also asked Werner to explain why negative groups in the complex did not lower the effective valence of the complex. Werner merely said that "the coordinated groups do not change the valence of the metal atom."

We have seen that as chemistry emerged from its early alchemical start, theory and graphics were simple. They explained the existing data but, as new facts became known, they had to be modified and expanded. Several early attempts to present comprehensive explanations of all phenomena fell far short of expectations. Before long, chemists, being trained in "classical chemistry," found it most difficult to think in original theoretical terms. Their patterns of explanations were developed as expansions of existing propositions. Training in chemistry demanded a thorough knowledge of the "established principles." No new ideas could be brought out until "absolute" proof could be shown. There was no avenue for expression of reasonable conjecture, hunches, and new theories without solid proof. Traditionalism was almost a prerequisite to being a scientist (*24*).

In the nineteenth century we have seen several trends of graphical representation in chemistry. The first was the circle, followed by circle with the letter symbol inside it; next was the letter alone. The letters were arranged in linear fashion. The lines were either single and all-inclusive or stacked one upon the other. At times the letter symbols were joined by brackets—other times dashes, and other times arcs. From time to time various systems were proposed which were synthesized from several previous ideas. Kekulé proposed elimination of all letters and circles and the use of only lines and arcs. Others tried to develop working models of the compounds. As each of these proposals fell short of expectations, chemists tried new modifications of established precepts.

It was not until Werner saw the bonding dilemma in a new light that progress could be made. It was indeed a combination of factors (personality, available data, and mental ability) that permitted Werner to advance chemical insight.

The type of work depicted by Werner and Jørgensen is most aptly described by George B. Kauffman (*32*). "In Jørgensen, the conservative, we have the classic type, the slow and deep-digging completer who produces with long deliberation and slowly develops a traditional theory to new consequences. In Werner, the liberal, we have the romantic type, the impulsive and brilliant initiator who produces prolifically and easily at an early age. Each needed the other. Science has need of both."

Acknowledgments

My appreciation to John Bailar, Jr., University of Illinois, and Dean F. Martin, University of South Florida, for editorial suggestions on the first manuscript; to George B. Kauffman, Fresno State College, for editorial suggestions and factual corrections on the second draft; and most of all to my wife for continuous helpful editorial commentary and constant encouragement. Without her help this paper would never have been completed.

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4

Some Lesser Known Aspects of the Work and Thought of Alfred Werner

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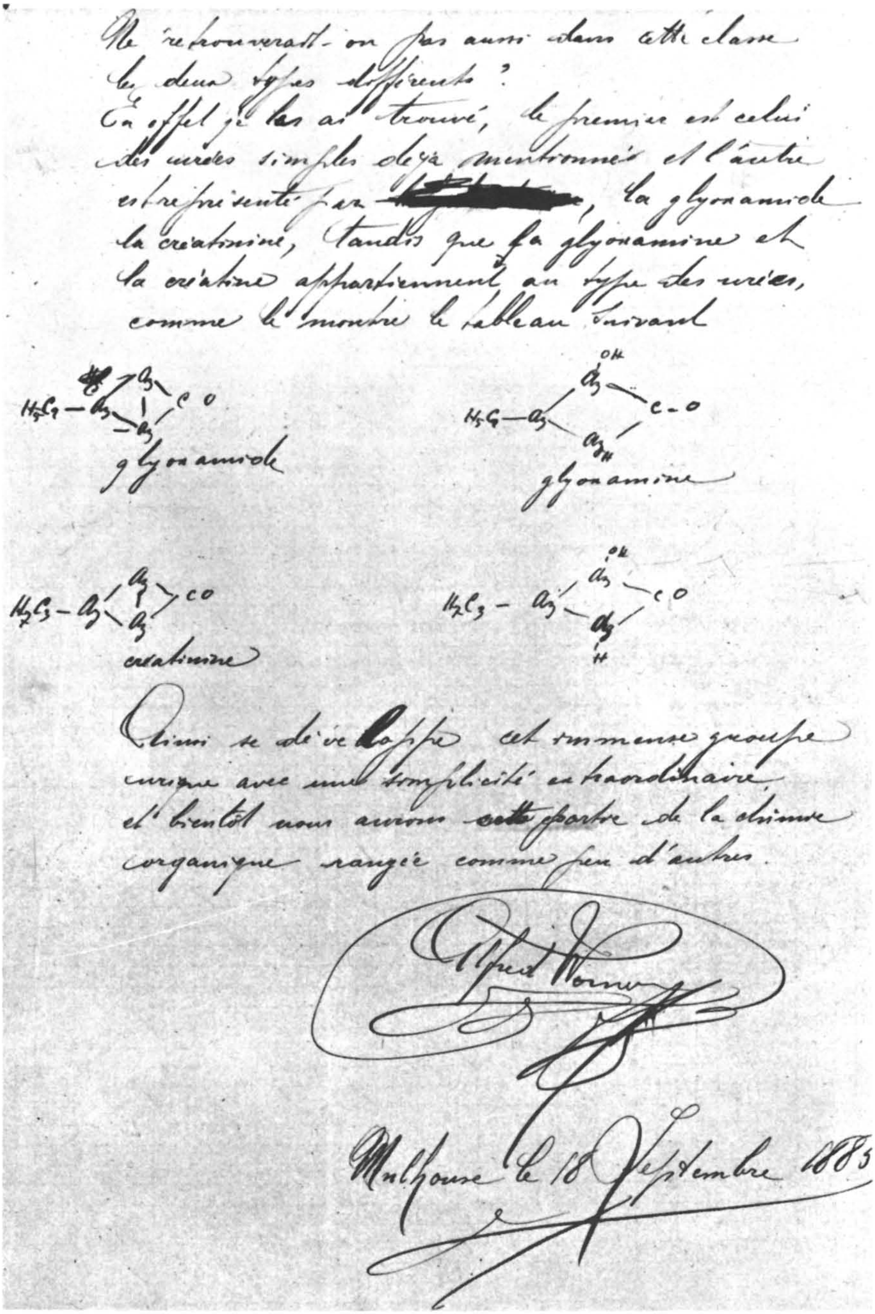
Werner's monumental research on coordination chemistry has tended to obscure his less spectacular achievements in other areas, organic as well as inorganic. From the many topics he dealt with during his almost 30-year-long research career, his relatively neglected works on trivalent nitrogen compounds and other organic substances, valence, the "benzene problem," ammonium and oxonium salts, acid-base theory, the hydrogen bond, and the periodic table are considered here.

Most of the contributions to this Centennial Symposium deal with various aspects of coordination chemistry, the field of which Alfred Werner is the undisputed founder and systematizer. That Werner's name is virtually synonymous with this area is attested to by the term "Werner complexes," colloquially used to designate coordination compounds. Yet such a close identification of a scientist with a given field of research can have its disadvantages, for it may obscure his other, less spectacular achievements. The purpose of this paper, then, is to correct this one-sided view of Werner and to illustrate his versatility by discussing briefly a few of his contributions to other areas, organic as well as inorganic. Among the topics treated here are trivalent nitrogen compounds and other organic substances, valence, the "benzene problem," ammonium and oxonium salts, acid-base theory, the hydrogen bond, and the periodic table.

Trivalent Nitrogen Compounds

Werner was trained primarily as an organic chemist at the Zürich Eidgenössisches Polytechnikum and was called to Universität Zürich to teach organic chemistry, yet these obvious facts are often overlooked by inorganic chemists. Furthermore, of Werner's first 30 publications (1890–



Ne retrouverait-on pas aussi dans cette classe
les deux types différents?
En effet je les ai trouvé, le premier est celui
des urées simples déjà mentionnés et l'autre
est représenté par [redacted], la glyoxamide
la créatinine, tandis que la glyoxamine et
la créatine appartiennent au type des urées,
comme le montre le tableau suivant

glyoxamide

glyoxamine

créatinine

Ainsi se développe cet immense groupe
urique avec une simplicité extraordinaire
et bientôt nous aurons ~~cette~~ partie de la chimie
organique rangée comme peu d'autres.

Alfred Werner

Mulhouse le 18 Septembre 1885

"Contribution de l'Acide Urique, de Séries de la Théobromine, Cafeine, et leurs Derivés,"
Mulhouse, Sept. 18, 1885

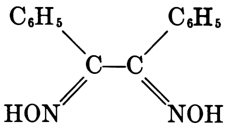
Last page of Werner's first original chemical work

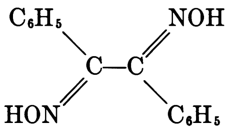
1896), the organic papers outnumber the inorganic ones by a ratio of two to one. It was only in 1898, after his reputation in coordination chemistry had already been established, that the number of his inorganic papers (21) reached that of his organic ones. His theoretical views on organic chemistry have even been the subject of a small, relatively unknown monograph (*6*) published at the turn of the century.

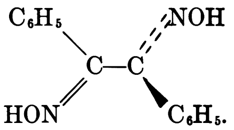
Despite his later preoccupation with coordination compounds, Werner's early interest in organic chemistry continued throughout his career. Almost one quarter (45) of his 174 publications deal with organic themes such as oximes; hydroxamic and hydroximic acids; phenanthrenes; hydroxylamines; azo, azoxy, hydrazo, and nitro compounds; and dyestuffs. Even at the height of his career, after his long-sought resolution of coordination compounds had unequivocally proven his octahedral configuration for cobalt, chromium, and rhodium to be correct, he repaid his debt to Pasteur by using these optically active inorganic compounds which had been resolved by means of organic substances (*93*) to resolve in turn dimethylsuccinic acid, an organic compound (*100*). Yet his first publication, "Ueber räumliche Anordnung der Atome in stickstoffhaltigen Molekülen" (*18*, *32*), excerpted from his doctoral dissertation, remains his most popular and important work in the organic field.

With this paper, co-authored with his teacher Arthur Hantzsch, the 24-year-old Werner entered into one of the most exciting disputes in the history of organic chemistry. This dispute with Victor Meyer (*43*) over the stereochemistry of trivalent nitrogen compounds remains much less familiar than Werner's justly famous battle with Sophus Mads Jørgensen over the constitution and configuration of coordination compounds (*28*, *31*, *33*), a topic which is discussed earlier in this symposium by Paul S. Cohen (p. 8). The organic controversy centered around the oximes—those crystalline derivatives, first discovered by Victor Meyer (*45*), which are so widely used in organic chemistry to characterize the parent carbonyl compound. It is commonplace that history repeats itself, and the history of chemistry is no exception to this rule. Just as Johannes Wislicenus' experimental investigations of the stereoisomeric lactic acids of 1873 (*126*, *127*) served as a direct stimulus for van't Hoff's classic theoretical essay of the following year (*22*) on the stereochemistry of carbon compounds, Heinrich Goldschmidt's discovery of a second benzildioxime (*16*) isomeric with his and Victor Meyer's benzildioxime (*17*) created the incentive for Meyer and Karl von Auwers' suggestion (*1*) that stereoisomerism was possible among nitrogen compounds which contained neither carbon-carbon double bonds nor asymmetric carbon atoms.

Meyer and von Auwers not only proposed structural formulas for the two benzildioximes, but they also predicted a third isomer, which they soon synthesized (*2*), as shown below:



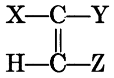




However, even a student with only the most elementary knowledge of organic chemistry will recognize that this formulation violates van't Hoff's so-called second proposition which states that free rotation is possible around a carbon-carbon single bond.

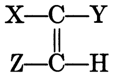
Werner and Hantzsch rejected Meyer and von Auwers' *ad hoc* hypothesis that two singly bonded carbon atoms could be connected in two different ways—one permitting rotation, and one restricting rotation. Instead they developed a surprisingly simple, general explanation for the isomerism of aldoximes, ketoximes, diazo compounds, hydroxamic acids, and other trivalent nitrogen compounds, based upon a direct transfer of Le Bel and van't Hoff's spatial concepts for the carbon atom to the nitrogen atom: "In certain compounds the three valences of the nitrogen atom are directed toward the corners of a (in any case irregular) tetrahedron whose fourth corner is occupied by the nitrogen atom itself."

According to Werner and Hantzsch, trivalent N thus fulfills a function similar to a CH group, and it therefore follows that "there can correspond to the two stereochemically isomeric carbon compounds of the form $XY \cdot C{=}(CH)Z$:



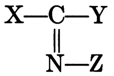
$$\begin{array}{c}X{-}C{-}Y\\ \|\\ H{-}C{-}Z\end{array}$$

and



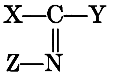
$$\begin{array}{c}X{-}C{-}Y\\ \|\\ Z{-}C{-}H\end{array}$$

two stereochemically isomeric carbon-nitrogen compounds of the form $XY \cdot C{=}(N)Z$:



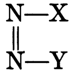
$$\begin{array}{l}X{-}C{-}Y\\ \quad\;\|\\ \quad\;N{-}Z\end{array}$$

and



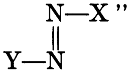
$$\begin{array}{r}X{-}C{-}Y\\ \|\quad\;\\ Z{-}N\quad\;\end{array}$$

Nitrogen compounds of the form $\begin{array}{c}NX\\ \|\\ NY\end{array}$ can likewise be compared with carbon compounds of the form $\begin{array}{c}(CH)X\\ \|\\ (CH)Y\end{array}$ and thus can be conceived as two stereochemical isomers:



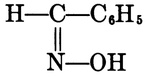
$$\begin{array}{l}N{-}X\\ \|\\ N{-}Y\end{array}$$

and



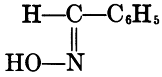
$$\begin{array}{r}N{-}X\\ \|\;\;\;\\ Y{-}N\;\;\;\end{array}$$"

According to the new theory, the two isomeric benzaldoximes receive the formulas



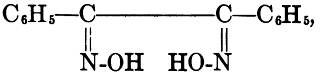
$H{-}\underset{\underset{N{-}OH}{\|}}{C}{-}C_6H_5$

and



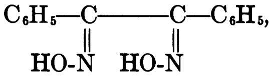
$H{-}\underset{\underset{HO{-}N}{\|}}{C}{-}C_6H_5$

and the three crucial benzildioximes receive the formulas



$C_6H_5{-}\underset{\underset{N\text{-}OH}{\|}}{C}{-}{-}{-}{-}\underset{\underset{HO\text{-}N}{\|}}{C}{-}C_6H_5,$

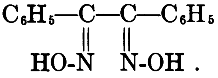
syn



$C_6H_5{-}\underset{\underset{HO\text{-}N}{\|}}{C}{-}{-}{-}\underset{\underset{HO\text{-}N}{\|}}{C}{-}C_6H_5,$

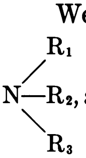
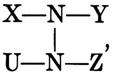
amphi

and



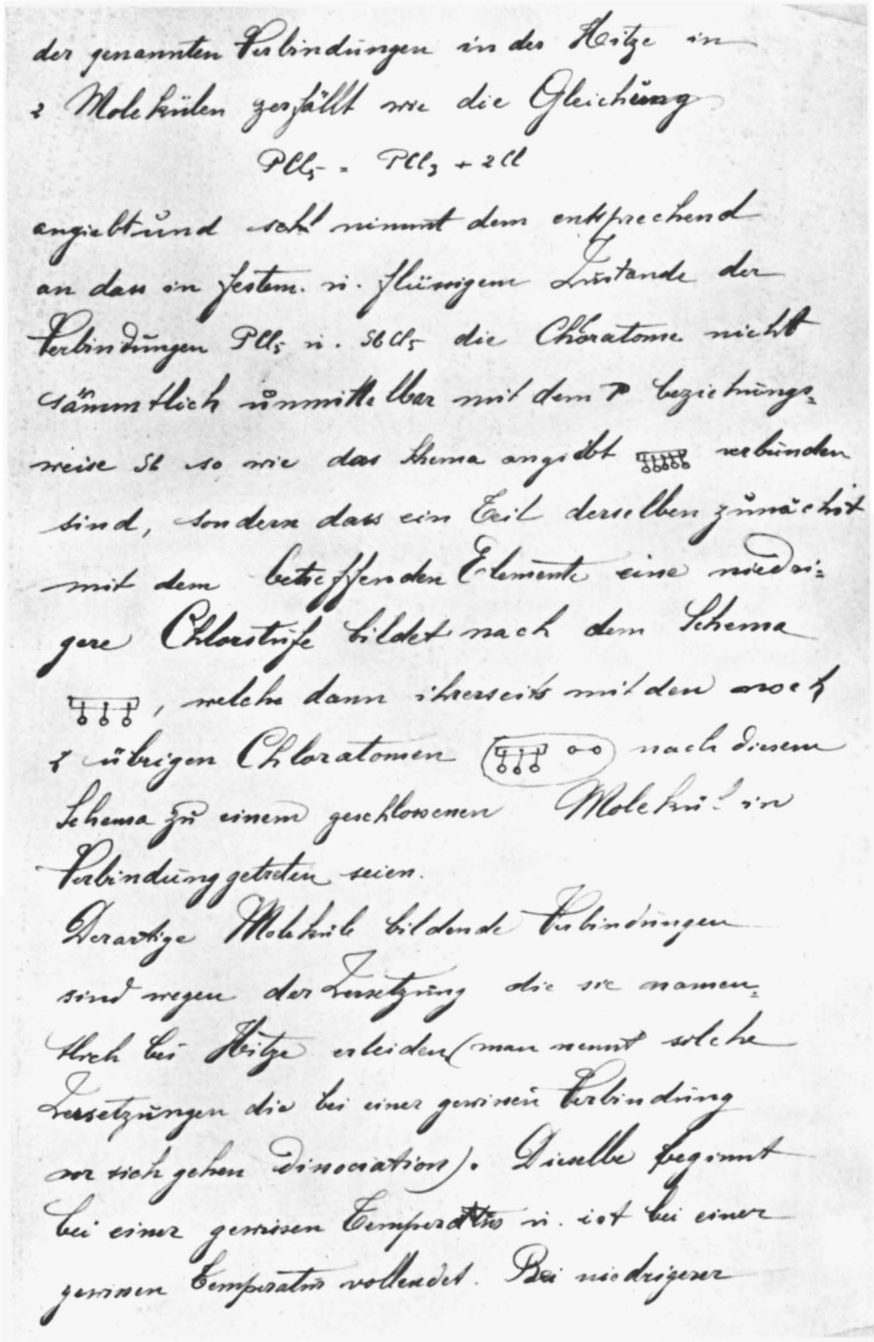
$C_6H_5{-}\underset{\underset{HO\text{-}N}{\|}}{C}{-}\underset{\underset{N\text{-}OH}{\|}}{C}{-}C_6H_5 .$

anti

Werner and Hantzsch also hypothesized that optical isomers of formula  $N\begin{array}{l}\diagup R_1\\ {-}R_2\\ \diagdown R_3\end{array}$, as well as geometric isomers of substituted hydrazines of the form  $\begin{array}{c}X{-}N{-}Y\\ |\\ U{-}N{-}Z\end{array}$, might exist. Such compounds of the first type, where R_1, R_2, and R_3 are unhindered groups, and of the second type have still not yet been found. The objection that, if their theory were correct a large number of organic nitrogen isomers should exist, whereas in fact only a very limited number of such theoretically possible isomers were known, can be applied also to carbon isomers.

The authors best summarize the advantages of the theory as follows: "It requires neither a new principle for the nature of valence nor the assumption of two different types of atomic bonding in order to explain the cases of isomerism in question. It proceeds from the concepts developed for geometrically isomeric carbon compounds, maintains completely van't Hoff's second proposition, and attributes a series of isomerisms which have heretofore been considered partly geometric, partly structural, and partly insufficiently explained to the same cause—*viz.*, to the different spatial arrangement of the radicals bound to nitrogen in relation to this atom itself."

Although Victor Meyer, Werner's most formidable adversary, withdrew his objections to Werner and Hantzsch's theory by the mid-nineties, attacks continued to appear in the literature until as late as 1920 (*46*). After resolutions in 1910 (*47, 48*) and 1923 (*52*), the significance of which was obscured by the possibility of isomerization of the compounds which were resolved, William Hobson Mills, the English stereochemist who is most familiar to inorganic chemists for his unequivocal proof of the square planar configuration for divalent platinum (*50*), succeeded (with B. C. Saunders) in synthesizing and resolving the optically stable compound:



der genannten Verbindungen in der Hitze in
2 Molekülen zerfällt wie die Gleichung

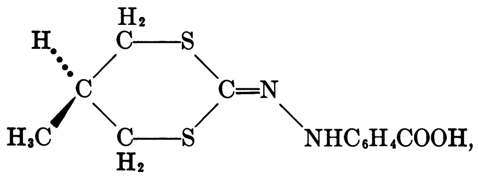
$$PCl_5 = PCl_3 + 2Cl$$

angibt und sch. nimmt dem entsprechend
an dass im festem u. flüssigem Zustande der
Verbindungen PCl_5 u. $SbCl_5$ die Chloratome nicht
sämmtlich unmittelbar mit dem P beziehungsweise Sb so wie das Schema angibt verbunden
sind, sondern dass ein Teil derselben zunächst
mit dem betreffenden Elemente eine niedrigere Chlorstufe bildet nach dem Schema
, welche dann ihrerseits mit den noch
2 übrigen Chloratomen nach diesem
Schema zu einem geschlossenen Molekül in
Verbindung getreten seien.

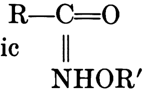
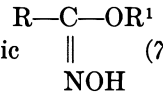
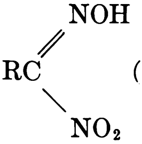
Derartige Molekül bildende Verbindungen
sind wegen der Zersetzung die sie namentlich bei Hitze erleiden (man nennt solche
Zersetzungen die bei einer gewissen Verbindung
vor sich gehen dissociation). Dieselbe beginnt
bei einer gewissen Temperatur u. ist bei einer
gewissen Temperatur vollendet. Bei niedrigerer

"Einleitung in die Chemie," Mulhouse 1883–84, p. 111

Page from notebook showing the formulation of PCl_5 as a molecular compound



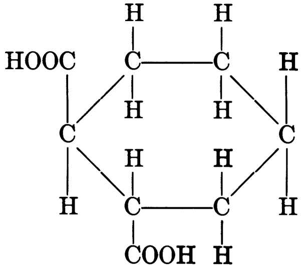
thus proving the nonlinearity of the >C=N-NH grouping and provided final and conclusive proof for the Werner-Hantzsch theory (*51*). The theory is compatible with the electronic theory of valence (*36*) and today, with only slight modification, is rightfully placed alongside the Le Bel and van't Hoff concept of the tetrahedral carbon atom as one of the foundations of stereochemistry.

Werner's contributions to the chemistry of oximes did not cease with the publication of his and Hantzsch's theory. Although Hantzsch's numerous subsequent researches, particularly on aromatic azo and diazo compounds, won general acceptance for the new theory, Werner himself experimented on oximes and related compounds and published papers describing the discovery of isomers which had been predicted by the theory (*70, 71, 75, 103*) and the use of methods such as the Beckmann rearrangement for assigning correct configurations to oximes (*106, 117*). He also synthesized and assigned configurations to compounds closely related to the oximes—*viz.*, substituted hydroxamic  $\mathrm{R{-}C({=}O){-}NHOR'}$ (*19, 72, 73*) and hydroximic  $\mathrm{R{-}C({=}NOH){-}OR^1}$ (*76, 77, 101, 102, 120, 122*) acid derivatives, nitrolic acids  $\mathrm{RC({=}NOH)NO_2}$ (*104*), and azoxazines and amine oximes (*112*). He used the benzhydroximic acids to synthesize another new class of compounds, the hydroxylaminealiphatic acids (*74, 109, 121*). Werner's organic work, however, was not limited to nitrogen compounds. He and his students devoted much experimental effort to the phenanthrenes and their derivatives (*80, 108, 111, 114, 115, 116*), as well as to organic synthetic reactions (*118, 119, 123*).

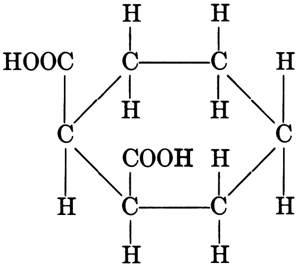
Werner's resolutions of inorganic coordination compounds, encompassing more than two dozen articles in the course of less than a decade, marked the summit of his career and are discussed in detail by Arthur W. Chester (Chapter 6), Bodie E. Douglas (Chapter 23), and other participants in this symposium. In fact, because of the recognition accorded to these works, Werner's resolutions of purely organic compounds may easily be overlooked. His earliest work in this field (1899) was the resolution of *trans*-

hexahydro-*ortho*-phthalic acid, an unusual compound containing two structurally identical asymmetric carbon atoms (*105*).

In three-, four-, five-, and six-membered ring systems, geometric and optical isomerism is possible since the rigidity of the ring prevents free rotation around its bonds. Werner's resolution provided a method for determining the configuration of such cyclic compounds. Although he was able to resolve the trans isomer, all his attempts to resolve the cis isomer proved fruitless, in accordance with his expectations.



trans



cis

One hundred publications and 14 years elapsed before Werner turned again to resolving organic compounds. This time, however, he used as a resolving agent one of his own recently resolved coordination compounds. By treating silver *dl*-dimethylsuccinate with either *d*- or *l*-tris(ethylenediamine)cobalt(III) bromide (*93*), he succeeded in resolving *dl*-dimethylsuccinic acid into its optical antipodes (*100*). On this occasion, inorganic chemistry came to the aid of her sister science, organic chemistry, rather than the reverse process which hitherto had been the usual procedure in resolving optically active compounds.

Thus, as we conclude our brief perusal of Werner's organic works, we see that, as he himself had stated on numerous occasions, there is no dividing line between organic and inorganic chemistry. The principles of his coordination theory have been successfully applied to many problems in organic chemistry and have explained the constitution and configuration of organic molecular compounds. Werner's belief in the unity of chemistry has been substantiated by the recent synthesis of metallocenes and similar organometallic compounds, which are discussed later in this symposium by Marvin D. Rausch (Chapter 32), M. Rosenblum and F. W. Abbate (Chapter 33), Rowland Pettit (Chapter 34), and Dean F. Martin (Chapter 35). The existence of these compounds amply demonstrates that the traditional barrier between organic and inorganic chemistry is artificial.

Valence

Valence is a topic which many major figures of chemistry have regarded as one of the most fundamental problems of their science. Among the contributors to the field are also such well-known names as Dalton, Wollaston, Davy, Berzelius, Liebig, Wöhler, Frankland, Kekulé, Couper, Pasteur, Williamson, Newlands, Mendeleev, Lothar and Richard Meyer, van't Hoff, Arrhenius, Helmholtz, Bohr, Kossel, Lewis, Langmuir, Sidgwick, Pauli, de Broglie, Schrödinger, Heitler, London, Hund, Pauling, and, of course, Werner himself.

Chemists have been guilty of using the single term valence to express more than one concept. Much of the inconsistency has arisen from the failure to distinguish between "affinity" or the force or intensity of combination (*Bindungsvermögen*) and "valence" or the numerical capacity for combination (*Bindungszahl*). Another source of confusion arises from the term valence used to refer to the number of bonds by which an atom in a molecule is joined to other atoms. In spite of the fact that numerous chemists repeatedly insisted that structural formulas were merely convenient devices to be regarded only in a purely formal sense, and not as actual structures, the view of valence as a number of bonds (*Valenzeinheiten, Einzelkräften, Affinitätseinheiten*), which mutually saturate each other, or even as the bonds themselves, has been widely held. This is largely because of Kekulé's views on the tetravalence of the carbon atom.

In his first publication (the inaugural dissertation, 1890) (*18, 32*), already discussed in connection with oximes, Werner repeatedly uses the term *Valenz* in a spatial sense to denote what should more accurately be called bonds. Scarcely more than a year later (1891), however, in his *Habilitationsschrift* "Beiträge zur Theorie der Affinität und Valenz" (*29, 97*), he states that "valence signifies an empirically determined numerical relationship independent of valence units." Throughout his career and in his many pronouncements upon valence, Werner was careful to distinguish between valence (a number, *Zahl*) and affinity (a force, *Kraft*), a distinction which is sometimes overlooked by chemists who are meticulous in other respects. Indeed, even Werner was on occasion guilty of failing to make the distinction.

Today it is fairly well known that Kekulé's theory of constant, indivisible directed single valence units (*Valenzeinheiten*) was too rigid and circumscribed to encompass all inorganic compounds, but what is often not realized is that it also encountered difficulty even in the field to which it was supposedly admirably suited—*viz.*, organic chemistry.

Werner objected to the older theory because it inadequately explained the racemization of optically active substances, the isomerization of geometric isomers, and the properties and reactions of cyclic compounds as well as of unsaturated compounds including olefins, acetylenes, benzene, and other examples of what later came to be known as conjugated systems. He therefore provided a simple and satisfactory explanation for these phenomena and related topics such as the structure of nitrogen compounds and the variability of the single carbon bond (*110*) (e.g., the labilization of α-hydrogen atoms adjacent to carboxyl groups in acids). Later (*69, 92*), he also applied his theory to explain the Walden inversion.

In his *Habilitationsschrift* (*29, 97*), the 24-year-old Werner boldly and completely rejected the old valence theory ("Separate valence units do not exist") and simultaneously laid the foundations for a totally new idea: "Affinity is an attractive force acting equally from the center of the atom toward all parts of its spherical surface." Applying this concept to organic chemistry, he concluded that "the stable arrangement of the four atoms bound to the carbon atom will be present when the bonding surfaces of the four atoms on the atomic sphere of the carbon atom are as large as possible without covering each other even partially [overlapping]."

By such simple reasoning and without introducing any *ad hoc* hypotheses such as directed valence forces, Werner logically deduced and explained the configurations of organic molecules which had been arrived at by van't Hoff (*22*), Wislicenus (*126, 127*), and others by more dogmatic means: "The four similar atoms bound to the carbon atom thus arrange themselves in the mutual position of the corners of a regular tetrahedron because, in this way, the greatest exchange of affinity between them and the carbon atom—i.e., the greatest bonding stability, occurs." The similarity of Werner's reasoning to that of modern theories of electron repulsion (*14, 15*), such as that discussed by R. J. Gillespie later in this symposium (Chapter 16), should be obvious.

The application of Werner's concept of affinity and valence to the phenomena mentioned above is difficult to summarize without considering numerous figures in detail. The following shows in some detail his explanation of the perennially popular "benzene problem."

"The Benzene Problem"

Since Faraday's discovery of benzene in 1825 (*12, 13*), devising a suitable structural formula which will successfully explain its unique aromatic properties has been a favorite parlor game for organic chemists. The first seriously considered structure is usually held to be the cyclic one proposed by Kekulé in 1865 (*34, 35*) on the basis of a dream akin to that which generated Werner's coordination theory. In order to explain the equivalence of the six hydrogen atoms, the obvious lack of reactivity, as compared with olefins, and in order to preserve the tetravalency of carbon which had become a *sine qua non* among orthodox organic chemists, a variety of alternative formulas was devised by Claus, Lothar Meyer, Ladenburg, Dewar, Körner, Richard Meyer, Thomsen, Armstrong, von Baeyer, Marsh, Herrmann, Sachse, Vaubel, Collie, Thiele, Erlenmeyer, Bloch, and Baly, Edwards, and Stewart, to mention only the most prominent proponents of structures.

It was only natural then that Werner, with his abiding interest in structural problems, should immediately apply his theory of nondirected valence forces to this intriguing but perplexing puzzle. He believed that the problem of the linking of the fourth valence force in benzene "cannot be solved wholly satisfactorily according to [the present] valence theory." His own particular treatment of "the benzene problem" not only appears in his *Habilitationsschrift* but it also forms the subject of his inaugural address for the Privat-Dozentur at the Eidgenössisches Polytechnikum (*94*) and is treated in the context of other proposed structures in his "Lehrbuch der Stereochemie" (*95*). The following excerpt from pp. 26–27 of the *Habilitationsschrift* (*29*, *97*) sets forth the gist of Werner's views:

"Let us imagine six carbon atoms bound in a ring. Since these carbon atoms are enclosed in the same ring, each of them comes within the spheres of action of the affinity of all the other atoms, and simultaneously an escape from these spheres of action will be prevented. Now, since in benzene each carbon atom has an equal amount of affinity available for the bonding of the other carbon atoms, the static condition of the molecule will be one in which all the carbon atoms, regardless of their mutual positions, are bound together by the largest possible amounts of affinity, even though [these amounts are] different.

"One may think of the affinity emanating from a carbon atom as being similar to an emission of light; one may assume, for example, that atom 1 (Figure 1) is luminous and illuminates the five other atoms. Then the two carbon atoms 2, found in the ortho position, will receive the greatest and of course equal amount of light from 1. The meta carbon atoms 3, on the

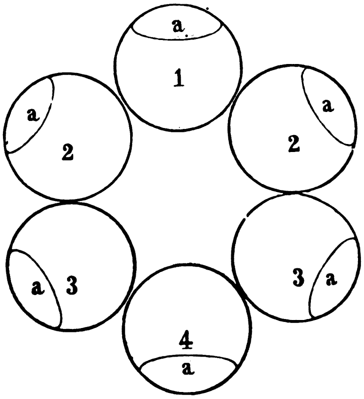


Figure 1. Werner's view of the benzene ring

other hand, will be placed largely in the shadow by the ortho carbon atoms and will therefore be illuminated only by very little light, which, in addition, will be weakened by [its traveling through] a greater distance. Finally, the para carbon atom 4 will indeed receive a significant amount of light, but its effect will be considerably weakened by its still greater distance from atom 1.

"[Something] quite similar will be true of the exchange of affinity. Thus, the greatest amount of affinity force will come into play and in equal amounts between the ortho carbon atoms. Only a very slight exchange of affinity will be able to take place between the meta carbon atoms. Also, this will be diminished by the very significant, even though unknown, decrease in affinity with [increasing] distance of the atoms. The para carbon atoms will be bound to each other by rather large amounts of affinity force, but the para bonding will have the least stability because of the relatively farthest distance of both atoms.

"Thus in the benzene molecule, one will be able to speak of neither single, nor double, nor diagonal (para) bonds in the ordinary sense of the word. Of the structural formulas [proposed] for benzene up to now, the concept which comes closest to this one is that which von Baeyer designated as the centric formula, of course, in terms of the usual theory."

By means of such assumptions, Werner was able to account for certain previously unexplained phenomena, such as the formation of Δ^2 tetrahydroterephthalic acid by reduction of $\Delta^{1,3}$ dihydroterephthalic acid. It must be admitted, however, that this so-called 1,4 addition to conjugated double bonds was later explained in a more satisfactory manner by Johannes Thiele's theory of partial valences.

Although the Werner *Benzoltheorie* had its advocates (*6*), it also had its critics. For example, A. W. Stewart raised two important objections to the Werner formula (*62*). First, the theory did not explain why six, and only six, carbon atoms are required to form a benzene nucleus and endow it with aromatic character. Secondly, it gave no clue to the relations between the ortho and para positions and among the meta positions other than the fact that the affinities between the atoms belonging to these two sets are not the same. In short, although Werner's structure for benzene has been superseded, his approach to the problem was an unusual and unique one. Indeed, we might not be too partisan if in Werner's refusal to acknowledge single directed valence forces we catch a glimpse of the current view of benzene which involves delocalized electrons.

Ammonium Salts

In the first section of this paper, we discussed Werner's views of the structure of trivalent nitrogen compounds. We shall now consider briefly his ideas on what was formerly known as quinquevalent nitrogen but now known as tetracovalent nitrogen. From the very inception of his coordination theory, Werner regarded metal ammines as "compounds which are formed from ammonia and metal salts according to the same reaction by which ammonium chloride is formed from hydrochloric acid and ammonia" (*30*, *98*). It is not surprising, therefore, that he should apply the tenets of this theory to ammonium salts which he logically regarded as "the simplest metal-ammines" (*98*).

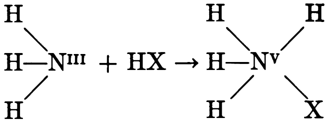
Before considering the spatial arrangement of the groups around the nitrogen atom in ammonium salts (configuration) we must first consider how, and in particular how many, groups are linked to the nitrogen atom (constitution). The three contending constitutional formulas for ammonium salts, together with the proposed schemes for their formation, are as follows:

Constant Valence Molecular Formula
(*Molekülformel*)

$$H_3N + HX \rightarrow [(H_3N)(HX)]$$

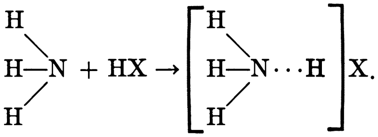
I

Variable Valence Formula
(*Valenzformel*)



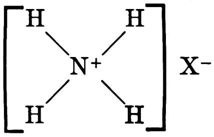
II

Werner's Auxiliary Valence Formula
(*Nebenvalenzformel*)



III

Formula I, according to which ammonium salts were regarded as "molecular compounds," was proposed by Kekulé as an attempt to preserve his dogma of constant valence. Formula II, proposed by Frankland and the advocates of variable valence, involved the formation of five bonds by nitrogen, a situation recognized as impossible by modern orbital theory. Formula III, the one which with minor modification to

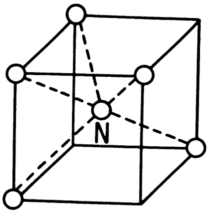


is universally accepted today, distinguishes sharply between ionizable and nonionizable valence a generation before Kossel and Lewis enunciated their concepts of electrovalence and covalence, respectively. Werner also was the first to recognize clearly a maximum coordination number of four for nitrogen and other elements in the second period (Li-Ne) of the periodic table. According to Werner, "the nitrogen of the ammonia still possesses a free auxiliary valence (*Nebenvalenz*) which is saturated by an auxiliary valence of the hydrogen of the HCl." He thus regarded nitrogen not as quinquevalent but as tetravalent. In a formal sense, the nitrogen is bound to the four hydrogen atoms by three main valences (*Hauptvalenzen*) and one auxiliary valence (*Nebenvalenz*), all of which are identical according to Werner.

In 1875 Victor Meyer, Werner's first scientific adversary, adduced experimental evidence favoring Formula II by discrediting Kekulé's formulation of ammonium salts as molecular or addition compounds of trivalent nitrogen (Formula I). He showed that the same quaternary ammonium salt was formed in the following two reactions (*44*):

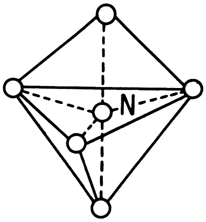
$$\begin{tikzcd}(CH_3)_2NH + 2C_2H_5I \arrow[dr] & \\ & N(CH_3)_2(C_2H_5)_2I + HI, \\ (C_2H_5)_2NH + 2CH_3I \arrow[ur] & \end{tikzcd} \qquad (1)$$

According to Kekulé's formula, however, two isomeric products, $(CH_3)_2(C_2H_5)N \cdot C_2H_5I$ and $(C_2H_5)_2(CH_3)N \cdot CH_3I$, should result. With the Kekulé formula effectively discredited, we can consider the spatial configurations proposed for the *Valenzformel* (II) and the *Nebenvalenzformel* (III). The three models suggested for quinquevalent nitrogen (Formula II) are as follows:



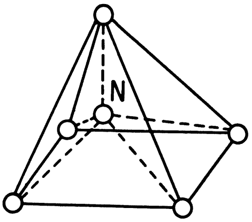
IV

Cube
van't Hoff, 1877 (*20, 21*)



V

Trigonal Bipyramid
Willgerodt, 1888 (*124, 125*);
Burch and Marsh, 1889 (*9*)

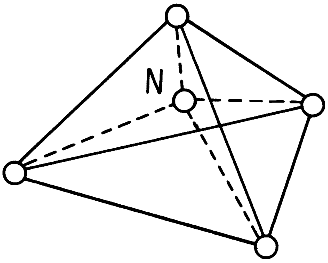


VI

Tetragonal Pyramid
Bischoff, 1890 (*5*)

Although not applicable to nitrogen, which is necessarily limited to a covalence of four, Structures V and VI have been found for a number of compounds of other elements (*14, 15*), but Structure IV has not been found to correspond to any compound exhibiting coordination number five.

Opposed to these three models in constitution as well as in configuration was Werner's regular tetrahedron, VII, which assumes four equivalent valence bonds instead of five valence bonds, not all of which are equal.

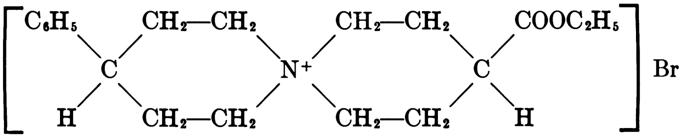


VII

Werner, 1893 (*30, 79, 98, 99, 116*)

We cannot permit ourselves the luxury here of considering the experimental evidence which resulted in the eclipse of all the quinquevalent models by Werner's tetracovalent model, but we can say that the technique of "isomer counting," i.e., the comparison of the number and types of isomers actually prepared with the number and types theoretically predicted for the different configurations, played a prominent role here just as it did in establishing Werner's octahedral configuration for cobalt(III). Also, the previously mentioned fact (Equation 1) that one and the same ammonium compound is formed, regardless of the path of the reaction or the order of introduction of ligands, shows the four valence bonds of nitrogen to be equivalent, thus eliminating the cubic (IV) and trigonal bipyramidal (V) structures. Although the tetragonal pyramidal model (VI) still implied the existence of more isomers than the experimental data justified, it was nevertheless widely accepted for many years until the work of Mills and Warren (1925) decided conclusively in favor of Werner's tetrahedral model.

After covalence and electrovalence were clearly distinguished, and after it had been recognized that strong electrolytes are ionized even in the solid state, the controversy over the configuration of ammonium salts became a struggle for supremacy between the idea of a tetragonal pyramid deprived of its fifth valence bond (X in Formula VI) and Werner's tetrahedral model (VII). Unfortunately, with very few exceptions, the successful resolutions of compounds of type [NABCD]X, while representing strong evidence in favor of a tetrahedral configuration, were also compatible with the tetragonal pyramidal model. The numerous resolutions of such compounds (*24, 25, 26, 38, 57, 58, 63, 64, 65, 66, 67, 68*) accomplished during Werner's lifetime, did not permit a definite decision to be reached. Six years after Werner's death, however, Mills and Warren's resolution (*53*) of 4-phenyl-4′-carbethoxy-bispiperidinium-1,1′-spirane bromide (*49*), shown below, into optical antipodes provided definitive proof for the tetrahedral configuration, inasmuch as a pyramidal configuration permitted geometric but not optical isomerism for this compound. The final, unassailable, and most direct proof was obtained three years later by x-ray diffraction.



Ralph W. G. Wyckoff, one of the contributors to this symposium volume, found that the nitrogen atom in tetramethyl and tetraethyl ammonium halides is surrounded tetrahedrally by the methyl or ethyl groups (*128*, *129*).

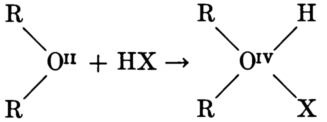
Oxonium Salts

Ammonium salts constitute only one type of a large class of compounds known as "onium salts." The monopositive cation of these salts consists of a central atom of an element from Periodic Group V(N,P,As,Sb,Bi), VI(O,S,Se,Te), or VII(Cl,Br,I), which is bonded covalently to hydrogen atoms, organic radicals, or a combination of these. Onium salts, in which oxygen is the central atom, are known as oxonium salts. Although Werner made a number of important experimental studies of oxonium salts, and even discovered several new types of such compounds (*78*, *90*), his theoretical views are of primary interest here.

Werner's paper, "Ueber die Constitution der Oxoniumsalze" (*113*), appeared concurrently with his article on ammonium salts (*116*). Because his views of these compounds are a direct application of his concepts of ammonium salts, and because he considered only the constitution of these compounds but not their configuration, his research on oxonium salts can be treated quite briefly. The three contrasting constitutional formulas and the proposed schemes of formation are strictly analogous to their ammonium salt counterparts as the reader can verify (*See* Formulas I, II, and III on p. 53):

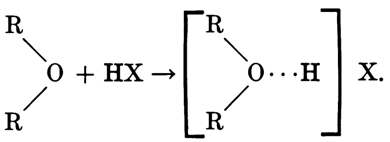
Constant Valence Molecular Formula (*Molekülformel*) $R_2O + HX \rightarrow [(R_2O)(HX)]$ VIII

Variable Valence Formula (*Valenzformel*)



IX

Werner's Auxiliary Valence Formula (*Nebenvalenzformel*)

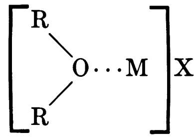


X

The Kekulé constant valence Formula VIII, which viewed oxonium compounds as molecular compounds formed by adding acid to an organic oxygen compound, was displaced by the Collie-Tickle (*10, 11*) and Baeyer-Villiger (*3, 4*) variable valence Formula IX involving tetravalent oxygen. Just as Werner postulated that the trivalent nitrogen atom in ammonia still possesses a residual affinity (*Nebenvalenz*), he maintained that the divalent oxygen atom in water, ethers, alcohols, aldehydes, ketones, and other organic oxygen compounds possesses a similar residual affinity. According to Werner, then, the oxygen in oxonium salts is not tetravalent but trivalent (two *Hauptvalenzen* and one *Nebenvalenz*).

Werner's concept of oxonium compounds has, of course, been amply confirmed, and its wide applicability has proven extraordinarily useful in treating large classes of compounds, especially dyestuffs, from a unified point of view. Its practical application in this area is treated in this symposium volume by David H. Wilcox, Jr. (Chapter 7). Werner's formulation X can be used to represent extremely varied types of substances, such as "addition compounds" of metal salts with organic compounds

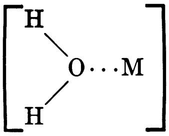
(H = M, i.e.,



X),

metal hydrates

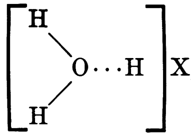
(R = H, H = M, i.e.,



X),

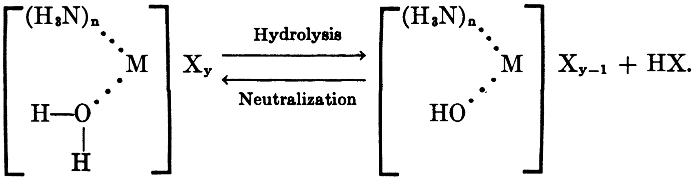
and the simplest inorganic oxonium salts, the hydrates of acids

(R = H, i.e.,



X,

hydronium salts). He also viewed metal aquoammines as oxonium salts and thus explained their behavior as acids on hydrolysis, as well as their re-formation from metal hydroxoammines by combination with acids (*see* below). Such relationships have brought us to our next topic.



(2)

Metal Aquoammine *Metal Hydroxoammine*

Acid-Base Theory

In his oxonium theory of acids and bases (*91*), Werner anticipated by 16 years the now generally accepted views of Brønsted (*7*, *8*) and Lowry (*40*, *41*), which accords that acids are proton donors and bases are proton acceptors. Yet, despite the fact that Werner was the first to emphasize the critical role of the solvent in acid-base phenomena, his contributions to this field are almost universally ignored.

The systematic study of acid-base properties of coordination compounds was initiated in 1906 by Werner's former student and co-worker, Paul Pfeiffer (*55*), who found that hydroxoammines of chromium could react with acids to form oxonium-like aquo salts which could in turn react with bases to reform the original compound:

$$[\mathrm{Cr\ py_2(H_2O)_2(OH)_2]Cl} \underset{2\mathrm{NH_3}}{\overset{2\mathrm{HCl}}{\rightleftarrows}} [\mathrm{Cr\ py_2(H_2O)_4]Cl_3}. \qquad (3)$$

Realizing the significance of Pfeiffer's results, Werner conducted a systematic and thorough search for similar compounds. Within a year he had prepared, investigated, and arranged in order of basicity 10 series of complex hydroxoammines of cobalt (*83*, *84*, *87*, *88*, *89*), chromium (*107*), ruthenium (*85*), and platinum (*86*) which showed relationships to their corresponding aquo salts that were analogous to those discovered by Pfeiffer. In a close approximation to the Brønsted-Lowry definition of a base, Werner attributed the decrease in basic strength of these compounds to differences in their affinities for hydrogen ions.

From the time of his first paper on the coordination theory in 1893 (*30*, *98*), Werner had been aware of the role of the solvent in electrolytic dissociation and had insisted that hydration, i.e., aquation, preceded ionization. In his paper, "Zur Theorie der Basen" (1907) (*91*), he applied this concept to his new definition of a base: "Any compound, which with water forms a hydrate which dissociates in aqueous solution into a complex positive ion and hydroxyl ions, is an anhydro base. . . . Aquo bases, or simply bases, are water addition compounds which in aqueous solution dissociate into hydroxyl ions." For example:

$$[\mathrm{Co(NH_3)_5OH]Cl_2} + \mathrm{H_2O} \rightarrow [\mathrm{Co(NH_3)_5H_2O]OH\cdot Cl_2} \rightarrow$$
$$[\mathrm{Co(NH_3)_5H_2O}]^{+3} + \mathrm{OH}^- + 2\mathrm{Cl}^- \qquad (4)$$

Hydroxo Compound	*Aquo Compound*
(Anhydro Base)	(Aquo Base)
(Contains non-dissociating hydroxyl groups)	(Contains dissociating hydroxyl groups)

In keeping with his emphasis on the role of the solvent, Werner postulated that the basic properties of an anhydro base result not from the *splitting off* of hydroxide ions, but rather from the *addition* of hydrogen ions. His definition, "Anhydro bases are compounds which in aqueous solution combine with the hydrogen ions of water and thereby displace the dissociation equilibrium of water to a limiting value of the hydroxyl ion concentration characteristic of them," is an obvious harbinger of the Brønsted-Lowry protonic concept of acids and bases. In other words, a hydroxo-aquo equilibrium forms the essential feature of Werner's theory. In direct contradiction to the Arrhenius view, it was now no longer necessary to restrict basic properties to hydroxyl-containing compounds.

Since Werner regarded metal hydroxoammines as metal hydroxides in which some of the hydroxyl groups had been replaced by ammonia molecules, he proceeded to extend his concept of bases to all hydroxide compounds. In this case, however, his characteristic urge to generalize, which had served him so well in his coordination theory, led to less fortunate results. Although his ideas were valid for coordination compounds and other substances containing hydroxyl groups bound covalently to the metal atom, he over-extended his concept by applying it to the ionic hydroxides of the alkali and alkaline earth metals. Thus, his assumption that the basic properties of ionic compounds were due to hydrogen ions from water being added to undissociated molecules of the metal hydroxide:

$$\underset{\textit{Anhydro Base}}{[NaOH]} + H_2O \rightarrow \underset{\textit{Aquo Base}}{[Na(H_2O)]OH} \rightarrow [Na(H_2O)]^+ + OH^-. \tag{5}$$

It is indeed unfortunate that Werner's attempted application of his acid-base concepts to compounds to which they did not apply aroused the antagonism of physical chemists and, consequently, retarded the acceptance of his views in the many areas in which they were valid.

Proceeding from the observation that certain metal aquoammines possessed acidic properties, i.e., underwent hydrolysis, as:

$$[Co(NH_3)_4(H_2O)_2]X_3 \rightarrow [Co(NH_3)_4(H_2O)OH]X_2 + HX, \tag{6}$$

Werner extended his concepts of anhydro and aquo bases to acids—for example,

$$\underset{\textit{Anhydro Base}}{PtCl_4} + 2H_2O \rightarrow \underset{\textit{Aquo Base}}{H_2[PtCl_4(OH)_2]} \rightarrow 2H^+ + [PtCl_4(OH)_2]^{-2}. \tag{7}$$

Just as he had done with bases, he generalized his concepts to include simple as well as complex compounds. For example, he accounted for the acidic properties of the hydrohalogen acids not by the incorrect Arrhenius dissociation:

$$HX \rightarrow H^+ + X^- \qquad (8)$$

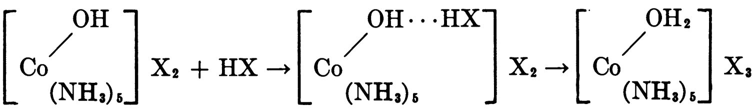
but rather by the reaction of the anhydro acid HX with water to form an aquo acid which then dissociates:

$$\underset{\textit{Anhydro Acid}}{HX + H_2O} \rightarrow \underset{\textit{Aquo Acid}}{H[X(H_2O)]} \rightarrow H^+ + [X(H_2O)]^-. \qquad (9)$$

Except for the fact that Werner considered the halide ion rather than the proton as hydrated, his postulated process is, in some respects, similar to the currently accepted Brønsted-Lowry view:

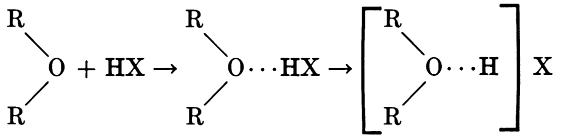
$$HX + H_2O \rightarrow [H{\cdot}H_2O]^+ + X^-. \qquad (10)$$

Werner also applied his ideas to hydrolysis, neutralization, basic salts, and other related topics. In view of our considerations earlier in this paper, it is interesting to note that Werner regarded neutralization reactions, in which hydroxo compounds react with acids to form aquo salts (*83*)



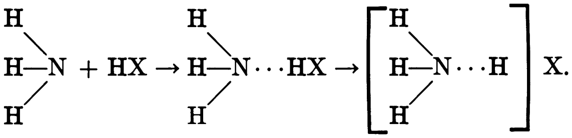
(11)

as completely analogous to the formation of organic oxonium salts by the reaction of organic oxygen compounds with acids (*113*)



(12)

and to the formation of ammonium salts from ammonia and acids (*116*)



(13)

Although some of Werner's ideas of acids and bases were only partially correct, many anticipated and are completely consistent with modern views. In applying his acid-base concepts to complexes, Werner was invariably correct. It was when he attempted to explain all acid-base phenomena, including those of simple compounds, by the same mechanism that he went astray. Nevertheless, after perusing the contributions of Pfeiffer, Bjerrum, Chugaev, Grinberg, Brønsted, Lowry, and others to the acid-base theory of complexes, it is clear that in this area of coordination chemistry, as in so many others, many of the theoretical and experimental foundations were erected by Alfred Werner.

The Hydrogen Bond

In other ways too Alfred Werner was ahead of his time. The concept of the hydrogen bond has customarily been attributed to Latimer and Rodebush (1920) (*37*) and to Huggins (1922) (*23*), but we find speculations about such a linkage in the previous work (1912) of Moore and Winmill (*54*) in their attempt to explain the weakly basic character of trimethylammonium hydroxide. However, the idea was adumbrated as early as 1909 by Werner in the second edition of his *magnum opus*, "Neuere Anschauungen auf dem Gebiete der anorganischen Chemie" (*96*):

"In any case, the existence of these [acid fluorides] and similar compounds is related to the fact that hydrogen fluoride is not monomolecular but bimolecular. [Association due to hydrogen bonding is now known to proceed beyond the bimolecular state—G. B. K.] In order to explain the bimolecular condition of hydrogen fluoride, the following constitutional formula is still frequently used today: $HF=FH$. This has contributed appreciably toward bestowing a certain illusion of validity to analogous formulas for double fluorides. But these formulas are undoubtedly incorrect, for the assumption of a reciprocal linkage of two fluorine atoms is highly improbable. For fluoro salts this follows from their analogy to other halogen salts, and in hydrogen fluoride the hydrogen must play a major role in forming polymeric molecules, for its substitution by alkyl [groups] nullifies the capacity for polymerization; the alkyl fluorides are monomolecular. However, this participation of hydrogen in the polymerization can only occur by virtue of the fact that it can participate as the central atom of a halogen acid anhydride. But then the constitutional formula $H(F \cdot H \cdot F)$ must be assigned to bimolecular hydrogen fluoride, and the acid fluorides showed be viewed as salts of hydrodifluoric acid, $R(F_2H)$. The properties of hydrofluoric acid, such as its weak strength and electrolytic conductivity, as well as the existence of acid fluorides, find a simple and suitable explanation in the proposed formula."

The Periodic Table

Beyond the shadow of a doubt, the most important unifying concept in chemistry is Mendeleev's periodic law. Hence, it is only natural that Werner, the great systematizer of inorganic chemistry, should turn his classificatory talent to the improvement and development of this most fundamental of chemical generalizations. Although his name is not usually associated with the periodic table today, Werner's particular version of the table was both popular and widely used, especially during the early decades of the present century. We must also remember that the Werner table, in common with those of others, has appeared in textbooks in grossly modified forms without being so designated by name (*59, 60, 61*).

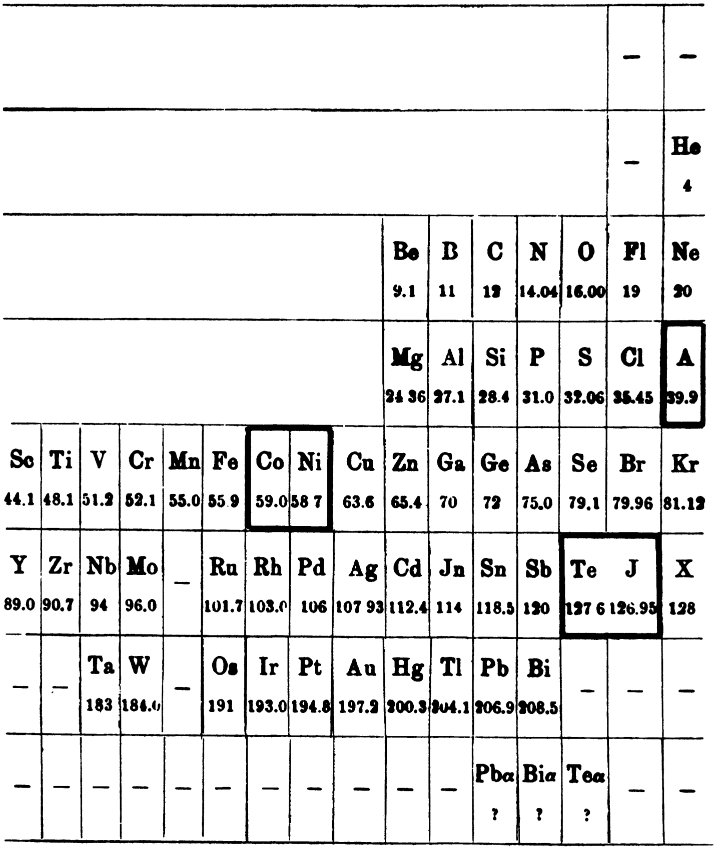
The difficulties experienced in fitting the iron-platinum metal group and the rare earths satisfactorily into the periodic table were attributed by Werner to the short form of most tables then in use and to the attempts in such tables to preserve and multiply what he considered to be trivial analogies. Accordingly, in 1905 (*81, 82*) he devised his own modification, which spread out the elements into what Mazurs, in his comprehensive survey of periodic tables (*42*), has called a long table with interrupted short and medium periods.

—																
H 1.008																
Li 7.03																
Na 23.05																
K 39.15	**Ca** 40.1															
Rb 85.4	**Sr** 87.6															
Cs 133	**Ba** 137.4	**La** 138	**Ce** 140	**Nd** 143.6	**Pr** 140.5	—	—	**Sa** 150.3	**Eu** 151.79	**Gd** 156	**Tb** 160	**Ho** 162	**Er** 166	—	**Tu** 171	**Yb** 173.0
—	**Ra** 225	**Laα** ?	**Th** 232.5	—	—	—	—	—	**U** 239.5	—	—	—	—	—	**Ac** ?	—

Figure 2. Werner's

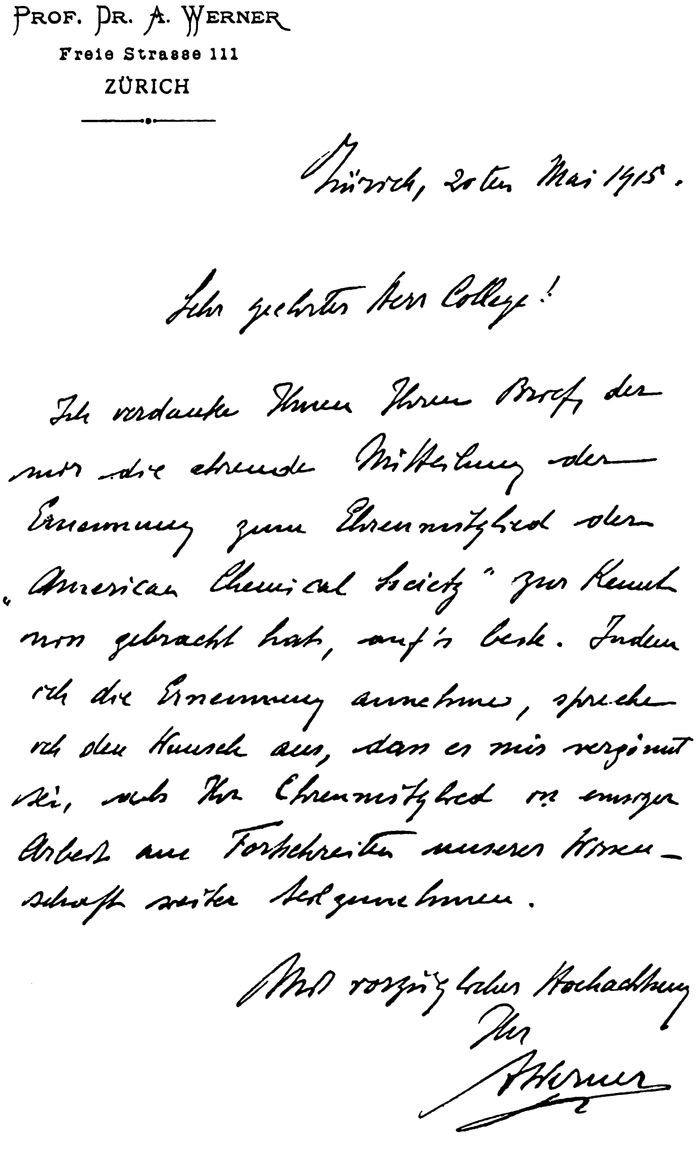
In what was one of the most successful long-form horizontal tables (Figure 2), Werner divided the elements into eight periods which occurred as four pairs of different but numerically related characteristic lengths. To the first two periods he allotted three elements each; to the third and fourth periods, eight elements each (3 + 5); to the fifth and sixth periods, 18 elements each (3 + 5 + [2 × 5]); and to the seventh and eighth periods, 33 elements each (3 + 5 + [2 × 5] + [3 × 5]). He showed that the mean difference in atomic weight between two consecutive elements increased from the third (Li-Ne) period (1.85) to the sixth (Rb-Xe) period (2.5), and he used this relationship to estimate by extrapolation the number of elements to be allotted to the other periods. In this manner, he arrived at a number of conclusions that would be regarded today as strange and bizarre.

For example, Werner estimated the mean difference in atomic weight between consecutive elements in the period containing H (atomic weight,



														–	–
														–	He 4
									Be 9.1	B 11	C 12	N 14.04	O 16.00	Fl 19	Ne 20
									Mg 24.36	Al 27.1	Si 28.4	P 31.0	S 32.06	Cl 35.45	A 39.9
Sc 44.1	Ti 48.1	V 51.2	Cr 52.1	Mn 55.0	Fe 55.9	Co 59.0	Ni 58.7	Cu 63.6	Zn 65.4	Ga 70	Ge 72	As 75.0	Se 79.1	Br 79.96	Kr 81.12
Y 89.0	Zr 90.7	Nb 94	Mo 96.0	–	Ru 101.7	Rh 103.0	Pd 106	Ag 107.93	Cd 112.4	Jn 114	Sn 118.5	Sb 120	Te 127.6	J 126.95	X 128
–	–	Ta 183	W 184.0	–	Os 191	Ir 193.0	Pt 194.8	Au 197.2	Hg 200.3	Tl 204.1	Pb 206.9	Bi 208.5	–	–	–
–	–	–	–	–	–	–	–	–	–	–	Pbα ?	Biα ?	Teα ?	–	–

periodic table



PROF. DR. A. WERNER
Freie Strasse 111
ZÜRICH

Zürich, 20ten Mai 1915.

Sehr geehrter Herr College!

Ich verdanke Ihnen Ihren Brief, der mir die ehrende Mitteilung der Ernennung zum Ehrenmitglied der „American Chemical Society" zur Kenntnis gebracht hat, auf's beste. Indem ich die Ernennung annehme, spreche ich den Wunsch aus, dass es mir vergönnt sei, als Ihr Ehrenmitglied an emsiger Arbeit am Fortschreiten unserer Wissenschaft weiter teilzunehmen.

Mit vorzüglicher Hochachtung
Ihr
A Werner

Courtesy Edgar Fahs Smith Memorial Library of History of Chemistry, University of Pennsylvania, Philadelphia, Pa.

Letter to Dr. Charles H. Herty, president of the American Chemical Society, acknowledging his election to honorary membership in ACS

Translation: I thank you most heartily for your letter which brings me the good news of my appointment as an honorary member of the American Chemical Society. In accepting the appointment, may I express the wish that as an honorary member I may have the privilege of participating in work which will advance the progress of our science.

1.008) and He (atomic weight, 4) as 1.5. He therefore considered it highly probable that an additional element, "perhaps the prototype of the negative element," should exist above F and between H and He. By assuming that each type of period occurs twice in the periodic table, he reached an even more far-fetched conclusion—*viz.*, that an additional period consisting of three as yet undiscovered elements should exist above the H-He period! Werner apparently persisted in these illusions throughout his lifetime, for although this first hypothetical period is depicted in the table only in the first (1905) edition of "Neuere Anschauungen," it is discussed in all editions with the exception of the fifth (posthumous) edition (1923). The hypothetical negative element is both shown in the table and discussed in the text of the first four editions.

Before judging Werner too harshly for what may strike us today as an almost mystical faith in the significance of numbers, let us not forget that Mendeleev himself had similarly predicted two elements lighter than hydrogen (*27, 39*). Indeed, before Moseley's discovery of atomic numbers in 1913, there was no certain way of predicting the exact number of possible elements, a fact which, for example, had rendered research on the elements, particularly the rare earths, extremely confusing. In attempting to establish theoretically the possible number of elements of different types then, Werner was merely pursuing a legitimate scientific activity—the search for regularity and order in nature.

In his periodic table, Werner arranged the elements in the order of increasing atomic weight, as was customary in that pre-Moseley period. However, he inverted the order so as to conform more closely to chemical properties in four cases—(1) Ar before K; (2) Co before Ni; (3) Te before I; and (4) Nd before Pr. The first three inversions had long been recognized by Mendeleev; in these cases, the apparent anomaly disappears when atomic numbers rather than atomic weights are used as the basis of classification. The fourth inversion, one original with Werner, is unjustified and resulted from his overzealous preoccupation with recurring numbers.

In his search for regularity, Werner noted that cases (1) and (3) occur at or near the end of his fourth and sixth periods, respectively, while cases (2) and (4) occur six or seven places beyond cases (1) and (3), respectively. Since Co precedes Ni in case (2), he assumed that Nd should likewise precede Pr in the corresponding parallel case (4). As further evidence for such an inversion, Werner cited the similarities in color of the salts (Co^{+2} and Nd^{+3}, pink; Ni^{+2} and Pr^{+3}, green).

Werner's great contribution regarding the periodicity of the elements lay in his recognition that periods are of different lengths and in his attempt to predict the number of elements in each period. He was able to deal satisfactorily with the transition elements and rare earths and to avoid periods containing two or more series, yet because the seventh (cesium) period of 33 elements determined the width of the table, and because the rare earths were arranged side by side, his table was unnecessarily long. This disadvantage was later overcome by Werner's ex-protégé, Paul Pfeiffer (*56*), who relegated the rare earths to a position at the bottom of the table. Though in some respects Werner's proposals were incorrect, in other respects they have been confirmed by the modern theory of atomic structure, in particular by the concepts of *Aufbauprinzip*, quantum numbers, and the Pauli exclusion principle.

Acknowledgment

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5

Alfred Werner and Cobalt Complexes

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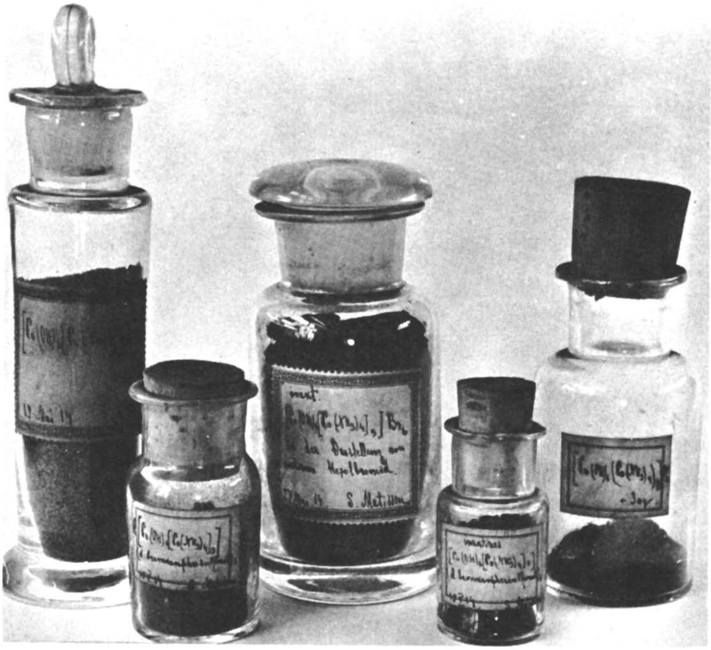
The experiments by Werner and his associates on cobalt coordination compounds accomplished two things: they increased the chemical knowledge in this extensive area (more than 700 compounds) and helped Werner develop his ideas on coordination theory and stereochemistry. It was only after he had received the Nobel Prize (1913) and after his death (1919) that his ideas of primary and secondary valence were confirmed. Unfortunately, Werner's span of active life was short (1893–1915). A listing is given of his co-workers who researched cobalt compounds. These resulted in 52 papers by Werner, 75 with co-authors, and at least 10 unpublished theses. Research to 1960 on cobalt coordination compounds has been summarized in "Gmelins Handbuch der anorganischen Chemie" (1963).

Alfred Werner (December 12, 1866–November 15, 1919) during his professionally active life (1893–1915) contributed extraordinarily to the knowledge of cobalt coordination compounds. These compounds, no doubt, helped him develop his ideas that resulted in the two theories that made him a leader in two phases of twentieth century chemistry: coordination theory and stereochemistry.

Werner presented his coordination theory in 1893, and his investigations and thoughts on cobalt compounds were presented in a series of 52 papers authored by him and 75 papers with associates (Table I). The names commonly used for these compounds are: complex ions, Werner complexes, coordinated complexes, coordination compounds, or simply complexes. His first lecture on cobalt compounds was probably the one given on "Neue Kobaltiake," September 1896, before the Schweizerische Naturforschende Gesellschaft of Zürich. A most important lecture in his life was no doubt his acceptance of the 1913 Chemistry Nobel Prize (*4*) in

Stockholm, Sweden. The last lecture, as the first, was given in Geneva, September 14, 1915, before the same society on "Cobalt Compounds with Asymmetric Cobalt and Carbon." It is perhaps significant that 12 of his papers in the *Berichte* between 1911 and 1914 carried the title "Toward the Knowledge of the Asymmetric Cobalt Atom." At least seven other lectures on cobalt compounds were given by Werner to national and international meetings (*2*). The most important of these papers is now available in translation (*3*). It is suspected that some researches on the cobalt compounds were not published in the years that Werner spent as a professor at Zürich (1893–1919) and are recorded only in theses at the University of Zürich (Table II). Shortly after his death, two of his biographers (*1*, *6*) mention that more than 200 thesis investigations had been made under his inspiration and supervision.

In 1898 there appeared an English translation of Werner's "Stereochemistry Among Inorganic Substances" (*7*). In this paper he pointed out that for "molecular compounds" constitution cannot be presented with the aid of valence unless one resorts to several secondary hypotheses, each applicable to only a limited number of compounds. He illustrated the differences in the chemical behavior of $Co(NH_3)_6Cl_3$ and $Co(NH_3)_5Cl_3$, as well as in their electrical conductivity in solution. He called attention to the series of intermetallic compounds intermediate between true molec-



Samples of tris[tetrammine-μ-dihydroxocobalt(III)]cobalt(III) salts, the first carbon-free coordinate compound to be resolved, 1914

Table I. Cobalt Compounds (*1*)

Year	*Co-Author*
1893–1896	A. Moliati
1897	P. Ferchland A. Klein R. Klein
1898	A. Mylius F. Beddow H. Grüger F. Steinitzer
1899	W. Spruck A. Vilmos
1900	F. Bräunlich R. Klien H. Müller
1901	L. Gerb A. Gubser C. H. Herty E. Humphrey
1903	N. Goslings
1904–1905	A. Grün E. Berl R. Feenstra A. Wolberg
1906	R. Feenstra E. Bindschedler
1907	E. Berl G. Jantsch E. Zinggeler A. Baselli F. Bräunlich F. Rogowina K. Dawe A. Fröhlich G. Jantsch C. Kreutzer E. Zinggeler
1910	E. Bindschedler & E. Welti
1910, con't.	J. Furstenberg M. Grigorieff E. Kindscher A. Salzer M. Pieper F. Steinitzer & K. Rücker
1911	V. L. King E. Scholze
1912	W. E. Böes L. Gerb, S. Lorie & J. Rapiport H. Hartmuth R. Bosshart F. Chaussy L. Cohn
1912	McCutcheon K. R. Lange P. Larisch G. Lindenberg M. Pokrowska C. Rix Y. Shibata R. Samanek G. Tschernoff
1913	M. Basyrin
1914	E. Bindschedler & C. Sackur R. Bosshart W. J. Bowis, A. Hoblik, H. Schwarz, & H. Surber H. Kuh & P. Wust
1915	E. Blatter, C. Sackur, H. Schwarz, & H. Surber
1918	P. Karrer S. Matissen
1921	J. E. Schwyzer & P. Karrer

ular compounds and double salts (double chlorides, fluorides, nitrites, etc.). He wrote, "There can be no doubt that the first salt contains three atoms of chlorine identical in properties and acting as ions, while the second contains only two that can act in that way.

"We have now to get an idea of the configuration of these groups MA_6; the most simple hypothesis that can be formulated is an octahedral arrangement, the metallic atom occupying the center of the octahedron. The six groups A will have their places at the corners.

"It is evident that this arrangement should give rise to certain cases of stereomerism, of which we shall consider at present only one, which experiment confirms."

From G. B. Kauffman, "Alfred Werner—Founder of Coordination Chemistry," Springer-Verlag, Berlin-Heidelberg-New York, 1966

Werner as a young Privat-Dozent, 1892 or 1893

Werner and his co-workers (Tables I and II) proceeded in a very systematic fashion, and a series of cobalt compounds was not only made but was also identified, and properties were noted or measured (color, chemical reaction, electrical conductivity, and optical properties). Some of his students and co-workers continued to investigate cobalt compounds after having accepted positions in other universities or returned to their native countries.

Table II. Theses at the University of Zürich on Cobalt Compounds, 1893–1921

Year	*Name*	*Gmelins Handbuch (Page)*	*Subject*
1904	P. Larisch	48, 133	"Über die Abhängigkeit der Löslichkeit von der Anzahl der Ionen bei den Kobalt-Chrom-, Rhodium-, Iridium-, und Platin-Ammoniaken"
1912	A. Gordienke	52, 56, 77, 88, 112, 149, 251, 252, 263, 353	"Untersuchungen über die Beziehungen zwischen Farbe und Konstitution chemischer Verbindungen"
1913	H. Seibt	149, 227, 228	"Über stereoisomers Difluoro- und Fluoro-ammin-diaethylendiaminkobaltisalze"
1914	J. Angerstein	74, 75, 77, 79, 100, 125, 135, 152, 155, 283, 353, 360	"Über die Absorptionsspektren von Metallammoniaken"
1915	W. Tupizina	242, 272	"Untersuchungen über die optische Aktivität von Kobaltverbindungen"
1919	R. von Arx	86, 183, 272	"Über aktive Isorhodanatommindiathylendiamin - Kobaltisalze"
	O. Dätwiler	264	"Zur Kenntnis der optisch-aktiven *cis*-Bromonitrodiaethylendiamin-Kobaltisalze"
	H. Fischlin	168, 169, 170, 259, 260	"Über optisch aktive Chloroaquodiaethylendiaminkobaltisalze"
	I. Wilbuschewitsch	140, 260, 270	"Über Diacido-diaethylendiaminkobaltisalze"
1921	C. Schleicher	52	"Über Absorptionsspektren von Komplexsalzen"

"Gmelins Handbuch der anorganischen Chemie," Eighth Edition, System No. 58, Part B, 1930, on "The Amines of Cobalt," is the only one of the separate volumes on metal amines in Gmelins' series that includes Werner's work. This book refers to the literature from 1799, the year of the discovery of the first cobalt-ammonium salt, to the year 1929. In this volume of 376 pages, more than 2400 cobalt compounds are listed, 700 of which refer to Werner and his associates. Some additional compounds and special investigations are available but, as mentioned earlier, are only available in thesis publications (Table II). The work on cobalt coordination compounds to 1960 has been summarized in "Gmelins Handbuch der anorganischen Chemie," System 58, Supplement to Part B, Section 1, 1963, and Section 2, 1964.

Although Werner's new chemical concept was developed in 1892 when he was only 26 years old and a Privat-Dozent at the Zürich Polytechnikum, general acceptance did not come until 1911. That year was probably the high point of Werner's career because it was then he resolved the racemic molecules of the 1,2-chloroammine bis (diethylenediamine) cobalt (III) salts. This discovery shook the chemical theory of the time. With this he proved the octahedral formula of a metal compound with 6-coordinate valency, for only this arrangement explained optical symmetry which he had proposed many years before.

With cobalt (III) complexes, all possible stereochemical changes have been observed. It is remarkable that Werner obtained his results by isolating the products of the reaction and estimating qualitatively the ratio of the isomers produced.

It is significant that Werner devised his concepts by considering the conductivity behavior and geometry of central metal atoms. He carefully tabulated lists of known compounds of the ammonia-complex type. Note the cobalt compounds listed on the abcissa in Figure 1. By using the metal as a central element, Werner surrounded it with a constant number—six molecules or ions in the case of cobalt compounds. He suggested that the attractions that held these molecules and ions to the central metal were secondary valences, which he termed "coordination number." The evidence for his interpretation was the conductivity behavior of these compounds (Figure 1). The conductivity is highest for those compounds that

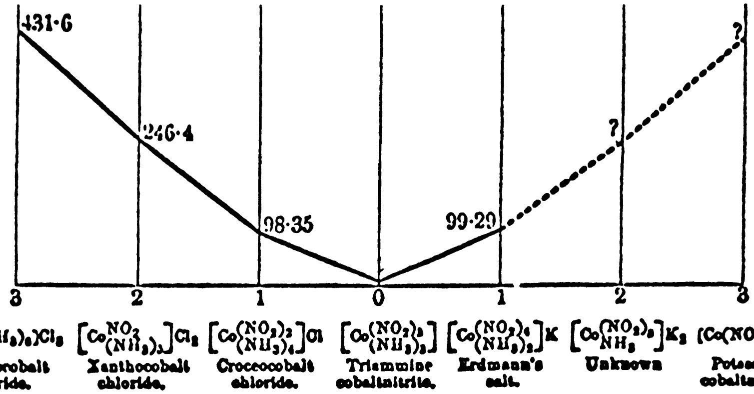


Figure 1. Conductivity of complex cobalt compounds

dissociate into the largest number of ions (considering the part within the square brackets as forming only one ion). As a negative ion enters the coordination sphere, the conductivity falls, reaching a zero value for $[Co(NH_3)_3(NO_2)_3]$, where dissociation is no longer possible.

Courtesy Frau Dr. Anna Elisabeth Ernst

Werner at his desk, ca. 1905

Besides explaining the ammonia complexes in this manner, Werner extended the same kind of reasoning to hydrates, cyanides, thiocyanates, amine complexes, cyanates, carbonyls, and similar compounds. He also reasoned that there must be isomerism owing to the arrangement of ions in the inner, or coordination, sphere and the outer sphere where ordinary, or primary, valence relations hold—e.g., $[Co(NH_3)_5CL]Br_2$ and $[Co(NH_3)_5Br]ClBr$.

Treating the 6-coordinate spheres in geometrical fashion, Werner demonstrated the possibilities for cis and trans isomerism. If the metal is considered to be at the center of a regular octahedron, the coordination valences will be directed to the six corners, giving two possible arrangements for the compound of the type MA_4B_2. According to Werner, then, a metal atom can combine with a definite number (usually four or six) of other atoms, ions, or molecules and coordinate them into a definite geometrical arrangement about itself.

While Werner's ideas of primary and secondary valence were not well received during his lifetime, shortly after his death (1920) they were confirmed by Kossel, who laid the foundation for the electronic theory of valence. Furthermore, at about the same time, Wyckoff and Dickinson both confirmed Werner's theory by x-ray diffraction studies of these types of compounds.

It is of interest that covalent compounds of bivalent cobalt can decompose H_2O with liberation of H_2, whereas the trivalent cobalt ion decomposes H_2O, liberating O_2, being one of the most powerful oxidizing agents known (*5*). These materials should have a use in modern aerospace problems.

In summary, it is now agreed that coordination concepts are valuable in explaining a wide variety of inorganic phenomena of theoretical and practical nature, such as the stabilization of unusual oxidation states, analytical implications of metal complexes, and the industrial use of complexing agents. Aside from the ammines and the hydrates, discussed mostly by Werner, there are many important types of coordination compounds, such as complex cyanides of heavy metals, metal carbonyls (formed in the catalysis of petroleum products and used to produce metals), and others.

The three symposia in 1966 are the tribute to Werner of a grateful generation of chemists. As a result many papers will be published in addition to two new books on his life and works (*2*, *3*).

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(1) Karrer, P., *Helv. Chem. Acta* **3**, 196 (1920). (This has an extensive, but not complete, bibliography of Werner's publications.)
(2) Kauffman, G. B., "Alfred Werner — Founder of Coordination Chemistry," Springer-Verlag, Berlin-Heidelberg, New York, 1966.
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(6) Pfeiffer, P., *J. Chem. Educ.* pp. 1090–1098, September, 1928.
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6

Polynuclear Complexes of Cobalt(III) Ammines

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The chemistry of non-peroxo polynuclear cobalt(III) ammines is reviewed with particular emphasis on Werner's major contributions. Modern work in this area has shown that Werner's conclusions regarding the structures of these compounds are substantially correct in spite of the relatively primitive techniques he had available. There is much current interest in polynuclear cobalt(III) complexes because of their relationship to oxygen carriers and intermediates in electron transfer reactions. Modern techniques such as spectroscopy and x-ray diffraction have been used to determine the electronic and molecular structures of these compounds.

Polynuclear cobalt(III) ammine complexes were first prepared as long ago as 1852, when Fremy (*6*, *7*) prepared the diamagnetic μ-peroxodecamminedicobalt(III) ion by oxidizing an aqueous ammoniacal cobalt(II) solution with air. In the next few decades, work centered on preparing the diamagnetic and paramagnetic μ-peroxo-dicobalt complexes (*14*, *26–28*, *39*). Because the μ-peroxo-dicobalt complexes have been adequately discussed in two recent reviews (*5*, *11*), they will not be discussed here.

In the first decade of the 20th century, Werner published a series of 10 papers in which he reported the results of extensive investigations on the preparations and structures of a large variety of polynuclear cobalt(III) ammine complexes (*29–34*, *36–38*, *40*). In the last paper of this series (*29*), Werner reviewed the results of his investigations by summarizing the results which led to his proposed structures.

The polynuclear cobalt(III) complexes which Werner prepared were principally ammines, although in some cases ethylenediamine was used as the ligand. The complexes contained a variety of bridging groups in

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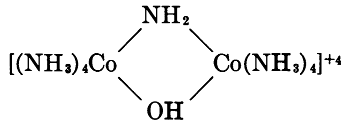
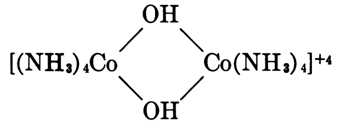
different combinations: peroxo, hydroxo, nitro, amido, acetato, and sulfato. The complexes contained two, three, or four cobalt atoms with up to six bridging groups. Some typical polynuclear cobalt(III) complex ions are:

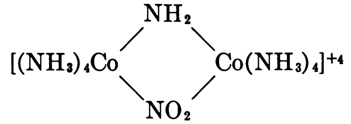
$$[(NH_3)_5CoNH_2Co(NH_3)_5]^{+5} \qquad (I)$$



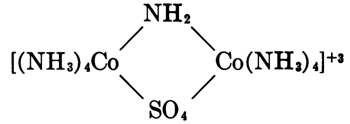
$$[(NH_3)_4Co\overset{NH_2}{\underset{OH}{\qquad}}Co(NH_3)_4]^{+4} \qquad (II)$$



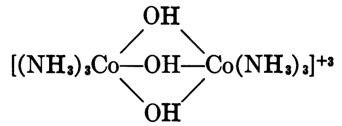
$$[(NH_3)_4Co\overset{OH}{\underset{OH}{\qquad}}Co(NH_3)_4]^{+4} \qquad (III)$$



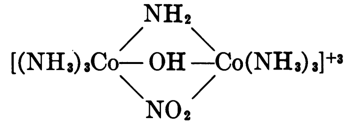
$$[(NH_3)_4Co\overset{NH_2}{\underset{NO_2}{\qquad}}Co(NH_3)_4]^{+4} \qquad (IV)$$



$$[(NH_3)_4Co\overset{NH_2}{\underset{SO_4}{\qquad}}Co(NH_3)_4]^{+3} \qquad (V)$$

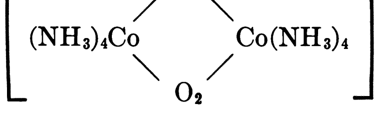


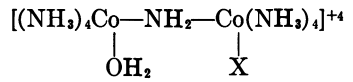
$$[(NH_3)_3Co\overset{OH}{\underset{OH}{-OH-}}Co(NH_3)_3]^{+3} \qquad (VI)$$



$$[(NH_3)_3Co\overset{NH_2}{\underset{NO_2}{-OH-}}Co(NH_3)_3]^{+3} \qquad (VII)$$

$$[Co\{(OH)_2Co(NH_3)_4\}_3]^{+6} \qquad (VIII)$$

The polynuclear complexes are generally prepared from intermediate products obtained from oxidizing aqueous ammoniacal cobalt(II) solutions in air. When air is bubbled through such solutions at a moderate rate for about eight hours, a solid originally called the Fuskosulfate, now known as Vortmann's sulfate, is obtained (*27*, *28*, *31*). This reddish-black solid contains as its principal component μ-amido-μ-sulfato-octamminedicobalt(III) sulfate (the sulfate of V) and small amounts of the binuclear peroxo complex  $\left[(NH_3)_4Co\overset{NH_2}{\underset{O_2}{\qquad}}Co(NH_3)_4\right](SO_4)_2$. Vortmann's sulfate may be converted to the sulfato nitrate (the nitrate of V) by treating it with nitric acid. Hydrolysis of the sulfato bridge with acid (HX) results either in formation of a hydroxo-bridge (II) or an unsymmetrical amido-bridged complex, such as



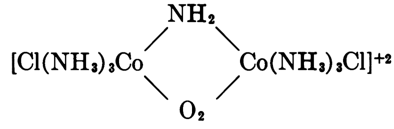
$$[(NH_3)_4\underset{\underset{OH_2}{|}}{Co}—NH_2—\underset{\underset{X}{|}}{Co}(NH_3)_4]^{+4}$$

which may be converted to the μ-amido-decamminedicobalt(III) ion (I) by treating it with liquid ammonia. In this way, Werner prepared many substituted amido-bridged complexes (*29*, *34*). The complete preparation has been given by Werner (*29*, *34*) and more recently by Vannerberg (*23*) and Chester (*3*).

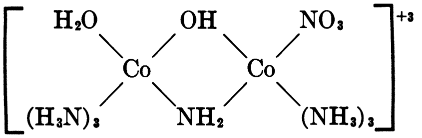
An aqueous ammoniacal cobalt(II) chloride solution oxidized very slowly with air yields small amounts of a solid known as the melanochloride (*26*, *27*). Werner proposed (*29*) that this solid contains as its major component the ion

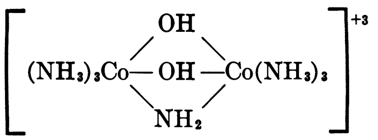
$$[(Cl)(H_2O)(NH_3)_3CoNH_2Co(NH_3)_3Cl_2]^{+2}$$

with small amounts of the ion



Werner found that melanochloride treated with various reagents led to a variety of doubly- and triply-bridged species incorporating an amido bridge. From the melanochloride, he prepared ions such as:





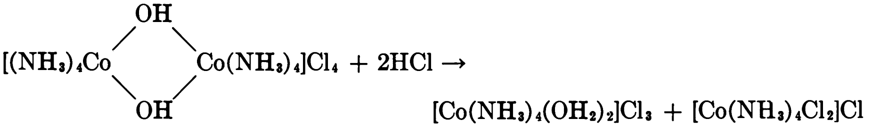
etc., as well as various unsymmetrical mono-bridged ions (*29*). The hydroxo bridges in these and other ions can be easily replaced with other simple anionic groups such as nitro, acetato, and oxalato by heating with the simple salts. However, Werner found no way to insert either amido or peroxo bridges; these bridges result only from the air oxidation.

The complex ions containing only hydroxo bridges (III and VI) are of interest because these are the only polynuclear cobalt(III) species which can be prepared directly from mononuclear cobalt(III) complexes. These ions are prepared by removing two moles of water from two moles of solid starting material—e.g., the sulfate of III is obtained by heating hydroxoaquotetramminecobalt(III) sulfate (*30*):

$$2[Co(NH_3)_4(H_2O)(OH)]SO_4 \rightarrow 2H_2O + [NH_3)_4Co(OH)_2Co(NH_3)_4](SO_4)_2$$

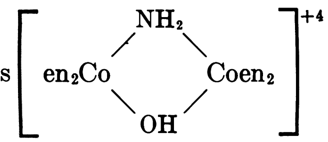
Werner proposed structures for the polynuclear complexes on the basis of both elemental analysis and chemical information. His primary chemical information was obtained from splitting the polynuclear complexes (usually by heating with concentrated acids) and determining the products. Thus, from reactions such as the following he was able to deduce the structures of the original compound. He also used the many interconversion reactions of the complexes to deduce their structures.

$$[(NH_3)_5CoNH_2Co(NH_3)_5]Cl + HCl \rightarrow [Co(NH_3)_6]Cl_3 + [Co(NH_3)_5Cl]Cl_2$$



$$[(NH_3)_4Co(OH)_2Co(NH_3)_4]Cl_4 + 2HCl \rightarrow [Co(NH_3)_4(OH_2)_2]Cl_3 + [Co(NH_3)_4Cl_2]Cl$$

$$[(NH_3)_3Co(OH)_3Co(NH_3)_3]X_3 + HX \rightarrow [Co(NH_3)_3(H_2O)_3]X_3 + [Co(NH_3)_3X_3]$$

It is of some interest to note that Werner was able to replace the NH_3 ligands with ethylenediamine only when the configuration on each end of the complex was that of a tetrammine fragment. Thus, he was able to prepare a complex such as  $[en_2Co(NH_2)(OH)Coen_2]^{+4}$ but was apparently unable to prepare unsymmetrically chelated species such as $[en_2(NH_3)CoNH_2Coen_2(NH_3)]^{+5}$. Even today such complexes cannot be prepared.

Perhaps Werner's *tour de force* in the area of polynuclear cobalt(III) complexes was his successful resolution of the "hexol" ion (VIII). He prepared this ion and its ethylenediamine analog by heating a basic solution of *cis*-diaquotetramminecobalt(III) sulfate and deduced its structure by observing that the acid cleavage gave back the *cis*-diaquo complex and cobaltous ion (*37*). He later resolved the ion into its optical antipodes with *d*-camphor sulfonic acid and *d*-bromocamphor sulfonic acid and obtained the D- and L- forms as the bromides (*35*). His successful resolution of this completely inorganic ion conclusively demonstrated the octahedral structure of mononuclear cobalt(III) complexes and put the octahedral structure on an equal footing with the tetrahedral.

Photograph by Herr Richard Taubenest

Partial view of Werner's collection of coordination compounds at Universitat Zürich

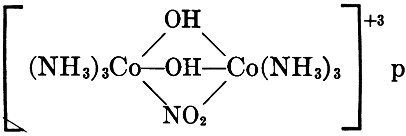
Since Werner's work, there have been relatively few reported investigations of polynuclear cobalt(III) complexes. Vannerberg has determined the structures of the di-μ-hydroxooctamminedicobalt(III) ion (III) (*24*) and the μ-amido-decamminedicobalt(III) ion (I) (*23*) by x-ray crystallography. Prout (*19*) has independently determined the structure of the dihydroxo compound. The structure of the dihydroxo compound may be described as two octahedra sharing one edge, as expected. In the case of the μ-amido complex, Vannerberg found that the Co-N-Co angle was 144° and that the two $Co(NH_3)_5$ groups were in an "eclipsed" configuration.

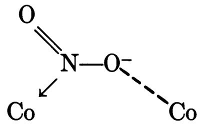
A recent Czechoslovakian patent (*1*) concerned with the separation of Ni and Co has reported isolation of a solid with the formula $[Co_2(NH_3)_{10}(SO_4)_2]SO_3 \cdot 2H_2O$. There seems to be no basis for formulating this compound as binuclear; it would seem more reasonable to assign the constitution as $[Co(NH_3)_5SO_4]_2SO_3 \cdot 2H_2O$.

The electronic spectra of bridged cobalt(III) complexes have been reported by Ohyagi (*18*) and by Inamura and Kondo (*13*). Ohyagi determined the visible and ultraviolet spectra of a large number of Werner's complexes but used relatively primitive (by modern standards) equipment. Inamura and Kondo examined the hydroxo-bridged complexes exclusively.

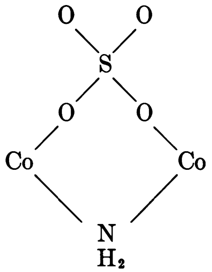
Reibel (*20, 21*) has investigated the polarography of some polynuclear ammines in connection with polarographic investigations of the peroxo-bridged complexes. He found a single stage, three-electron reduction to Co^{+2} for the polynuclear complexes.

Infrared spectra have been reported by Blyholder and Ford for hydroxo-bridged complexes (*2*), Vannerberg (*25*) for a variety of complexes, and Hewkin and Griffith (*12*). The IR spectra of polynuclear and mononuclear cobalt(III) ammines differ little because the dominant bands are due to the NH_3 ligands. However, Blyholder and Ford (*2*) assign a strong band at 530 cm.$^{-1}$ to a motion of the cobalt-oxygen four-membered ring, and Vannerberg (*25*) has assigned some weak bands to vibrations of the -NH_2- and -OH- bridging groups.

Infrared studies provide a means of determining the mode of attachment of various polyatomic bridging groups, such as nitro and sulfato. Nakamoto and co-workers (*16*) have found that the nitro group in the ion  $\left[(NH_3)_3Co\overset{OH}{\underset{NO_2}{\text{—OH—}}}Co(NH_3)_3\right]^{+3}$ probably bridges through a nitrogen and an oxygen atom:



Nakamoto *et al.* (*17*) and Tanaka *et al.* (*22*) have demonstrated that the sulfato bridge in the sulfato nitrate (nitrate of V) has C_{2v} symmetry and is thus bidentate. The structure of the bridging group in V is then most likely shown as:



Such a structure would, however, result in highly strained, bond angles. Thus, positive proof must wait upon single crystal x-ray diffraction studies.

The bridging acetato group has not been investigated in polynuclear cobalt complexes. The acetato ion may bridge through one or both of the carboxyl oxygens. Although it seems likely that both oxygens are involved in bridge formation, such a structure needs to be confirmed. As in the sulfato bridge, a bidentate bridge would result in a highly strained structure because the acetato group always occurs with other (smaller) bridging groups (OH^-, NH_2^-), unlike the acetate dimers observed with other metal ions (e.g., cupric acetate).

In a recent study of the electronic and vibrational spectra of the μ-amido-decamminedicobalt(III) ion (I), Chester and Brubaker have assigned the spectral bands on the basis of molecular orbital and normal coordinate analysis calculations (*34*). They concluded that the two halves of the ion (the $Co(NH_3)_5$ groups) are electronically independent of each other and assigned the electronic transitions on the basis of a simple tetragonal crystal field with axial compression. The calculations also supported the conclusion that the bonds in the Co-N-Co bridge are very similar to simple $Co\text{-}NH_3$ bonds.

Mast and Sykes (*15*) have recently investigated the kinetics of interconversion reactions of some binuclear cobalt(III) ammines. They have reported both chemical and kinetic evidence for the existence of the diaquo complex $[(H_2O)(NH_3)_4CoNH_2Co(NH_3)_4(H_2O)]^{+5}$, a complex not previously prepared. Garbett and Gillard have reported similar interconversions with ethylenediamine ligands (*8*) and have assigned optical configurations (*9*).

A thorough review of the preparations and physical properties of the polynuclear cobalt complexes is given in "Gmelins Handbuch der anorganischen Chemie" (*10*).

In spite of the many modern techniques available to the chemist, the known chemistry of polynuclear cobalt(III) complexes is essentially that deduced by Werner 60 years ago. Since his work, no new polynuclear cobalt complexes have been prepared and characterized and no new reactions uncovered. Modern work in this area is being aimed at attaining a better understanding of the electronic structures inherent in polynuclear ions, which would be of value in a variety of active fields. The chemistry of polynuclear complexes is important in such new areas as synthetic oxygen carriers, electron transfer reactions, and transition metal catalysis. The fact that these new investigations are solidly based on Werner's pioneer investigations testifies to the genius with which he opened up a new area of coordination chemistry, with only the simple chemical techniques available to him. His work in the area of polynuclear cobalt(III) ammine complexes should continue to serve as a model of "solid" research for some time to come.

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7

Werner and Dyes

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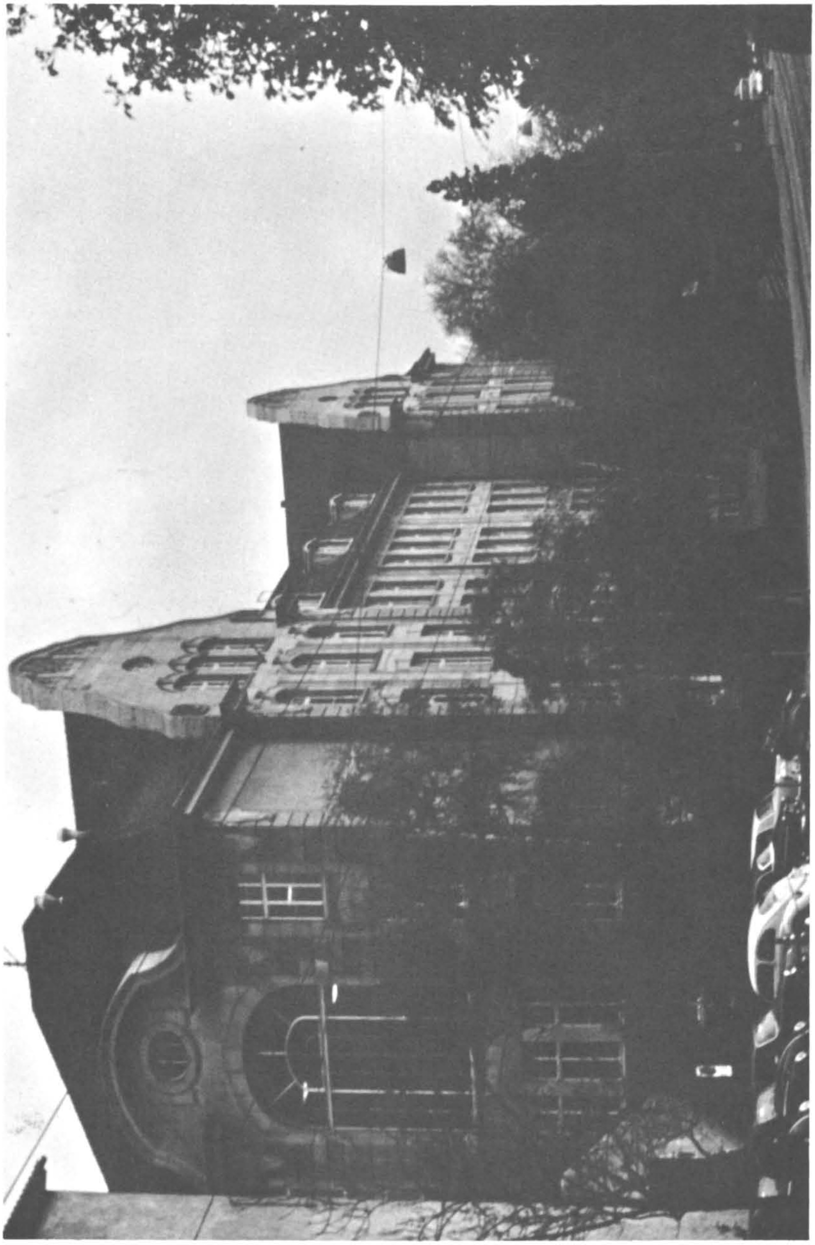
Alfred Werner was born in Mulhouse, the great Alsatian textile dyeing center. Here he formed a lifetime friendship with Emilio Noelting, an outstanding dye chemist. Later, at Zurich Federal Technical College, the great school for dye researches, he studied under Arthur Hantzsch of aromatic diazo compounds fame. Werner's first paper, with Hantzsch, was on the spatial arrangement of compounds with carbon and nitrogen bonded together. Out of this work came the "variable valence" idea which culminated in the coordinated structures. Werner wrote three papers on the theory of mordant dyeing. However, it was in the subsequent application of the coordination concept to certain chemical classes of dyes—e.g., phthalocyanines and ortho hydroxy azo compounds—that its value lies.

Kekulé's theory of "constant or fixed" valency undoubtedly helped Werner and Hantzsch develop their theories of the stereoisomeric forms of oximes and diazo compounds. However, Werner soon felt that Kekulé's ideas were too rigid and, being convinced that sufficient facts were now at hand to justify a new theory, outlined one for "variable" valency. He then spent the rest of his life producing experimental proofs. This is not the whole story, but it can serve to introduce Alfred Werner. Two of his pupils may be quoted: Paul Pfeiffer (*29*): " 'A Contribution to the Constitution of Inorganic Compounds,' . . . marks Werner as the founder of the modern views in this field and insures to him a rank in the history of chemical thought equal to that of August Kekulé." Ernst Berl (*3*): "Werner's coordination theory was developed in 1893 and explains the composition of compounds of first and higher order—the so-called 'molecular compounds', . . . It was afterward applied with success to organic problems and is the most important enlargement of Kekulé's doctrine of valence."

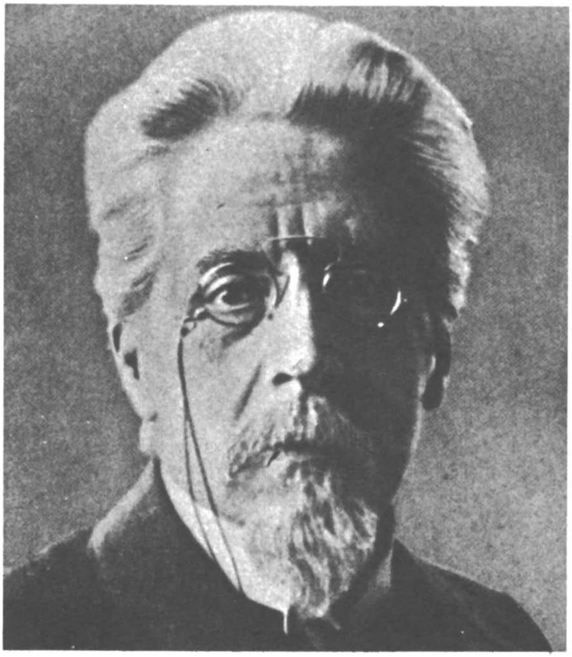
Alfred Werner was born December 12, 1866, at Mulhouse in Alsace, the son of a factory foreman. His mother was Jeanette Tesché before her marriage. Young Werner took what little money he could earn and set up a chemical laboratory in a part of his father's barn. Here he ran some experiments, wrote them up, and submitted the paper to Emilio Noelting for criticism, along with the naive inquiry as to how long it would take to become a professor. The city of Mulhouse was the center of the Alsatian dyeing industry, and Professor Noetling (*30*), a great dye chemist, was director of the school of chemistry at Mulhouse. Noelting's answer came back saying that the chemical work was neat in appearance, but that there was still much to be done, and that becoming a professor takes time. This reply did not cause Werner to lose his enthusiasm for chemistry (*13*, *23*, *27*). After a period in the army he matriculated at the Zurich Polytechnical Institute in 1886. This is where Noelting had studied under Victor Meyer and Emile Kopp. Alfred Werner found three great teachers and researchers there: Arthur Hantzsch, Georg Lunge, and Frederic Pearson Treadwell. Hantzsch (*11*) had been a student under Rudolph Schmitt at Dresden and, thus, came by his great interest in diazo compounds quite naturally. Georg Lunge (*2*) had been a pupil of Robert Bunsen at Heidelberg after first obtaining his doctor's degree at Breslau. Treadwell (*31*) was an American, from Boston, who had graduated *summa cum laude* under Bunsen at Heidelberg. He and his son, William Dupré Treadwell, taught analytical chemistry for a total of 74 years at Zurich. This is surprising since they came from seafaring stock.

In 1889 Werner obtained his diploma as a technical chemist and remained as an assistant to Lunge while working for his doctor's degree under Hanztsch. The problem concerned the spatial arrangements of atoms in nitrogen compounds. Kekulé in 1867 had suggested isomerism which his student, J. H. van't Hoff (*26*), had developed and which culminated in his "Spatial Chemistry" in 1875. Werner, knowing of such views, suggested to Hantzsch that nitrogen compounds must exist in different spatial forms just like carbon compounds and put forth the idea that the three valence forces of nitrogen are positioned near the three corners of a tetrahedron, while the nitrogen atom itself occupies the fourth corner. By the following day Hantzsch decided that Werner was right, and they then proceeded along this line of thinking (*3*). Subsequently, in 1890 they published the first paper on the stereochemical configuration of oximes: "On the Spatial Arrangement of Atoms in Nitrogen-Containing Molecules." This was followed in the same year by two further papers entitled: "Notes on the Stereochemical Isomers of Nitrogen Compounds." This idea of the structure of doubly bonded carbon-nitrogen compounds and its elaboration has been regarded by Gilbert T. Morgan as Werner's



University of Zurich Chemical Institute

Werner and Students, 1911



Arthur Hantzsch (from Berichte, 1941)

most important contribution to organic chemistry (*23*). Werner's doctorate thesis was accepted by University of Zurich in 1890 and bore the same title as the first joint paper.

Lunge, noting the progress of his young assistant, said to him, "My dear Werner, you are fired as my assistant. You are too good for this position. I will use my influence to convince your father to let you continue your studies elsewhere and devote yourself to teaching and research." Werner then was able to go to Paris where he spent one semester studying with Marcellin Berthelot at the College de France. Berl is convinced that Lunge provided the money for the time in Paris (*2*).

Upon his return to Zurich, Werner sought a position at the Polytechnic Institute and offered in support his "Contribution to the Theory of Affinity and Valence." In this was his theory of affinity and valency and the constitution of inorganic compounds propounded. Morgan relates (*23*) that Kekulé's theory of constant or fixed valency, which had proved of fundamental importance in the development of organic chemistry, was more or less accepted as the guiding principle in explaining the constitution of inorganic compounds. In this respect it was not helpful; sufficient evidence had already accumulated to show that a theory of variable valency was more in accord with known facts. Werner discarded the idea of constant valency with a fixed number of valency units of equivalent strength operating in certain definite directions and assumed that the chemical affinity of an element was distributed uniformly over the surface of its spherical atom in such a manner that, according to the circumstances attending chemical combination, this affinity could be divided up in a great variety of ways into few or many valency units of varying intensities. Pfeiffer (*3*) felt that in this thesis Werner had disposed of many traditional notions and laid the foundations of a new valence theory. In the fall of 1893, Werner was appointed successor to Victor Merz and, two years later, a full professor at Zurich University.

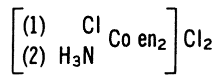
Like many good teachers, Werner spent much time during the evenings preparing his lecture notes; on one particular night he went to sleep with this on his mind and dreamed his coordination theory. According to Pfeiffer, Werner awoke at two o'clock with a start, realizing that he had found the long-sought solution—similar to the way in which Kekulé was inspired for his benzene theory. He arose from his bed and by five o'clock in the afternoon had worked out the essential points of the coordination theory. Berl (*2*) added that "within one week, working day and night," Werner worked out and wrote down the theory of inorganic compounds which was published in 1892 (actually 1893) (*46*, *48*). This publication contains all the elements of his future work, carried out until 1915 when he became ill. Werner's brain had subconsciously worked out his coordination theory of complex compounds. It was in this publication that optical isomers of inorganic molecular compounds were predicted (*3*, *46*, *48*).

The coordination theory which Werner had outlined was subjected in his laboratory to many strict and discerning tests. The results drew many students to Werner at Zurich.

One early pilgrim was Charles Holmes Herty, born in Milledgeville, Ga., a former student of Ira Remsen at Johns Hopkins. Ten years later, Herty came to Zurich to work with Werner for one semester. The result was a joint authorship of the fourth paper, "A Contribution to the Constitution of Inorganic Compounds," published in 1901 (*47*). Herty then moved on to Berlin where he spent a semester with Otto N. Witt. Witt was one of the great dye chemists (*6*, *50*). Herty, after returning home, always championed the cause of American dyes and other organic chemicals. Our splendid, growing organic chemical industry owes much to him.

In 1909 at Zurich Werner had the pleasure of working and teaching in the new chemical institute that he had planned. His work was proceeding with singular success, and the number of his students continued to multiply. One of these pupils was Victor Louis King, born in Nashville, Tenn. and educated at Dartmouth and Columbia. It was his good fortune to be given the problem of finding optically active compounds, and he successfully solved it by preparing the first one. Werner had foreseen the possibility of such compounds, but it was not until 1911 that the resolution of 1:2-chloroamminodiethylenediamine cobaltic chloride was accomplished with the aid of *d*-bromocamphorsulfonic acid (*17*, *18*, *45*).

1:2-Chloroamminodiethylenediamine cobaltic chloride



$$\left[\begin{matrix}(1)\ \mathrm{Cl} \\ (2)\ \mathrm{H_3N}\end{matrix}\ \mathrm{Co\,en_2}\right]\mathrm{Cl_2}$$

Pfeiffer wrote: "This constituted the experimental proof of one of the important deductions of his theory, and in consequence the great significance of the coordination theory for chemical systematics was generally recognized" (*27*). Then Morgan continued with: "This striking confirmation of Werner's views of the configuration of coordination compounds was speedily followed by other analogous resolutions, and optically active compounds of octahedral symmetry are known which contain cobalt, chromium, iron, iridium, platinum, rhodium, and ruthenium as the central metallic atoms (*23*). King wrote about his experience as follows (*16*): "I was extremely fortunate in being able to work out this problem successfully and was able to do it partly because I spent the entire periods otherwise known as vacation to work in the university. After I had essentially developed the possibility of proof, all the tremendous facilities of the university were placed at my disposal. For the work at Zurich, which was published over Werner's name and mine in the reports of the German Chemical Society, I received not only the *summa cum laude* honor but special honors in addition, which were written into my sheepskin. Immediately after the conclusion of this work I was invited by Willstatter of the

Polytechnicum in Zurich and by Pictet of the University of Geneva, to work on some problems with them and to publish the results with them. I elected to work with Willstatter and had the pleasure of working on an attempt to prove that naphthalene was a derivative of benzene. This was of particular interest because while the association with Werner was with a man of tremendous perception, the association with Willstatter was with a man who was primarily a brilliant technician. Willstatter was a man who fairly scintillated with skill and technique of investigation, and the work with him on the reduction of naphthalene with hydrogen proved to be the foundation of the industry which later fluorished in Germany with the production of such solvents and oils for motor spirit consumption as tetralin and decalin. This work was published at length in the German Chemical Society reports. During my stay in Zurich, I made the acquaintance of Lunge, Treadwell, Bamberger, Einstein, etc., and the prominence given to the work which I was doing gave me an opportunity to have a great deal of fellowship with these men, all of whom are famous in chemistry. In my spare time I worked with Dr. Baudisch and together we published a few articles on a material called cupferron which created some interest in America in connection with certain analytical methods."

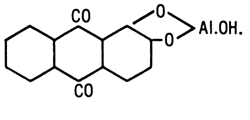
King returned to the United States in 1915 and went to work with Thomas A. Edison. When our country entered World War I, he was asked by Bernard Baruch and Charles McDowell to act as chief of the dyes and intermediates section of the War Industries Board. Through this work he became associated with the Calco Chemical Company, where I came to know him. King was closer to the development and manufacture of dyes and intermediates than was Herty. However, they were two valiant knights who fought lustily to protect and develop the American dye industry.

Pfeiffer wrote (*27*): "Especially in his younger years, Werner made it a practice to discuss the newer work appearing in the literature or his own investigations for hours with his assistants, and he demanded that sharp criticism be exercised during these sessions. His assistants did not always find it easy to follow the trend of his thought, for he had a fabulous memory which extended over the whole field of chemistry, both inorganic and organic, and he could pass from one subject to another with great facility. If the topic chanced to be, say, the isomerism of inorganic complex compounds, the discussion in a few moments would very likely be centered around analogous phenomena exhibited by terpenes, alkaloids, or dyestuffs."

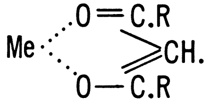
Werner received the Nobel prize in 1913, and about this time began to suffer from arteriosclerosis, but he did not become seriously ill until 1915. Then his assistants, Paul Karrer and Paul Pfeiffer, took over for him until his death on November 15, 1919. Karrer remained at the University of Zurich where his work with the vitamins has brought fame to him and additional fame to the University. Pfeiffer later went to the University of Bonn where he had the chair once held by Kekulé.

The direct contributions made by Werner to dyeing and dyes do exist and must be acknowledged even though they are not extensive. Werner began as a pupil of Hantzsch, and together they worked to extend the concepts of spatial chemistry to the carbon-nitrogen bond, and just as it was extended to the nitrogen-nitrogen bond Werner began to lose interest. This situation was, of course, due to the ascending elaboration of his coordination complexes. He lectured only on organic chemistry until 1902, at which time he then took over the inorganic teaching as well. His papers on the chemistry of phenanthrene (*38*, *39*), on the primary and secondary valences and the constitution of ammonium compounds (*40*), as well as the constitution of oxonium compounds (*41*), were published in 1902.

Back in 1899, Werner and Stiasny (*49*) had studied the action of nitric acid on azobenzene and produced a series of nitro-azobenzenes and nitro-azoxybenzenes, but Werner carried the work no further. Werner then became interested in the analogy between the lakes of mordant dyes and the metallic derivatives of β-diketones and proposed the view that mordant dyes were internal metallic complexes. This resulted in three papers published in the 1908–09 period. The first (*42*), reporting the complex metal salts formed from oximes, diketones, and several metals, came to the conclusion that the formation of mordant dyes depends on the formation of complex metal salts. He found that dyes capable of combining with mordants possessed both a salt-forming complex and a group capable of forming a coordinate link with a metal ion.



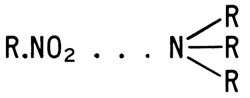
Cycloid structure for alizarin lake



Coordinate linkage for mordant dyes

In a second paper (*43*), Werner reiterated his belief that the cycloid structure of Liebermann's theory (*21*) does not explain the peculiar properties of lakes, as it only affords the metal an opportunity of combining with the organic body by means of its primary valencies.

The final paper (*44*) reported the finding that nitro compounds such as trinitromesitylene and tetranitromethane give colors with aromatic hydrocarbons and amines. Saturated aliphatic compounds give no color with tetranitromethane, but unsaturated aliphatic compounds act like hydrocarbons as long as the ethylene link does not adjoin a carboxyl group. Werner concluded that the colored compounds result from the interaction of subsidiary valencies associated with the nitro group on one hand, and the ethylene or the nitrogen atom on the other, and gave the following structure:

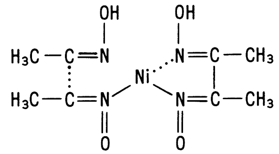


None of Werner's colored compounds were good dyes, but the significant point is that his student, Paul Pfeiffer (*51*, *52*), adopted the coordinate theory of Werner and applied it with success to an expanding group of new and old colored compounds. The applications of the coordinate theory of metal complexes may be separated into the following divisions:

1. Analytical separations
2. Sequestering agents
3. Inorganic dyes and pigments
4. Mordant dyes
5. Metallized azo dyes
6. Fixing of dye to natural fibers
7. Fixing of dye to synthetic fibers

Analytical Separations

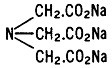
There are quite a number of organic oximes and ketones which are useful in analysis because they form colored, insoluble, coordination complexes with many metals. Cupferron, already mentioned by King, and dimethylglyoxime, whose nickel complex was established by Pfeiffer (*51*), are typical.



Nickel chelate of dimethylglyoxime

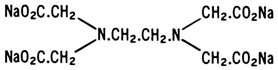
Sequestering Agents

Sequestering agents are any compounds that form water-soluble metal complexes. They are also known as chelating agents, a name given them by Gilbert T. Morgan (*37*). While many carbon structures have been proposed, only two seem to have been exhaustively studied by Pfeiffer (*28*, *29*), Schwarzenbach (*32*, *33*), Martell (*22*), and others. These are nitrilotriacetic acid, NTA, and ethylenediaminetetraacetic acid, EDTA. The original commercial names were Trilon A and B, respectively (*12*).



$$\mathrm{N}\left\langle\begin{matrix}\mathrm{CH_2.CO_2Na}\\ \mathrm{CH_2.CO_2Na}\\ \mathrm{CH_2.CO_2Na}\end{matrix}\right.$$

NTA



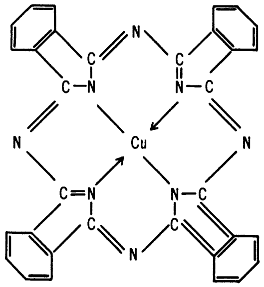
$$\left.\begin{matrix}\mathrm{NaO_2C.CH_2}\\ \mathrm{NaO_2C.CH_2}\end{matrix}\right\rangle\mathrm{N.CH_2.CH_2.N}\left\langle\begin{matrix}\mathrm{CH_2.CO_2Na}\\ \mathrm{CH_2.CO_2Na}\end{matrix}\right.$$

EDTA

As the versatile applicability of these compounds increased, more manufacturers began to make them, with the resulting multitude of trade names. The tetrasodium salt of ethylenediaminetetraacetic acid appears to be the most versatile complexing agent, with one mole reacting with one mole of a divalent metal ion. It is used in scouring textile material, in preparation of print pastes, in dyeing with disperse colors when hard water is used in the process, etc.

Inorganic Dyes— and Pigments

Many inorganic coordination compounds are highly colored, but only a few have amounted to much as commercial items or processes. There was a mineral khaki prepared by treating the fabric with mixed iron and chromium salts, making alkaline, and aging. Prussian blue, a valuable pigment which is a complex of iron cyanides, has been used in dyeing. Then there are the white lead and phosphotungstic and phosphomolybdic acid complexes with triphenylmethane dyes to give strong and fast pigments. With the advent of copper phthalocyanine, Monastral blue, we have a coordination complex which is very valuable as a pigment, and its soluble derivatives are valuable as dyes.

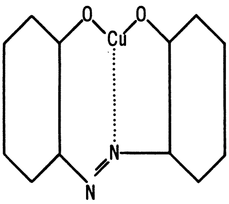


Copper phthalocyanine

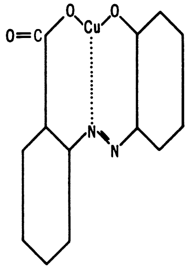
Mordant Dyes

Among the organic dyes and dyeing methods in this category are some which were in use long before there was anything more than an empirical understanding of the relation between the dye and the metal. Obviously, an understanding of mordant dyes as internal metallic complexes has brought improved methods for obtaining dyeings with better tinctorial and fastness properties.

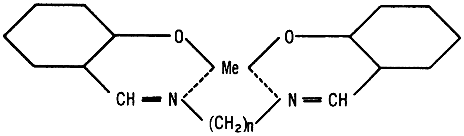
Mordant dyes are believed to be compounds which contain groups capable of acting as electron-pair donors or which contain intramolecular hydrogen bonds capable of reaction with metal ions to form coordinate covalent bonds. Examples of these donor groups are: —OH, —COOH, =O, =NOH, —NH$_2$, and —H. There must be two such groups in ortho or peri positions to each other on condensed benzene rings or, in the case of azo and azomethine dyes, in the ortho positions to the —N=N— and —N=C— linkages. In mordanting, the formation of the metal complex may not be complete, so that in practice there may be present both the coordination complexes and simple metal salts of the dyes.



Copper complex of o,o′-dihydroxyazobenzene

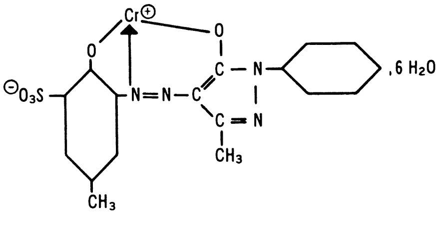


Copper complex of o-hydroxyazobenzene-o′-carboxylic acid



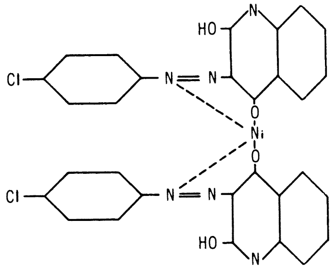
Metal complex of azomethine compound (51)

The type of complex can vary depending upon the dye, the metallic ion, and the reaction conditions. There are too many to be covered here, but commercial examples of the more familiar types might be considered. The first is the 1:1-chromium complex of acid alizarin red C, a zwitterion type (*34*):



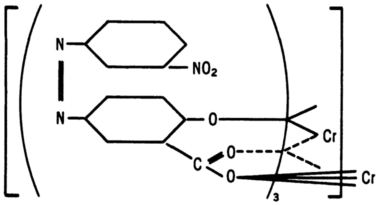
Acid alizarin red C

The second example is a 1:2-nickel complex of C.I. Pigment Green 10 (*19*):



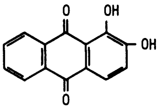
C. I. Pigment Green 10

A third is the chromium complex of alizarin yellow 2G, one of the large group of azosalicylic acid metal complexes (*25*):



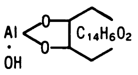
Alizarin yellow 2G

The mordant dyes cannot be left without first giving the pictorial development of the constitution of alizarin and Turkey red lakes. The structure of alizarin, 1,2-dihydroxyanthraquinone (*9*):



Alizarin

The aluminum lake as suggested by Lieberman in 1893 (*20*):

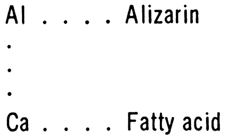


Lieberman 1893

Schlieper's interpretation of alizarin red in 1903 (*10*) is shown on the following page. Morgan in 1920 suggested the metallized complex (*23*) shown below.

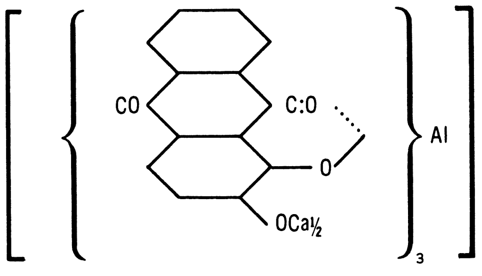
Normal dyed *Dyed hot*

Schlieper 1903



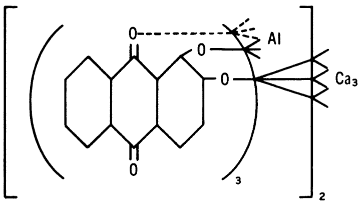
Normal dyed, oiled, and steamed

Schlieper 1903



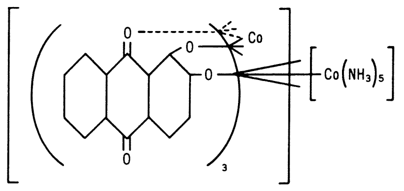
Morgan 1920

Morgan gave his improved formula in 1921 (*24*):



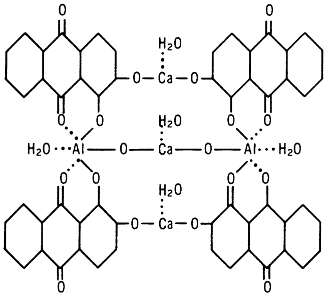
Morgan 1921

In 1921 Morgan represented the cobalt alizarin complex (*24*):

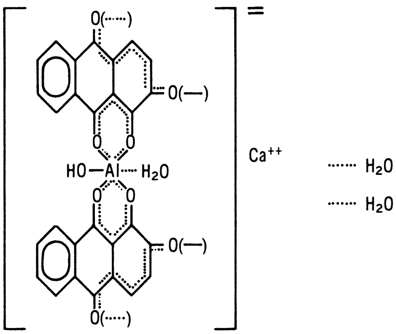


Morgan 1921—Cobalt complex

By 1940 Fierz-David suggested the structure shown on the next page for Turkey red lake (*7*). Kiel and Heertjes in 1965 gave the model for calcium aluminum alizarate (*15*), shown also.



Fierz-David 1940

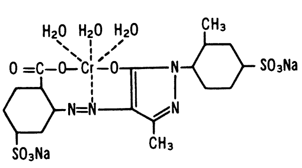


Kiel and Heertjes 1965

Metallized Azo Dyes

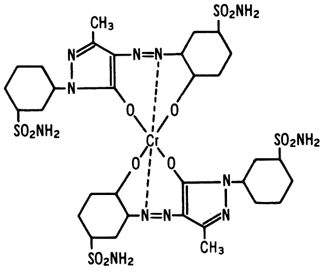
Pre-metallized azo dyes were introduced shortly before World War I, and shortly before World War II metallized wool dyes, known commercially as Neolan and Palatin, came on the market. They were completely metallized azo dyes with shades ranging from yellow to black and were coordinated complexes of chromium. Three examples include (*35*):

Neolan Yellow BE, a 1:1 chromium complex:

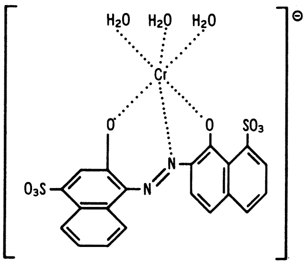


Neolan Yellow BE

Neolan Orange R, a 1:2 chromium complex, and Neolan Blue 2G, a 1:1 chromium complex, are shown on the following page.



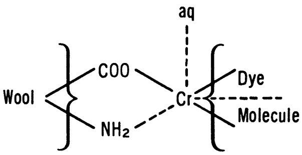
Neolan Orange R



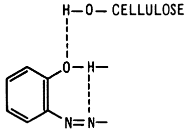
Neolan Blue 2G

Fixing of Dye to Natural Fibers

There is evidence that there exist interactions between dye, metal, and fiber. In the case of wool, when a 1:1 chromium dye complex is present the possibility of covalent linkage between the metal atom and polar groups in the wool molecule exists (*8*):



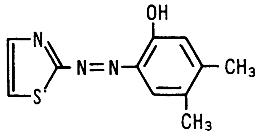
With cotton (cellulose), the direct dyes usually contain *o*-hydroxy- or aminoazo compounds, in which chelation assists in the production of hydrogen bonds between the dye and the cotton (*1*):



Such bonding implies that chelation of the proton with the azo group increases the accessibility of the electron pair involved in the hydrogen bond with the cotton. The chelation of a metal ion would probably result in the formation of a more stable chelate ring but would also introduce the probability of delocalizing the electron pair as well as converting the dye to a cation.

Fixing of Dye to Synthetic Fibers

A pertinent example of the application of Werner's coordination complexes to the coloring of synthetic fibers is exhibited in the case of polypropylene fibers containing nickel. The minute nickel particles have been evenly dispersed throughout the fiber by a chelate "stabilizer," so that upon dyeing with azo disperse dyes bearing the same *o*-substituents, as noted above, a fast deep color is formed (*4*). This example,



is said to give fast deep green shades (*36*).

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8

Some Recent Developments in Coordination Chemistry

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This paper describes catalysts of the type $(R_3Q)_2MX_2$ *(R is an alkyl, aryl, or phenoxy group; Q is P, As, or Sb; M is Ni, Pd, or Pt; X is a halogen or halogenoid. Where M is Pd or Pt, a compound* $M'X_2$ *or* $M'X_4$ *is added (M' = Si, Ge, Sn, or Pb (but preferably Sn, which forms the compound* $(R_3Q)_2M(SnX_3)X$*.) In the presence of such a substance, polyunsaturated compounds, especially esters of long chain fatty acids, are hydrogenated until one double bond remains. The hydrogenation is preceded by cis-trans rearrangement of the double bonds and migration of the double bonds along the carbon chain to form a conjugated system. Another research project has shown that certain bacteria can utilize the nitrogen from* D-*[Coen₃]Cl₃, but that* L-*[Coen₃]Cl₃ inhibits their growth.*

It is common to liken a good deed or a wise word to a pebble dropped into the surface of a lake; it sets up a series of waves which travel outward in an ever-widening circle toward some distant and perhaps unknown shore. The analogy is a good one, not only because it is so apt, but also because it raises in each listener's mind a pleasant and sometimes nostalgic picture. We might properly apply this analogy to Werner's theory of the structure of coordination compounds, for certainly it has exerted an ever-widening influence on all branches of chemistry, both pure and applied. It has taken over the major part of inorganic chemistry, has so modified our concepts of bonding that large areas of physical chemistry have been changed, has found a steadily increasing number of applications in biochemistry, has become the backbone of analytical chemistry, and has been more and more widely applied to many aspects of organic chemistry. Nor can Werner's contribution be measured only in terms of ideas—tremendous as that contribution is. It must be measured also in terms of the training of his students, many of whom became distinguished chemists in several fields of chemistry—Yuji Shibata and T. P. McCutcheon in inorganic chemistry, Paul Karrer and Paul Pfeiffer in organic chemistry, Arturo Miolati in physical chemistry, Edmund Stiasny in leather chemistry, Charles H. Herty in industrial chemistry, and John Read, the chemical historian, to name only a few.

Like other analogies, the likening of Werner's theory to the generation of waves when a pebble is dropped into quiet water is not perfect, for the ripples in the lake gradually fade away, whereas the coordination theory has steadily gained in importance and usefulness. The waves are becoming stronger and stronger. It is impossible to measure Alfred Werner's influence on chemistry, both because it is still growing, and because it is woven into the fabric of modern chemistry that one cannot separate it from the contributions of others. Suffice it to say, Werner was one of the few great geniuses of chemistry and certainly the greatest of modern times. All here today are his disciples, and each one of us owes him a great debt.

As is well known, Werner was trained as an organic chemist and, at the time he applied himself to the problem of the structure of complex inorganic compounds, he had very little experience in inorganic chemistry. His theory was not based on his own experimental work but entirely on the experiments of others. How much time he had spent in the study of inorganic complexes, we do not know, except that it was relatively little. His reading was extensive enough, however, to allow him to see a large number of relationships clearly and to synthesize them into the coordination theory which sprang fully grown from the mind of its creator. The experimental work came later. There were many chemists who found fault with the theory, and Werner had to devise and perform a host of experiments to substantiate his ideas. Fortunately, he was able, eventually, to establish the truth of the coordination theory beyond any doubt. It is but fitting that we should honor him in this centennial symposium. The number of papers which have been offered and the range of the topics which they cover tell, far better than I can, the impact which Werner has had.

In this lecture, I should like to outline briefly two pieces of research in coordination chemistry which have held our attention recently. The first of these involves a series of complexes which catalyze the isomerization and hydrogenation of poly-unsaturated systems in a quite specific way. The original goal of the research was to devise a method of hydrogenating the poly-unsaturated esters in soybean oil without producing the fully saturated compounds.

This work has been done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract was supervised by the Northern Utilization Research and Development Division of the Agricultural Research Service. The details of the experimental work, all of which has been done by Hiroshi Itatani, are being published elsewhere. The results of the work have been highly satisfactory, not only from a practical point of view, but also in opening several interesting fundamental questions to which we hope to find answers. The chief properties of these catalysts are:

1) They convert cis double bonds to trans double bonds.

2) They cause the double bonds to move along the hydrocarbon chain, probably in a random fashion, until the double bonds become conjugated.

3) They bring about the reduction of all but one of the double bonds. If any further hydrogenation takes place, it is extremely slow and, in most cases, can be disregarded.

4) Under properly selected conditions, reduction does not take place—only isomerization to the conjugated system.

5) When methanol or a mixture containing methanol is used as the solvent, hydrogenation takes place even in the absence of elemental hydrogen. In that case, the hydrogen is furnished by the alcohol which is converted to aldehyde. Tetrahydrofuran can also furnish hydrogen, and there is some evidence that even benzene can play this role.

Although the generality of these five properties has not been fully explored, the available evidence indicates that the reactions are not confined to the long chain esters but are applicable to a range of compounds.

6) In the hydrogenation of the long chain esters in alcohol solution, ester interchange is quite extensive.

The catalysts which I wish to describe are of the type $(R_3Q)_2MX_2$, where R represents an alkyl or aryl group; Q, phosphorus, arsenic, or antimony; M, nickel, palladium, or platinum; and X, a halogen or halogenoid. When M is palladium or platinum, an excess of a compound $M'X_2$ or $M'X_4$ is added (M' = silicon, germanium, tin, or lead). The catalyst which we have studied most extensively is a mixture of $(\phi_3P)_2PtCl_2$ and $SnCl_2$ which gives the complex $(\phi_3P)_2Pt(SnCl_3)Cl$, in which the tin atom is bonded directly to the platinum atom (*3*, *9*). The fact that an excess of tin(II) chloride must be present suggests that there is an equilibrium,

$$(\phi_3P)_2PtCl_2 + SnCl_2 \rightleftharpoons (\phi_3P)_2Pt(SnCl_3)Cl,$$

and the recent isolation of $[Pt(SnCl_3)_5]^{-}{}_3$ by R. D. Cramer *et al.* (*4*) suggests that the substitution of $-SnCl_3$ for $-Cl$ may go further, with the formation of $(\phi_3P)_2Pt(SnCl_3)_2$. There is no experimental evidence, however, to indicate that this occurs. Under hydrogenation conditions, $(\phi_3P)_2Pt(SnCl_3)Cl$ is reduced to $(\phi_3P)_2Pt(SnCl_3)H$, which has been isolated as an orange-yellow crystalline solid. This is apparently the actual hydrogenation agent. We believe that the -$SnCl_3$ ligand alters the nature of the Pt-H bond to such an extent that the hydrogen atom is readily lost to the organic substrate. We were formerly of the opinion that the platinum and the tin both attached themselves to carbon-carbon double bonds (*2*), but this is evidently not correct because dicyano-bistriphenylphosphine-palladium(II), $(\phi_3P)_2Pd(CN)_2$, and the halo-nickel complexes, $(\phi_3P)NiX_2$, exert the same type of catalytic effects without the addition of tin(II) chloride. The -$SnCl_3$ ligand, like the -CN ligand, apparently alters the nature of the Group VIII metal sufficiently to produce the unusual catalytic effects which, in the case of the nickel complexes, are achieved even with the halo-complexes.

The addition of $SnCl_4$, $GeCl_4$, $GeCl_2$, $PbCl_2$, or $SiCl_4$ to $(\phi_3P)_2PtCl_2$ also effects a change in the catalytic properties of the $(\phi_3P_2PtCl_2$ for, on hydrogenation, the mixtures give larger yields of monoene than does that of $(\phi_3P)_2PtCl_2$ alone. Understandably, the addition of tin(IV) chloride gives almost the same results as the addition of tin(II) chloride.

The germanium compounds are not as effective as the tin compounds. Hydrogenation of methyl linoleate in their presence gives monoene and no stearate, but it also yields a few per cent of other unidentified products. Such materials are not observed when tin chloride is the additive. Lead(II) chloride is less effective for reduction than either germanium(II) or germanium(IV) chloride, and it, too, produces unidentified products. Presumably, $GeCl_2$ and $PbCl_2$ form the ligands -$GeCl_3$ and -$PbCl_3$, though evidence on this is still lacking. The fact that the addition of $SiCl_4$ gives a catalyst which is very similar to that containing $PbCl_2$ is unexpected, and the mode of its action is not yet clear. This is an interesting problem. Conceivably, the silicon can expand the coordination sphere and form the ligand -$SiCl_5$, or the silicon may be reduced to form the ligand -$SiCl_3$. Either of these results would be surprising.

The R_3Q ligands were introduced into the complex to give greater solubility in organic solvents, but, in addition, they play a definite role in forming the catalyst, as is illustrated in Table I. The reactions shown in Table I were all carried out under the same conditions, using methyl linoleate (1.0 g., 3.4 mmoles) as the substrate. The catalyst consisted of the platinum compound (0.34 mmole) and, except in the first two cases, $SnCl_2 \cdot 2H_2O$ (1.7 mmoles). The solvent was a mixture of 30 ml. of benzene and 20 ml. of methanol. The reaction was carried out for 5 hrs. at 90°C. under a pressure of 39.1 atm. of hydrogen. The "dienoate" of the product may not be linoleate, for isomerizations take place easily.

Frankel *et al.* (*8*) have found that the Group V ligand is not essential, and that a mixture of H_2PtCl_6 and $SnCl_2$ is even more selective than is $(\phi_3P)_2Pt(SnCl_3)Cl$. In all probability, the platinum is reduced to the +2 state and forms a complex of the type $H_2[Pt(SnCl_3)_xCl_{(4-x)}]$, and this, upon further hydrogenation, goes to $H_2[Pt(SnCl_3)_xCl_{(4-x-y)}H_y]$.

Table I. The Effect of Varying the Group V Ligand

	Product						
Catalyst	*Unidentified*	*Stearate*	*Monoene*	*Dienoate*	*Cis-trans*[a]	*Trans-trans*[a]	*Trans*[b] (%)
$(\phi_3P)_2PtCl_2$			4.1	95.9			10.3
$(\phi_3As)_2PtCl_2$			47.5	48.0	4.5		43.6
$(\phi_3P)_2PtCl_2$ + $SnCl_2 \cdot 2H_2O$			14.4	42.2	20.4	22.8	64.6
$(\phi_3As)_2PtCl_2$ + $SnCl_2 \cdot 2H_2O$			66.5	19.6	6.6	7.3	74.5
$(\phi_3Sb)_2PtCl_2$ + $SnCl_2 \cdot 2H_2O$	1.4		14.5	74.6	6.8	1.8	77.2
$((\phi O)_3P)_2PtCl_2$ + $SnCl_2 \cdot 2H_2O$		6.2	87.9	5.9			81.8
$(Bu_3P)_2PtCl_2$ + $SnCl_2 \cdot 2H_2O$			2.4	78.4	11.2	8.0	39.2

[a] Cis-trans means cis, trans conjugated dienoate; trans-trans means trans, trans conjugated dienoate.

[b] Trans % means trans isomer (%) as elaidate.

In general, the palladium compounds are more active for hydrogenation than are their platinum analogues. We have used them in the selective hydrogenation of soybean oil methyl ester, which contains approximately 4.2% stearate and 11.5% palmitate, the remainder being linoleate and linolenate. Under conditions similar to those outlined for Table I, but using a mixture of $(\phi_3P)_2PdCl_2$ and $SnCl_2 \cdot 2H_2O$, the linoleate and linolenate were reduced completely to monoenic esters in three hours, the product consisting of stearate, 4.1%; palmitate, 12.0%; and monoenic esters, 83.9%. Even at pressures as low as 13.6 atm., the same result was obtained in the same length of time. At lower temperatures, however, hydrogenation was not complete, as is shown in Table II.

As with the platinum analogue, the palladium compound is activated by the addition of $GeCl_2$, but not as much as by $SnCl_2 \cdot 2H_2O$. For example, in an experiment comparable with the first one in Table II, but using germanium instead of tin, the figures for the last five columns are 50.1%, 20.2%, 4.1%, 10.1%, and 38.8%.

The dicyano-palladium complex $(\phi_3P)_2Pd(CN)_2$ is a remarkably effective catalyst for reduction to monoene, even without adding tin(II) chloride. (It does not combine with tin(II) chloride.) At 90°C., in 12 hrs., it gave 82.8% monoene. At the same time, the percentage of stearate in the product rose to 5.4%, indicating that the dicyano-palladium compound is not quite as selective as the tin-containing catalysts. An attempt

Table II. Reduction with $(\phi_3P)_2PdCl_2$ and $SnCl_2 \cdot 2H_2O$

		Product						
Temp. (°C.)	*Time (Hours)*	*Palmitate*	*Stearate*	*Monoenate*	*Dienoate*	*T or[a] cis-trans*	*Trans-[a] trans*	*Trans[b] (%)*
original oil		11.0	4.4	27.7	49.3	7.6		0.
90	3	12.0	4.1	83.9				69.6
60	3	11.9	4.4	32.2	36.2	7.9	7.3	14.4
60	5	11.8	4.4	32.1	32.8	9.1	9.8	19.8
60	12	11.9	4.3	83.8				71.6
40	12	11.5	4.5	30.2	39.0	8.0	6.8	14.3
24	9	11.4	4.4	29.2	35.5	8.5	10.0	17.4

[a] T or cis-trans means trienoates, including linolenate and cis, trans conjugated dienoate. Trans-trans means trans, trans conjugated dienoate.

[b] Trans % means trans isomer (%) as elaidate.

to hydrogenate methyl oleate with the dicyano complex under these same conditions converted 2.3% of the material to stearate and 2.7% to dienoate. This suggests that the dicyano-palladium catalyst (and perhaps other catalysts of this series) brings about a disproportionation of the substrate. This is a surprising result which must be studied further.

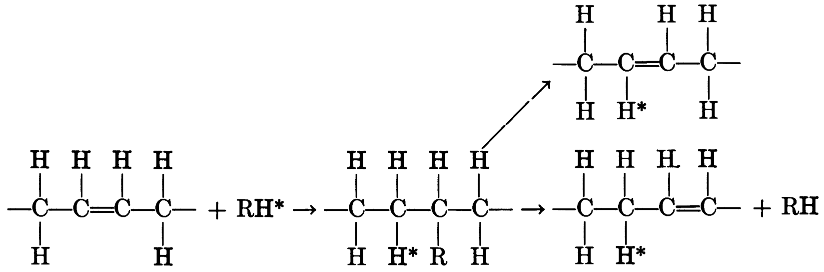
Surprisingly, $(\phi_3As)_2Pd(CN)_2$ is not as effective as its phosphine analogue, $(\phi_3P)_2Pd(CN)_2$, for in 12 hrs. it gave only 38.7% monoene. In general, the platinum compounds are activated more by arsines and stibines than by phosphines, but the reverse is true for the palladium compounds. For example, a mixture of $(\phi_3Sb)_2PdCl_2$ and tin(II) chloride does not catalyze the hydrogenation of dienote, although the corresponding platinum catalyst is reasonably active. Mixtures of triphenylphosphine-palladium dichloride with tin(II) chloride or germanium(II) chloride do not reduce methyl oleate at all, though they may bring about rearrangement from the cis to the trans form. No study has yet been made of this aspect of the reaction.

The bis-triphenylphosphine nickel halides are not activated by tin(II) halides. However, the iodide, $(\phi_3P)_2NiI_2$, is an effective catalyst for the hydrogenation of methyl linoleate to the monoene stage. The bromide is less effective, and the chloride has very little catalytic power. None of these nickel compounds has much ability to bring about isomerization. The nickel compounds are unstable in alcoholic solutions, and the experiments reported in Table III were carried out in either benzene, tetrahydrofuran, or toluene.

As Tables I, II, and III show, isomerization of the esters from the cis forms to the trans forms takes place readily, especially with the platinum complexes. The results will be described in more detail elsewhere. It has also been shown (7) that movement of the double bonds along the chain takes place, and that the monoenate mentioned in the tables is a mixture of mono-unsaturated esters. The double bond appears most abundantly near the center of the chain but is present throughout nearly its whole length. The isomerization precedes reduction and, under some conditions, can be achieved without reduction. In such a case, the isomerization leads to the formation of a conjugated system. The isomerization is important, not only because of its possible value in the synthesis of conjugated compounds, but also because it is necessary if selective hydrogenation is to take place. It probably does not depend upon the presence of more than one double bond, and certainly does not depend upon the presence of two double bonds close to each other because the 9,15-methyl dienoate, $C_{17}H_{31}COOCH_3$, is readily hydrogenated to the methyl monoenoate, $C_{17}H_{33}COOCH_3$, in the presence of $(\phi_3P)_2Pt(SnCl_3)Cl$.

As has already been mentioned, the palladium and nickel catalysts can cause hydrogenation in the absence of elemental hydrogen, in which case the solvent serves as the source of hydrogen. Good yields can be obtained if the solvent contains methanol, and even in THF or benzene poor yields of product can be isolated. Table IV shows some typical results.

The details of the mechanism of this catalysis are still not clear, and many experiments remain to be done. Currently, we believe that migration along the carbon chain involves the reversible addition of a hydrido complex to the double bond. This is supported by the isolation of the isoprene complex, $[(\phi_3P)_2PtCl(C_5H_9)]$, from the hydrido platinum complex, $[(\phi_3P)_2Pt(SnCl_3)H]$ (*1*). The loss of tin(II) chloride in that example may be only incidental, for more recent experiments indicate that hydrocarbon adducts containing the -SnCl₃ ligand can be isolated. If this assumption is correct, both cis-trans isomerization and movement of the double bond can be brought about as follows:



$$-CH_2-CH=CH-CH_2- + RH^* \rightarrow -CH_2-CHH^*-CHR-CH_2- \rightarrow -CH_2-CHH^*-CH=CH- + RH$$

$$-CH_2-CHR-CHH^*-CH_2- \nearrow -CH_2-CH^*=CH-CH_2-$$

(RH* represents the hydrido catalyst. The hydridic hydrogen is distinguished by an asterisk.)

When two double bonds become conjugated, the conjugated system attaches itself to the catalyst—perhaps through a temporary expansion of the coordination sphere (*10, 11*). This addition is irreversible, but the addition compound is split by the hydrogenating agent shown below on

Table III. Hydrogenation of Methyl
Bis-triphenylphosphine Nickel

Catalyst	*Temp. (°C.)*	*Time (Hrs.)*	*Solvent*	*Unidentified*	*Stearate*
$(\phi_3P)_2NiI_2$	90	3	ϕH		1.1
	90	3	THF		
	140	3	ϕCH_3		2.0
$(\phi_3P)_2NiBr_2$	90	3	ϕH	2.1	3.1
	90	3	THF	1.3	3.1
	140	3	ϕCH_3	1.6	5.1
	90	12	ϕH	2.2	5.8
$(\phi_3P)_2NiCl_2$	90	3	ϕH	0.6	
	90	3	THF		

[a] Hydrogen pressure = 39.1 atm.

page 112. Before it decomposes, the product of this reaction may allow movement of the double bond along the chain or cis-trans isomerization, but it is not able to undergo further hydrogenation.

The second piece of work I wish to mention is a quite different sort, involving attempts to achieve the optical resolution of tris-ethylenediamine cobalt(III) chloride, $[Coen_3]Cl_3$, by bacterial action. Many chemists have studied the physiological action of metal complexes, and Dwyer and his

Table IV. Reactions in the

Substrate	*Catalyst*	*Solvent*	*Palmitate*	*Stearate*
Soybean oil Methyl ester	$(\phi_3P)_2PdCl_2 + SnCl_2 \cdot 2H_2O$	ϕH-MeOH	10.6	4.7
	$(\phi_3P)_2PdCl_2 + GeCl_2$	ϕH-MeOH	12.1	5.7
	$(\phi_3P)_2Pd(CN)_2$	ϕH-MeOH	10.6	7.7
Methyl Linoleate	$(\phi_3P)_2NiI_2$	THF		1.4
	$(\phi_3P)NiBr_2$	ϕH		1.6
	$(\phi_3P)_2PtCl_2 + SnCl_2 \cdot 2H_2O$	ϕH-MeOH		
	$(\phi_3As)_2PtCl_2 + SnCl_2 \cdot 2H_2O$	ϕH-MeOH		

[a] N_2 pressure = 27.2 atm.

[b] (a) 90°C. for three hours; (b) 90°C. for 12 hours; (c) same blank as in Table II; and(d) 90°C. for five hours.

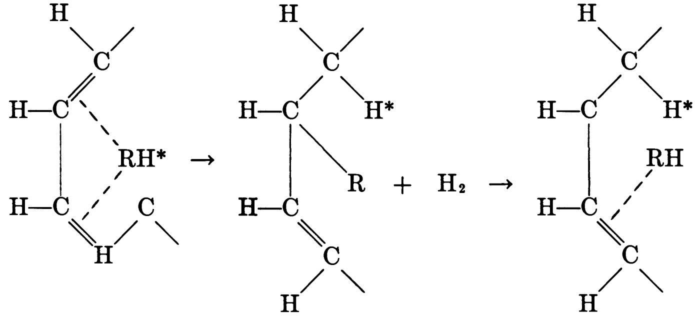
Linoleate (1.0 g., 3.4 mmoles) with Halides (0.64 mmoles)[a]

Product				
Monoenoate	*Dienoate*	*Cis-trans*	*Trans-trans*	*Trans* (%)
83.5	15.4			84.7
83.2	16.8			58.5
88.8	9.2			65.4
53.0	40.0	1.8		40.9
38.7	48.7	3.3	4.9	37.5
73.2	20.1			50.5
80.5	11.5			57.0
1.6	97.8			6.0
	100.			2.1

co-workers have observed that optical isomers have different effects (*6*). We have sought to study the converse of that problem—the action of biological systems on optically active complexes. Our work was begun by M. J. S. Crespi (*5*) and has been continued by John Geldard under NSF Grant G386. We are greatly indebted to I. C. Gunsalus for his consultation and help with the experimental work. The description here is very brief, as details will be published elsewhere.

Absence of Elemental Hydrogen[a]

Product					
Monoenoate	*Dienoate*	*T or cis-trans*	*Trans-trans*	[b]	*Trans* (%)
83.2	1.5			(a) (c)	62.3
38.8	32.4	4.4	6.6	(a) (c)	23.6
53.2	27.5	1.0		(b) (c)	44.5
55.3	39.1	2.0	2.2	(a)	43.7
22.4	69.2	4.0	2.8	(b)	23.9
4.9	48.3	21.0	25.8	(d)	61.2
51.6	24.8	9.7	13.9	(d)	61.6



When dilute solutions of D- and L-$[Coen_3]Cl_3$ containing the trace elements and enzymes essential for bacterial growth are treated with *Pseudomonas aeruginosa,* the bacteria grow in the flask containing the D-isomer but not in the one containing the L-isomer. Even under the best conditions, the growth is poor, and it has been found that the bacteria utilize only the nitrogen (or part of it) from the coordinated ethylenediamine. If they are to continue to grow, a source of carbon such as succinate must be added to the broth. The ethylenediamine molecule is not completely destroyed but is converted to some other compound which is also a coordinating agent—perhaps $NH_2CH_2COO^-$ which, in the extreme case, could be further utilized to form $C_2O_4^{-2}$. A very interesting feature of the reaction is that the bacteria do not grow in a solution of the racemic complex, and it has been shown that the L-isomer inhibits their growth, so *this* complex cannot be resolved by *these* bacteria. Nonetheless, the result is an interesting one and suggests that a whole field of bacterial inorganic chemistry is available for study. Is the result here reported a general one, or could this complex be resolved by other bacteria? Are there other complexes more amenable to bacterial resolution? Might it be possible to synthesize complexes by bacterial degradation of other complexes? What if the ligands are themselves optically active? (The answer to this last question is being sought by L. D. Applequist.) Unfortunately, however, few students are trained both in the chemistry of inorganic coordination compounds and in bacteriology. Further development of this problem must therefore await such persons who wish to undertake it.

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9

Werner Coordination and Crystal Structure

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The early interaction between Werner's coordination theory and crystal structure is discussed in terms of the problems about valence that then prevailed.

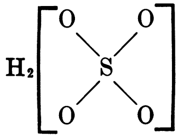
Werner's theory of coordination must be counted one of the great steps forward in our understanding of chemical combination. Concerned with the distribution of atoms in molecular complexes and coming not long before the discovery of x-ray diffraction, it was particularly important for those of us who were then beginning crystal analysis. This analysis, in establishing for the first time exactly where the atoms are in a solid, offered the most direct check imaginable of how correct Werner's notions about valence were, and, conversely, the ideas about coordination arising from this theory could suggest many compounds that it would be profitable to examine with x-rays.

We can best understand this interaction between theory and experiment in the light of the actual problems of chemical combination to which coordination theory was then addressed. They were entirely different from those which occupy us today. Inevitably, valence theory has passed through a series of stages in accord with the prevailing state of chemical knowledge. The first objective of chemistry was necessarily determining the composition of compounds. With the adoption of the atomic theory, these compositions were expressed through formulas which stated the amounts of the elements found to be present. As a second stage, these compositional formulas developed into structural formulas which sought also to express the relations of atoms to one another within a compound. The structural formulas of organic chemistry and the Werner type formulas we can write for the more complicated inorganic compounds are such summary statements of what has been learned about atomic associations. Nowadays, we know what these associations are or how to establish them experimentally. This has made it possible to move into the third, current stage which, as we all know, defines the forces responsible for the bondings we observe.

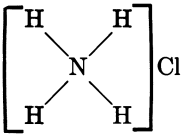
Although early chemical analyses told the proportions of different chemical elements in a compound, they had little to say about atomic relationships. Structural chemistry and the ideas about valence it incorporates developed rapidly around the preoccupation with organic compounds that began a century ago. Most of the elements entering into such compounds have fixed powers of combination and this fact, together with the idea of the tetrahedral carbon atom, set the form which valence theory had acquired by the end of the last century. For the inorganic chemist, however, this theory failed to explain two frequently encountered sets of phenomena: (a) the multiple valence of many elements other than carbon, oxygen, and hydrogen; and (b) the innumerable stable "addition compounds" formed from simple molecules.

The multiple combining powers of many elements for oxygen and their very different valences referred to hydrogen and to oxygen were early recognized. Thus, it was seen that in H_2S sulfur was, like oxygen, divalent, but that in SO_2 and SO_3 it was tetra- and hexavalent. Similarly, chlorine was monovalent in HCl and NaOCl, but tri-, penta-, and heptavalent in chlorites, chlorates, and perchlorates. The multiplicity of valence thus expressed was an empirical fact of inorganic chemistry long before Werner propounded his theory of coordination (*17*). This theory stated it succinctly, but satisfying explanations emerged only later through electron theories of valence arising out of the facts of x-ray spectroscopy and the theory of Bohr.

Coordination may be said to have had its beginnings in the attempt to understand such simple "molecular compounds" as $SO_3 \cdot H_2O$ and $NH_3 \cdot HCl$. Obviously there was little meaning to representing these common substances as molecules held together by some form of "secondary valence." Especially after the development of electrochemistry it was apparent that sulfuric acid should be expressed as



even though sulfur was hexavalent, and ammonium chloride was expressed as



though nitrogen had a valence of five. One of the slightly more complicated series of compounds used by Werner to illustrate his coordination theory included the numerous ammoniates and hydrates of platinic chloride. He pointed out that among the ammoniates $PtCl_4 \cdot 2NH_3$ is not dissociated in aqueous solution, but that $PtCl_4 \cdot 2NH_4Cl$ is. The latter does not, however, yield Cl^- anions; instead it dissociates into NH_4^+ and $PtCl_6^{2-}$. On the other hand, there are other ammoniates, $PtCl_4 \cdot 3NH_3$ and $PtCl_4 \cdot 4NH_3$, which in solution are dissociated to yield Cl^- anions and to include the platinum as part of complex cations. The properties of all these were expressed by him through writing their formulas as $[(NH_3)_2PtCl_4]$, $(NH_4)_2{}^+[PtCl_6]^{2-}$, $[(NH_3)_3PtCl_3]^+Cl^-$, and $[(NH_3)_4PtCl_2]^{2+}$-$Cl_2{}^-$. The characteristics of a large number of compounds of tetravalent platinum are well stated by such coordination formulas in which a central platinum atom is always directly bound to six neighboring atoms. In some, water molecules replace ammonia molecules in the foregoing formulas; in others, six-fold coordination may be provided by atoms of cyanide, nitro, or oxalate radicals, or of relatively complex molecules such as thiourea, ethylenediamine, dimethylglyoxime, or acetylacetone. Werner not only noted that in all these cases a $[Pt \cdot 6X]$ cluster behaved as an undissociated unit, even though the normal valence of platinum remained four, but that a similar six-fold coordination occurs around many other elements, including chromium, cobalt, iron, iridium, vanadium, and molybdenum. He also pointed out that metallic coordination is not always six. It is sometimes eight while, for such metals as beryllium and nickel and the nonmetallic boron and nitrogen, it is four. Many of the compounds for which coordination formulas were written show an isomerism analogous to that found among organic compounds; he explained this by saying that the coordinated radicals and atoms are distributed at the corners of polyhedra: an octahedron for six-fold and a tetrahedron for four-fold associations.

Werner's book contains these essentially spatial formulas for hundreds of obscure as well as common inorganic compounds. At the time, it was argued that the composition of many of these substances needed verification and further study; nevertheless, the coordination formulas in his compilation continue to this day to suggest useful experiments, and many of the properties they predict have since been verified. In evaluating the work of Werner we must never lose sight of the fact that the writing of meaningful formulas, and not an "explanation" of valence forces, was the goal within reach of the structural chemistry of his time. Though coordination formulas did make understandable many of the new facts being brought to light by physical chemistry, they were not immediately accepted as representing the actual atomic associations.

With the discovery of x-ray diffraction and the opportunity this gave to determine exactly where the atoms are in a crystal, there arose an unexpectedly direct way to ascertain the measure of reality behind the Werner theory and its implied equivalence of some primary and secondary bonds.

As a graduate student majoring in inorganic chemistry, I chose to study the structure of sodium nitrate (*18*) as part of my doctoral thesis because it seemed important to find out how a pentavalent nitrogen atom was related to the oxygen atoms which, together with it, formed the nitrate ion. Due mainly to the insights of electrochemistry, we no longer wrote the formula of this salt as $Na_2O \cdot N_2O_5$, but we still needed to discover if the three nitrogen-to-oxygen bonds were equivalent. I then chose ammonium chloroplatinate (*19*) as a crystal that should provide a clear-cut test of Werner coordination.

Soon after this structure was worked out and published, Dickinson (*9*) published the atomic arrangement in the isomorphous chlorostannate, and similar confirmations of this type of structure were offered by Scherrer, Stoll (*12*, *13*), and Bozorth (*5*). All these studies agreed in showing that the six halogen atoms of the molecule formed part of a complex anion centered around the metallic atom. All six chlorine atoms in $(NH_4)_2PtCl_6$, for instance, were crystallographically identical. They were equally distant from the metal atom, and hence there was no difference in the bonds they formed with it. Furthermore, chlorines were found to be at the corners of a regular octahedron having the platinum atom at its center. A more complete agreement with the predictions of the Werner theory could scarcely have been imagined.

Subsequent studies of crystal structures provided, and are still supplying, other confirmations. We showed early that the molecules of water and of ammonia in most crystalline hydrates and ammoniates have the same association with a metallic atom as do the coordinated atoms and radicals of a complex ion. For example, $[Ni \cdot 6NH_3]Cl_2$ (*20*) has the same crystal structure as ammonium chloroplatinate with $[Ni \cdot 6NH_3]$ in place of $[PtCl_6]$; and there are numerous hydrates, such as $NiSO_4 \cdot 6H_2O$ (*1*, *7*), in which the water molecules are octahedrally distributed about the metal atom. As an additional point it was later found, as Werner had predicted, that in $NiSO_4 \cdot 7H_2O$ (*2*) this octahedral coordination still exists, the seventh water lying elsewhere in the structure unattached to metal.

It is impractical to list even representative examples of the different types of compound that crystal structure investigations have shown to be appropriately represented by coordination formulas; nevertheless the following, randomly chosen from among recent determinations, are typical. In contrast to the coordinated complex ions discussed above, crystals of compounds such as $CoCl(NO_2)_2 \cdot 3NH_3$ (*15*) and the two, cis and trans, forms of $PtCl_4 \cdot 2NH_3$ (*3*, *4*, *8*) are built of definite molecules that do not dissociate in solution. Among compounds of somewhat greater complexity we have in $NiCl_2 \cdot 4(NH_2)_2CS$ (*6*, *10*) an octahedral coordination of nickel provided by the chloride ions and four sulfur atoms of the thiourea molecules; the same coordination is supplied in ferric acetylacetonate (*11*) by two oxygen atoms from each of three acetylacetone groups and in nickel nitrate tris-ethylenediamine (*14*, *16*) by the two nitrogens of each $H_2N(CH_2)_2NH_2$ molecule. Results such as these have put the basic correctness of coordination theory beyond dispute; its formulation will remain permanently useful even though crystal structure methods have advanced until we no longer need rely on its predictions.

The terminology of coordination has quite naturally found a place in our everyday descriptions of crystal structures. Thus, we refer to the coordination of an atom as *n*-fold, or more specifically as triangular, square, tetrahedral, octahedral, cubic, etc. Often it is convenient to go a step further and state the relation of these coordination figures to one another throughout the crystal, which can then be imagined as built up by their sharing of corners, edges, or faces. We have learned from the study of crystal structures that the coordination of an atom is often related to its characteristic combining power, i.e., its valence. This is illustrated by the square coordination of the platinum atom in its Pt^{2+} condition and by the fact that in the Pt^{4+} state the planar $[PtCl_4]^{2-}$ association is converted into a $[PtCl_6]^{2-}$ octahedron by adding two more chlorine neighbors on a line normal to the plane of the Pt^{2+} complex. It is significant that a square coordination for the Pt^{2+} and an octahedral association for the Pt^{4+} atoms are preserved whatever may be the four and six atoms that are coordinated.

On the other hand, we have found that there are many types of crystal in which the coordination is set, not by chemical valence, but by the relative sizes of an atom and its immediate neighbors—that is to say, by considerations of close packing. This is the case both with simple ionic compounds and with compounds like hydrates where a metal atom and its enveloping water molecules are held together by dipolar attractions of some sort rather than by directed valence bonds. Thus, among their hydrates, the coordination about the small Be^{2+} is tetrahedral, that around the larger Ca^{2+} usually octahedral, while around the still larger Ba^{2+} it may be nine or more. Often we can decide from the experimental results if the observed coordination is caused by packing or directed valence. Valence must, for instance, be responsible for the different coordinations of platinum in its divalent and tetravalent compounds, as well as for the tetrahedral coordination about Cu^{+} atoms as contrasted with the square, or distorted, octahedral coordination that occurs about Cu^{2+}. In contrast, the tetrahedral coordination of oxygen about silicon, which prevails throughout silicate chemistry, is to be expected whether or not a strongly directional character is attributed to the Si-O bond; evidently a knowledge of crystal structure does not always give the answer we seek.

With the development of quantum mechanics, however, this knowledge is providing much of the experimental basis for explanations of the nature of chemical bonds. The first steps, taken by applying quantum mechanical ideas to the earlier electron theories of valence reinforced by the quantitative measurements of spectroscopy, identified many bonds in terms of the electrons that could form them. Thus, hybridization of one *s* and three *p* electrons was shown to account for the tetrahedrally distributed four equal bonds (sp^3 bonds) of the carbon atom. Similarly, we have become accustomed to attribute a square coordination to the presence of four sp^2d bonds obtained when one s, one d, and two p electrons are hybridized. Six equal bonds of the type sp^3d^2 can be constructed from the available valence electrons of many of the atoms and ions that show octahedral coordination, such as Pt^{4+} or Co^{2+}. We have, however, come to realize that it is often necessary to consider all the chemically active electrons of a molecule when seeking to account quantitatively for any one bond. The development of molecular orbital and crystal field theories is now making this possible. It obviously does not lie within the province of this brief historical review to discuss this newest phase of valence theory, but in conclusion I do want to emphasize the essential role of Werner coordination in preparing the ground for it. It showed how to write realistic formulas for innumerable complex inorganic substances that were not previously comprehensible and thus has gained for itself a permanent place through the qualitative pictures it supplied of molecular structure and the atomic associations that prevail in crystalline solids.

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10

The Development of Coordination Chemistry at the University of Cambridge, 1925-1965

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The period 1925–1965 bridges the time between the early, simple Werner studies and the modern largely theoretical structural studies of coordination chemistry. The main work at Cambridge was on the complexes formed by what were then novel polyamines, such as 1,2,3-triaminopropane, tris(2,2′,2″-triaminotriethyl)amine, bis(2,2′-diaminodiethyl)amine, etc., and applying sulfamide as a chelating agent, which led to the optical resolution of the second entirely inorganic compound to be thus resolved, and the first systematic application of tertiary phosphines and arsines to coordination compounds, a development which has since dominated the greater part of all coordination studies. The application of novel ligands, such as NNN′N′-dimethylethylenediamine, 1,4-dimethylpiperazine, and 2-phenylisophosphindoline, which form stable coordination compounds under conditions which might have been expected to give products of marked instability, is briefly discussed.

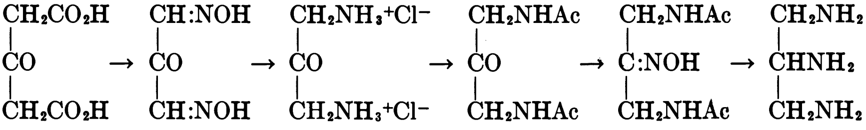
The period 1925–65 is of considerable interest because it formed a kind of bridge between the simple Werner theories and the modern study of the electronic structure of coordination compounds; it was a period moreover when many new types of coordination compounds were discovered and many new structures elucidated. In Cambridge, it is a source of pride that the use of tertiary phosphines and arsines in the study of coordination compounds and the elucidation of their structure originated in the University laboratories. I am qualified to write about the Cambridge coordination studies during this period, for I participated in most of them.

In the years immediately following the First World War, interest in coordination chemistry in Britain had fallen to a low ebb. This was due possibly to the wartime cessation of academic research work but probably more to the fact that, apart from a very few chemists who almost fanatically spurned Werner's work, most chemists accepted Werner's theories and conclusions as affording a very thorough and virtually complete interpretation of coordination compounds, a class of compounds which in any case appeared to represent a comparatively small portion of the overall chemical field. In England, interest in these compounds was however still maintained almost entirely by G. T. Morgan (later Sir Gilbert Morgan) and his co-workers at Birmingham University and, on the more theoretical side, by N. V. Sidgwick of Oxford University.

Sir William Pope, professor of chemistry at Cambridge University, had however been considering various aspects of Werner's work and its possible extension, for when I had finished my doctoral work under his supervision (1923), he suggested that I should synthesize 1,2,3-triaminopropane (VI), the use of which as a coordinating agent to metals might open up a field comparable to that which ethylenediamine had provided in Werner's hands.

Triaminopropane had already been synthesized by Curtius and Hesse (*9*), but their method gave rather poor yields and involved the possibly hazardous handling of tricarballylic acid triazide.

Pope's first suggestion for this synthesis, namely the condensation of 1,2,3-tribromopropane with potassium phthalimide, failed because the tribromopropane under these conditions very readily lost hydrogen bromide with the production of phthalimide. I ultimately synthesized the triamine by converting citric acid by the action of sulfuric acid into acetone dicarboxylic acid (I) which, with nitrous acid, gave the di-isonitroso-acetone (II); this when reduced with stannous chloride gave diaminoacetone stannochloride which, after treatment with hydrogen sulfide, gave the dihydrochloride(III). The latter was converted into the diacetamidoacetone(IV), then into the oxime (V) which, when reduced with aluminum amalgam and hydrolyzed with hydrochloric acid, gave the trihydrochloride of the triaminopropane(VI). The overall yield of the stannochloride from the citric acid was 37%, the yield of III from the stannochloride was 90%, and that of the remaining stages was almost theoretical. The synthesis of this triamine was thus considerably longer and more laborious than Werner's preparation of ethylenediamine, but with the aid of a young assistant (F. C. Baker) I was able to prepare considerable quantities of the



$$\begin{array}{c} CH_2CO_2H \\ | \\ CO \\ | \\ CH_2CO_2H \end{array} \rightarrow \begin{array}{c} CH{:}NOH \\ | \\ CO \\ | \\ CH{:}NOH \end{array} \rightarrow \begin{array}{c} CH_2NH_3^+Cl^- \\ | \\ CO \\ | \\ CH_2NH_3^+Cl^- \end{array} \rightarrow \begin{array}{c} CH_2NHAc \\ | \\ CO \\ | \\ CH_2NHAc \end{array} \rightarrow \begin{array}{c} CH_2NHAc \\ | \\ C{:}NOH \\ | \\ CH_2NHAc \end{array} \rightarrow \begin{array}{c} CH_2NH_2 \\ | \\ CHNH_2 \\ | \\ CH_2NH_2 \end{array}$$

(I) (II) (III) (IV) (V) (VI)

crystalline triamine trihydrochloride. The application of the triamine in coordination chemistry very richly rewarded our synthetic labors (*29*).

We found that when an aqueous solution of chloropentamminocobalt(III) dichloride, $[(NH_3)_5ClCo]Cl_2$, was boiled with two equivalents of the triamine, the cold concentrated solution deposited the orange crystals of bis(triaminopropane)cobaltic trichloride (VII; X = Cl), which when treated in aqueous solution with sodium iodide deposited the orange-brown tri-iodide (VII; X = I) (*29*), and with sodium thiocyanate deposited the pale brown trithiocyanate (VII; X = SCN) (*28*). The almost colorless crystals of bis(triaminopropane)rhodium(III) tri-iodide (VIII; X = I) were similarly prepared (1925) (*29*).

$[Co\{NH_2CH_2CH(NH_2)CH_2NH_2\}_2]X_3$
(VII)

$[Rh\{NH_2CH_2CH(NH_2)CH_2NH_2\}_2]X_3$
(VIII)

$[Ni\{NH_2CH_2CH(NH_2)CH_2NH_2\}_2]X_2$
(IX)

$[Zn\{NH_2CH_2CH(NH_2)CH_2NH_2\}_2]I_2$
(X)

$[Pt\{NH_2CH_2CH(NH_2)CH_2NH_2\}_2]X_2$
(XI)

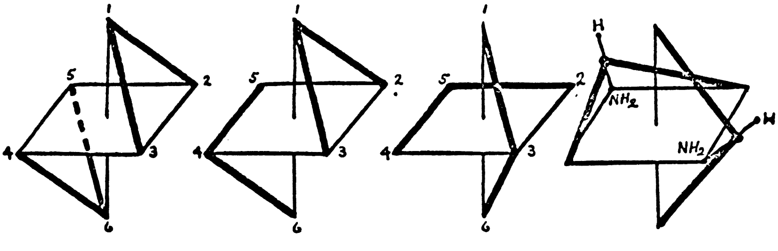
A, hot ethanolic solution of nickel succinimide, when treated with the triamine, then concentrated and added to aqueous sodium iodide, deposited the pale red bis(triaminopropane)nickel di-iodide (IX; X = I); the deep red sulfate (IX; 2X = SO_4) was similarly prepared (*28*).

Aqueous zinc nitrate similarly treated gave the colorless crystalline bis(triaminopropane)zinc di-iodide (X) (*20*). An aqueous solution of sodium tetrachloroplatinate(II), $Na_2[PtCl_4]$, when treated with two equivalents of the triamine, heated until clear, and then concentrated and added to aqueous sodium bromide and iodide gave the colorless bis(triaminopropane)-platinum(II) dibromide (XI; X = Br), m.p. 270–271°C., and the di-iodide (XI; X = I), m.p. 266–267°C., respectively. The fact that in these salts (which were sufficiently stable for recrystallization from hot water) the divalent platinum was showing the exceptional coordination number of 6—i.e., that it was coordinated to all six amino groups of the two triamine molecules, was shown by the addition of the dibromide to an excess of sodium picrate, both in cold aqueous solution, whereby only the dipicrate (XI; X = $C_6H_2N_3O_7$) was precipitated; had any amino groups remained uncoordinated, they also would have formed picrates (1928) (*19*).

The characteristic property of most of these salts was their high stability under various conditions. For example, they could be boiled in aqueous solution for long periods without change; in this respect the zinc compound (X) contrasts markedly with its ammonia analogue, $[Zn(NH_3)_6]I_2$, which on exposure to air at room temperature loses ammonia to give the tetrammino compound $[Zn(NH_3)_4]I_2$. This stability in hot aqueous solution is matched by their thermal stability for they all have high melting or decomposition points—usually about 280–300°C. Furthermore, the cobalt compound (VII; X = Cl) is obtained when the above preparation is carried out using only one equivalent of the triamine; no intermediate compound of type $[NH_2CH_2CH(NH_2)CH_2NH_2Co(NH_3)_3]Cl_3$ was detected.

At the time of this work, many chemists considered that a metallic ion of a particular valency had a stable coordination number and definite coordination configuration, these being presumably dependent primarily on the electronic distribution within the compound. The stability of the above bis-triaminopropane compounds made chemists admit (some very reluctantly) that an additional factor is involved—namely, that a metallic atom may adjust its coordination number and its coordination configuration to the spatial demands of a suitable multi-bridging ligand. The dimensions of the triamine molecule clearly allow two molecules to fit firmly around the 6-coordination octahedron, and the metal (e.g., zinc(II), platinum(II)) adapts itself to this requirement to obtain maximum stability. These considerations are now of course the accepted commonplace factors of coordination chemistry.

The possible configurations of the 6-coordinate octahedron when fully coordinated to two molecules of the triamine have points of interest (*28*). There are three possible configurations. In the first (Figure 1), the triamine occupies the 2,1,3:4,6,5 positions, and this isomer has a plane of symmetry. In the second (Figure 2), the triamine occupies the 2,1,3:5,4,6 positions, and this isomer is dissymmetric and should be capable of optical resolution. In both these isomers, the triamine is coordinated to a triangular face of the octahedron; in the third isomer (Figure 3) the triamine is coordinated around a square cross-section of the octahedron and occupies the 1,3,6:4,5,2 positions. This third isomer would appear to have a plane of symmetry; however the triamine molecules would not be



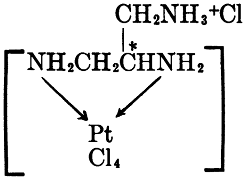
Figures 1, 2, 3, and 4. The various orientations of two molecules of 1,2,3-triaminopropane around the 6-coordinate octahedron placed symmetrically to the two square planes of symmetry of the regular octahedron because the central coordinating amino group should give a lateral displacement to the central carbon atom (Figure 4) and thus prevent the triamine molecule coinciding with the apparent plane of symmetry. In the first isomer (Figure 1) this lateral displacement occurs in the plane of symmetry, which is thus not affected.

Theoretically, therefore, the cations in each of the salts (VII), (VIII), (IX), (X), and (XI) could exist in three forms, two of which should be susceptible to optical resolution. All these salts formed excellent and apparently homogeneous crystals. An attempt (*28*) to resolve the trichloride (VII; X = Cl) by fractional recrystallization of the corresponding (+)-camphorsulfonate gave a trichloride having a very faint rotation, and the similar use of the (+)-3-bromocamphor-8-sulfonate and the (+)-camphor-α-nitronate gave completely negative results. It is probable that the configuration (Figure 1) is the stable common arrangement in all such salts (1926).

The application of the triamine to hexachloroplatinic(IV) acid, H_2PtCl_6, led to very interesting results. This acid in hot aqueous solution, when treated with the free base, underwent reduction with deposition of platinum but, when boiled with the triamine trihydrochloride, gave canary-yellow crystals of composition XII. It was clear therefore that

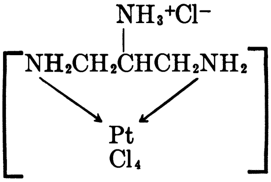
$$\text{NH}_2\text{CH}_2\text{CH(NH}_2\text{)CH}_2\text{NH}_2\text{, PtCl}_4\text{, HCl}$$

(XII)



$$\left[\begin{array}{c}\text{NH}_2\text{CH}_2\overset{\overset{\text{CH}_2\text{NH}_3^+\text{Cl}^-}{|_*}}{\text{C}}\text{HNH}_2\\ \searrow\ \swarrow\\ \text{Pt}\\ \text{Cl}_4\end{array}\right]$$

(XIII)



$$\left[\begin{array}{c}\text{NH}_2\text{CH}_2\overset{\overset{\text{NH}_3^+\text{Cl}^-}{|}}{\text{C}}\text{HCH}_2\text{NH}_2\\ \searrow\ \swarrow\\ \text{Pt}\\ \text{Cl}_4\end{array}\right]$$

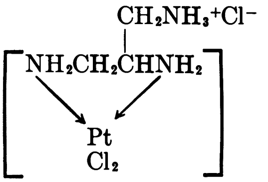
(XIV)

in this salt only two of the three amino groups had coordinated with the platinum and that the third group had formed a hydrochloride. The homogeneous product could therefore be one of two possible compounds—namely XIII, in which the 1,2-amino groups had coordinated with the platinum and the 3-amino group had formed an ammonium cation and XIV, in which the 1,3-amino groups had coordinated and the 2-amino group had formed the ammonium cation (*16*).

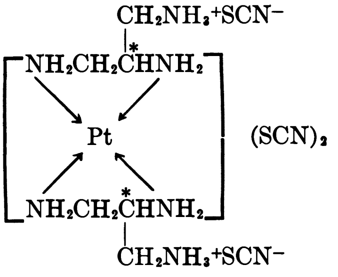
The determination of the structure of the salt was not difficult because in XIII the central (C*) carbon atom has become asymmetric, whereas the cation in XIV has a plane of symmetry. The chloride was therefore converted into the (+)-camphorsulfonate, which after fractional recrystallization from water gave the optically pure (−)-tetrachloro-(triaminopropane-mono-(+)-camphorsulfonate)platinum, having in aqueous solution (15°C.) $[M]_{5461}$ − 426°. This salt, treated in aqueous solution with concentrated calcium chloride solution, deposited the (−)-tetrachloro-(triaminopropane-3-monohydrochloride)platinum(IV) (XIII), having $[M]_{5461}$ − 502°. The racemic hydrochloride was similarly converted, using the (−)-camphorsulfonic acid, into the optically pure (+)-tetrachloro(triaminopropane-mono-(−)-camphorsulfonate)platinum, having [M] + 424°, which furnished the corresponding hydrochloride, having [M] + 501°. [The compound, XIII, is now termed tetrachloro(2,3-diaminopropylammonium)platinum(IV) chloride.]

This resolution (1927) showed that the salt must have the constitution XIII, and furthermore that the five-membered ring system of XIII was more stable than the six-membered ring system of XIV because the compound XIII was formed to the apparently complete exclusion of the compound XIV. This was moreover the first decisive example of a carbon atom becoming asymmetric by the operation of a coordinate link (*17*, *30*).

The analogous platinous salt, XV, was subsequently (1928) obtained by treating potassium tetrachloroplatinate(II), $K_2[PtCl_4]$, in hot aqueous solution with triaminopropane trihydrochloride. This salt was converted into (+)-dichloro(triaminopropane-mono-(+)-3-bromocamphor-8-sulfonate)platinum, having after fractional crystallization $[M]_{5461}$ + 522°, and furnishing the (+)-dichlorotriaminopropane-3-monohydrochloride)platinum (XV), [M] + 195°. The use of the (−)-sulfonic acid gave the corresponding salts having [M] − 524° and [M] − 192°, respectively (*19*).



(XV)



(XVI)

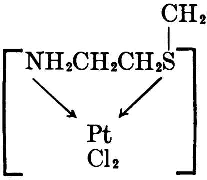
It is noteworthy that ammonia or ethylenediamine reacts similarly with both the compounds, XIII and XV, withdrawing hydrogen chloride, whereupon the liberated amino group coordinates with the platinum, evicting a chlorine atom, thus giving trichloro-triaminopropaneplatinum (IV) chloride, $[Cl_3\{NH_2CH_2CH(NH_2)CH_2NH_2\}Pt]Cl$, and the corresponding chloro-triaminopropaneplatinum(II) chloride, respectively (*17*, *19*).

When, however, an aqueous solution of potassium tetrachloroplatinate(II) is treated with an excess of the triaminopropane base and then concentrated, the solution when then treated with aqueous potassium thiocyanate containing acetic acid gives the colorless bis(triaminopropane-3-monothiocyanate)platinum(II) dithiocyanate (XVI) (*19*). There is little doubt, therefore, that the solution contains the cation (XI) because with sodium bromide and iodide it deposits the salts XI (X = Br) and XI (X = I) (p. 122), but that the presence of even a weak acid enables the 3-amino group of each triamine molecule to break away from the platinum, and thus with potassium thiocyanate to give the salt, XVI. This salt has two asymmetric carbon atoms (C*), and might therefore exist as a racemic or as a meso form. Although the compound appeared to be homogeneous, the possibility of it being the meso form dissuaded us from attempted optical resolution (1928).

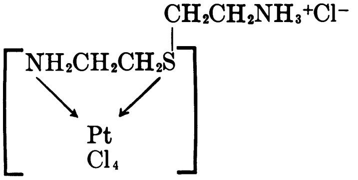
When an excess of the triamine base was added to copper sulfate in cold aqueous solution, the latter became deep violet in color. Addition of potassium iodide solution now precipitated the slate-blue tetrakis(triaminopropane)copper(II) hexaiodide (XVII, where "ptn" represents one molecule of the triamine); alternatively, the addition of potassium

$[Cu_3ptn_4]I_6$

(XVII)



(XVIII)



(XIX)

thiocyanate precipitated the corresponding hexathiocyanate. In these compounds, the copper has retained its coordination of 4, and three copper atoms are thus fully coordinated by the 12 amino groups of the four triamine molecules (*16*). When, however, the above deep violet solution was treated with aqueous potassium thiocyanate containing acetic acid, the more soluble bis(triaminopropane-3-monothiocyanate)copper(II) dithiocyanate (precisely similar to the salt (XVI)) was precipitated (*16*).

The discovery of salts such as XIII, XV, and XVI, in which only two of three potentially coordinating groups were actually linked to the metallic atom, led to a new aspect of the stereochemistry of sulfur. I found that when a solution of 2,2′-diaminodiethylsulfide dihydrochloride, $S(CH_2CH_2NH_2)_2$, 2HCl in one equivalent of *N*-hydrochloric acid was added to a solution of potassium tetrachloroplatinate(II), the mixture when boiled deposited crystals of the composition $Cl_2PtS(CH_2CH_2NH_2)_2$, HCl. This immediately suggested that this compound was dichloro-(2,2′-diaminodiethylsulfide monohydrochloride)platinum(II) (XVIII); if so, the sulfur atom became asymmetric and the compound should have been resolvable. All attempts to resolve this compound failed however. It was therefore dissolved in cold dilute hydrochloric acid and treated with hydrogen peroxide, when the tetrachloro-(2,2′-diaminodiethylsulfide monohydrochloride)platinum(IV) (XIX) slowly crystallized. This compound still contained an asymmetric sulfur atom. The failure of initial attempts to resolve this compound, like those of the compound XVIII, were undoubtedly due to the very low optical stability of these compounds, particularly in hot solutions. On one occasion I mixed cold aqueous solutions of XIX and of ammonium (+)-camphorsulfonate and set the solution aside for several days; a heavy deposit of the yellow (+)-tetrachloro-(2,2′-diaminodiethylsulfide mono-(+)-camphor-sulfonate)platinum(IV) (XIX) slowly formed. These crystals were the optically pure salt, having $[M]_{5461}$ + 1070°. This salt, treated with calcium chloride, both in ice-cold aqueous solution, yielded the (+)-chloride (XIX), having $[M]_{54\,61}$ + 1110°; this rotation, when the solution was maintained at 15°, fell to +849° (after 8 hours), + 330° (24 hours), + 140° (32 hours), and after 50 hours was not detectable (1930) (*21*).

The salt, XIX, when in boiling aqueous solution readily deposited the salt, $[Cl_3PtS(CH_2CH_2NH_2)_2]Cl$—a reaction comparable to that shown by the salts XIII and XV.

This work showed that the stereochemistry of the 3-covalent sulfur in these metallic coordination compounds was not essentially different from that in the sulfinic esters, the sulfoxides, and the sulfilimines, which were resolved by Phillips *et al.* (*4*, *13*, *47*).

While the above work on the coordinated derivatives of 1,2,3-triaminopropane was in progress, we were also investigating (1925) the derivatives of 2,2′,2″-triaminotriethylamine(XX) (*31*). This very interesting tetramine, the preparation of which we were able to improve, separates from cold concentrated hydrochloric acid solution as the monohydrated

$N(CH_2CH_2NH_2)_3$
(XX)

$HN^+(CH_2CH_2NH_3^+)_3\,4Cl^-,\ H_2O$
(XXI)

$N(CH_2CH_2NH_3^+)\ 3Cl^-$
(XXII)

$[Cl_2trenPt]Cl_2$
(XXIII)

$[Cl_2trenPt][PtCl_6]$
(XXIV)

$[trenPt]I_2$
(XXV)

tetrahydrochloride (XXI); the combined inductive effect of the positive charges on the three primary amine groups tend however to deactivate the tertiary amine group, and the tetrahydrochloride (XXI) on exposure to air effloresces with the formation of the stable anhydrous trihydrochloride (XXII) (*31*).

Treatment of these hydrochlorides under suitable conditions with hexachloroplatinic(IV) acid gave two hydrated salts, 2 tren, $3H_2PtCl_6$ and 2 tren, $4H_2PtCl_6$, (where "tren" indicates one molecule of the tetramine), corresponding to the tri- and tetra-hydrochlorides, respectively. When an aqueous solution containing the first of these salts and an excess of the trihydrochloride of the base was boiled for 14 hours, it yielded the stable orange-colored dichloro-tetramine-platinic(IV) dichloride (XXIII). In this compound, the base is coordinating as a tetramine; this is shown by the two chloride ions, which could be replaced by simple double decomposition by two iodide ions or by the hexachloroplatinate ion (XXIV) (*31*). The tertiary nitrogen atom of the tetramine is therefore apparently showing a greater power for coordinating to a metal than for salt formation with an acid, although tertiary monoamines do not usually form stable coordination salts. However, the primary amino groups when coordinated would carry very weak positive charges compared with those in the hydrochloride, and the tertiary amine would be only very slightly deactivated; the only compact coordinated arrangement of the tetramine around an octahedron would bring the tertiary amine group in close contact with a coordinating position. Finally, a tertiary nitrogen atom may develop comparatively strong coordinating power if it forms part of a suitable chelating group—in this case three such groups having the tertiary nitrogen in common. The last factor was not appreciated until 1958 when Mann and Watson showed that *NNN′N′*-tetramethylethylenediamine, $(CH_3)_2NCH_2CH_2N(CH_3)_2$, acts as a strong chelating ligand (p. 142).

When potassium tetrachloroplatinate(II), K_2PtCl_4, was heated with two equivalents of the free base "tren," treatment of the clear colorless solution with potassium iodide gave the cream-colored triaminotriethylamineplatinum(II) di-iodide dihydrate, which in a vacuum over phosphoric anhydride gave the anhydrous di-iodide (XXV). The structure of this salt was puzzling. Its low solubility precluded molecular weight determinations, but assuming that the simple formula, XXV, was correct it followed that if the divalent platinum atom had its usual planar configuration, one of the chelating 2-aminoethyl groups must have spanned the diagonal of the square, which would have involved considerable strain and probably have been impossible. Alternatively, no strain would be involved if the platinum had adopted a tetrahedral configuration, a possibility which many chemists in 1926 found difficult to accept. I had always thought that the di-iodide in hot aqueous solution had increased its coordination number to 6 by coordination with water to give a salt, [tren $Pt(H_2O)_2]I_2$, in which the tetramine would have a strainless coordination around four neighboring points of the octahedron, and that on crystallization these water molecules were shed to give a nonionic compound of structure [tren PtI_2] (*31*).

The tetramine base when added to ethanolic nickel succinimide gave rise to two distinct cations, for the solution when treated with aqueous potassium thiocyanate deposited deep blue crystals of the tetramine-nickel(II) dithiocyanate (XXVI), but with aqueous potassium iodide gave deep violet crystals of the tris-tetramine-bis-nickel(II) tetraiodide (XXVII). Both were readily decomposed by acids (1926) (*26*).

$[\text{tren Ni}](SCN)_2$	$[\text{tren}_3\ Ni_2]I_4$	$[\text{tren Ni}]SO_4$
(XXVI)	(XXVII)	(XXVIII)

The dithiocyanate (XXVI) was converted into the readily soluble sulfate (XXVIII); the molecular weight and the conductivity of this salt in aqueous solution provided strong evidence that it was the monomer (XXVIII). Clearly, however, the nickel complex in this salt could readily adopt the tetrahedral configuration, of which many examples have been described in recent times.

Although the dithiocyanate (XXVI) is ionic in aqueous ethenolic solution, a later x-ray analysis (1959) showed that in the crystalline state the nickel atom is at the center of an octahedron, being coordinated to the four amino groups of the tetramine and to the nitrogen atoms of the two thiocyanate groups, the interatomic distances being Ni-N(primary) 2.20, Ni-N(tertiary) 2.13, and Ni-N(NCS) 2.06 A. (*48*).

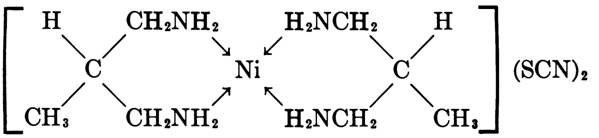
The cation in the salt, XXVII, might well have been dissymmetric, but although several derivatives were investigated no evidence of optical resolution was obtained (*26*).

3,3′,3″-Triaminotripropylamine (XXIX) was also prepared. This tetramine forms a stable tetrahydrochloride (XXX), for the inductive effect of the positive poles on the three primary amine groups cannot now be effectively transmitted to the tertiary nitrogen atom, which therefore is not deactivated. When ethanolic nickel succinimide was similarly treated with the base (XXIX), the solution on addition of potassium thiocyanate deposited the lilac-blue tetramine-nickel(II) dithiocyanate (XXXI) (where "trpn" represents one molecule of the tetramine), and potassium iodide gave the corresponding di-iodide. A cation analogous to XXVII was apparently not formed (*27*).

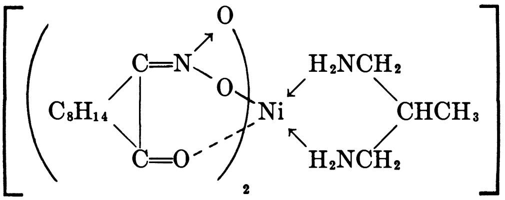
$N(CH_2CH_2CH_2NH_2)_3$	$HN^+(CH_2CH_2CH_2NH_3^+)_3\ 4Cl^-$	$[\text{trpn Ni}](SCN)_2$
(XXIX)	(XXX)	(XXXI)

In seeking decisive evidence for the configuration of the 4-coordinate nickel complex (1927), a number of salts was made in which the nickel was coordinated with two molecules of the following diamines:

$CH_3CH(CH_2NH_2)_2$, $(HO)CH(CH_2NH_2)_2$, $BrCH(CH_2NH_2)_2$,
$(SCN)CH(CH_2NH_2)_2$, and $H_2NCH_2CH_2N(C_2H_5)_2$.



(XXXII)



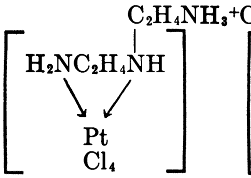
(XXXIII)

The salts, such as XXXII, were all of such a type that had the nickel been planar, cis-trans isomers could have been formed. Had the nickel been tetrahedral, however, the salts should have been resolvable. These salts were all beautifully crystalline blue compounds showing no indication of geometric isomers and also showing no indication of optical resolution! It is noteworthy however that an attempt to replace the SCN ions in XXXII by camphornitronate groups gave deep green covalent products of composition corresponding to XXXIII. Three of the above diamines gave products of this type and color. Their structures would probably repay renewed investigation by modern methods (*18*).

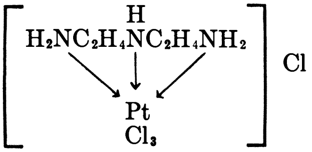
In assessing work of this type, the present younger chemist should bear in mind that the coordination chemists at this time had available for their structural studies virtually only one instrument—namely, the polarimeter; the help obtainable from absorption spectra was meager, and that from x-ray structure studies, although potentially very great, was severely limited by the rarity of these instruments in active operation.

One of the last of the polyamines to be used in Cambridge was 2,2′-diaminodiethylamine, $(H_2NCH_2CH_2)_2NH$, which had to be synthesized for this purpose (1934) (*23*).

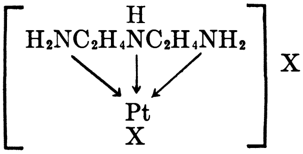
This base (as the trihydrochloride) reacted with hexachloroplatinic(IV) acid to form the salt, XXXIV, in which the central nitrogen atom becomes asymmetric; attempts to resolve it not unexpectedly failed as this group would almost certainly have very low, optical stability. The salt, XXXIV, when treated with silver salts, lost hydrogen chloride with the formation of the salt, XXXV. With potassium tetrachloroplatinate(II), the salt, XXXVI (X = Cl), was obtained and was more readily isolated after treatment in solution with sodium bromide or iodide as the cream-colored XXXVI (X = Br) or XXXVI (X = I), respectively. The free base reacted with aquopentamminocobaltic trichloride to give the



(XXXIV)



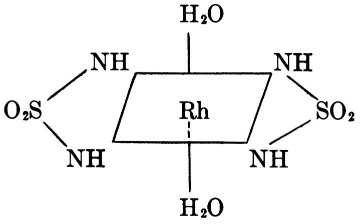
(XXXV)



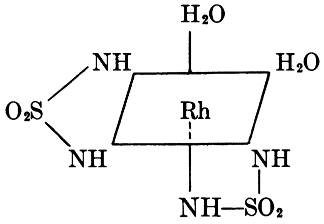
(XXXVI)

$[Co\{(H_2NC_2H_4)_2NH\}_2]$ ion, isolated as the dark brown, crystalline tri-iodide (*22*).

A little earlier I had made an excursion into pure inorganic chemistry by studying the chelating possibilities of sulfamide $(H_2N)_2SO_2$. At that time (1933), and indeed at the present time, very few even experienced chemists had seen the diamide of one of the commonest inorganic acids. Its chelating power could have been foretold with moderate confidence. When sodium hexachlororhodium(III), Na_3RhCl_6, was added to an excess of sulfamide, both in warm aqueous solution, fine yellow crystals of sodium disulfamido-diaquorhodium(III), $Na[(H_2O)_2Rh\{(HN)_2SO_2\}_2]$, were obtained. This anion could have had the water molecules in the trans (or 1, 6) positions (XXXVII), or in the cis (or 1, 2) positions (XXXVIII). The former, XXXVII, has planes of symmetry, whereas XXXVIII is dissymmetric. The sodium salt was converted under carefully controlled conditions into the yellow (+)-2-phenyl-ethylamine salt, which was then reconverted back to the sodium salt, having $[M]_{5780}$ + 31° in aqueous solution. Again using very carefully controlled conditions, the racemic sodium salt was converted into (+)-nor-ψ-ephedrine salt, which slowly separated over two days. This crop in turn gave the sodium salt, having $[M]_{5780}$ − 33.5°. This form was also obtained by the use of the (−)-2-phenylethylamine salt (*22*).



(XXXVII)

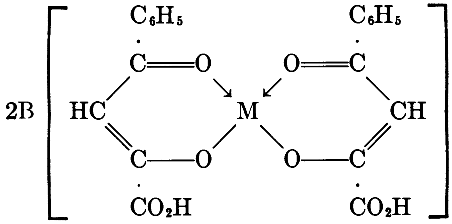


(XXXVIII)

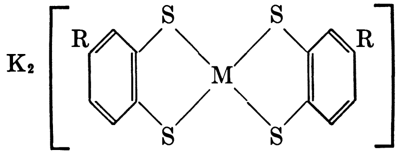
This resolution showed decisively that the anion had the cis (or 1, 2) structure, XXXVIII. Its achievement allowed me to have the honor of joining Alfred Werner as one of the two chemists who have resolved a purely inorganic compound into optically active forms.

This work incidentally also brought me enquiries from several chemical firms regarding the preparation of sulfamide, which they hoped might form a series of polymers comparable with those of urea. They had, however, not appreciated the fact that the two acid diamides have widely different chemical properties, and this idea proved fruitless.

W. H. Mills, in one of his stereochemical investigations, used benzoylpyruvic acid, $C_6H_5COCH_2COCO_2H$, as a chelating agent and, with Gotts in 1926, coordinated this acid with beryllium(II), copper(II), and zinc(II) to obtain, with various optically-active alkaloids, salts of the type, XXXIX, where M represents the metal and B one molecule of the alkaloid base neutralizing the $\cdot CO_2H$ group. The brucine salt of the beryllium complex was obtained in two forms which, in solution, underwent rapid mutarotation to give the same rotatory value. One form, when rapidly treated in ethanolic solution with dimethylamine hydrochloride, deposited brucine hydrochloride almost quantitatively, and the filtered solution of the dimethylamine salt XXXIX (M = Be, B = $(CH_3)_2NH$), then underwent rapid and almost complete racemization. These results provided strong evidence for the tetrahedral configuration of the 4-coordinated beryllium atom. The strychnine salt of the cupric anion (XXXIX; M = Cu) and the brucine salt of the zinc anion (XXXIX; M = Zn) also showed mutarotation in solution. There has since been ample evidence for the tetrahedral configuration of the 4-coordinate beryllium and zinc atoms and for the planar configuration of the 4-coordinate cupric atom, and Mills and Gotts' observations on their cupric compound have never been satisfactorily explained (*43*).



(XXXIX)

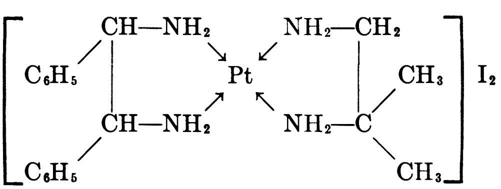


(XL)

Mills and Clark (1936) investigated the salts (XL) which 4-coordinated mercury(II), cadmium(II), and zinc(II) form with toluene-3,4-dithiol

(XL; R = CH_3) and with 1-chlorobenzene-3,4-dithiol (XL; R = Cl). These 4-coordinated metals have the tetrahedral configuration, and the salts of type XL should be resolvable. The salts with optically active bases were each separated into two forms, apparently diastereoisomers of very low optical stability, and replacement of the active base by an inactive cation always gave an inactive salt (*42*).

Mills and Quibell (1935) prepared a compound which was stereochemically of novel type to obtain evidence for the configuration of the 4-coordinate platinum(II) atom (*45*). For this purpose they coordinated



(XLI)

one molecule of meso-1,2-diphenylethylenediamine and one of 1,1-dimethylethylenediamine to platinum to give the salt, XLI. If the four valencies of the platinum atom are planar, this cation is dissymmetric, whereas if the valencies are tetrahedrally arranged the cation has a plane of symmetry. The optical resolution of this compound gave decisive evidence for the planar configuration of the platinum atom, and it was followed in 1939 by the resolution of the analogous palladium(II) compound (*44*).

In 1934 I started an investigation, the results of which were to have a very considerable influence on a high proportion of future coordination research. Sugden (*52*) had suggested (1929) that metals were coordinated to ligands by a single link, and he based this view on his interpretation of the parachors of aluminium and beryllium acetyl- and propionyl-acetonates. This type of linkage seemed improbable, and I sought a series of more simple nonchelated coordination compounds, the parachors of which could be investigated in some detail (*32*). The parachor determination was based on a surface-tension measurement which was carried by the bubble method on the liquid material. Hence, the coordination compounds had to be fusable without decomposition. After much seeking, I recollected the compounds of type $PtCl_2, 2PCl_3$ and $PtCl_2, PCl_3$ obtained by Schützenberger *et al.* in 1870–72 by the action of phosphorus pentachloride on spongy platinum (*49*, *50*, *51*). These compounds could be melted but hydrolyzed rapidly in air with evolution of hydrogen chloride. When, however, they were added to anhydrous methanol or ethanol, they gave crystalline esters of type $PtCl_2,2P(OCH)_3)_3$ and $PtCl_2,P(OCH_3)_3$. The molecular weight of the latter was subsequently found to correspond to $2PtCl_2,2P(OCH_3)_3$. These esters were reasonably stable in air but hydrolyzed in the presence of hot water. To obtain compounds which would offer greater resistance to air and not undergo hydrolysis, and which would contain a metal unlikely to give rise to cis-trans isomerides, I used tertiary alkyl phosphines and prepared a series of homologous compounds starting with $PdCl_2,2P(C_2H_5)_3$ and going up to $PdCl_2,2P(n\text{-}C_5H_{11})_3$. These were stable compounds, readily recrystallized from organic solvents and having sharp melting points. With the aid of a young research student, Donald Purdie, we measured the parachors of these compounds, the melting points of which fell from 139°C. for the ethyl member to 47°C. for the *n*-amyl member. Our idea was to subtract the sum of the parachors of the constituent atoms of each molecule (excluding that of the palladium which was unknown) from the molecular parachor, the difference being that of the palladium atom plus two coordinate links. This difference proved experimentally to have the value 22 for the ethyl member, which fell to −12 and −14 for the butyl and amyl compounds, respectively (*32*).

Similar homologous series of trialkylarsinepalladium(II) dichloride and of dialkylsulfide-palladium dichloride compounds gave results of the same pattern (1935). Looking back now upon the considerable volume of work in this investigation (*32*), it is clear that structural theory was insufficiently developed at that time to allow any precise interpretations of our results. The latter, however, destroyed any evidence for singlet links in coordination compounds.

This work and that which immediately followed in the Cambridge laboratories did however represent the first application of tertiary phosphines and arsines to the study of the properties and reactions of coordination compounds.

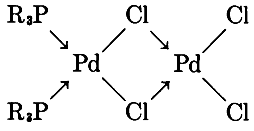
In the course of this work we found that a dichloro-bis(trialkylphosphine)palladium(II), when boiled in ethanol with ammonium tetrahcloropalladate(II), readily gave the double compound shown below. Their arsenic analogues behaved similarly.

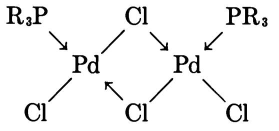
$$[(R_3P)_2PdCl_2] + (NH_4)_2[PdCl_4] = [R_3P, PdCl_2]_2 + 2NH_4Cl.$$

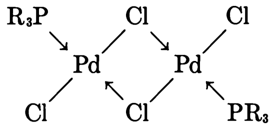
The compounds of type $[(R_3P)_2PdCl_2]$ when heated under reduced pressure distilled unchanged, but their arsenic analogues when thus treated lost tertiary arsine and again gave the double compound:

$$2[(R_3As)_2PdCl_2] = [R_3As, PdCl_2]_2 + 2R_3As.$$

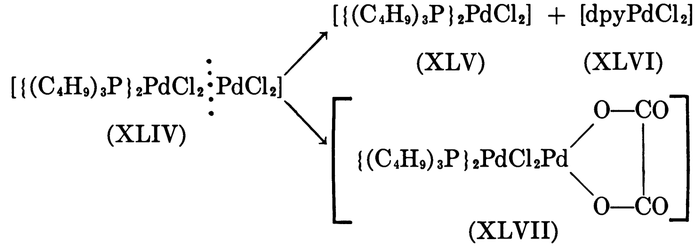
These bridged compounds were uniformly darker in color than their mononuclear precursors, but were also soluble in organic solvents and gave crystals of sharp melting points (*33*). Each bridged compound could theoretically have three isomeric forms—the unsymmetric (XLII), and the cis (XLIIIA) and the trans (XLIIIB) symmetric forms.

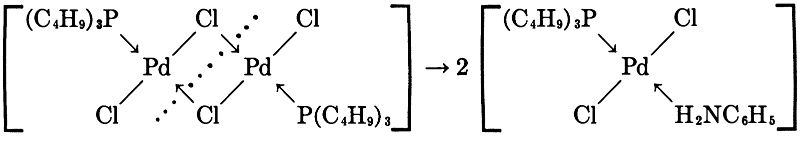

(XLII)


(XLIIIA)


(XLIIIB)

The early evidence (1936) indicated that all three forms probably existed in tautomeric equilibrium. The dipole moments (measured under Sidgwick's direction at Oxford) of the simple compounds $[\{(C_2H_5)_3P\}_2PdCl_2]$ and $[\{(C_2H_5)_3As\}_2PdCl_2]$ were 1.05 and 1.04 D, respectively. Those of $[\{(C_4H_9)_3P\}_2(PdCl_2)_2]$ and $[\{(C_4H_9)_3As\}_2(PdCl_2)_2]$ were 2.34 and 2.52 D, respectively. To give two examples of the chemical evidence for tautomerism, the *n*-butyl member appeared to have the unsymmetric structure, XLIV, for when treated with 2,2′-dipyridyl it gave the compounds (XLV) and (XLVI), and when treated with potassium oxalate gave the oxalato compound (XLVII). It also appeared to have the symmetric structure, XLIIIA or B, for with aniline (2 moles) it gave solely the phosphine-aniline compound, XLIX (*33*).





(XLVIII)

(XLIX)

Later, the structure of the trimethylarsine-palladium bromide compound, $[\{(CH_3)_3As\}_2(PdBr_2)_2]$, was determined by x-ray crystal analysis (Mann and Wells, 1938) and found to possess the trans symmetric structure, XLIIIB, with a planar molecule (*40*). It should be added that each of the many bridged compounds prepared in these investigations appeared to be entirely homogeneous in the crystalline state.

Meanwhile attention had been paid to the copper(I) iodide-tertiary phosphine and arsine derivatives (*36*). An aqueous solution of potassium iodide containing cuprous iodide, when shaken vigorously with, for example, triethylphosphine, rapidly deposited white pellets of composition

$(C_2H_5)_3P$,CuI, and triethylarsine similarly gave an analogous compound of composition $(C_2H_5)_3As$,CuI. These compounds when recrystallized from benzene have sharp melting points. Their molecular weights, determined in boiling acetone or freezing 1,2-dibromoethane, showed however that they were tetramers—e.g., $[(C_2H_5)_3P,CuI]_4$. An x-ray examination showed that the tetrakis(monoiodo-triethylarsine-copper(I)) had a structure (Figure 5) in which four cuprous atoms are at the apex of a tetrahedron. The four iodine atoms lie each at the center, but above the plane, of one face of the tetrahedron. Beyond each cuprous atom is an arsenic atom lying on the elongation of the axis joining the center of the tetrahedron to the copper. The three ethyl groups are then joined to each arsenic atom so that the tetrahedral angle is subtended both at the arsenic and the first (or α) carbon atom of the ethyl groups. Each set of three ethyl groups linked to an arsenic atom are thus bent umbrella-wise over this atom (*36*).

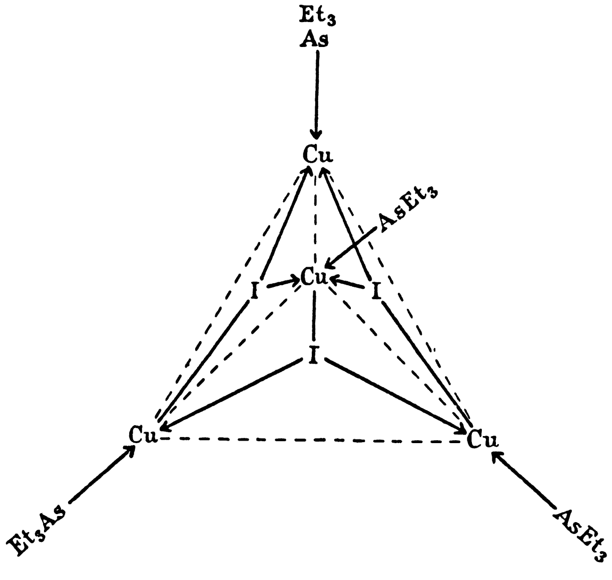


Figure 5. Tetrakis (monoiodo-triethylarsine copper(I))

The broken lines represent the edges of the tetrahedron formed by the four copper atoms, the apex formed by the central copper atom being tilted to show all the bonds joined to this atom. The iodine atoms are depicted on the faces of the tetrahedron in order to show their linkage to the neighboring copper atoms. Actually, they lie well above the plane of the tetrahedral faces. The iodine atom on the rear face of the tetrahedron is not shown. The unbroken lines without barbs represent covalent links; those with barbs represent coordinate links. These are formal linkages, but all the Cu-I links are of course identical (36).

The most recent IUPAC name for the above compound is tetra-μ_3-iodo-tetrakis [triethylarsine copper (I)].

The structure therefore shows the tetrahedral configuration of the copper(I) atom, the coordinated arsenic atoms, and the carbon atoms, and shows that the 3-covalent iodine atom can be regarded as a triangular pyramid—i.e., as if it were lying at one apex of a tetrahedron with its three valencies directed towards the other three apices (*36*).

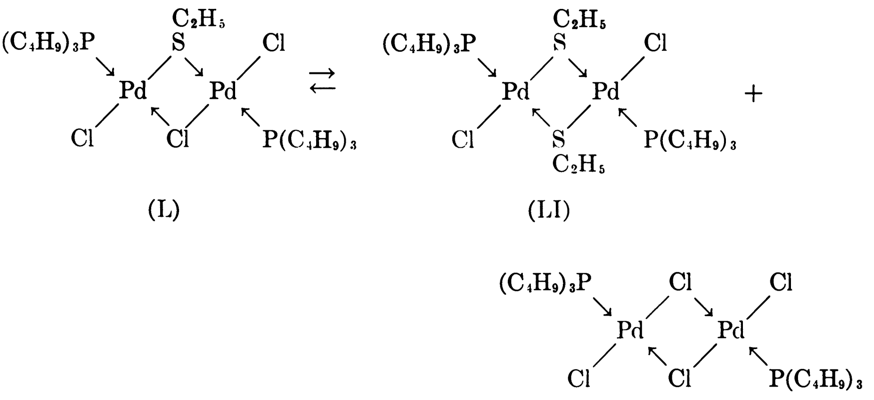
This coordinated structure, which was entirely novel in 1936, is not limited to copper(I) iodide derivatives. Silver(I) iodide forms similar tetrameric compounds with tertiary phosphines and arsines, and since tetrakis(monoiodo-tri-*n*-propylarsinesilver), $[(C_3H_7)_3As,AgI]_4$, is strictly isomorphous with tetrakis(monoiodo-triethylarsinecopper), the two series have identical structures (*41*).

Gold(I) halides, however, form monomers of type $[R_3P{\rightarrow}AuX]$ and $[R_3As{\rightarrow}AuX]$ which can be distilled at low pressures. X-ray crystallographic analysis shows that these compounds have almost certainly linear molecules (*41*). These aurous compounds very readily add on one molecule of a halogen or of a mixed halogen to give the corresponding auric compounds, and all the 10 compounds of formula $[(C_2H_5)_3P{\rightarrow}AuX_3]$, $[(C_2H_5)_3P{\rightarrow}AuX_2X']$, and $[(C_2H_5)_3P{\rightarrow}AuXX'X'']$ were prepared and their relative stabilities investigated (Mann and Purdie, 1940) (*35*).

An x-ray crystal structure investigation of the most stable member, tribromo-triethylphosphinegold(III), carried out in the Cavendish Laboratory of Physics at Cambridge, showed that the 4-covalent auric atom had the planar configuration (Perutz and Weisz) (*46*).

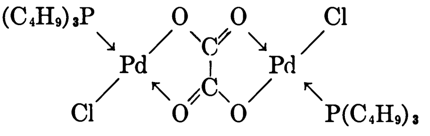
In 1937 another young research worker, Joseph Chatt, joined me. It was already known that the bridged tri-*n*-butylphosphine-palladium(II) chloride compound (XLVIII), when treated with one equivalent of ethylthiol, gave the compound considered to be L (*33*). Treatment with a second equivalent was now shown to give the compound LI. The compound, L, in certain solvents, forms an equilibrium with LI and LII; for example, when a benzene solution of L is warmed, the yellow color darkens as the orange-red compound, LII, is formed and reverts to the yellow color on cooling. This equilibrium is further shown by mixing cold equimolecular ethanolic solutions of LI and LII, when the least soluble (L) slowly crystallizes out. The chemistry of the compounds L and LI was investigated in some detail (*7*).

It had earlier (1936) been assumed that the bridged dichloro-oxalate (XLVII) must necessarily have the oxalato group chelated to adjacent cis positions (as Werner had assumed in simpler compounds), although A. E. Finn's determination of the dipole moment of the compound, XLVII, had made him suggest that it had the trans-symmetric structure, LIII, possibly in equilibrium in solution with the corresponding unsymmetric

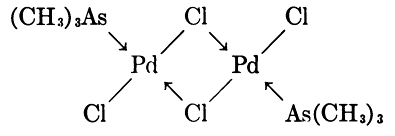


(L) (LI) (LII)

and cis-symmetric forms (*33*). In the compound, LIV, the Pd-Pd distance was known to be 3.4 A. (*40*). An x-ray crystal structure examination of the dichloro-oxalato compound showed that in this compound the Pd-Pd distance was about 5.48 A., and the structure was certainly LIII, with a 4-covalent oxalato group (1938) (*3*).



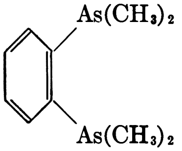
(LIII)

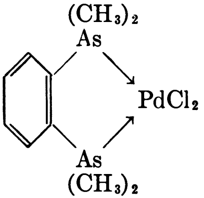


(LIV)

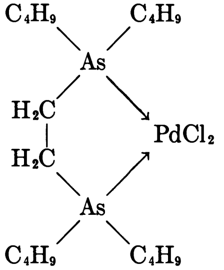
The mechanism of various reactions of the dichloro-bridged compounds was investigated, and the splitting effect of 2,2′-dipyridyl, for example in converting XLIV into a mixture of XLV and XLVI, was shown to be indecisive evidence for the unsymmetric structure XLII or XLIV (*3*).

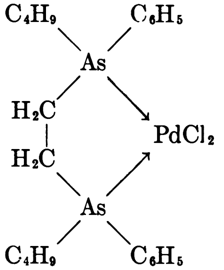
To obtain further evidence regarding the existence of the unsymmetric structure, XLII, *o*-phenylenebisdimethylarsine (LV) was synthesized for the first time (1939) and used for the preparation of the monopalladium(II) compound, LVI, in which the two arsine groups must be chelated in the 1,2 positions—i.e., this compound forms the left-hand portion of the structure XLII (*2*). If the chlorine atoms in the compound LVI are to form a bridge with another $PdCl_2$ unit, the product must have the unsymmetric structure, XLII. In practice, no bridged compounds could be obtained from the compound, LVI, the compact stable structure of which was emphasised. To ensure that this failure was not caused by the size or nature of the groups in the diarsine, LV, the compounds dichloro-bis(di-*n*-butyl-

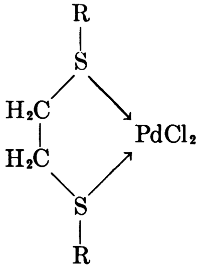

(LV)


(LVI)

phenylarsine)palladium, $[\{(C_4H_9)_2C_6H_5As\}_2PdCl_2]$, and dichloro-bistriphenylphosphinepalladium, $[\{(C_6H_5)_3As\}_2PdCl_2]$, were synthesized and found to form the normal bridged compounds very readily. The latter were incidentally the first bridged compounds to be prepared from arsines or phosphines carrying aryl groups. Furthermore, the ethylene-diarsine compounds, LVII and LVIII, and the ethylenedisulfide compounds, LIX ($R = C_2H_5$ or n-C_8H_{17}), would not form bridged compounds. [The compound LVIII existed in two forms, m.p. 172–174°C. and 185–186°C., one of which must have been the racemic and the other the meso form.]


(LVII)


(LVIII)


(LIX)

In view of these results, a far more detailed investigation of the probable mechanism of various reactions which had earlier (*33*) been cited as evidence for the unsymmetric and symmetric structures, XLII and XLIIIA and B, was undertaken, and it became clear that these reactions did not provide unambiguous evidence on these points (*2*).

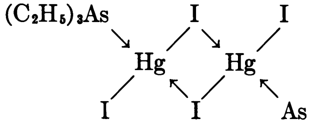
Our diarsine (LV) has since been used by many workers in the coordination field as an invaluable chelating agent for the preparation of compounds of type LVI and of other types.

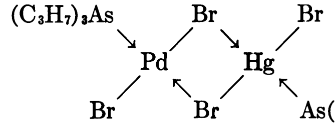
An investigation of the tertiary phosphine and arsine derivatives of cadmium(II) and mercuric halides (1940) was brought to an end by the Second World War; nevertheless, it proved such a rich vein that the results can only be very briefly summarized (*12*).

Cadmium halides gave three classes of crystalline compounds, of type (A) $[(R_3P)_2CdX_2]$, (B) $[(R_3P)_2(CdX_2)_2]$, and (C) $[(R_3P)_3(CdX_2)_2]$.

Mercuric halides gave compounds of types analogous to (A), (B), and (C) and also gave two additional classes, (D) $[(R_3P)_2(HgI_2)_3]$ and (E) $[(R_3P)_2(HgX_2)_4]$. These five classes in the mercuric series were usually given also by the comparable arsines; the stability of individual members often depended largely on the halide employed.

X-ray examination showed that the class B compound, $[\{(C_2H_5)_3As\}_2(HgI_2)_2]$, has the bridged trans-symmetric structure, that each mercuric atom has four groups arranged tetrahedrally around it, and that the molecule has a center of symmetry (LX). It is therefore structurally similar to palladium compounds of type XLIIIB, except that the latter has a planar molecule. The structure of the compound of class (D), $[\{(C_4H_9)_3As\}_2(HgBr_2)_3]$, was also determined.


(LX)

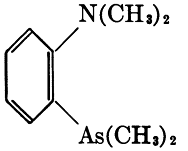

(LXI)

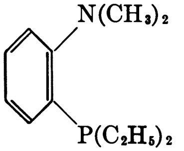
These results enabled us (*34*) to prepare several bridged compounds having two different metals. One of these was di-μ-bromo-dibromobis(tri-*n*-propylarsine)mercury(II)palladium(II) (LXI), in which the palladium portion is of course planar and the mercuric portion is tetrahedral.

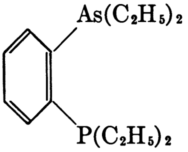
The wide variety of compounds recorded in these papers would probably richly repay further x-ray crystal analysis.

The rapid development of synthetic methods in the organo-phosphorus field (and to a lesser extent in the organo-arsenic field), which occurred after the Second World War, enabled us to prepare a number of compounds closely allied to our original diarsine (LV) and to study their value as chelating ligands.

The main types (1955–57) are exemplified by *o*-dimethylaminophenyldimethylarsine (LXII) (*37*), *o*-dimethylaminophenyldiethylphosphine (LXIII) (*38*), *o*-diethylphosphinophenyldiethylarsine (LXIV) (*15*), and 4-methyl-*o*-phenylenebis(diethylphosphine) (*10, 14*).


(LXII)


(LXIII)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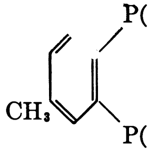
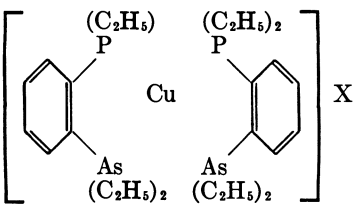
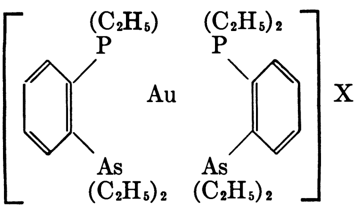

(LXV)

The results obtained in the use of the amine-arsine (LXII) and the amine-phosphine (LXIII) are too detailed and intricate to allow a clear summary; both compounds could act as chelate ligands or could coordinate solely by the arsine and phosphine groups, respectively.

The products obtained from the phosphine-arsine (LXIV) proved to be of considerable interest (*5*). This ligand combined with copper(I) chloride, bromide, and iodide to give the bis-(*o*-diethylphosphinophenyldiethylarsine)copper(I) halide (LXVI, X = Cl, Br or I); the stabilities of these three salts increased from the chloride to the iodide. Other coordinated products were obtained under different conditions.



(LXVI)



(LXVII)

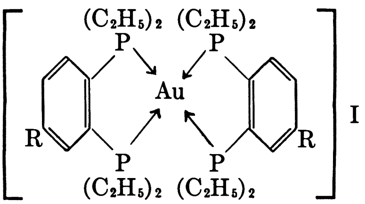
Silver iodide dissolved in aqueous potassium iodide gave the silver compound analogous to LXVI, but even the iodide had only moderate stability.

Tetrachloroauric(III) acid in aqueous ethanol reacted with an excess of the phosphine-arsine undergoing reduction and chelation to give the cation, LXVII, precipitated as the colorless, highly stable iodide. The 4-coordinate aurous atom in this compound has the tetrahedral configuration, and attempts were made to resolve the cation into optically active forms. Fractional recrystallization of eight salts having different optically-active anions failed to give any indication of resolution.

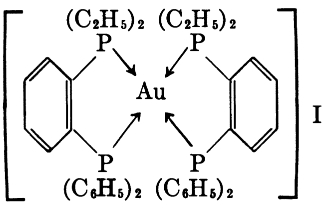
X-ray investigation of the salt, LXVII (X = I), and its copper(I) analogue, LXVI (X = I), showed that, although the positions of the arsenic and the phosphorus atoms are clearly defined, the atoms of the two elements cannot be differentiated owing to an apparently random distribution—i.e., sites which for convenience can be labeled A and B may at one place in the crystal be occupied by arsenic and phosphorus, but crystallographically equivalent sites A′ and B′ may be occupied by P and As, or by As and P, respectively, the random distribution being quite distinct from the regular arrangement to be expected in a racemate.

This random distribution would almost certainly cause the two diastereoisomers formed with an optically-active anion to form mixed crystals which could not be separated by fractional crystallization (*5*).

In later work (1964), Davis and Mann (*11*) prepared the stable colorless iodides LXVIII (R = CH_3 and C_6H_5) and LXIX. The iodide ion in the salt, LXVIII (R = CH_3), was replaced in turn by nine optically-active anions, but again fractional crystallization gave no evidence of resolution; similar experiments with the salts, LXVIII (R = C_6H_5) and LXIX, gave the same result.

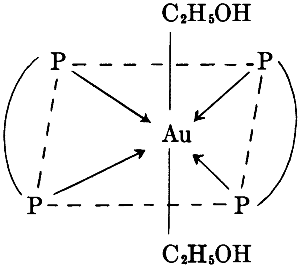


(LXVIII)



(LXIX)

The numerous salts of these three cations had varying solubilities in different organic solvents, but almost all had high solubility in cold ethanol and methanol. This may indicate that the cation has united with the alcohol to give a 6-coordinate cation, indicated as LXX, which is stable



(LXX)

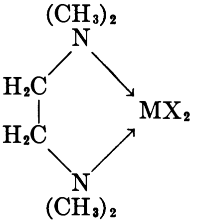
in solution but discards the ethanol when the cation is precipitated as the iodide or picrate.

The auric salt similar in composition to LXIX, but having a planar configuration and a trivalent cation, and other kindred auric compounds were studied (*11*).

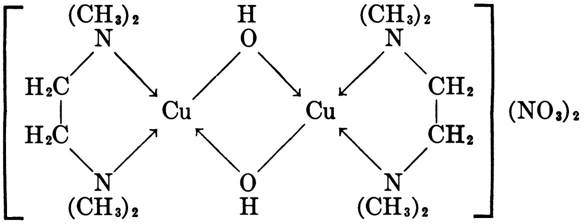
Fresh light on the comparative chelating powers of various types of ligand arose from our discovery (Mann and Watson (1958)) that *NNN'N'*-tetramethylethylenediamine (p. 128) and 1,4-dimethylpiperazine will coordinate very stably with various divalent metallic atoms, although simple tertiary amines seldom coordinate other than weakly with metals (*39*).

The tetramethylethylenediamine gave the yellow-orange LXXI (M = Pd,X = Cl) and the deep orange LXXI (M = Pd,X = Br); both these compounds could be recrystallized unchanged from water even when it contained an excess of the free diamine. The diamine gave the pale yellow derivatives, LXXI (M = Pt, X = Cl) and LXXI (M = Ir, X = Cl), and the two deep green copper(II) derivatives, LXXI (M = Cu, X =

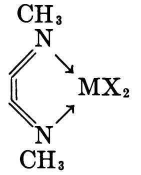
SCN) and LXXI (M = Cu, X = $C_6H_2O_7N_3$), the last being a very rare example of picrate groups being directly coordinated to a metal. Copper nitrate gave the deep blue hydrated di-μ-hydroxybis(*NNN'N'*-tetramethylethylenediamine)dicopper(II) dinitrate (LXXII). The formation of compounds of type LXXI is not restricted to divalent metals having a planar 4-coordinate configuration, for cadmium gave the less stable colorless compound, LXXI (M = Cd, X = Cl).



(LXXI)



(LXXII)



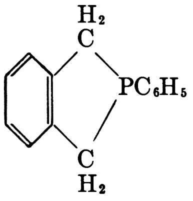
(LXXIII)

1,4-Dimethylpiperazine gave similarly colored compounds (LXXIII) with $PdCl_2$, $PdBr_2$, $PtCl_2$, and $IrCl_2$. In all the compounds (LXXIII), the dimethylpiperazine has necessarily adopted the "boat" configuration.

All the compounds of types LXXI and LXXIII showed negligible conductivities in nitrobenzene solution. The lack of any compound having two molecules of either diamine coordinated to one atom of the metal is almost certainly due to the steric hindrance of the first molecule of the diamine (*39*).

The very considerable stability of compounds of type LXXI and LXXIII, in spite of the fact that LXXI has two tertiary alkylamine groups and LXXIII has two very similar groups, indicates that if a group having normally a very weak coordinating power can be associated with another such group in a molecule which is dimensionally suitable for chelate coordination, each group will mutually reinforce the coordinating power of the other—and that to a far greater extent than chemists had thereto realized.

A final mention should be made of the tertiary phosphine, 2-phenylisophosphindoline (LXXIV), which is not difficult to make (*25*) and which has a remarkable power of giving coordinated metallic derivatives which are stable, although the metal is showing an unusual coordination number often associated with instability (1958) (*6*, *7*, *8*).



(LXXIV)

$[(C_{14}H_{13}P)_2MX_2]$

(LXXV)

$[(C_{14}H_{13}P)_3MX_2] \rightleftarrows [(C_{14}H_{13}P)_3MX]X$

(LXXVI) (LXXVII)

With the dihalides of platinum(II), palladium(II), and nickel(II), this phosphine, of formula $C_{14}H_{13}P$, gives the normal 4-coordinate derivatives, LXXV (M = Pt, Pd, or Ni; X = Cl, Br, or I), but also gives 5-coordinate derivatives, LXXVI. The latter are stable in the crystalline state and in certain solvents—e.g., dichloromethane, but in ethanol and nitrobenzene undergo considerable ionization to LXXVII. An ethanolic solution of the dichloro-Pt or Pd compounds when treated with sodium picrate and sodium perchlorate deposits the salts $[(C_{14}H_{13}P)_3MCl]C_6H_2N_3O_4$ and $[C_{14}H_{13}P)_3MCl]ClO_4$, respectively. The palladium derivatives, LXXVI, exist in different forms; the dibromide, for example, occurs as a yellow and a red form, and the latter has been shown by x-ray crystal analysis to have a 5-coordinated palladium atom in a square pyramidal configuration (Figure 6) (*8*).

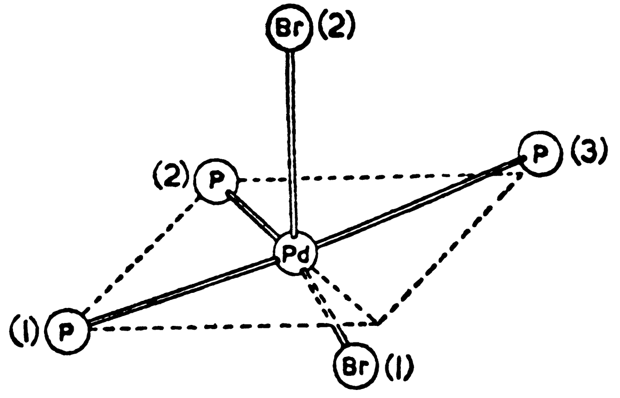


Figure 6. Tris (2-phenylisophosphinodoline)dibromopalladium (LXXVI; M = Pd, X = Br) (red form)

The rectangle can be considered to be drawn in the ideal plane defined by the atoms Pd, P(1), P(2), and P(3) which are nearly coplanar, although the atom P(3) is slightly raised above this plane. The atom Br(1) is slightly below the plane (8).

The platinum in the dihydrated derivatives of type LXXVI is undoubtedly 6-coordinated, and of formula $[(C_{14}H_{13}P)_3(H_2O)_2PtCl]Cl$ and $[(C_{14}H_{13}P)_3(H_2O)_2PtSCN]SCN$; the coordinated and the ionic SCN groups in the latter are readily detected by their different UV absorption bands (*8*).

The phosphine combines with cobalt(II) dihalides to give the 5-coordinate derivatives, LXXVIII, but these do not undergo ionization in organic solvents. Rhodium(III) trihalides give normal 6-coordinate compounds, LXXIX, whereas sodium hexachloroiridate(IV), Na_2IrCl_6,

$[(C_{14}H_{13}P)_3CoX_2]$
(LXXVIII)

$[(C_{14}H_{13}P)_3RhX_3]$
(LXXIX)

$[(C_{14}H_{13}P)_3IrHX_2]$
(LXXX)

$[(C_{14}H_{13}P)_3IrX_3]$
(LXXXI)

gives the hydride dichloride, LXXX (X = Cl), which with chlorine gives the trichloride, LXXXI (X = Cl). The compounds, LXXX and LXXXI, where X = Br, were similarly prepared (*7*).

$[C_{14}H_{13}P, CuI]_4$
(LXXXII)

$[C_{14}H_{13}P, AuX]$
(LXXXIII)

$[(C_{14}H_{13}P)_2MX]$
(LXXXIV)

$[(C_{14}H_{13}P)_3MX]$
(LXXXV)

$[(C_{14}H_{13}P)_4Cu]X$
(LXXXVI)

The phosphine reacts with copper(I) iodide to give the tetramer, LXXXII; silver(I) iodide gives a similar less stable product, and gold(I) halides give the normal monomers, LXXXIII. The halides of all three metals give the 3-coordinate compounds, LXXXIV, of which the iodo members are the most stable. The gold(I) iodide derivative, LXXXIV (M = Au, X = I), is remarkable in existing in organic solvents as a covalent trigonal plane structure and in the crystalline state as a largely ionized salt (*6*).

The halides of all three metals give the covalent 4-coordinate derivatives, LXXXV, but—quite exceptionally—only copper(I) gives 4-coordinate salts, such as LXXXVI (X = NO_3 or ClO_4). As we have previously seen, gold(I) halides require two molecules of an active chelate ligand to give stable salts of this type (*5, 11*).

This very brief account of some of the coordination derivatives of 2-phenylisophosphindoline will indicate its remarkable powers as a coordinating ligand, for which an explanation has been suggested (*8*).

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The Nomenclature of Coordination Compounds from Pre-Werner Times to the 1966 IUPAC Report

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Concurrently with the development of the coordination theory, Alfred Werner proposed a system of nomenclature for coordination compounds. Most of the aspects of this nomenclature system are still in use today: the o-ending for negative ligands, order of classes of ligands, termination for complex anions, designation of bridging groups, and distinction among structural isomers. However, current usage for indicating the oxidation state of the central ion (or charge on the complex ion) differs from that proposed by Werner. Further, several terms useful in describing coordination compounds have been added: ligand, chelate, multidentate, etc. Nevertheless, the Werner system has been adapted with only slight alteration to keep pace with the rapid growth and increased scope of coordination chemistry. Recently proposed expansion of the system by the IUPAC Commission on the Nomenclature of Inorganic Chemistry gives promise of dealing with even more varied and complicated compounds.

The major purpose of this paper is to trace the development of nomenclature practices in the broad area of coordination compounds from the near chaos before the enunciation of the coordination theory by Alfred Werner to the present day. A secondary purpose of this paper is to give an insight into the manner in which nomenclature principles develop and become standard practice. It will be shown how, once a sound basis for a system of nomenclature was enunciated, it has been possible to modify and extend practices to cover a rapidly expanding field of knowledge.

Table I. Names Based on Color[a]

Name	*Color*	*Formula*
flavo	brown	*cis*-$[Co(NH_3)_4(NO_2)_2]^+$
croceo	yellow	*trans*-$[Co(NH_3)_4(NO_2)_2]^+$
luteo	yellow	$[Co(NH_3)_6]^{3+}$
praseo	green	*trans*-$[Co(NH_3)_4Cl_2]^+$
roseo	rose-red	$[Co(NH_3)_5H_2O]^{3+}$
purpureo	purple-red	$[Co(NH_3)_5Cl]^{2+}$
violeo	violet	*cis*-$[Co(NH_3)_4Cl_2]^+$

[a] These names were proposed by Fremy in 1840 (*14*, *15*).

Nomenclature before Werner (to 1897). The Lavoisierian system of nomenclature, even with the Berzelius modifications, provided no suitable names for that class of compounds which later was designated coordination compounds. Names based on the patterns for double salts and addition compounds were not satisfactory because the properties of these materials were not those consistent with the patterns provided. Consequently, names based on properties, especially color (Table I), or the names of prominent investigators became popular (*2*) because they, at least, did not commit the user to any theory of their structure. The developments in organic chemistry after 1860 did not contribute to the understanding of these strange compounds, so there was no carry-over to them of the nomenclature developments in organic chemistry.

Despite Werner's antipathy for names based on color, such names were generally used well into the present century. For example, the name "luteo," originally proposed for $[Co(NH_3)_6]^{+3}$, was generalized to include $[Co(en)_3]^{+3}$, $[Co(bipy)_3]^{+3}$, $[Co(trien)_2]^{+3}$, and other cobalt compounds in which six amine nitrogen atoms are coordinated to cobalt (or even other metal ions) in the "luteo series." As long as cobalt and chromium were the only metal ions included, the reference to color had real meaning. However, to consider colorless $[Ru(NH_3)_6]^{+3}$ (*16*) as a member of the "luteo series" was, to say the least, somewhat ambiguous.

Proposals of Werner (1897). Early in his investigation of coordination compounds, Werner offered a systematic scheme of nomenclature which surmounted all of the previous difficulties. Further, the basic principles of that scheme of nomenclature, although considerably modified, persist today. Werner stated the principles of his system thus (*33*, *38*):

1. Names obtained from the color of the compounds are to be avoided.
2. The name of the resulting complex is to be made up by placing side by side the names of the components.
3. The names of the atoms (or radicals) which are linked to the central metallic atom are to be placed before the name of this central atom. When carrying this out the following order is to be preserved: The names

of the acid residues come first, then follow the names of the groups which resemble ammonia, and directly before the name of the metallic atom are to be placed the number of ammonia molecules.

4. The molecule of ammonia is to be expressed by the word ammine (spelt with a double m), in order to distinguish it from the organic amine. Water, after Palmaer's suggestion is expressed by aquo.

5. The names of the acid residues which are not in the first binding zone are placed after the name of the central metallic atom.

However, more was involved than was given in those simple statements. Werner was not satisfied with the inorganic nomenclature practices of his time for even binary compounds and had earlier adopted a series of suffixes (or infixes) to indicate valence (*34*):

> It would be even more simple if all those compounds of the same valency had their names ending in the same letter or suffix, thus:

MeX	a-	Compound	(monovalent)
MeX_2	o-	"	(divalent)
MeX_3	i-	"	(trivalent)
MeX_4	e-	"	(tetravelent)
MeX_5	an-	"	(pentavalent)
MeX_6	on-	"	(hexavalent)
MeX_7	in-	"	(heptavalent)
MeX_8	en-	"	(octavalent)

He incorporated these into his suggestions for the nomenclature of coordination compounds. The result was names such as these (*33*):

$[Cr(NH_3)_6](NO_3)_3$	Hexamminchromi nitrate
$[CoCl(NO_2)(en)_2]Br$	Chloronitritodiethylendiamincobalti bromide
$[Co(OH_2)_2(NH_3)_4]Cl_3$	Diaquotetrammincobalti chloride
$[Pt(OH)_2(NH_3)_4]Cl_2$	Dihydroxotetramminplate chloride

Werner did not place as much emphasis on names for complex anions as he did for complex cations and neutral entities. Consequently, such names as ferrocyanide and cobaltinitrite persisted almost to the exclusion of the more consistent hexacyanoferroate and hexanitritocobaltiate. However, it is entirely clear in papers published after those enunciating his principles for nomenclature that he inaugurated practices which are still followed today.

Werner's contributions did not end with the items so far mentioned. He utilized the terms cis and trans (*40*) and developed a numbering system for designating isomers (*39*). In his study of polynuclear compounds, he introduced the symbol μ- for designating bridging groups (*36*) and the infix -ol designating bridging >OH (*37*). In order to account for the presence of water in some hydrates in excess of the normal coordination number of the cation concerned, Werner postulated the coordination of double water molecules, H_4O_2 (*35*). He designated these as bisaquo groups.

Post-Werner Period (1919–1930). Following Werner's time, all writers on coordination compounds used names based, to at least some extent, upon his system of nomenclature, although there were many loose practices. The device which Werner introduced to indicate valency and which was used by some of his contemporaries did not find general acceptance. Perhaps the difficulties of remembering six different suffixes and of pronouncing them so that they would be clearly understood were too great. Some other practices became common. The attached groups became known as ligands. (The term ligand is a very popular one today. Occasionally one even finds ligancy used in place of coordination number (*4*).) Also the center of coordination, perhaps by analogy to the benzene nucleus, was often called the nuclear atom. Two important terms were introduced by Sir Gilbert Morgan. These were chelate (*25*) and multidentate (*26*). Both were adjectives to describe the character of coordination groups. Today chelate is widely used not only as an adjective but also as a noun and as a verb. Further, the noun may be used to designate the attached ligand (chelated group), the free ligand (chelating group), or the entity resulting from chelation (metal chelates). As illustrations of the abuse of chemical terms, two cases stand out in the author's mind: the person who thought that the term chelate referred only to those compounds containing rings formed through hydrogen bonds and another who spoke of a monodentate chelate group. Chernyaew (*5*, *6*) devised a structural nomenclature scheme by indicating which groups in a coordination structure were in trans positions.

International Union of Pure and Applied Chemistry (IUPAC) (1919–1940). From this point forward, any account of the growth of nomenclature practices for coordination compounds is of necessity concerned with activities of the International Union of Pure and Applied Chemistry. This body appointed a Committee for the Reform of Inorganic Chemical Nomenclature which published rules for naming inorganic compounds in 1940 (*19*, *20*, *21*). (There have been some confusing changes of titles during the history of the International Union. It was founded in 1919 as the International Union of Pure and Applied Chemistry but later dropped the qualifying adjectives (*29*) only to return to the original name still later. The original Commission on the Reform of Inorganic Chemical Nomenclature became the Commission on the Nomenclature of Inorganic Chemistry.

Many have wondered why the appearance of a report on inorganic nomenclature was delayed so long, whereas that on organic nomenclature was published in 1930. (Both commissions were appointed in 1919.) The reason is quite simple. The organic commission had the advantage of many years of prior cooperative effort in the development of a systematic nomenclature, whereas the inorganic commission had to pioneer for such cooperative effort. The large number of organic compounds and the varied types very early created among organic chemists an interest in nomenclature. Conversely, there were no such barriers to mutual understanding within the body of inorganic chemistry. Actually, there were some preliminary reports of the inorganic commission (*8*, *23*, *24*).

This set of rules was based upon a report drawn up by H. Remy (*32*) on behalf of the German Chemical Society and in collaboration with some of its members of whom A. Stock was the most active. The portion of the rules devoted to coordination compounds amounts to little more than half a page of the *Journal of the American Chemical Society.* In essence, the rules endorsed the nomenclature practices introduced by Werner with the substitution of Stock numbers to indicate valence in place of the cumbersome vowel suffixes of Werner. The amount of page space devoted to coordination compounds in the rules is no indication of the influence of the rules upon practice in the naming of coordination compounds. In a few years, systematic names had almost completely displaced unsystematic names which had been firmly established.

General Items Involved in Coordination Nomenclature. In following the development of nomenclature practices for coordination compounds, one needs some frame of reference to compare the continuities and changes. This is perhaps most easily done by reference to a set of principles or rules which has been used by the author on other occasions (*10*, *11*, *13*). We shall follow the changes in the statement of a given rule while the specific field covered by the rule does not change. Prior to the time of Werner, there was no basis for a systematic nomenclature. The rules and practices established by Werner might be expressed as a number of simple rules (*13*).

Rule 1. *Order of Listing Ions.* The cation is named first, followed by anion.

Rule 2. *Characteristic Endings of Coordination Groups.* Neutral groups have no characteristic ending; negative groups have the ending *-o*.

Rule 3. *Order of Classes of Ligands.* The ligands are placed before the central atom(s) with anionic ligands first, followed by neutral ligands. Among the latter, NH_3 is expressed by *ammine* and H_2O as *aquo.* (The final *-o* does not indicate a negative group in this instance.)

Rule 4. *Order within Classes of Ligands.* Ammonia is listed last among the neutral groups.

Rule 5. *Use of Numerical Prefixes.* (Werner used the prevalent practices: di-, tri-, etc., but introduced bisaquo for a doubled water molecule, H_4O_2.)

Rule 6. *Terminations for Anions.* The suffix -ate is used as in sulfate, etc.

Rule 7. *Designation of Oxidation Numbers.* (Werner used his own vowel suffixes.)

Rule 8. *Bridging Groups.* The Greek letter μ- is placed in front of the name of the bridging group: μ-amino, μ-diamino, μ-peroxo-amino. (Werner designated bridging >OH by -ol.)

Rule 9. *Designation of Point of Attachment.* This is covered by Rule 10.

Rule 10. *Designation of Structural Isomerism in the Ligand.* Ligand isomerism is indicated by separate names for the isomeric ligands: -SCN, thiocyanato *vs.* -NCS, isothiocyanato; -NO_2, nitro *vs.* -ONO, nitrito.

Rule 11. *Designation of Geometrical Isomerism in the Coordination Sphere.* Axial substitution in Ma_4b_2 is designated as trans and corner substitution by cis. Otherwise, the trans isomer was 1,6- and the cis 1,2-.

Rule 12. *Designation of Optical Isomerism.* (Werner used the practice of his time for organic compounds.)

Rule 13. *Coordination of Groups in Lower Functionality than Usual.* (The examples known to Werner were simple and presented no problem.)

Other general aspects of the nomenclature of coordination compounds became important after Werner's time. Rules for these will be given at the appropriate places. They are:

Rule 14. *Direct Linkage of Coordination Centers*
Rule 15. *Coordinated Oxide Ions*
Rule 16. *Abbreviations in Formulas*
Rule 17. *Extended Structures*
Rule 18. *Homoatomic Aggregates*

The rules specifically stated by Werner covered Rules 1, 3, and 7 directly and Rules 2 and 4 by implication. Practices introduced by Werner covered Rules 5, 6, 8, 10, 11, 12, 13, and 16 to at least some extent. The IUPAC Commission in its 1940 report covered Rules 1, 2, 3, 5, 6, and 7 (*19*, *20*, *21*). The practice covered by Rule 7 marked the only significant departure from Werner's proposals. In place of the vowel suffixes of Werner, the charge on the central atom (ion) was designated by a Roman numeral (Stock system).

Review Following IUPAC Report (1945–48). During World War II a small group of inorganic chemists working at one of the laboratories maintained by the Manhattan District reviewed the entire subject of the nomenclature of coordination compounds. The result of the study was to formulate rules under general aspects (the forerunners of those used here) for the practice of the IUPAC Commission, to formulate additional ones covering other practices of Werner and his followers, and finally to suggest additional practices as rules (*13*). There were a few definite proposals in this publication: the ending -ium for positively charged, coordinated groups (Rule 2); aqua instead of aquo (so that only anionic ligands had a terminal -o) (Rule 2); use of multiplicative prefixes (Rule 5);

the addition of zero to the Stock numbers for zerovalent compounds (Rule 7) (*3*); use of italicized symbols for indicating the point of attachment of a ligand to the central atom (Rule 9); a way to indicate direct linkage of two centers of coordination: $(EtNH_2)_4ClPt\text{-}PtCl(EtNH_2)_4$ = *sym*-dichlrooctakis(ethylamine)biplatinium(IV) ion (Rule 14); and avoidance of uranyl, etc., in names of coordination entities (Rule 15). The publication had the desirable effect of focusing attention on the problems of inorganic nomenclature, generally, and especially upon those within the field of coordination compounds.

Ewens and Bassett Proposals (1949). Shortly after World War II the International Union Commission was reactivated and this time included an American representative, Alexander Silverman. In order to present some of the problems of inorganic nomenclature to chemists generally, Ewens and Bassett (both were members of the IUPAC Commission) published an article pointing out some of the problems of inorganic nomenclature and suggesting solutions (*9*). They endorsed an ending for positively charged ligands and aqua for water as a ligand (Rule 2). They argued strongly for the order: cationic, neutral, anionic, in listing ligands (Rule 3) and proposed a definite order of ligands within groups (Rule 4). Two of their proposals were especially important: one was the designation of the actual charge on the ion, tetracyanonickelate(4-) for $Ni(CN)_4^{-4}$ instead of using Stock numbers (Rule 7), and the other was the use of "poly" to designate extended chain structures for many solid coordination compounds (Rule 17).

ACS Symposium, 1951. As part of the program of the ACS meeting at the time of the IUPAC meeting in New York, a symposium on nomenclature was held. The nomenclature of coordination compounds was discussed in relation to general inorganic nomenclature (*10*). Rules 1–16 were presented and discussed at that time. A few items are worthy of mention:

Rule 2.	Aqua and the ending -ium for cationic ligands were recommended.
Rule 3.	The order cationic, neutral, anionic was favored in agreement with Ewens and Bassett.
Rule 4.	The following orders for listing groups were proposed: neutral groups: (1) chelate groups; (2) simple groups; negative groups: (1) $O^=, OH^-$; (2) organic groups in order of decreasing complexity; (3) polynuclear inorganic anions; (4) mononuclear anions in the order of decreasing complexity.
Rule 7.	It was recognized that the Stock system had become firmly established.
Rules 8–11.	The recommendations given in the previous summary were confirmed. It was further proposed that the

functionality of a multiply bridging group be indicated thus: μ^4-.

Rule 13. Additional examples given.
Rule 14. Few examples known at that time.
Rules 15–16. As in previous summary.

IUPAC Revised Rules, 1953–57. The above items among many other were considered by the IUPAC in Stockholm in 1953 and a tentative set of rules was issued from that meeting (Comptes Rendus 17th Conference). Further items and criticisms were considered in Zurich 1955, Reading 1956, and Paris 1957; finally in 1957 the IUPAC Commission adopted a revised version of the rules for naming inorganic compounds (*7*, *27*). A section of the rules (nearly four pages) was devoted to coordination compounds. Beyond the items covered in the 1940 rules, the following were included in the 1957 version:

Rule 2. The ending -o for negative groups was accepted with aquo for neutral water as an exception. Shortened forms for several simple amines were accepted. Organic anionic groups are to end in -ato.
Rule 3. The order negative, neutral was retained.
Rule 4. Detailed orders of preference which are hard to remember were given.
Rule 5. The use of multiplicative prefixes and parentheses was accepted.
Rule 7. Negative Stock numbers and zero were recognized. The Ewens-Bassett charge numbers were rejected.
Rule 8. The use of -μ-amido- and -di-μ-amido- was adopted for bridging groups.
Rule 9. The italicized symbols for elements were recommended to indicate point of attachment.
Rule 11. The prefixes *asym-* and *sym-* were endorsed.
Rule 14. This was omitted as a rule but one example was given.
Rule 15. Acceptance of this was implied in report.
Rule 17. Substitution of *catena-* for *poly-* in extended chain structures.

ACS Symposium, 1959. When an IUPAC Commission makes a report, the report is first published in the *Comptes Rendus, IUPAC*. Following this initial publication, when the Rules are tentative, there is an official publication of the rules by IUPAC and of national versions (especially in languages other than English and French). During these waiting periods, copies are frequently shared with others. In order to acquaint Americans with the new version of the rules and with problems still remaining, a symposium on inorganic nomenclature was held in September, 1959 by the Divisions of Inorganic Chemistry and of Chemical Literature. I was asked to discuss coordination compounds and took occasion to summarize what the new rules covered and what remained to be done. Inasmuch as these papers were not published until 1964, the summary of coordination compound nomenclature had to be completely rewritten because of developments that had taken place in the interim (*11*). Comments on some of the important nomenclature innovations during this period are in order.

Practices of Chernyaew and of "Gmelins Handbuch." In 1928 Chernyaew introduced a method for designating groups in trans positions and thus incorporated space orientation into names and linear formulas (*5*, *6*). This practice was used greatly in the Russian literature but did not seem to catch on elsewhere. However, when faced with the tremendous task of compiling the literature on coordination compounds of platinum the editors of "Gmelins Handbuch" (*11*) adopted a system which was essentially an abbreviated form of the Chernyaew method for designating groups in trans positions and in an equatorial plane.

The editors of "Gmelins Handbuch" have also adopted a uniform pattern for using abbreviations (*17*, *18*). Details are given in a recent publication (*12*).

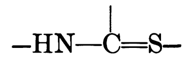
Chemical Abstracts Subject Index, 1962. The Index to Vol. 56 of *Chemical Abstracts* inaugurated some definite changes in inorganic nomenclature practices related to indexing. The 1957 IUPAC Report was adopted with certain exceptions. Some of these exceptions merit mention here.

Rule 2.	Different names for a few common ligands: hydro, hydroxy, peroxy, mercapto, thio, dithio, hydroperoxy. In case of doubt, the charge on a ligand is indicated thus: tartrato(3-) for $^-OOCCH(O^-)CH_2$-COO^-. Organic radicals listed with neutral groups.
Rule 4.	Ligands listed alphabetically within classes. The ligands CO and CN^- are considered to be organic.
Rule 5.	Non-simple ligands require multiplicative prefixes and parentheses while simple ones do not. Elaborate (and somewhat arbitrary) bases for distinguishing between simple and non-simple.
Rules 9, 11, 14, 16, and 17.	Not mentioned.
Rule 13.	Designation of the charge of a coordinated anion is useful in indicating coordination in lower functionality than usual: tartrato(2-) *vs.* tartrato(3-).

General System of Locant Designators (1965). Although, after Werner, a number system of locant designators for designating structures has been used to some extent, the true potential of such a system was never developed. Further, the system was never extended to configurations other than square planar and octahedral and was used with multinuclear compounds to only a limited extent. A good deal of interest in the use of locant designators resulted from two papers by McDonald and Pasternak (*22*, *28*). They developed a linear-formula notation for coordination entities which included all known configurations. They also indicated how this could be extended into a system of nomenclature.

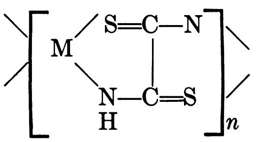
Present Status Summary, 1964–5. The delay in the publication of the 1959 symposium papers made it possible to summarize not only the 1957 IUPAC Report but also the 1962 statement of practices of *Chemical Abstracts* and other developments (*11*). In fact, it was necessary to write an addendum after the publication of the summary (*12*).

Rule 8. Refinements in the indication of bridging were suggested: μ_3-iodo to indicate attachment to three centers of coordination; μ-methylphosphido(2-) to indicate charge on a bridging group; and μ^4- or $\mu(4)$- to indicate the functionality of a bridging group such as

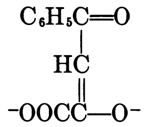


$$\begin{array}{c}-S{=}C{-}NH-\\ |\\ -HN{-}C{=}S-\end{array}$$

in an extended structure:



Rule 9. At times it is necessary to designate not only the heteroatom in a ligand chain but also the carbon atoms to which coordinated groups are attached:



Benzoylpyruvato-O^{α}, O^{γ}-

or benzoylpyruvate-O^1, O^3-

The preparation of numerous compounds in which there are direct carbon to metal bonds at times necessitates a means to distinguish between pi- and sigma-bonding. This has been done by the use of σ- (*1*) and π- (*30, 31*): $Fe(\pi\text{-}C_6H_5)(\sigma\text{-}CH_2CH{=}CH_2)(CO)_2$, π-cyclopentadienyl-σ-alkyldicarbonyliron.

Rule 14. Not only are there now many examples of bonds between like metal atoms but also between unlike metal atoms.

Rule 17. The study of coordination polymers has produced many examples of extended structures, some of them quite complicated.

The review also pointed out some inconsistent practices in names for organic ligands, the need for agreement of organic ligand names with accepted organic nomenclature practices, and inconsistent practices in the eliding of vowels (e.g., pentammine *vs.* pentaammine).

The addendum to the "Present Status" summary discussed the matter of locant designators (Rule 11), the coordination of ligands in less than their maximum functionality (Rule 13), abbreviations (Rule 16), and the coordination of tautomeric forms of a ligand.

The 1966 Revision of the IUPAC Rules. In 1963 I was asked to become a titular member of the IUPAC Commission on the Nomenclature of Inorganic Chemistry. My first assignment was to prepare a manuscript covering a numbering system for coordination compounds. I had been busy with the revision of a critique of nomenclature in this field, and the assignment only extended the activities in which I was engaged. At the Toulouse meeting of the Commission (1964), general agreement was obtained on several features of coordination nomenclature. A subcommission (Chatt, Prue, Fernelius) was assigned the task of preparing a set of rules covering the entire subject but, in the instance of several major matters, alternatives were to be provided for the convenience of the entire commission in reaching final decisions. By March 1965 a draft of rules was available for a meeting of the subcommission. There was remarkable agreement among the members of the subcommission and they were able to extend the coverage of the proposed rules beyond anything that had been envisioned. A revised draft was made available to the meeting of the full Commission in Paris in July. Choices were made on the alternates requested and further revisions adopted. It was possible to present a final copy to the Council of the Union for adoption as tentative rules. These are now in proof and should be published shortly. Let us see what they involve.

In general, the elision of vowels is to be avoided.

Rule 2. Aqua, mercapto, methylthio, and hydrido were adopted. The approval of aqua settled a long time inconsistency and of mercapto and methylthio brought complete agreement between the Inorganic and Organic Commissions. Efforts to adopt chlorido, bromido, etc., in place of the simpler chloro, bromo, etc., were successful. There is still much unhappiness about hydrido.

Rules 3 and 4. All groups are to be listed alphabetically regardless of charge, type, bridging character, etc. While this order is very convenient for a given language it does lead to different orders in different languages. The nomenclature committee of the German Chemical Society decided to follow the 1957 Rules at this point regardless of any action taken by the IUPAC Commission.

Rule 5. The use of multiplicative prefixes and parentheses will follow organic and *Chemical Abstracts* practices. The British are not as rigid on this matter as the Americans.

Rule 7. The Ewens-Bassett system of designating the charge on a coordination ion is accepted as an alternate to the Stock system for indicating the oxidation state of the central atom.

Rule 8. The use of μ_3-, etc. for indicating bridging of three or more centers is accepted as well as the use of locants to designate positions bridged in a homoatomic aggregate (Rule 18).

Rule 9. Locants may be used to designate positions of attachment: tartrato(3-)-O^1,O^2 *vs.* tartrato(4-)-O^2,O^3.

Rule 11. The prefixes *fac-* and *mer-* (facial and meridianal) are accepted. Letters are to be used as locant designators around a center of coordination. Their use has been extended to (1) multidentate ligands (even branched ones), (2) all known configurations around a central atom, and (3) multinuclear entities (provided they are not branched).

Rule 12. The designation of absolute configurations is under serious study. In the meantime, individual optical isomers can be designated by the use of locants.

Rule 13. This need is now fully covered by the practice of Rule 10 and amplification of *Chemical Abstracts* practice (Rule 9).

Rule 14. The wide variety of compounds involving direct bonding between centers of coordination can be treated by one of the following practices:

$[Re_2Br_8]^{2-}$	bis(tetrabromorhenate)(2-) ion
$(C_6H_5)_3AsAuMn(CO)_5$	pentacarbonyl {(triphenylarsine) aurio}-manganese

Rule 15. Current practice has removed the need for any such rule.

Rule 16. The standardization of abbreviations is under study.

Rule 17. The application of above rules permits the naming of a wide variety of extended structures.

Rule 18. The structures of homoatomic aggregates is indicated in names such as these:

$Os_3(CO)_{12}$	dodecacarbonyl*triangulo*triösmium
B_4Cl_4	tetrachloro*tetrahedro*tetraboron
$[Nb_6Cl_{12}]^{2+}$	dodeca-μ-chloro*öctahedro*hexaniobium(2+) ion
B_8Cl_8	octachloro*dodecahedro*öctaboron

Items Remaining to be Covered. Despite the growth of nomenclature practices for coordination compounds and their standardization, many problems still remain. Perhaps the most important is the preparation of a small reference manual with full discussion of principles and a multitude of examples. The entire question of asymmetry in coordination compounds needs careful study including the designation of absolute configurations. For those compounds having π bonds some means of indicating which of several multiple bonds present in the ligand are involved in the π bonding to the central atom. In other structures, a means for indicating the number of atoms involved in the delocalization of electrons which participate in the bond to the central atom is needed. The very interesting sandwich compounds containing borane aggregates await systematic names.

Ideally, the principles of a nomenclature system should remain unchanged for long periods of time. It cannot be said that the naming of coordination compounds today is the same as it was when Werner was active in the field. There have been many additions, extensions, and alterations. However, the same basic patterns proposed by Werner are still followed. If Alfred Werner were to return by some magic to a symposium such as this, I am sure he would have little difficulty visualizing structures from the names. I am sure he would be amazed, however, at the enormous expansion of the field he pioneered. That our present nomenclature practices reflect the bases he proposed is a true measure of his foresight and genius.

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12

Invariance and Distortions of Octahedral Chromophores

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Octahedral chromophores MX_6 can be identified in many crystalline or vitreous materials, solutions, or salt melts. An instantaneous picture, obtained by spectroscopic measurements, allows dynamic distortion of the Jahn-Teller or Gillespie-Nyholm type to be detected, though a crystal structure may show a much higher time-average symmetry. The few limitations of the concept "central atom oxidation state" are analyzed, and second-sphere influences from ion-pairs, externally coordinated atoms, and the ambient medium in general are discussed. Frequently, the internuclear distances are shorter and the coordination numbers lower in organic solvents than in water. Accumulated spectroscopic evidence should warn classical physico-chemists against taking complex formation constants too seriously and should encourage further thinking about species in solution.

One of the main characteristics of inorganic chemistry is that the regularities observed normally have exceptions. One such regularity thoroughly studied by Werner was the situation that the central atom M, having a definite oxidation state, and the nearest neighbor ligand atoms X in a chromophore MX_6 retain octahedral symmetry for a long time, and that the physical properties such as light absorption of MX_6 are comparatively independent of the next-nearest neighbors. This paper amplifies each of these statements and discusses the general question whether classical physico-chemical ideas can be applied at all to complexes in solution.

Exclusive Octahedral Symmetry

The 2 *p* group atoms, such as beryllium, boron, carbon, and nitrogen, are sufficiently small and have such an electronic structure that tetrahedral symmetry of chromophores MX_4 is by far the most common. Because 5- and 6-coordinated carbon compounds (now by a somewhat tautological definition called electron-deficient) were much less known in Werner's time, this invariance constituted the main background for making approximate invariance of octahedral symmetry of MX_6 plausible for larger central atoms M. The five regular polyhedra have fascinated geometricians since the ancient Greeks, and chemists certainly thought it appropriate for the first two regular polyhedra to represent the most common chromophores. Werner extrapolated this idea and predicted that MX_8, such as $Mo(CN)_8^{-4}$, ought to be cubic. Actually, the x-ray crystallography later developed showed that continued lattices such as CaF_2 can have this coordination, whereas isolated complexes either are Archimedean antiprisms or have lower symmetry, as one also would predict from a reasonable repulsive potential of the interaction between the ligands. On the other hand, the regular icosahedron MX_{12} is represented with good approximation (*127*) in $[Mg(H_2O)_6]_3[Ce(NO_3)_6]_2 \cdot 6H_2O$, where $Ce(III)O_{12}$ is formed by six bidentate nitrate ligands. It is fascinating to note that Werner (*123*) recorded this compound as containing $Ce(NO_3)_6^{-3}$, though he probably assumed there were six unidentate ligands. Werner was not always particularly lucky when he discussed rare earths. He gave arguments (*123*) for Pr coming after Nd in the Periodic Table. This was based on the fact that Co(II) and Nd(III) aqua ions are pink and Ni(II) and Pr(III) aqua ions are green. The whole argument, however, if it had any significance, should be applied to pink Er(III) and green Tm(III). His preference for octahedral coordination influenced physicists in recent years to assume no solvation of lanthanide tris-β-diketonates. The line emission of fluorescent europium(III) compounds can be used for liquid lasers, and only very reluctantly the physicists admitted that solvent molecules or a fourth diketonate anion are present, increasing the coordination number to over six (*28*, *79*, *95*, *100*).

In the case of closed-shell systems such as $Al(H_2O)_6^{+3}$, AlF_6^{-3}, SiF_6^{-2}, PCl_6^-, SF_6, $SnBr_6^{-2}$, $Sb(OH)_6^-$, $Te(OH)_6$, and XeO_6^{-4}, there is little doubt that the coordination number $n = 6$ is determined by the relative atomic size and that the octahedral symmetry is determined by the minimum energy obtained for a wide range of conceivable ligand-ligand repulsion potentials. In molecular orbital (M.O.) theory, there is no need to assume that six orbitals are involved to roughly the same extent in the bonding of six ligands (*31*), and the hybridizations d^2sp^3 or sp^3d^2 are not plausible at all. In central atoms containing a partly filled *d* shell, we recognize positive reasons for preferential octahedral coordination. The presence of a lower subshell of three degenerate orbitals (in Cartesian coordinates of the type *xy*, *xz*, and *yz*) explains the great stability of octahedral, low-spin d^6-systems such as Co(III), Rh(III), Ir(III), and Pt(IV). For reasons related to the Jahn-Teller effect discussed below, d^3-systems such as V(II), Cr(III), Mn(IV), Mo(III), Tc(IV), Ru(V), Re(IV), and Ir(VI) are also excellent examples, the three electrons having parallel spin in the lower sub shell. In the conventional electrostatic model of the ligand field, it is not feasible to compare the relative stability of chromophores MX_n of highly different symmetry or coordination number *n*. Such a comparison is possible in the angular overlap model (*49*, *62*, *98*, *99*) where it can be shown that for identical M-X distances the total σ-anti-bonding effect on all five *d* orbitals is proportional to *n*. Hence, the main condition for the most stable symmetry of a chromophore containing a partly-filled *d* shell is that the σ-anti-bonding properties are concentrated as much as possible on the empty and half-filled *d* orbitals. This is what remains of the concept "ligand field stabilization" in M.O. theory. Seen from this point of view, it is quite legitimate for d^1- and d^2-systems to distort from regular octahedral symmetry and, in particular, to contain one or two oxide ligands at short internuclear distances as in $VO(H_2O)_5^{+2}$, $MoOCl_5^{-2}$, $RuO_2Cl_4^{-2}$, and $OsO_2(OH)_4^{-2}$, because even the π-anti-bonding *d* orbitals can remain unoccupied.

Actually, a comparison of the chromophores reported (*45*) shows that Cr(III) is always octahedrally coordinated, except in certain polytungstates where the rigidity of the oxide skeleton is sufficient to produce tetrahedral $Cr(III)O_4$ and $Co(III)O_4$. Even multidentate phosphines, which frequently produce trigonal-pyramidic, 5-coordinate complexes (*118*), produce the chromophore fac-$Cr(III)P_3Cl_3$. Kauffman (*66*) has translated a very interesting paper by Werner which apparently has never been submitted for publication. In analogy with the octacyanides of Mo(IV), Werner at one time suggested that 8-coordination of Cr(III) occurs in a series of compounds of the type $[Cren_2Cl_4]H$ and $[Cren_2Cl_3(ClO_4)]H$. The University of Zürich was kind enough to supply Kauffman and myself with samples of these unusual compounds. The reflection spectra leave no doubt that an octahedral chromophore occurs, and it is highly probable that it is fac-$Cr(III)N_3Cl_3$. As seen in Table I, the two spin-allowed transitions correspond to absorption maxima having wavenumbers very accurately the arithmetic mean of those of $Cren_3^{+3}$ and $CrCl_6^{-3}$. (In this isolated complex, a comparison is probably more adequate with the salt (*30*) of $CrCl_6^{-3}$ than with the polymeric (*97*) $CrCl_3$.) Hence, the values of the spectrochemical parameter, $\Delta = 17700$, and the nephelauxetic parameter, $B = 590$ cm.$^{-1}$ ($\beta_{35} = 0.64$), are exactly the mean values agreeing with Tsuchida's rule of average environment (*33*, *115*, *116*). Though the reflection spectra generally give broader bands than the solution spectra (and Werner's compounds hydrolyze rapidly in aqueous solution), it is

Table I. The Wavenumbers of the Two Absorption Maxima Corresponding to the Two First Spin-Allowed Transitions for Octahedral $3d^3$-Systems and Racah's Parameter of Interelectronic Repulsion B

(in cm.$^{-1}$)

Cren$_3^{+3}$	21900	28500	620
$CrCl_6^{-3}$	13200	18700	560
$[CrCl_3]_n$	13700	18900	510
[Cr(en)(enH)Cl$_3$]ClO$_4$	17700	23900	590
[Cr(en)(enH)Cl$_3$]Cl	17100	23400	615
[Cr(en)(enH)Cl$_3$]$^+$ calc.	17550	23600	590
[CrenCl$_4$]$^-$ calc.	16100	21970	580
[Cren(H$_2$O)Cl$_3$] calc.	16800	22950	600

striking that they are not broader than those of unsubstituted chromophores, Cr(III)X$_6$. This agrees with the cubic holohedrized symmetry (*98*) of the fac-Cr(III)N$_3$Cl$_3$, whereas the mer-isomer would be expected to show band splittings (*3, 35, 101*). In Werner's time, ethylenediamine was always considered a bidentate ligand, but the chemical composition of the salts suggests that enH$^+$ = $NH_2CH_2CH_2NH_3^+$ is a unidentate ligand, as well as the structure [Cr(en)(enH)Cl$_3$]ClO$_4$ of the perchlorate. There remains only one chemical difficulty for this proposal, and that is the observation that the chloride does not immediately precipitate AgCl with Ag$^+$, apparently excluding an external chloride ion [Cr(en)(enH)Cl$_3$]$^+$Cl$^-$. However, Werner (*123*) discovered that the sulfur atoms of the ambidentate thiocyanate ligands are capable of binding silver ions so strongly that—e.g., Co(NH$_3$)$_5$NCSAg^{+3} does not precipitate Cl$^-$, though a soluble Co(NH$_3$)$_5$NCSAgCl^{+2} cannot be excluded. Werner (*123*) also prepared [AgCl$_2$Co(NH$_3$)$_4$]SO$_4$. Hence, it is conceivable that the three chloride ligands of Cr(en)(enH)Cl$_3^+$ are capable of binding Ag$^+$—only decomposing slowly to AgCl.

In other words, the tendency towards invariant coordination number of certain central atoms, such as Cr(III), is even more pronounced than Werner expected. Perhaps the concept of molecular adducts influenced him a little too much; his favorite example of PtCl$_4$ attaining the maximum coordination number six in PtCl$_4$X$_2$ by adding two ligands is obscured by the fact that PtCl$_4$ probably is a polymeric structure containing Pt(IV)Cl$_6$ chromophores. (Thus, solid TcCl$_4$ contains bridged Tc(IV)Cl$_6$ chromophores (*21*). Falqui (*22*) reported a cubic lattice with a = 10.45 A. of PtCl$_4$ and identified the structure as a packing of tetrahedral molecules in analogy to TiBr$_4$. The diamagnetism and nonvolatility make this proposal less probable; the crystals might be K$_2$PtCl$_6$-type (H$_3$O)$_2$PtCl$_6$.)

Delépine (*17*) demonstrated that IrCl$_4$ does not exist. What is sold under this name, even 50 years later, is actually H$_2$[IrCl$_6$]·6H$_2$O. In aqueous solution, however, the neutral complex [IrCl$_4$(H$_2$O)$_2$] may exist (*10*). Werner also wrote sulfuric acid as the adduct SO$_3$·H$_2$O, whereas we consider it a dioxo-dihydrox complex of sulfur(VI) (*45*). Werner's ideas at this point are more acceptable with $TiCl_4$ and $SnCl_4$ existing as monomeric, volatile substances.

Labile and Robust Octahedral Complexes

Some, but not all, octahedral complexes retain their constitution for a long time; the classical studies of the low rate of racemization of optically active complexes of bidentate ligands and the modern studies of the exchange of isotopically marked unidentate ligands are completely convincing (*71*). Because of the specific form of the Arrhenius equation, the reaction rates at room temperature are extremely dramatic functions of the activation energy, and the classification into labile and robust complexes does not necessarily correspond to extremely different numerical values of the activation energy. One may say the same thing another way: the order of magnitude of duration of intramolecular vibrations is 10^{-13} sec. Hence, a mean life of three years corresponds to one out of 10^{21} vibrations required for dissociating the molecule, whereas a mean life of one sec. is equivalent to one out of 10^{13} vibrations only.

The question of the constitution of aqua ions is a particularly complicated one. Werner emphasized the importance of S. M. Jørgensen's studies of an isolated water ligand in complexes such as $Co(NH_3)_5H_2O^{+3}$ and $Co(NH_3)_5OH^{+2}$. A few hexaaqua ions are sufficiently stable to be studied with isotopic exchange techniques, and Cr(III) (*113*) and Rh(III) (*86*) have half-lives of a few days at room temperature. One of the byproducts of the identification of transitions in the partly-filled *d* shell, by studying the absorption spectra, is the firm conviction that aqua ions such as $Mn(H_2O)_6{}^{+2}$ (*34, 80*) and $Ni(H_2O)_6{}^{+2}$ (*8, 32*) are perfectly normal constituents of the aqueous solution or solid salt hydrates, though their half-lives in solution at room temperature can be shown (*12, 19*) to be 2.10^{-7} sec. and 10^{-4} sec., respectively. The interesting point is that the absorption spectra indicate beyond any doubt that the solution indeed contains the chromophores, $Mn(II)O_6$ and $Ni(II)O_6$, deviating only to a small extent from regular octahedral symmetry because of the vibrations. Because distorted forms would show much higher absorption bands, even a small concentration would be detected by broad background absorption between the maxima characterizing the octahedral species. There is some evidence in chloride melts at higher temperature (*27*) that several 3 *d* group, central atoms are surrounded by a varying number of chloride ligands—most of the time having very low symmetry.

In the case of colorless aqua ions, one has to use other techniques. The *bona fide* existence of $Be(H_2O)_4{}^{+2}$, $Al(H_2O)_6{}^{+3}$, and $Ga(H_2O)_6{}^{+3}$ is indicated by nuclear magnetic resonance experiments (*12*). Eigen (*19*) reviewed the various techniques available for very short-lived aqua ions. The alkaline metal ions, Ba(II), Sr(II), Ca(II), and surprisingly enough

Cu(II), Cd(II), and Hg(II) have half-lives of a definite water ligand around 10^{-9} sec., whereas La(III) and Zn(II) are 3.10^{-8} sec., and Mg(II), 10^{-5} sec., —slightly more than Co(II), Fe(II), and Mn(II). Unfortunately, the coordination number cannot be determined for the very short-lived species, and it is quite conceivable that it is not defined. What is observed is the average stay of a definite water ligand.

Spectroscopic studies are very valuable for obtaining almost instantaneous pictures of the situation. We may, as a Gedanken-experiment, concentrate our attention on an absolutely instantaneous, but complete, description of a given solution or crystal. If one visualizes that nearly all the Mn(II) or Cr(III) central atoms are surrounded by six ligand atoms at nearly identical distances and close to the axes of a suitably chosen Cartesian coordinate system, we have indeed approximately octahedral chromophores. It is immediately evident that this is a particularly fortunate case; central atoms such as Na(I) or Ba(II) are suspected of having six, seven, eight, . . . neighbor atoms in distorted symmetries. In idealized crystal structures, obtained by time-averaging this instantaneous picture (and also in practice by averaging the content of each unit cell), the coordination number n is well-defined if all M-X distances are identical. In this sense, sodium(I) has $n = 6$ in NaCl and iron(II), $n = 10$ in $Fe(C_5H_5)_2$. In other cases, n may be less well-defined; it is a matter of personal preference whether cubic body-centered tungsten has $n = 8$ or 14, six W-W distances being somewhat longer than the eight shortest distances. It is also clear that in solution or in molten salt, n may readily lose its physical significance.

The spectroscopic evidence for deviation from octahedral symmetry is particularly alarming for copper(II) (*54*). The aqua ion in solution and in salts known to contain $Cu(H_2O)_6^{+2}$ has an absorption spectrum as though it were strongly tetragonally distorted (*33*), two water molecules being at a considerably greater distance than four water molecules in a square. However, there is evidence from the temperature dependence of the anisotropy of g factors obtained by electron spin resonance that the choice of the tetragonal axis changes rapidly, though not as rapidly as the process of optical excitation. This might contribute to the unusually rapid exchange of water with the solvent. There is no doubt that this distortion is connected with the Jahn-Teller effect; however, our opinions are not too clear at present. It is important to note that not only σ-anti-bonding electrons can be responsible for the Jahn-Teller distortions such as found in the $3d^4$-systems, Cr(II) and Mn(III), and the $3d^9$ Cu(II); the π-anti-bonding electrons are effective in $3d^1$ Ti(III) (*29*, *92*) and high-spin $3d^6$ Fe(II) and Co(III) (*14*). The latter example of two adjacent absorption bands at a position where only one is predicted for octahedral symmetry is especially interesting because it also occurs in the cubic crystal K_2NaCoF_6.

The intensity of absorption bands in chromophores apparently having a center of inversion, such as octahedral MX_6, is normally ascribed to two effects (*111, 112, 117*): vibronic coupling with electronic states of opposite parity (in actual practice corresponding to the electron transfer bands (*31*)) and actual hemihedric distortions of the equilibrium symmetry. When we return to our instantaneous picture, it is not easy to distinguish accurately between the two causes, especially so for solutions. The Laporte-forbidden transitions are induced by the small deviations from regular octahedral symmetry, but whether or not these deviations oscillate around a set of nuclear positions having a center of inversion is not easy to determine. Gillespie and Nyholm (*24, 25*) pointed out that many *s* and *p* group central atoms are surrounded by a set of ligands distinctly lacking a center of inversion and that for many purposes the lone pairs present seem to replace an equal number of ligands. Hence, the stereochemistry of—e.g., lead(II), is much more complicated than that of barium(II) (*81*). However, PbS, PbSe, and PbTe crystallize in NaCl lattice. It is legitimate to ask whether these compounds are not statistical averages of distortions either in the six directions along the four-fold axes or in the eight directions along the three-fold axes. Careful crystallographic measurements are needed to distinguish this situation from that prevailing with NaCl—where the vibrational motion has its maximum probability density in the middle of each unit cell. Orgel (*81*) notes that TlI crystallizes in the cubic CsCl lattice at room temperature but distorts to a lower symmetry by cooling. Actually, the zero-point vibration at 0°K. may still have too large an amplitude to allow a macroscopic distortion of PbS.

In the transition group complexes containing a partly filled *d* shell, it is possible that a reminiscent Gillespie-effect contributes to the intensity of Laporte-forbidden transitions. Thus, the absorption band of $Co(NH_3)_6^{+3}$ has roughly the same oscillator strength as that of $Co(NH_3)_5Cl^{+2}$, and there is some evidence (*54*) that Cu is above the plane of the four ammonia molecules, not only in the tetragonal-pyramidic $Cu(NH_3)_5^{+2}$, but also in an instantaneous picture in $Cu(NH_3)_4^{+2}$, which would constitute essentially a Gillespie effect.

Besides these discrepancies between crystallographic results and the instantaneous evidence obtained by spectroscopic measurements, there occurs another interesting discrepancy between classical physico-chemical and spectroscopic investigations. A very characteristic case is that of normal anion complexes and the outer-sphere ion-pairs in solution. This distinction is clear-cut in stable complexes (*23*) such as $[Cr(H_2O)_6]^{+3}SO_4^{-2}$ and $[Cr(SO_4)(H_2O)_{4\text{ or }5}]^+$. In the case of lanthanide chlorides, it is well-known that spectroscopic evidence (*42, 75*) for inner-shell complexes $NdCl(H_2O)_x^{+2}$ indicates a formation constant hundreds of times smaller than that of the ion pair $Nd(H_2O)_9^{+3}$ Cl^-. In organic solvents the inner complexes are relatively more abundant (*2, 42*). In certain cases, one also finds anisotropic complexes (*55*) with anions at anomalously long distances from the central atom but not separated by solvent molecules, as are the genuine, outer-sphere, ion pairs. (*See also* discussion by Griffiths and Symons (*26*).) This is particularly frequent for copper(II), which seems to add anions perpendicular to the plane of the four strongly bound ligands (*2*). The electron transfer spectra of such species have higher wavenumbers than those of the normal complexes—similar to the higher wavenumber (*72, 73, 102*) of the ion pair $Co(NH_3)_6^{+3}$, I^- being relative to $Co(NH_3)_5I^{+2}$.

One could write an heroic epic about the discussion between certain Scandinavian chemists who believe only in complex formation constants determined in strong salt solutions and certain American chemists who believe only in constants for extremely dilute solutions. Because I am not a good Scandinavian, and because I work in an American research institute in Geneva, I might suggest the compromise that, in a certain sense, thermodynamic arguments are not valid for either of the two cases. It is quite evident that the original argument applies to equilibria between simple component crystalline, liquid, and gaseous phases. In treating solutions, it is possible that each solvent contains a definite standard form of a given solute and that the properties of the solute do not vary appreciably once the concentration of the solute is below a given level, depending upon the degree of deviation from the ideal. One has to be careful when applying this proposition. For example, it is necessary to dilute a solution of N_2 at room temperature greatly before the free energy of two nitrogen atoms is lowered; one would not, however, expect a similar strong bonding between two metal atoms in a dilute amalgam.

Applying physico-chemical arguments, one may consider the extreme of stable, readily identifiable molecules (e.g., by isotopic marking), such as SF_6, or perfect equilibrium in solution. Frequently, one is interested in an intermediate case. The equilibrium is presumed for some but not all possible reactions. The favorite anion ClO_4^- would be able to oxidize Fe(II) to Fe(III), but this does not change its use as a constant salt medium for studying the hydrolysis of $Fe(H_2O)_6^{+2}$. If one studies the absorption spectrum of a definite anion such as $IrBr_6^{-2}$ in a variety of solvents, one observes small spectral shifts which can be interpreted as being due to a small variation of the Ir-Br distance (*48*). Similar shifts are observed for $IrCl_6^{-2}$ in lattices such as K_2PtCl_6, Cs_2PtCl_6, Cs_2SnCl_6, etc. (*39*). This spectroscopic effect corresponds closely to the classical concept of standard state of solution in a definite solvent. One may argue that $IrBr_6^{-2}$ in water and in dichloroethane is not exactly the same species and, in general, that the same molecule in two situations, where the populated part of the ground state potential surface is different because of interactions with the surroundings, represents in a sense two species.

Physico-chemical textbooks are ostensibly adapted to neutral species and refrain from determining energies of individual ions (*6*), though this concept is quite appealing to spectroscopists (*31*). However, in water, in molten salts, and in intermediate cases of concentrated solutions of deliquescent salts, it is an experimental fact that certain metallic or hydrogen electrodes work according to Nernst's law. This is much less true for mixtures of water and organic solvents and usually not the case for anhydrous organic solvents. Returning to our instantaneous picture of the aqueous solution containing various dissolved ions, it is quite clear that nearly all the spectroscopic effects are connected with direct central atom ligand contacts, such as $Fe(H_2O)_5Cl^{+2}$, whereas ion pairs of the type $Fe(H_2O)_6{}^{+3}$ Cl^- may decrease the activity of both $Fe(H_2O)_6{}^{+3}$ and Cl^- without spectacular spectroscopic effects. In dilute aqueous solution, Debye and Hückel's theory is usually a fair approximation, whereas N. Bjerrum pointed out that long-range, ion-pair interaction can considerably influence the behavior of salts in solvents having lower dielectric constants.

One must accept that spectroscopic and classical physico-chemical techniques are complementary and cannot always furnish the information desired. In the case of ions such as Li^+, Ag^+, or Ba^{++} in aqueous solution, one does not know at present whether they are predominantly connected with a definite number of water molecules or not, whereas $Be(H_2O)_4{}^{+2}$, $Mg(H_2O)_6{}^{+2}$, and a large number of transition group ions are quite well known. In the classical opinion, no way is known to determine the solvation number of a solute in dilute solution. On the other hand, spectroscopic measurements make it certain that $Ni(NH_3)_6{}^{+2}$ occurs in the whole concentration range from strong aqueous ammonia to liquid, anhydrous ammonia. This type of statement is less safe for multidentate ligands; $Nien_3{}^{+2}$ might form $Nien_4{}^{+2}$, $Nien_5{}^{+2}$, and finally $Nien_6{}^{+2}$ with unidentate ligands in anhydrous ethylenediamine and, as seen in the last chapter, the spectra of the chromophores $Ni(II)N_6$ are not expected to be widely different (*33*). In all cases, the definite constitution of solutes stops at some distance from the central atom. The arrangement of water molecules around $Cr(H_2O)_6{}^{+3}$ in aqueous solution is probably as variable as around Cs^+ or $N(CH_3)_4{}^+$.

The meaning of a complex formation constant is not as clear-cut as one can wish. The behavior of aqua ions which may be either definite species such as $Ni(H_6O)_6{}^{+2}$ or vague representations of the "standard solute in dilute solution has already been discussed." One then must discuss the question: When is a ligand bound to a central atom? Certainly, this problem does not occur for most complexes of multidentate ligands, but weak complexes are not in an easy position. Prue (*89*) correctly emphasized that without any specific attraction between two molecules, for purely topological reasons, one would find a complexity constant of 0.2 liter/mole from contact charge-transfer spectra in typical conditions. If one finds a smaller formation constant, the two molecules repel each other systematically. This behavior is also common in molten salts, and it is rather surprising to physical chemists that spectroscopic techniques frequently, but not always, suggest that definite chromophores exist. If equilibrium occurs, the instantaneous picture is always the same except for fluctuations predicted by statistical mechanics which are too small to be detected; we obtain a radial distribution function the same as that from x-ray diffraction of liquids. It is true that in many cases this radial distribution has a relatively sharp maximum at a short distance corresponding to direct contact between the central atom and the first neighbor atom. The angular distribution (which is indirectly referred from absorption spectra of ions such as $Ni(H_2O)_6^{+2}$), combined with the radial distribution, then allows us to judge whether a definite chromophore MX_n of definite symmetry is predominant. The vibrational behavior of such a chromophore can be analyzed according to normal modes (*121*) and allows the individual species to be considered. In other cases, such an analysis would not be possible.

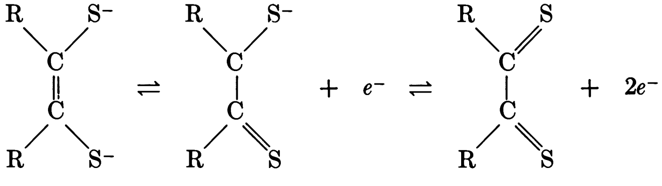
Well-defined Oxidation States

Using various vowels according to definite rules, Werner classified complexes with the central atom oxidation state being the integers from +1 to +8. However, he admits that such a classification sometimes can be difficult (*123*), as in the iron(II) complex $Fe(CO)(CN)_5^{-3}$ and in a few cases, impossible such as $Fe(NO)(CN)_5^{-2}$. It is worth more careful analysis (*51*) to determine why inorganic chemists are able in nearly all cases to define oxidation states. It is certainly true that only very few monatomic cations in chemical compounds are known to carry nearly as much positive charge as the oxidation number indicates; this is probably valid only for alkali metal ions and for the heavier alkaline earth metal ions when occurring in fluorides. The oxidation state is more a spectroscopic quantity related to the preponderant electron configuration. It is well-known in quantum chemistry (*50*) that the wavefunction of a system containing two or more electrons is not normally a well-defined configuration in the strict sense but is mixed with other configurations—frequently having two electrons in tightly contracted orbitals with positive energy. However, it is possible to define the *preponderant configuration* as that configuration which classifies correctly the symmetry types and other quantum numbers of the ground state and the lowest excited levels. Thus, the neon atom has the preponderant configuration $1s^22s^22p^6$, and the first excited levels can be classified according to the configurations $1s^22s^22p^5(nl)$.

In transition group complexes where the ligands are "*innocent*"—i.e., do not have partly occupied subshells in their preponderant configuration, the oxidation state of the central atom can be determined from the number of electrons in the partly filled shell of the preponderant configuration.

Thus, a large number of complexes of V(II), Cr(III), Mn(IV), Mo(III), Tc(IV), Ru(V), Re(IV), Os(V), and Ir(VI) has absorption spectra (*9, 31, 40, 63, 68, 97, 111, 112*) clearly showing all the details characterizing d^3 systems in octahedral symmetry, allowing Roman numerals to be fixed to indicate the oxidation states. The nephelauxetic effect—i.e., the decrease of interelectronic repulsion parameters relative to the corresponding gaseous ion (indicating an expansion of the partly-filled shell)—suggests (*44, 56*) in most cases a fractional charge on the central atom in the interval between 1 and 2.5. The theoretical estimate of this fractional charge has varied quite a bit. Pauling's hybridization theory for covalent chromophores MX_n assumes the central atom charge to be n units lower than the oxidation state if ionic structures were without importance; however, because of the highly different electronegativities, it was then argued that the central atom is approximately neutral and not negatively charged. The electrostatic model of the ligand field theory began with the assumption that the central atom carries as much positive charge as the oxidation state. On the other hand, the Wolfsberg-Helmholz model for M.O. calculations (which have been quite popular in recent years) normally results in central atom charges between zero and 1. However, a closer analysis (*50, 60, 84*) shows that if the interatomic coulomb terms—i.e., the Madelung potential, are taken into account much higher positive charges are predicted which agree with the nephelauxetic effect.

A typical case of a ligand which frequently is not "innocent" is NO. The possibility of its occurring as NO^+, NO, or NO^-, having its own partly filled shell in the preponderant configuration and the rather baroque stereochemistry (*45*), makes this apparently simple ligand highly complicated. Recently, a great number of complexes has been prepared with ligands L of the general configuration:



where R = H, CF_3, CN, C_6H_5, etc. These ligands are sometimes "innocent"—e.g., in d^8 complexes ML_2^{-2}, where M = Ni(II), Pd(II), or Pt(II)—and the preponderant configuration of the ligand corresponds to the left-hand form L^{-2}. However, when these species are oxidized (*106, 109*) to ML_2^- and ML_2, it is by no means clear whether the oxidation state of the central atom increases to M(III) and M(IV) or whether it is defined at all. The tris-coordinated complexes suffer the same difficulties. VL_3^{-2}, VL_3^-, and VL_3 have been prepared (*15, 120*). Since vanadium(VI) is an unacceptable oxidation state, the latter form must contain contributions from L^- and L. Actually, the nuclear hyperfine structure of electron-spin, resonance curves seems to indicate that the unpaired spin ($S = \frac{1}{2}$) of VL_3 is concentrated on the central atom, and the complex may perhaps be V(IV) of L_3^{-4}. On the other hand, the unpaired spin is situated mainly on the ligands in VL_3^{-2}, which might be a V(III) complex of L_3^{-5}. One can argue (*41*) that the collectively oxidized forms of the ligands L_3^{-4} and L_2^{-2} lack two electrons in a particularly unstable M.O., having as many node planes as the *g* and *f* orbitals, respectively, and which is not stabilized by adjacent, empty orbitals of the central atom. Such linear combinations with a great number of node planes also seem to produce electron transfer bands at unusually low wavenumber (*82*) in $Yb(C_3H_3)_3$. Finally, it can be mentioned that the crystal structures of ReL_3 ($R = C_6H_5$) and MoL_3 ($R = H$) have been shown (*20, 110*) to contain trigonal, prismatic chromophores MS_6. This is an interesting case of deviation from the much more frequent octahedral symmetry; it may be noted that Pauling found trigonal, prismatic coordination $Mo(IV)S_6$ in the $4d^2$ system MoS_3.

The sulfur-containing ligands are only non-"innocent" if they contain conjugated double bonds; the absorption spectra of xanthates, dialkyldithiocarbamates, and dialkyldithiophosphates (*47, 67*) indicate octahedral chromophores, $Cr(III)S_6$, $Co(III)S_6$, $Rh(III)S_6$, and quadratic chromophores, $Ni(II)S_4$ and $Pd(II)S_4$, with well-defined oxidation states of the central atoms. Conjugated, carbon-containing ligands have another characteristic property—i.e., whereas most electron transfer bands correspond to an electron jumping from filled M.O., mainly localized on the ligands, to the empty or partly-filled shell, belonging mainly to the central atom, aromatic ligands such as dipyridyl or acetylacetonate form complexes with reducing central atoms having "inverted" electron transfer bands where an electron jumps from the partly- or completely-occupied shell to low-lying, empty orbitals of the ligands (*37, 125*). It is quite conceivable that complicated heterocyclic ligands such as porphyrins have ionization energies of the highest, filled orbitals and electron affinities of the lowest, empty orbitals comparable to those of the partly filled shell of a typical central atom. Hence, the reduction products of—e.g., M(II)phthalocyanines (*18, 70, 114*), may not have well-defined oxidation states.

Besides this type of non-"innocent" ligand related to biological problems (*59*), another situation where oxidation states are difficult or impossible to define involves metallic alloys or low-energy-gap semiconductors. The 4*f* and 5*f* group elements usually have preponderant configurations containing an integral number of electrons in the partly-filled shell, as one can infer from the magnetic moments and other physical properties, but this is not normally the case for *d* group elements. There is a close connection between Pearson's concept (*58, 83*) of soft and hard Lewis acids and bases and the innocence of ligands; the non-innocence is an extreme case of the high density of low-lying, excited states favoring softness.

Interactions between Chromophores and Surroundings

The study of absorption spectra has demonstrated the unusual invariance of octahedral chromophores, $Cr(III)X_6$, in glasses and minerals (*4*, *77*). Empirical evidence from glass-making (*124*) has been extended, and one can study e.g. the equilibria between blue $Co(II)O_4$ and pink $Co(II)O_6$ or between purple $Ni(II)O_4$ and yellow-green $Ni(II)O_6$ in borate and silicate glasses (*65*). Similar observations can be made on molten chlorides (*27*) and sulfates (*64*). Relations between the crystal structure and absorption spectra of mixed oxides (*61*, *87*, *90*, *103*, *104*, *105*) and fluorides (*91*) have been carefully evaluated. In this connection, Clark (*11*) discussed the invariance of the chromophores, $M(II)Cl_6$ and $M(III)Cl_6$, in solid halides and halide complexes.

The main conclusion of these studies is the influence of the internuclear distance, the compressed chromophores having larger orbital energy differences in the partly-filled shell, and more pronounced nephelauxetic effect. Unexpectedly, the electron transfer spectra move to lower wavenumbers in the compressed chromophores (*1*, *39*). Similar conclusions can be drawn from the spectral shifts in organic solvents (*5*, *48*). An interesting question is why certain organic solvents, such as acetonitrile, stabilize low coordination numbers of halide complexes (*45*). Thus, one can study $CeCl_6^{-2}$, $CeBr_6^{-2}$, 4*f* group MX_6^{-3} having spectra different from the aqua ions (*93*), and 5*f* group MX_6^{-2} in such solvents (*16*, *94*).

Much remains to be done in the field of complexes of mixed ligands. All the ruthenium(III) (*12*) and rhodium(III) (*126*) chloro-aqua complexes have been separated by ion-exchange techniques, and the mixed complexes, $OsCl_aBr_{6-a}^{-2}$ and $IrCl_aBr_{6-a}^{-2}$, by electrophoresis (*7*, *88*). Labile mixed complexes such as bismuth(III) (*78*) and uranium(IV) (*38*) chloro-bromides have been studied by spectrophotometry, but the conclusions are obviously more difficult to obtain.

In a few cases, one observes narrow absorption bands caused by the co-excitation of solvent (*36*) or aqua ligand (*85*) vibrations. It is worth emphasizing how relatively rare this phenomenon is—again showing a considerable isolation of the individual chromophore. In the case of crystalline solids, the energy band description encounters insurmountable difficulties in the case of fairly localized transitions (*50*, *53*, *57*).

However, if chemical bonds are formed between a ligating atom and a next-nearest neighbor atom, from the point of view of the central atom, considerable inductive effects can occur. Werner (*107*, *122*) used the argument about the yellow chromophore, $Co(III)N_6$, in $Co(NH_3)_6^{+3}$ and $Co(NH_3)_5(NO_2)^{+2}$ and the red chromophore, $Co(III)N_5O$, in $Co(NH_3)_5(H_2O)^{+3}$ and $Co(NH_3)_5(ONO)^{+2}$. Inductive effects are already perceived by comparing the brick-red, aqua pentammine with cherry-red $Co(NH_3)_5OH^{+2}$, but Werner's argument would have been destroyed by the purple azide complex $Co(NH_3)_5(N_3)^{+2}$. However, these differences are related to the different number of lone pairs on the ligand; this effect is conspicuous in sulfur-containing ligands (*47*). Werner's discovery of the ligand NCSAg was mentioned, and the yellow color of $Co(NH_3)_5NCSH^{+3}$ found in concentrated sulfuric acid (*69*) and the high spectrochemical position (*96*, *119*) of the ligand $NCSHg^+$ are other examples. The solid $Co(NCS)_4Hg$ contains the tetrahedral chromophores (*13*) $Co(II)N_4$ and $Hg(II)S_4$, and the ligand $NCSHgCH_3$ also exists (*108*).

Werner (*123*) stressed pertinently the importance of such "complexes of higher order." It is indeed admirable that he developed inorganic chemistry so extensively without crystal structures available. Actually, it is in his spirit that modern inorganic chemists frequently attempt to prepare definite chromophores (*43*) in order to study absorption spectra and other physical properties and to obtain understanding of chemical bonding. Thus, the octahedral chromophores $Cr(III)Se_6$, $Rh(III)Se_6$, and $Ir(III)Se_6$ are normally only found in black semiconductors. If they are protected against polymerization in $(C_2H_5O)_2PSe_2^-$, however, the absorption spectra of the tris-diethyldiselenophosphates can be obtained (*52*), indicating rather extreme conditions of covalent bonding. Sulfur-containing ligands (*45*, *47*, *74*) are particularly illustrative for this purpose.

A final paradox may show how difficult it is to apply the mass-action law in a consistent way. A solution of UCl_4 in molten Al_2Cl_6 has an absorption spectrum corresponding to *n* larger than 6 (*76*). Addition of alkali metal chlorides *decreases* *n* to 6, the typically octahedral complex being formed probably according to:

$$U(Cl_2AlCl_2)_4 + 6\,Cl^- = UCl_6^{-2} + 4\,AlCl_4^-$$

the former, bridged complex then containing the chromophore $U(IV)Cl_8$.

The M.O. treatment of halides and noble gas complexes has been reviewed (*46*).

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13

Coordination in the Second Sphere

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The concept of coordination in the second sphere was introduced by Werner. All authors agree that such outer-sphere association exists in solution, but they disagree about the kind and the extent of this association. Some advocate a second-sphere coordination which is closely analogous to the inner-sphere coordination. The data which support this hypothesis are not very convincing and can be criticized in various ways. The present author finds that the electrostatic theories of N. Bjerrum, Fuoss, and Kraus, according to which the formation of the ion-associates is a result of coulombic attraction, both qualitatively and quantitatively, give the most trustworthy picture of the outer-sphere association. However, this does not exclude the fact that some preferred mutual orientation exists in the ion pairs.

In the third edition of his famous "Inorganic Chemistry," Alfred Werner introduces the concept of coordination in the second sphere and distinguishes between the following possibilities:

(1) A group in the second sphere is directly coordinated to a ligand in the first sphere.

(2) A complex with fully occupied first sphere has residual affinity to attach groups (addition compounds in the second sphere).

(3) An added group is attached at the same time to the complex and to a group in the second sphere of the original complex (substitution reaction in the second sphere).

As an example of the first kind of outer-sphere complex formation, Werner (*44*) studied the interaction of thiocyanato complexes of cobalt (III)ammines with silver ions. In these complexes nitrogen is bound to the metal, and the sulfur atom in the thiocyanate group is free to complex metal ions with affinity to this atom. In most cases 1:1 complexes are formed (*41*); D. N. Purohit, Rajasthan, has in this laboratory with a silver electrode determined that the formation constants for the addition of silver ions to various thiocyanatochromium(III) and cobalt(III) complexes are of the 10^4 order of magnitude.

This type of reaction is a special case of the more general category—reactions of coordinated ligands—which has recently been discussed (*19*). However, one has the feeling that the concept "second-sphere coordination," as understood by modern research workers, no longer includes this category of important reactions.

The second possibility considered by Werner comes more closely to what is understood today by second-sphere coordination. As an example of this kind of outer-sphere coordination, Werner (*43*) mentions the addition compounds of tris(acetylacetonato) complexes of trivalent metals with various amines. Strangely enough Werner also considers double salts of the Carnallite type formulated as $[\mathrm{Me(OH_2)_6}]^{\mathrm{Cl_2}}_{\mathrm{ClK}}$ to be compounds of this category. Such double salts are today interpreted as lattice compounds, but it must be remembered that Werner was without any knowledge of crystal structures and had to draw his conclusions from the stoichiometrical composition of the solid compounds alone. In order to explain Werner's viewpoints with regard to his third kind of second-sphere coordination, one may consider the fact that a great number of tris(ethylenediamine) complexes of divalent metals crystallize with two moles of water while, on the other hand, tris(ethylenediamine)cobalt(III) halides crystallize with three moles of water. Werner expresses this through formulas of the type:

$$[\mathrm{Ni\ en_3}]\begin{matrix}\mathrm{(OH_2Cl)}\\ \mathrm{(OH_2Cl)}\end{matrix}, \qquad [\mathrm{Co\ en_3}]\begin{matrix}\mathrm{(OH_2Cl)}\\ \mathrm{(OH_2Cl)}\\ \mathrm{(OH_2Cl)}\end{matrix}$$

In a similar way the seventh mole of water in $NiSO_4 \cdot 7H_2O$, for example, and the fifth mole of water in $CuSO_4 \cdot 5H_2O$ are considered to be bound to the sulfate ion in the second sphere. With our present knowledge of the crystal structures of these salts (*2*, *3*), this interpretation is not far from being correct. In crystal lattices one always has an ordered configuration in the second sphere, and the question discussed in recent years is to what extent one has an arranged and spatially well-defined configuration in the second sphere also for complex ions in solution.

Outer-sphere Association in Solution

One way, in some cases usable, of obtaining qualitative information about compound formation in solution is to determine the ionic or molecular weight of the association products either by diffusion or dialysis experiments. Brintzinger and co-workers have developed the last-mentioned method and determined the ionic weights of complex ions in strong salt solutions using selected reference ions of opposite sign (*10–13*). From their data they draw far-reaching conclusions with regard to the constitution of complex salts in aqueous solution. Thus Brintzinger and Osswald (*12*) think they have proof that complex cobalt(III) cations such as $Co(NH_3)_6^{+3}$, $Co(NH_3)_5Cl^{+2}$, and $Co(NH_3)_4SO_4^{+}$ form two-shelled complexes of the general type $[Coa_6]X_4^{-v}$ with anions such as SO_4^{-2}, $C_2O_4^{-2}$, and HPO_4^{-2} but curiously enough not with $S_2O_3^{-2}$. According to ionic weight determinations of Brintzinger and Osswald the complex formation is nearly complete in 1–2 molar solutions of the anions in question. Other unexpected results of Brintzinger and co-workers are that the divalent metal ions of the first transition group in 2*M* $(NH_4)_2SO_4$ or Na_2SO_4 have ionic weights corresponding to the general formula $Me_2(SO_4)_4^{-4}$ (*10*), and that the tris(ethylenediamine)cobalt(III) ion, contrary to $Co(NH_3)_6^{+3}$ and $Cren_3^{+3}$, is found to have an ionic weight corresponding to the formula $Co_2en_6^{+6}$ (*13*). These results, as also many other results from the work of Brintzinger, must be taken with all possible reservation for various reasons (*38*), but mainly because they were carried out with filters whose pores were too narrow (*40*). Pore size is very critical, and those which are too narrow sometimes cause ionic weights which are too high. Thus, Kiss and Acs (*23*), by repeating the measurements of Brintzinger and co-workers using better filters, showed the nonexistence of the complex $[Co(NH_3)_5Cl](SO_4)_4^{-6}$ and found that $Co(NH_3)_5Cl^{+2}$ in 2*M* $(NH_4)_2SO_4$ has an ionic weight corresponding to the cobalt(III) complex itself (found 174, calc. 180) to be compared with the value 563 found by Brintzinger and Osswald (*11*). Further, Kiss and Acs (*23*) have disproved the existence of the binuclear complex $Me_2(SO_4)_4^{-4}$ and found that $CuSO_4$ in 2*M* $(NH_4)_2SO_4$ has an ionic weight corresponding to the complex $Cu(SO_4)_2^{-2}$. They have also confirmed that $Coen_3^{+3}$ is not dimeric, in agreement with J. Bjerrum's redox potential measurements of the couple $Coen_3^{+3}/Coen_3^{+2}$ (*6*).

Thus, Brintzinger's dialysis measurements are not reliable even as qualitative evidence for coordination in the second sphere. However, Laitinen *et al.* (*25*) have obtained such evidence from polarographic investigations of hexamminecobalt(III) ions in various supporting electrolytes. The half-wave potential of $Co(NH_3)_6^{+3}$ is found to be shifted towards more negative values in the presence of certain ions—e.g., SO_4^{-2}, and diffusion rates are slower than in a pure chloride or nitrate medium. To explain these findings, the authors assume that the ions of the supporting electrolytes are clustered about the central complex owing to electrostatic attraction similar to that on which the ion-association concept of Bjerrum (*9*) and of Fuoss and Kraus (*17*) is based.

In Bjerrum's theory (*9*), two ions of opposite charge constitute an ion pair if they are closer together than a certain critical distance:

$$q = \frac{z_1 z_2 e^2}{2\,D\,k\,T}$$

where z_1 and z_2 are the ion charges, e the charge of the electron, D the dielectric constant of the solvent, k is Boltzmann's constant, and T the Kelvin temperature. According to this criterion considerable ion-pair formation must be expected to occur in aqueous solutions in the case of highly charged cations and anions. Such ion association has also been found in numerous cases (*39*), and methods as different as those of solubility, conductivity, and spectrophotometry usually give values for the association constant which agree fairly well (*33*). In the case of aquo cations it is not always easy to distinguish between coordination in the inner sphere (normal complex formation with more or less covalent bonding) and the outer-sphere association. However, from the Bjerrum's theory it is possible to calculate the dimension of the ion pair from the experimental association constants extrapolated to zero ionic strength, and because the crystal radii are known one can estimate whether or not the water shell around the cation is penetrated by the anion. For example, the ion pair of the trivalent ions $La(H_2O)_n^{+3}$ and $Fe(CN)_6^{-3}$ in mixed solutions of water and organic solvents has been shown to be an outer-sphere complex in agreement with Bjerrum's theory (*20*). More recently the relaxation methods developed by Eigen and co-workers (*15*) have made it possible to analyze the problem in more detail and to determine the association constant for the inner-sphere as well as for the outer-sphere complex. Using this technique, Behr and Wendt (*4*) have in aluminum sulfate solutions at an average ionic strength $I \sim 0.1M$ estimated the following values for the two kinds of constants:

$$K_{1\,\text{out}} = \frac{[Al(H_2O)_6^{+3}, SO_4^{-2}]}{[Al(H_2O)_6^{+3}][SO_4^{-2}]} = 19 \pm 3\ M^{-1}$$

$$K_{1\,\text{in}} = \frac{[AlSO_4^{+}, aq]}{[Al(H_2O)_6^{+3}][SO_4^{-2}]} \backsim 0.6\ M^{-1}$$

A ligand such as SCN^- shows a relatively higher tendency to inner complex formation than does SO_4^{-2} (*36*). Fronaeus and Larsson (*16*) assume that the C—N stretching frequency is nearly the same for the free ligand as for thiocyanate bound in the outer sphere, and under this assumption they estimated from infrared absorption measurements the inner- and outer-sphere association constant in the nickel(II)-thiocyanate system at average ionic strengths to be:

$$K_{1\,\text{in}} = 12 \pm 2\ M^{-1}, \qquad K_{1\,\text{out}} = 3 \pm 2\ M^{-1}$$

For the special case of the metal ions in the first transition group, the absorption spectra in the visible and ultraviolet can also be used as criteria

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to distinguish between substitution in the first and the second sphere (*45*). Thus the ligand field bands characteristic of these ions are changed only by substitution in the first sphere (*8*), while the electron transference bands also are influenced by the substitution in the second sphere (*30*). In the $Cu(H_2O)_6^{+2}$, SO_4^{-2}-system the ligand field band in the near infrared, which is responsible for the blue color of the solutions, depends only slightly on the sulfate ion concentration—contrary to the electron transference band in the ultraviolet. By careful analysis of the concentration influence on this band in lithium sulfate solutions, with $\sqrt{I}$ varying from 0.2 to 2.6, Näsänen (*34*) obtained the following expression for the association constant of the ion pair at 25°C.:

$$\log K_1 = 2.10 - \frac{4.05\sqrt{I}}{1 + 1.62\sqrt{I}} + 0.052\,I$$

Owing to the tetragonal distortion of the cupric ions (*7*), this ion pair must be considered an anisotropic complex as defined by Jørgensen (*22*)—i.e., an intermediate between an inner- and outer-sphere complex.

In the case of the octahedral robust complexes of cobalt(III) and chromium(III), substitution in the first sphere is hindered. This type of complex ion is, therefore, especially suitable for studying association in the second sphere. The hexammine and tris(ethylenediamine) cobalt(III) ions have especially been used for this kind of study. For the association of these ions with anions, such as sulfate and thiosulfate, the ion-pair constant is of the order of magnitude of 10^3 M^{1-} at $I = 0$, somewhat smaller for $Coen_3^{+3}$ than for $Co(NH_3)_6^{+3}$ (*21*), but strongly dependent on the ionic strength. Thus Posey and Taube (*37*), from spectrophotometric measurements in the ultraviolet, obtain the following expression for the association constant of the ion pair $[Co(NH_3)_6]SO_4^+$ in solutions with $\sqrt{I}$ varying from 0.04 to 0.3:

$$\log K_1 = 3.32 - \frac{6.10\sqrt{I}}{1 + 2.00\sqrt{I}}$$

The rather polarizable thiosulfate ion has a much higher influence on the ultraviolet absorption of the cobalt(III)-ammine complexes than the much less polarizable sulfate ion (*24*), but it is noteworthy that the stability of the ion pairs formed with the first mentioned ion is even smaller than those formed with the sulfate ion (*18*). This supports the electrostatic nature of the second-sphere association.

Using Bjerrum's theory, Monk and co-workers (*18, 21*) calculated the radii of the ion pairs in question to have the expected order of magnitude 4–5 Å. From the theory it can also be estimated that the constant for the formation of a triple ion $[Coa_6]X_2^-$ of the considered type and dimensions:

$$K_2 = \frac{[[\mathrm{Coa_6}]\mathrm{X_2}^-]}{[[\mathrm{Coa_6}]\mathrm{X}^+][\mathrm{X}^{-2}]}$$

at zero ionic strength is about 100 times smaller than K_1 for the formation of $[\mathrm{Coa_6}]\mathrm{X}^+$. However, K_2 depends much less on the ionic strength than K_1 and, if $[\mathrm{Coa_6}]\mathrm{X_3}^{-3}$ is formed, which *a priori* is not very probable, then the value of

$$K_3 = \frac{[[\mathrm{Coa_6}]\mathrm{X_3}^{-3}]}{[[\mathrm{Coa_6}]\mathrm{X_2}^-][\mathrm{X}^{-2}]}$$

should even increase with increasing ionic strength.

R. Larsson recently has found evidence for a relatively rapid stepwise association in the second sphere for complexes of the above type. Thus, anion-exchange investigations of Larsson and Tobiason (*29*) with the hexammine cobalt(III) ion in sodium sulfate and thiosulfate solutions showed that three sulfate ions or thiosulfate ions were taken up in about $1M$ solutions of the ligands. These results were supported by another method. It is well-known since the days of Werner (*42*) that the optical rotation of dissymmetric complex ions is sensitive to the nature of the accompanying ions, and, as pointed out by Kirschner and co-workers (*1*), this may be due to ion association. Larsson (*26*) studied the change in the optical rotation of the D-tris(ethylenediamine)cobalt(III) ion in sulfate and thiosulfate solutions. It was here characteristic that the curves, which gave the molar rotation as a function of the anion concentrations, went through a minimum for $C_{\mathrm{Na_2X}} \sim 0.05M$. This gave some evidence for the formation of $[\mathrm{Coen_3}]\mathrm{X}^+$ and $[\mathrm{Coen_3}]\mathrm{X_2}^-$, and Larsson assumed that a considerable amount of $[\mathrm{Coen_3}]\mathrm{X_3}^{-3}$ was formed at higher concentrations. In an attempt to exclude the influence of activity factors, Larsson and Johansson (*28*) repeated the measurements of the $\mathrm{Coen_3}^{+3}$, $\mathrm{S_2O_3}^{-2}$-system in an approximately constant salt medium (I = $2M$ ($\mathrm{NaClO_4}$)). The curve had here a somewhat different appearance from the curve in pure thiosulfate solution. The minimum was less pronounced, occurred already for $C_{\mathrm{Na_2S_2O_3}} \sim 0.005M$, and was followed by a plateau for $C_{\mathrm{Na_2S_2O_3}} \sim 0.04$–$0.06M$ before the curve increased smoothly. Larsson believed that the deviations from a monotonically increasing curve were a result of stepwise outer-sphere association, and by analysis of the curve he arrived at the following set of constants:

$$K_1 = 150, \qquad K_2 \backsim 50, \qquad K_3 \backsim 20, \qquad K_4 \backsim 1.$$

This result seemed to support Larsson's hypothesis (*27*, *29*) that the same criterion shall apply to the outer sphere of coordination as to the inner one—i.e., the ligands must be assumed to occupy a limited number of so-called coordination sites which are spatially well-defined. However, from an electrostatic point of view, it seems improbable that the voluminous tris(ethylenediamine)cobalt(III) ion should associate with such a relatively high affinity with four thiosulfate ions in 2*M* $NaClO_4$. Therefore, in cooperation with Inge Olsen, the author (*35*) has examined the system by a more traditional method. The association was followed spectrophotometrically in mixtures of sodium perchlorate and sodium thiosulfate at a constant ion normality ($C_{Na^+} = 2.88M$). Measurements were made at five wavelengths in the ultraviolet, and the data were treated as described by J. Bjerrum (*5*). It was found that the formation of the ion pair $[Coen_3]S_2O_3^+$ was sufficient to explain the data at least up to about 0.5*M* $Na_2S_2O_3$. The ion-pair constant was calculated to be $K_1 = 1.3 \pm 0.1$, a value which is more than 100 times lower than Larsson's value for K_1 in the same system. The most simple explanation of this discrepancy is that the irregularities found in the concentration dependence of the rotation are only indirectly caused by second-sphere coordination. According to recent views (*14*), the dextro- as well as the levo-form of $Coen_3^{+3}$ exists as an equilibrium mixture of four conformations, each with its own optical rotation. If now the equilibrium between the different conformations is disturbed by the ion-pair formation, a minimum in the rotation curve is easily understood. Therefore, the measurements ought to be repeated with the optically active tris(diamine) complex of 1,2-cyclohexanediamine which exists in one conformation only. In any case, it is noteworthy that the minimum is less pronounced in solutions with a high concentration of $NaClO_4$, and Olsen and the author (*35*) have found that the minimum disappears completely in mixtures of $Na_2S_2O_3$ and Na_2SO_4 at a constant molarity of one. In this medium the rotation of D-$Coen_3^{+3}$ at 546 and 578 mμ shows no anomaly and changes linearly with the mole fraction from 1*M* Na_2SO_4 to 1*M* $Na_2S_2O_3$.

The idea that the instantaneous equilibrium between the different conformations of dissymmetric complex ions could be influenced by ion-pair formation finds some support in recent experiments of Mason and co-workers with diastereoisomeric cobalt(III) complexes. Thus, Mason and Norman (*31*) have shown that the circular dichroism spectra of D-$Co(d\text{-}pn)_3^{+3}$ and L-$Co(d\text{-}pn)_3^{+3}$ (pn = propylenediamine) are differently changed by oxo-anions such as PO_4^{-3}, SO_4^{-2}, and $S_2O_3^{-2}$. According to these authors the oxo-anion and D-$Co(d\text{-}pn)_3^{+3}$ (or D-$Coen_3^{+3}$), but not L-$Co(d\text{-}pn)_3^{+3}$, should have a preferred mutual orientation in the ion pairs. At low concentrations the effect of sulfate and thiosulfate ions on the circular dichroism of D-$Co(d\text{-}pn)_3^{+3}$ is similar to that of phosphate but with these anions at concentrations $> 0.2M$ the previous changes are reversed—probably due to breaking down the specific orientation of the ion pair in the denser ionic atmosphere. It is also interesting that Mason and Norman (*32*) have found that $Co(NH_3)_6^{+3}$ associated with *d*-tartaric acid produces a pronounced Cotton effect. These results show that some mutual orientation exists in the outer-sphere association products, probably as a consequence of chelate hydrogen bonding. Future work in this field is awaited with interest.

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The Role of Coordinate Covalence in Nonmolecular Solids

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This paper describes a coordinated polymeric model of nonmolecular solids which pictures each atom as joined to each neighbor of opposite kind by a polar covalent bond. The covalent bond energy is taken as the geometric mean of the two homonuclear single bond energies, adjusted for bond length. The ionic bond energy is determined using a modified Born-Mayer equation. The weighting coefficient for the ionic contribution is the ratio of partial charge to oxidation number. The total atomization energy is the weighted sum of covalent and ionic contributions. Calculated and experimental values agree well for more than 100 solid halides and chalcides. The coordinated polymeric model is superior to the simple ionic model in its applicability over a complete polarity range.

The purpose of this paper is to present a more useful model of nonmolecular solids, such as formed by combination of a metal with a nonmetal. This model had been proposed earlier (*7*) on the basis of preliminary evidence; more recent work (*8*) has now provided quantitative confirmation.

From our knowledge of the electronic structure of their atoms, we can predict a reasonable formula for the simplest molecule that might be formed by a metal combined with a nonmetal. For example, we can recognize the univalence of both potassium and chlorine atoms and predict that the simplest molecule will have the molecular formula, KCl. However, a single bond in such a molecule would use only one electron from each atom, leaving unused both vacant orbitals on the potassium and electron pairs on the chlorine.

An extremely important principle of chemical bonding (*10*) that unfortunately is seldom stated explicitly is: Chemical combination tends to continue in the direction where fullest possible use of all available orbitals and electrons is made. A single molecule of KCl is therefore a potentially reactive species. If more than one are brought together, condensation must occur, in which otherwise unused electron pairs of chlorine become attracted to otherwise vacant orbitals of potassium. Such condensation is greatly enhanced by the nature of the original single bond between potassium and chlorine. Because the chlorine was initially much more electronegative than the potassium, it acquired much more than half a share in the two valence electrons at the expense of the potassium. This resulted in a partial negative charge on chlorine and a partial positive charge on potassium. An effect of negative charge is to enhance the availability of electron pairs for coordinate bond formation (*10*). An effect of positive charge is to increase the availability of outer vacant orbitals to accept electron pairs from donor atoms (*10*). Thus, the initial electronegativity difference between potassium and chlorine in particular, and between metal and nonmetal in general, tends to assist in the further condensation of the simplest molecules to form crystalline aggregates of significant stability. High bond polarity, however, is not essential to this condensation, the primary cause of which is the proximity of atoms having outer lone pairs to atoms having outer vacant orbitals.

We may therefore regard the formation of a crystalline solid by combination of a metal with a nonmetal as involving first, formation of simple molecules satisfying the capacity of the component atoms for normal covalence, followed by coordinate covalence to make maximum use of remaining orbitals and electron pairs. The individuality of the initial simple molecules is destroyed by such a process because the distinction among the several bonds of each atom of one of the elements to each atom of the other element must disappear. In the example of KCl, each atom becomes surrounded by six of the other elements in a symmetrical octahedral cluster in which no one of the six partial bonds can be favored over the other five.

If this model of a binary solid is correct, a quantitative analysis of the bonding should be possible. Let us therefore turn to bond energies, beginning with the simplest case of a diatomic molecular compound. For example, consider HBr. Here two different atoms have joined by a single covalent bond. The initially higher electronegativity of bromine ensures that this bond must be polar. We find it convenient to describe this bond qualitatively as the resultant of a "covalent" contribution and an "ionic" contribution. Quantitatively the problem has been, until recently (*8*), very difficult. Let us assume that each atom makes a constant contribution to nonpolar covalence that is measured by its homonuclear single covalent bond energy. In a nonpolar heteronuclear covalent bond, then, following Pauling (*6*), we may evaluate the energy as the geometric mean of the two homonuclear bond energies. The energy for H_2 is 104.2 kcal. per mole and for Br_2, 46.1. The geometric mean of these is 69.2. However, the bond in HBr is polar and with polarity comes bond shortening. If we take the nonpolar covalent radius of hydrogen to be 0.32 A., as it seems to be in all but the hydrogen molecule, and that of bromine to be 1.14 A., the nonpolar bond length R_c is 1.46 A. The observed bond length R_o in HBr is 1.41 A. Closer interaction corresponds to greater bond strength so the nonpolar covalent energy 69.2 must be corrected by the factor $R_c/R_o = 1.46/1.41 = 1.03$; $1.03 \times 69.2 = 71.6$ kcal. per mole. This would be the bond energy if the atoms at the observed distance were attached by a single nonpolar covalent bond. If the molecule were completely ionic, its bond energy would be $330\ e^2/R_o$ or 234 kcal. per mole. If we can determine the relative contributions of covalent and ionic bonding, we can add them to get the total bond energy:

$$E = t_c E_c + t_i E_i = \frac{t_c R_c \sqrt{E^{AA} E_{BB}}}{R_o} + \frac{t_i 330\ e^2}{R_o} \tag{1}$$

where t_c and t_i are the weighting coefficients whose sum is 1.

For molecular compounds, t_i is given by the average of the partial charges on the two atoms forming the bond (*8*). In HBr the partial charges are 0.12 and −0.12 (*11*), so t_i is 0.12 and t_c is 0.88. The total bond energy is then

$$E = 0.88 \times 71.6 + 0.12 \times 234 = 91 \text{ kcal. per mole}$$

which agrees reasonably well with the experimental value of 88 kcal. per mole. This method has been applied successfully to bonds in nearly 100 molecular binary compounds (*8*), providing evidence that the fundamental concepts are sound.

For application to nonmolecular solids, the bond description is similar but certain modifications are needed. First, the covalent energy must be multiplied by the equivalent number n of two electron covalent bonds per formula unit that must be broken for atomization. The evaluation of n will be discussed in detail presently. Second, the ionic energy must be evaluated as the potential energy over the entire crystal, corrected for the repulsions among adjacent electronic spheres. This is done by using the Born-Mayer equation for lattice energy, multiplying this expression by an empirical constant, a, which is 1 for the halides and less than 1 for the chalcides, as follows:

$$E = E_c + E_i = \frac{t_c n \sqrt{E^{AA} E_{BB}}\ R_c}{R_o} + \frac{t_i 330\ z_{+e} z_{-e}{}^{2} Mka}{R_o} \tag{2}$$

Here M is the Madelung constant, and k is the repulsion coefficient (*1*). The charges on the ions are z_{+e} and z_{-e}. The coefficient t_i is the ratio of partial charge to oxidation number of either ion. For example, in $MgCl_2$, the charge on Mg is 0.56, and that on Cl is −0.28, from which $t_i = 0.28$ or $0.56/2 = 0.28$. When E_{AA} and E_{BB} are in kcal. and Rc and R_o are in Angstrom units, E is the atomization energy in kcal. per mole.

Equation 2 has been applied to more than 110 solid binary compounds, with calculated atomization energies agreeing within an average of about 3% with the experimental values. Before discussing the problem of evaluating n and a, let us consider some typical examples. Basic data for all calculations reported here are taken chiefly from standard references (*3*, *4*, *13*, *14*, *16*).

Calculating Atomization Energies of Typical Binary Solids

KCl. The electronegativities of potassium and chlorine are 0.41 and 4.93, respectively. By applying the principle of electronegativity equalization and the postulate of the geometric mean to the compound KCl, the electronegativity in the compound is found to be the square root of 0.41 x 4.93, or 1.42. If the chlorine had acquired complete control of an electron, its electronegativity would have decreased by 4.62. In becoming part of KCl, chlorine has decreased in electronegativity by 4.93 − 1.42 or 3.51. The partial charge on chlorine is defined (*11*) as the ratio of the actual electronegativity change to the change that would correspond to acquisition of unit charge: $3.51/4.62 = 0.76$, which is assigned a negative sign corresponding to the fact that the electronegativity decreased. The "ionicity" of KCl is therefore 76%, and t_i is 0.76, with t_c being 0.24.

For the atomization of KCl, six bonds per atom pair must be broken. Since only eight electrons are available, however, these six are equivalent to only four normal covalent bonds, or $n = 4$. The observed bond length, R_o, is 3.14 A., whereas the covalent radius sum, R_c, is 2.95 A. The dissociation energy of K_2 is 13.2 and of Cl_2, 58.2 kcal. per mole. The geometric mean of these is the square root of 13.2 x 58.2, or 27.7. The covalent contribution to the total bonding energy is then calculated as follows:

$$E_c = \frac{0.24 \times 27.7 \times 4 \times 2.95}{3.14} = 25 \text{ kcal. per mole}$$

If KCl were ionic, its repulsion coefficient would be $1 - \rho/R_o = 1 - 0.311/3.14 = 0.90$. For all halides, $a = 1$. The rock salt structure of KCl has a Madelung constant of 1.75. The ionic contribution is then calculated as follows:

$$E_i = \frac{0.76 \times 330 \times 1.75 \times 0.90}{3.14} = 126 \text{ kcal. per mole}$$

The total atomization energy is the sum of the covalent contribution and the ionic contribution, 25 + 126 = 151 kcal. per mole. The experimental heat of atomization of KCl is equal to the sum of the standard heats of atomization of the separate elements at 25°C., 21.4 + 29.1 = 50.5, minus the standard heat of formation of KCl, which is −104.2 kcal. per mole: 50.5 −(−104.2) = 154.7 kcal. per mole, in good agreement with the calculated value.

In this particular example, if we had assumed the simple ionic model without a covalent contribution, the Born-Mayer equation would have provided a lattice energy (*5*, *15*):

$$U = \frac{330 \times 1.75 \times 0.90}{3.14} = 165.4 \text{ kcal. per mole}$$

To convert this to atomization energy, we subtract the ionization energy of potassium, 100.5, and the electron affinity of chlorine (*2*), −84.8: 165.4 − 100.5 − (−84.8) = 149.7 kcal. per mole, almost the same as with the coordinated polymeric model. Both models provide reasonably accurate bond energy information if the covalent contribution is relatively small, and for KCl it is less than 17%. However, whereas the ionic model becomes less and less satisfactory as the covalent contribution increases, the coordinated polymeric model can be applied over a complete range of ionicity, as will be amply demonstrated.

Before proceeding to the next example, let us examine the dependence of energy as calculated by Equation 2 on an accurate estimation of partial charge. If the correct charge on chlorine in KCl were 0.71 instead of 0.76, t_i would be 0.71, and t_c would be 0.29. Then E_c would be 30, and E_i would be 118, giving a total of 148 kcal. per mole. A difference of 0.1 electron would similarly change E_c to 35 and E_i to 109 for a total of 144. Evidently in this example, error of less than 0.05 electron in the partial charge estimation would not cause a serious error in total bond energy, although in many compounds even an error of 0.02 electron would have a significant effect (*8*). Nevertheless, the agreement between calculated and experimental atomization energies suggests that the estimated ionicity of KCl must be nearly correct. In general, accurate atomization energies could not be calculated by using Equation 2 unless partial charges were essentially correct.

AgBr. Partly because the Born-Mayer equation fails in application to this compound, AgBr is generally agreed to have considerably greater "covalent character" than KCl. The electronegativity of silver is 2.57, and that of bromine is 4.53. The geometric mean of these is 3.41, from which we observe that bromine has become lower in electronegativity by 4.53 − 3.41 = 1.12. If bromine became bromide ion, its electronegativity would be reduced by 4.43. The partial charge on bromine in AgBr is defined as the ratio of the electronegativity change in joining silver to the electronegativity change in becoming bromide ion: 1.12 divided by 4.43, or −0.25. The compound is only 25% ionic, and t_i is 0.25, with t_c being 0.75.

The internuclear distance in the crystal, R_o, is 2.88 A., and the covalent radius sum R_c is 2.48. The Ag—Ag bond energy has been estimated, from data for all the silver halides, to be about 19 kcal. per mole. The dissociation energy of Br_2 is 46.1 kcal. per mole, from which the geometric mean for AgBr is found to be 29.5. The six bonds that must be broken for atomization, per formula unit, of this rock salt structure utilize only four electron pairs, from which $n = 4$. The covalent contribution is:

$$E_c = \frac{0.75 \times 29.5 \times 4 \times 2.48}{2.88} = 76 \text{ kcal. per mole}$$

The Madelung constant is again 1.75, and the repulsion coefficient is calculated to be 0.89. The ionic contribution is therefore:

$$E_i = \frac{0.25 \times 330 \times 1.75 \times 0.89}{2.88} = 45 \text{ kcal. per mole}$$

The sum, 121, is in excellent agreement with 119 kcal. per mole determined from the experimental standard heats of atomization of silver, 68, and bromine, 26.7, and the standard heat of formation of AgBr, −24.0 kcal. per mole: $68 + 26.7 - (-24.0) = 118.7$.

If we had assumed the simple ionic model here, the Born-Mayer equation would have given a lattice energy of 178.4 kcal. per mole. The ionization energy of silver is 176.2 and the electron affinity of bromine (*2*) is −79.1, from which the atomization energy of AgBr is 81.3 kcal. per mole, in error by nearly 40 kcal. Efforts to modify the Born-Mayer equation to take other factors into account (*5*) have not produced satisfactory results for such compounds.

MgO. The electronegativity of magnesium is 1.99, and that of oxygen is 5.21, giving a geometric mean of 3.22. This corresponds to an electronegativity decrease of $5.21 - 3.22 = 1.99$ for oxygen. Formation of O^- would produce a decrease of 4.75. Therefore the partial charge on oxygen in MgO is 1.99 divided by 4.75, or −0.42. This is equivalent to 21% ionicity; hence, t_i is 0.21, and t_c is 0.79. The hypothetical homonuclear single bond energy for magnesium has been estimated (*8*) as 46.1. The O—O energy is 33.2, giving a geometric mean for Mg—O of 39.1. The observed bond length R_o is 2.10, the covalent radius sum 2.03, and $n = 4$, as in the preceding examples. The covalent contribution to the atomization energy is then:

$$E_c = \frac{0.79 \times 39.1 \times 4 \times 2.03}{2.10} = 119$$

With a Madelung constant of 1.75 and a repulsion coefficient k = 0.82, we can calculate the ionic contribution, remembering that here a has the value for oxides, 0.63, and the ions each bear a charge of 2.

$$E_i = \frac{0.21 \times 330 \times 1.75 \times 2 \times 2 \times 0.82 \times 0.63}{2.10} = 119$$

The total atomization energy is then 238 kcal. per mole, compared with the experimental value of 239. Note that in this 21% ionic compound, covalent and ionic contributions to the atomization energy are equal.

Here the lattice energy calculated on the basis of the simple ionic model is about 902 kcal. per mole. Literature values (*5*, *15*) range from 907 to 983. This lattice energy cannot be converted accurately to atomization energy because of uncertainty as to the two-electron affinity of oxygen. Assuming 170 for this (*5*), with 524 for the sum of the ionization energies of magnesium, we get 902 − 170 − 524 = 208 for the atomization energy, in error by 30 kcal. per mole.

TiO_2. The electronegativity of titanium is 1.40 (*12*), and that of oxygen is 5.21. The geometric mean is the cube root of 1.40 x 5.21 x 5.21 or 38, = 3.36. The electronegativity of oxygen has decreased by 5.21 − 3.36 = 1.85; compared with 4.75 it would have decreased in becoming O^- ion. The partial charge on oxygen is defined as the 1.85 divided by 4.75 = −0.39. The value of t_i is therefore 0.20, and t_c is 0.80. From bond energies of gaseous tetrahalides, the homonuclear single covalent bond energy for titanium is found to be 14.4. The O—O energy is 33.2, leading to a geometric mean of 21.8 kcal. per mole for Ti—O. R_o is 1.96 and R_c is 2.05. In the rutile structure of this compound, each oxygen atom has a coordination number of 3, and titanium offers more than the usual four orbitals for accepting electron pairs. The value of n is therefore taken as 6. We may then calculate the covalent energy:

$$E_c = \frac{0.80 \times 21.8 \times 6 \times 2.05}{1.96} = 110 \text{ kcal. per mole}$$

The Madelung constant is 2.41, $z+$ is 4, and $z-$ is 2. The repulsion coefficient is estimated as 0.84. As for other oxides, a is 0.63. From these data, the ionic contribution can be calculated as follows:

$$E_i = \frac{0.20 \times 330 \times 2.41 \times 2 \times 4 \times 0.84 \times 0.63}{1.96} = 344 \text{ kcal. per mole}$$

The sum, 454 kcal. per mole, agrees well with the experimental value of 456.

Al_2O_3. The electronegativity of aluminum (*12*) is 2.25. The geometric mean for Al_2O_3 is therefore the fifth root of 2.25 x 2.25 x 5.21 x 5.21 x 5.21, or 3.72. The electronegativity of oxygen has been reduced by 5.21 − 3.72 = 1.49, which signifies a partial charge on oxygen of 1.49 divided by 4.75 = −0.31. This corresponds to t_i 0.16 and t_c 0.84. The Al—Al single bond energy, obtainable from data for the gaseous halides, is 47.8, which gives a geometric mean of 39.8 for Al—O. The number of covalent bonds to be broken for atomization, four for each oxygen, is 12, and R_o is 1.85, R_c 1.98. From these data, the covalent energy is calculated:

$$E_c = \frac{0.84 \times 39.8 \times 1.98}{1.85} = 429$$

The Madelung constant for corundum, α-Al_2O_3, is 24.24, and k is estimated as 0.84. The ionic energy then is:

$$E_i = \frac{0.16 \times 330 \times 24.24 \times 0.84 \times 0.63}{1.85} = 366$$

Here we find the total atomization energy calculated as 795 kcal. per mole to be significantly higher than the experimental value of 733. A possible explanation of this discrepancy can be found by examining the structure more closely. The corundum structure closely resembles that of sodium chloride but with every third metal atom missing. The bond angles to oxygen are therefore only 90° instead of 109°, bringing the bonds to only about 87% as far apart as in the tetrahedral coordination which is more normal for oxygen. We should therefore expect covalence to be weaker than ordinary. How great a weakening should be expected is not known, but it is interesting to note that a reduction of E_c by about 10% would lead to an atomization energy agreeing reasonably well with the experimental. Whatever the true correction, it should be in the direction of lessening the difference between calculated and experimental values.

The Number of Covalent Bonds

Assigning the value of n, the equivalent number of covalent bonds per formula unit that must be broken in atomization sometimes involves complications that are not yet fully understood. In any major group metal-nonmetal combination, one may picture each metal atom as providing four (or more) orbitals for bonding to nonmetal atoms. The coordination about the metal atom is never less than 4, and may be 6 or 8, but these numbers do not necessarily indicate the number of two-electron bonds or their equivalent. One may likewise picture each nonmetal atom as providing (with help from the metal) four electron pairs, and no matter to how many neighbors these are spread out, the maximum equivalence in terms of electron pair bonds cannot exceed 4 per nonmetal atom. However, in layer structures, such as represented by $CdCl_2$ and CdI_2 where each nonmetal atom has a coordination number of 3, and in chain structures like that of $BeCl_2$ where each nonmetal is coordinated to only two metal atoms, fewer than four electron pairs per nonmetal atom may be involved in the bonding.

Let us consider first the binary halides and chalcides of 1:1 composition. These involve 8:8 coordination, as in CsCl, 6:6 coordination, as in NaCl, or 4:4 coordination, as in ZnS. In all such compounds only eight valence electrons are available per formula unit, which suggests the maximum of the equivalent of four covalent bonds no matter what the coordination number. Data are available for 55 such compounds, for 38 of which the atomization energy is clearly in good agreement with $n = 4$. The remaining 17 compounds, however, have atomization energies closely corresponding to $n = 3$. These include all the halides of lithium and sodium, and the sulfides and selenides of beryllium, magnesium, zinc, cadmium, and manganese. The question raised here is why in these particular compounds is the covalence equivalent only to 3 instead of 4?

In 1:2 or 2:1 compositions, the principal structures involve 8:4 or 4:8 coordination, as in CaF_2, 6:3 coordination, as in rutile or layer arrangements, or 4:2 coordination, as in the beryllium halide chains of tetrahedra. Since each nonmetal atom may be regarded as contributing (with the help of the metal) eight valence electrons, we may expect a maximum of four covalent bonds (or their equivalent) per nonmetal atom per formula unit. In the antifluorite structures, represented here only by the alkali metal oxides and sulfides, the maximum value of n should be 4. Empirically, n is observed to be 4 for Na_2O, K_2O, and Rb_2O, but in Li_2O and all the alkali metal sulfides the calculated atomization energy does not equal the experimental value unless n is taken as 6, which, as will be discussed below, may or may not have fundamental significance. In the fluorite structure, a maximum covalence of 8 can be predicted, but this is never observed, presumably because even though the nonmetal atoms possess eight pairs of electrons per formula unit for sharing, the single metal atom cannot provide eight orbitals to accommodate them. Here the limitation is that of the metal. For fluorides of calcium, strontium, and barium, and for $BaCl_2$, n is indeed 4. However, for $SrCl_2$ and CdF_2, n is evidently 3. For ZrO_2, where more than four orbitals are available on the metal, $n = 6$.

In the $PbCl_2$ type of structure, each metal atom has nine nonmetal neighbors, but again the covalence is limited by the metal. For all the seven compounds of this type for which data are available, namely the bromides and iodides of strontium and barium as well as the lead halides except iodide, $n = 4$.

Table I. Number of Covalent Bonds per Formula Unit

(*empirical–maximum*)

	F	*Cl*	*Br*	*I*	*O*	*S*	*Se*
Li	3-4	3-4	3-4	3-4	6-4	6-4	
Na	3-4	3-4	3-4	3-4	4-4	6-4	
Be	3-4	3-4	3-4	3-4	4-4	3-4	
Mg	4-4	3-4	3-4	3-4	4-4	3-4	3-4
Zn	3-4	3-4	3-4	3-4	3-4	3-4	3-4
Cd	3-4	3-4	3-4	3-4			3-4
K	4-4	4-4	4-4	4-4	4-4	6-4	
Rb	4-4	4-4	4-4	4-4	4-4	6-4	
Cs	4-4	4-4	4-4	4-4	4-4	6-4	
Tl(I)	4-4	4-4	4-4	4-4			
Cu(I)	4-4	4-4	4-4	4-4			
Ag(I)	4-4	4-4	4-4	4-4			
Ca	4-4	3-4	3-4	4-4	4-4	4-4	4-4
Sr	4-4	3-4	4-4	4-4	4-4	4-4	4-4
Ba	4-4	4-4	4-4	4-4	4-4	4-4	4-4
Pb(II)	4-4	4-4	4-4	4-4		4-4	
Mn(II)	4-4	4-4	4-4	4-4	4-4	3-4	3-4
Pb(IV)					4-4		
Te(IV)					4-4		
Ti(IV)					6-6		
Zr(IV)					6-8 ?		

In the rutile structure, covalence is again limited by the availability of orbitals on the metal. Ten compounds of this type have been studied. In four of these, MgF_2, MnF_2, PbO_2, and TeO_2, $n = 4$. In SnO_2, TiO_2, and TiS_2, $n = 6$, showing presumably availability of outer and inner *d* orbitals to supplement the usual 4. But n appears to equal 3 in ZnF_2, $CaCl_2$, and $CaBr_2$. The latter two seem anomalous from any viewpoint, but it may be observed that they do have distorted structures which may account for their having lower bond energy than calculable for $n = 4$.

One may recognize again in layer structures the limitation on covalence set by the metal, even though its coordination number is 6. Here we find that $n = 4$ for CaI_2, PbI_2, $MnCl_2$, $MnBr_2$, MnI_2, and Cs_2O (where the central oxygen limits the covalence). For the bromides, chlorides, and iodides of magnesium, zinc, and cadmium, however, n clearly equals 3. Similarly, in the chains of tetrahedra, which are formed by $BeCl_2$, $BeBr_2$, and BeI_2, and possibly $ZnCl_2$, the coordination number of the metal is 4, but the covalence number n is 3.

Table I summarizes the situation with respect to n by listing the assigned value of n together with its maximum value, as limited by availability either of orbitals or electrons, for 104 compounds. In 63 of these, the covalence corresponds to the maximum as limited by the number either of electron pairs or orbitals. The bond number of 6 for the alkali metal sulfides seems at first quite unreasonable since the sulfur atom would have, with the help of the metal atoms, only four electron pairs to share. It may be worth considering, however, that sulfur is more negative by far in these compounds than in any other known combination. In such condition it *might* be able to provide two more electron pairs from its underlying shell, which at any rate would not overload the metal atoms, with three covalent bonds apiece. However, such a use of underlying electrons is at present unrecognized elsewhere, and some more plausible explanation would seem desirable.

The chief problem presented by Table I is, as mentioned above, the rationalization of the tendency for, especially, lithium, sodium, beryllium, magnesium, zinc, and cadmium to form only three coordinate covalent bonds at one time even though surrounded by four donor atoms or their equivalent. One may note that the first four of these elements consist of the smallest metal atoms and cannot go beyond the third shell in bonding. They are at least the best candidates for reduced bonding within their respective groups. As for zinc and cadmium, these are so much more electronegative that they do not permit the nonmetal to enhance its donor ability by acquiring high negative charge. A general relationship between partial negative charge on the nonmetal and its coordination number in the crystal has previously been pointed out (*7*). This may well be a contributing factor in the reduction of *n* in these compounds. So, although quantitative prediction of *n* is not always possible, its empirical values are usually not unreasonable. Additional study of this problem should, if

Table II. Calculation of Atomization Energies of Solid Fluorides

Compound	$-100\delta_F$	R_o	R_c	n	M	k	E_c	E_i	E	E_o
LiF	74	2.01	2.06	3	1.75	0.85	25	179	204	203
NaF	75	2.31	2.26	3	1.75	0.87	19	162	181	180
KF	85	2.66	2.66	4	1.75	0.88	13	163	176	174
RbF	88	2.82	2.83	4	1.75	0.89	10	160	170	170
CsF	89	3.01	2.97	4	1.75	0.90	9	153	162	164
TlF	49	2.59	2.27	4	(1.75)	(0.88)	44	96	140	136
CuF	38	1.85	1.89	4	1.64	0.83	70	92	162	160
AgF	38	2.46	2.06	4	1.75	0.87	56	78	134	136
BeF_2	29	(1.52)	1.62	3	4.44	(0.83)	105	232	337	342
MgF_2	34	1.97	2.02	4	4.76	0.84	111	228	339	341
CaF_2	47	2.36	2.46	4	5.04	0.87	84	288	372	370
SrF_2	51	2.50	2.64	4	5.04	0.87	74	295	369	367
BaF_2	56	2.68	2.70	4	5.04	0.88	57	306	363	366
ZnF_2	24	2.03	2.03	3	4.82	0.84	81	158	239	246
CdF_2	27	2.34	2.20	3	5.04	0.87	64	166	230	229
PbF_2	29	(2.29)	2.18	4	(4.62)	0.86	75	167	242	244
MnF_2	33	2.14	1.89	4	4.82	0.85	84	210	294	294

successful, reveal important features of bonding in such solids that at present are not thoroughly understood.

The Chalcide Factor, a

A second and more perplexing problem in calculating bond energies is presented by the necessity of factor a for chalcides. This has the value 0.63 for oxides, 0.60 for sulfides, and about 0.42 for selenides. In other words, the calculated atomization energies of chalcides are always higher than the experimental values. If the covalent energies are assumed correct, the calculated ionic energies are found to exceed the experimental and must be corrected by the factor a. Among possible sources of this discrepancy, in Equation 2, the most evident is the repulsion coefficient k. Indeed, it is remarkable that k values for the halides appear so satisfactory. However, since no chalcides come even close to complete ionicity, no empirical determination of k is likely to represent accurately the entirely hypothetical ionic condition. Until more thorough understanding of bonding in solids becomes possible, we may assume that the interionic repulsions involving dinegative ions are unexpectedly high, leading to substantially lower ionic energy than otherwise. There is little question of the validity of factor a because all available data are in good agreement.

Summary of Calculated Energies, and the Advantages of the Coordinate Covalent Model

The calculation of atomization energies of nonmolecular solids is summarized in Tables II for fluorides, III for chlorides, IV for bromides, V for iodides, VI for oxides, VII for sulfides, and VIII for selenides. The successful application of Equation 2 to such a large number and variety of nonmolecular compounds strongly supports the coordinate covalent or coordinated polymeric model. It seems probable that more complex compounds such as sulfates and carbonates are also of this nature.

This model has the great advantage of bridging smoothly the transition from even to uneven electron sharing, permitting quantitative evaluation of the magnitudes of the separate covalent and ionic contributions. That it also establishes beyond any reasonable doubt the essential validity of the concepts of electronegativity equalization and partial charge should be obvious, for here and elsewhere (*8*) are now reported about 200 examples of successful bond energy calculation that would have been impossible if the partial charge values were not at least approximately correct.

In summary, when metal and nonmetal atoms combine, their valence electrons, which may include all outer-shell electrons of both kinds of atoms, become shared in accordance with their initial electronegativities and in such a way as to provide maximum utilization of orbitals. Through equali-

Table III. Calculation of Atomization Energies of Solid Chlorides

Compound	$-100\delta_{Cl}$	R_o	R_c	n	M	k	E_c	E_i	E	E_o
LiCl	66	2.57	2.33	3	1.75	0.88	36	130	166	165
NaCl	67	2.81	2.53	3	1.75	0.89	30	122	152	153
KCl	76	3.14	2.95	4	1.75	0.90	25	126	151	155
RbCl	79	3.29	3.10	4	1.75	0.90	21	125	146	152
CsCl	81	3.47	3.24	4	1.76	0.90	18	124	142	151
TlCl	41	3.31	2.54	4	1.76	0.91	55	65	120	121
CuCl	29	2.30	2.16	4	1.64	0.86	91	59	150	143
AgCl	29	2.77	2.33	4	1.75	0.89	79	54	133	128
$BeCl_2$	23	2.02	1.89	3	4.09	0.85	126	130	256	258
$MgCl_2$	28	2.46	2.29	3	4.49	0.87	103	147	250	247
$CaCl_2$	40	2.74	2.73	3	4.73	0.89	84	202	286	290
$SrCl_2$	44	3.02	2.91	3	5.04	0.90	72	218	290	295
$BaCl_2$	49	3.18	2.97	4	(4.8)	0.90	76	219	295	305
$ZnCl_2$	18	2.52	2.30	3	(4.09)	(0.87)	99	84	183	189
$CdCl_2$	21	2.76	2.47	3	4.49	0.89	84	100	184	178
$PbCl_2$	23	2.99	2.53	4	(4.62)	0.88	90	104	194	191
$MnCl_2$	27	(2.52)	2.16	4	4.49	0.88	111	140	251	240
$AlCl_3$	19	2.30	2.24	3	8.30	(0.87)	125	196	321	332

Table IV. Calculation of Atomization Energies of Solid Bromides

Compound	$-100\delta_{Br}$	R_o	R_c	n	M	k	E_c	E_i	E	E_o
LiBr	61	2.75	2.48	3	1.75	0.88	37	112	149	151
NaBr	62	2.98	2.68	3	1.75	0.90	30	108	138	135
KBr	72	3.29	3.10	4	1.75	0.91	26	114	140	138
RbBr	75	3.43	3.25	4	1.75	0.91	23	115	138	137
CsBr	76	3.62	3.39	4	1.76	0.91	20	111	131	136
TlBr	36	3.44	2.69	4	1.76	0.91	54	55	109	112
CuBr	25	2.46	2.31	4	1.64	0.87	85	48	133	133
AgBr	25	2.88	2.48	4	1.75	0.89	76	45	121	119
$BeBr_2$	20	2.16	2.04	3	(4.09)	0.86	118	107	225	220
$MgBr_2$	25	2.60	2.44	3	4.38	0.88	97	122	219	213
$CaBr_2$	36	2.94	2.88	3	(4.73)	0.89	78	170	248	257
$SrBr_2$	41	3.21	3.06	4	4.62	0.90	89	175	264	264
$BaBr_2$	45	3.30	3.12	4	(4.8)	0.91	74	197	271	276
$ZnBr_2$	15	2.63	2.45	3	4.49	0.88	93	74	167	163
$CdBr_2$	17	(2.87)	2.62	3	4.38	0.89	81	76	157	155
$PbBr_2$	20	3.19	2.87	4	(4.62)	0.89	88	85	173	166
$MnBr_2$	23	(2.72)	2.31	4	(4.38)	0.89	102	108	210	210

zation of electronegativities, which is equivalent to the equalization of valence orbital energies, the atoms acquire partial charge. We may picture a binary compound of metal with nonmetal as consisting of an orderly crystalline array of partially charged atoms, not ions, held together by a

Table V. Calculation of Atomization Energies of Solid Iodides

Compound	$-100\delta_I$	R_o	R_c	n	M	k	E_c	E_i	E	E_o
LiI	53	3.03	2.67	3	1.75	0.90	38	91	129	121
NaI	54	3.23	2.87	3	1.75	0.90	31	87	118	113
KI	63	3.53	3.29	4	1.75	0.91	30	93	123	118
RbI	66	3.66	3.44	4	1.75	0.92	27	95	122	117
CsI	68	3.83	3.58	4	1.76	0.92	23	95	118	117
TlI	28	3.64	2.88	4	1.76	0.91	55	41	96	98
CuI	17	2.62	2.50	4	1.64	0.88	85	31	116	123
AgI	17	2.81	2.67	4	1.64	0.90	82	29	111	109
BeI_2	14	(2.37)	2.23	3	(4.09)	(0.87)	112	69	181	180
MgI_2	19	2.81	2.63	3	4.38	0.89	92	87	179	173
CaI_2	30	3.15	3.07	4	4.38	0.90	101	124	225	221
SrI_2	34	3.37	3.25	4	(4.62)	0.91	89	140	229	226
BaI_2	39	3.51	3.31	4	(4.8)	0.91	72	160	232	237
ZnI_2	9	2.75	2.64	3	4.38	(0.89)	91	42	133	132
CdI_2	12	2.99	2.81	3	4.38	0.90	78	52	130	126
PbI_2	14	3.12	2.87	4	4.38	0.90	86	58	144	139
MnI_2	17	2.95	2.50	4	4.38	0.89	98	74	172	176

Table VI. Calculation of Atomization Energies of Solid Oxides

Compound	$-100\delta_O$	R_o	R_c	n	M	k	E_c	E_i	E	E_o
Li_2O	80	2.00	2.07	6	5.04	0.83	111	174	285	278
Na_2O	81	2.40	2.27	4	5.04	0.85	55	149	204	210
K_2O	90	2.79	2.67	4	5.04	0.88	44	149	193	188
Rb_2O	92	2.92	2.84	4	5.04	0.88	43	146	189	177
Cs_2O	93	(2.86)	2.98	4	4.38	0.89	42	133	175	175
BeO	35	1.60	1.62	4	6.37	0.77	147	115	262	279
MgO	42	2.10	2.03	4	1.75	0.82	120	120	240	239
CaO	57	2.40	2.47	4	1.75	0.85	103	149	252	253
SrO	62	2.57	2.65	4	1.75	0.86	96	150	246	239
BaO	67	2.75	2.71	4	1.75	0.86	79	156	235	234
ZnO	29	1.80	2.04	3	5.99	0.87	96	90	186	174
CdO	32	2.36	2.21	3	1.75	0.89	70	88	158	147
MnO	41	2.22	1.90	4	1.75	0.86	90	118	208	218
Al_2O_3	31	1.85	1.98	12	24.24	(0.84)	435	344	779	733
Ga_2O_3	19	(1.98)	1.98	12	25.03	0.84	381	220	601	567
SnO_2	17	2.10	2.13	6	2.41	0.85	186	146	332	329
PbO_2	18	2.22	2.27	4	2.41	0.86	97	140	237	231
TeO_2	13	2.03	2.10	4	2.41	0.85	129	115	244	242
TiO_2	39	1.96	2.05	6	2.41	0.84	110	344	454	456
ZrO_2	44	2.20	2.18	6	2.52	0.86	160	360	520	526

combination of coordinate covalence and ionic attraction. We may look upon coordinate covalence as a force holding the atoms together by attrac-

Table VII. Calculation of Atomization Energies of Solid Sulfides

Compound	$-100\delta_S$	R_o	R_c	n	M	k	E_c	E_i	E	E_o
Li_2S	67	2.47	2.36	6	5.04	0.86	141	115	256	251
Na_2S	68	2.83	2.56	6	5.04	0.86	108	103	211	211
K_2S	76	3.20	2.96	6	5.04	0.89	89	106	195	212
Rb_2S	80	3.31	3.13	6	5.04	0.90	86	109	195	189
Cs_2S	80	3.48	3.27	6	5.04	0.90	79	103	182	185
BeS	24	2.10	1.92	3	1.64	0.82	132	61	193	200
MgS	30	2.60	2.32	3	1.75	0.86	110	69	179	185
CaS	44	2.84	2.76	4	1.75	0.87	133	94	227	220
SrS	49	3.00	2.94	4	1.75	0.88	123	102	225	214
BaS	55	3.17	3.00	4	1.75	0.88	102	108	210	214
ZnS	16	2.34	2.33	3	6.55	0.87	114	38	152	146
CdS	20	2.52	2.50	3	1.64	0.88	100	46	146	128
PbS	22	2.96	2.58	4	1.75	0.88	101	46	147	135
MnS	28	(2.2)	2.21	3	1.75	0.86	107	76	183	182
TiS_2	29	(2.52)	2.36	6	2.19	(0.88)	130	182	312	325

Table VIII. Calculation of Atomization Energies of Solid Selenides

Compound	$-100\delta_{Se}$	R_o	R_c	n	M	k	E_c	E_i	E	E_o
MgSe	31	(2.64)	2.53	3	1.75	(0.88)	95	52	147	150
CaSe	46	(2.97)	2.91	4	1.75	(0.90)	108	68	176	168
SrSe	51	(3.10)	3.08	4	1.75	(0.90)	100	73	173	167
BaSe	57	(3.32)	3.15	4	1.75	(0.90)	84	74	158	165
ZnSe	18	(2.72)	2.42	3	1.64	(0.87)	82	26	108	114
CdSe	22	(2.95)	2.58	3	1.64	(0.88)	71	30	101	101
MnSe	30	(2.3)	2.34	3	1.75	0.86	100	54	154	144

tion of the different nuclei for the same shared electrons. The ionic attraction results from the fact that the equalization of orbital energies essential to covalence imparts opposite charges to adjacent atoms which therefore attract one another. The covalent contribution to the total bond energy is a measure of the importance of the role of coordinate covalence in nonmolecular solids. As shown by the data herein, this role is usually highly significant.

Indeed, the simple ionic model seems no longer acceptable, except for crystals of complex ions which afford no possibility of additional coordinate covalence. Limitations of the ionic model have long been recognized and become increasingly apparent, but most attempts to improve it have begun with modifying the ionic model. By recognizing that the components of binary solids are usually more nearly atomic than ionic, a much simpler and, I believe, more useful concept of the bonding has evolved. The coordinated polymeric model of such solids has the great advantage of providing a uniform concept of bonding applicable to nonmolecular compounds ranging from zero to maximum polarity. At the same time, with appropriate minor modification, it can be applied to molecular compounds as well. Although many difficult problems remain to be solved, the basis is thus established for a comprehensive theory of bonding that is both practical and informative.

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15

Coordination Number, Electronic Configuration, and Ionic Charge as Discrete Variables in Coordination Chemistry

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A formal system for organizing coordination chemistry is developed centering around the recognition of coordination number, electronic configuration, and ionic charge as discrete, independent, and non-transmutative variables. Using these and other discrete variables, matrices may be developed which permit the orderly listing of coordination compounds of a given metal or type. Furthermore, changes in the values of these discrete variables during chemical reactions of coordination compounds may be used to classify such reactions into seven types: a) Isoelectric exchange, b) Positive-moving exchange, c) Negative-moving exchange, d) Reduction, e) Oxidation, f) Oxidative addition, and g) Reductive elimination.

Since 1958 the author has been actively engaged in synthesizing novel transition-metal organometallic compounds. Possible new types of compounds, as well as the relationship between known types of compounds, have been considered. It became increasingly apparent that the principles governing properties of coordination compounds, although individually understood, had not yet been clearly organized. Originally, this paper intended to summarize and relate the factors influencing the chemistry of cyclopentadienylmetal carbonyls, one of the principal subjects of the author's researches. However, a formal structure to the chemistry of coordination compounds had to be developed before it could be properly used to account for the chemistry of the cyclopentadienylmetal carbonyls or any other special class of compounds. This paper thus develops such a formal structure.

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Discrete and Continuous Variables

Discrete variables refer to the numbers of items of types which cannot be divided without undergoing qualitative as well as quantitative change. Thus, a metal atom in a coordination compound can only be surrounded by an integral number of ligands. The coordination number (designated as C) is therefore a discrete variable. Furthermore, the total number of electrons arising from the central metal atom and the coordinated ligands must also be an integer. The electronic configuration (designated as E) is thus also a discrete variable. Finally, a coordination complex can either be neutral, anionic, or cationic. If it is anionic, an integral number of cations must be present to preserve neutrality of the compound. Similarly, if it is cationic, an integral number of anions must be present to preserve neutrality of the compound. Thus, ionic charge (designated as Q) is also a discrete variable. By contrast, other variables such as charge distribution and bond strength are continuous variables because they can assume any value within given limits.

The following basic principle underlies the formal structure developed in this paper:

> All coordination compounds are too complex for exact mathematical computations of their properties. Even calculations with extensive simplifying approximations can be too complex. Thus, the values of *continuous* variables are always uncertain. However, by contrast, the values of *discrete* variables can be found exactly because each discrete variable may have only a limited number of separated specific values. If coordination compounds of a given metal in an n-dimensional matrix are arranged where each of the n dimensions represents the value of one of n independent discrete variables, the effects of the continuous variables, as well as of the discrete variables, can be understood more readily because our studies can focus on a specific region of this matrix. The following terms are used in considering the details of this matrix.

Definitions

Types of Ligands. Only ligands bonded to a metal by means of only one electron-pair bond (i.e., monodentate) are considered in this paper. Ligands bonded to a metal by means of more than one electron-pair bond may be divided into two types:

a) LOCALIZED CHELATING LIGANDS. An n-dentate chelating ligand has non-adjacent atoms which are bonded to the central metal atom. For analysis here, an n-dentate chelating ligand is considered as n different monodentate ligands occupying a total of n coordination positions.

b) DELOCALIZED π-COMPLEXING LIGANDS. These ligands have more than two adjacent atoms donating more than one electron pair to the central atom, generally by delocalized π bonding. The π-cyclopentadienyl ligand is the most common example. For simplicity, this paper does not discuss in detail complexes with these ligands.

The calculation of a) electrons donated by a ligand, and b) the oxidation state of the central metal atom are defined below.

a) NUMBER OF ELECTRONS DONATED BY A MONODENTATE LIGAND. Consider the neutral two-electron M-L bond as being formed by *neutral* M (metal) and L (ligand) fragments. If both electrons arise from the ligand, the ligand is a two-electron donor. If both electrons arise from the metal, the ligand is a zero-electron donor. If one electron arises from the metal and one from the ligand, the ligand is a one-electron donor. Further examples are discussed below.

b) OXIDATION STATE OF THE CENTRAL METAL ATOM. With the central metal atom in an oxidation state with a) value of zero, consider the various two-electron bonds between the central metal atom and the ligands surrounding it as being formed from neutral metal and ligand fragments. For each electron in these bonds arising from the neutral metal atom, add $+1$ to the oxidation state. For the oxidation state thus found add (algebraically) the ionic charge of the coordination complex.

With these definitions, it is possible to classify all monodentate ligands into one of the following five types:

a) THREE-ELECTRON DONOR (DESIGNATED AS T). In forming a bond with the metal atom, the neutral ligand T first transfers one electron completely to the metal atom forming the cation T^+. This cation T^+ then acts as a two-electron donor to form the M-T bond. Thus, the neutral ligand T donates a total of three electrons to the metal atom and contributes -1 to its oxidation state. The only two examples of "localized" monodentate three-electron donor ligands are the nitrosyl and arylazo ligands. Characteristic of both of these ligands is the stability of the species T^+.

b) TWO-ELECTRON DONOR (LEWIS BASE))DESIGNATED AS L). In forming the M-L bond, the ligand L contributes both electrons and zero to the oxidation state of the metal atom. Lewis bases, including trialkylamines, tertiary phosphines, carbon monoxide, alkylisocyanides, and dialkylsulfides, fall into this very common category.

c) ONE-ELECTRON DONOR (DESIGNATED AS X). In forming the M-X bond, the ligand X contributes one electron and $+1$ to the oxidation state of the metal atom. Halides, pseudohalides, and alkyl groups fall into this very common category.

d) ZERO-ELECTRON DONOR (LEWIS ACID) (DESIGNATED AS Z). The ligand Z contributes neither electron to the two electron M-Z bond but $+2$ to the oxidation state of the central metal atom. Lewis acids, especially derivatives of tricovalent boron, such as BH_3 and the oxide ion O^{-2}, fall into this category.

e) ONE-ELECTRON ACCEPTOR (DESIGNATED AS N). The nitride ligand as present in $[OsO_3N]^-$ and related compounds is the sole representative of this category. This ligand accepts one electron from the metal atom and contributes neither electron to the two electron M-N bond but adds +3 to the oxidation state of the central metal atom.

Most of the ligands in the complexes under consideration will be either two-electron donors L or one-electron donors X. The ability to classify all ligands into these very few types simplifies the fitting of known coordination compounds of a given metal into a very simple matrix.

Types of Discrete Variables. Discrete variables can be either *transmutative* or *non-transmutative.* Changing of a transmutative discrete variable, while holding all others constant, changes (transmutes) the central metal atom. However, changing of a non-transmutative discrete variable while holding all others constant does not change the central metal atom. The most important transmutative discrete variable is the atomic number of the central metal atom, designated as A. The three, non-transmutative variables of importance in this paper are coordination number (C), electronic configuration (E), and ionic charge (Q).

The three independent, non-transmutative variables are defined as follows:

a) COORDINATION NUMBER (C). The variable C corresponds to the number of monodentate ligands surrounding the central metal atom. Hexacoordinate complexes ($C = 6$) are often favored.

b) ELECTRONIC CONFIGURATION (E). The variable E is the sum of the outer metal nonbonding electrons and the electron pairs of the metal-ligand bonds. For compounds with the favored "rare gas" electronic configuration, E is 18. For square planar complexes of the late transition metals, the electronic configuration E is 16.

c) IONIC CHARGE (Q). The variable Q is the net charge on the coordination complex.

The variable "oxidation state" (designated as O) is also a discrete variable, but it is a *dependent* one rather than an independent one because O depends on C (coordination number), A (number of outer electrons of the neutral free central metal atom which is closely related to its atomic number), and E (electronic configuration as defined above) as follows:

$$O = 2C + A - E.$$

Thus, the oxidation state is defined exactly once A, C, and E are specified.

The CEQ-Matrix

Consider the compounds of a given metal such as rhenium. Then consider a three-dimensional matrix with the three independent, discrete variables: electronic configuration (E), coordination number (C), and ionic charge (Q) corresponding to the three dimensions. The known rhenium complexes can be placed in this matrix in the appropriate cells corre-

Table I. *CEQ* Matrix for Rhenium

Electronic Configuration, E

13	14	15	16	17	18	19	*Coordination Number, C*
					$[\mathrm{Re^{VII}X_9}]^{-2}$ $\mathrm{ReH_9}^{-2}$		9
				$[\mathrm{Re^{VI}X_8}]^{-2}$ $\mathrm{Re(CN)_8}^{-2}$	$[\mathrm{Re^{V}X_8}]^{-3}$ $\mathrm{Re(CN)_8}^{-3}$		8
					$[\mathrm{Re^{III}L_3X_4}]^{-}$ $\mathrm{Re(CO)_3Br_4}^{-}$		7
	$[\mathrm{Re^{V}L_6}]^{+5}$ $[\mathrm{Re^{V}X_6}]^{-}$ $\mathrm{Re(NH_3)_6}^{+5}$, $\mathrm{ReF_6}^{-}$	$[\mathrm{Re^{IV}L_4X_2}]^{+2}$ $[\mathrm{Re^{IV}X_6}]^{-2}$ $\mathrm{Re(diars)Cl_2}^{+2}$ $\mathrm{ReCl_6}^{-2}$	$[\mathrm{Re^{III}L_6}]^{+3}$ $[\mathrm{Re^{III}L_4X_2}]^{+}$ $\mathrm{Re(NH_3)_6}^{+3}$ $\mathrm{Re(diars)_2Cl_2}^{+}$	$\mathrm{Re^{II}L_4X_2}$ $\mathrm{Re(diars)_2Cl_2}$	$[\mathrm{Re^{I}L_6}]^{+}$ $[\mathrm{Re^{I}X_6}]^{-5}$ $\mathrm{Re(CO)_6}^{+}$, $\mathrm{Re(CN)_6}^{-5}$		6
					$[\mathrm{Re^{-I}L_5}]^{-}$ $\mathrm{Re(CO)_5}^{-}$		5

sponding to the values of the variables C, E, and Q. In order to cover a large number of rhenium complexes with a given number of entries the generalized ligand designations T, L, X, and Z as defined previously are used.

Table I shows a simplified version of such a *CEQ* matrix for rhenium. In order to obtain a more convenient two-dimensional table, the axis corresponding to the ionic charge Q has been eliminated. Instead, in each box corresponding to definite values of C and E, the extremes of different values of Q are given. For example, in the box $E = 18$, $C = 6$, the two species $[Re^{I}L_6]^+$ ($Q = +1$) and $[Re^{I}X_6]^{-5}$ ($Q = -5$) are shown. In addition, each box contains specific examples of the species illustrated by the general formulas.

Hexacoordinate species ($C = 6$) with the rare gas configuration ($E = 18$) are particularly favored. Therefore, in the *CEQ*-matrix the row corresponding to $C = 6$ and the column corresponding to $E = 18$ are outlined in double lines. In the rhenium *CEQ*-matrix (Table I), as well as the other *CEQ*-matrices given in this paper (Tables II to VII), the complex types are concentrated along the $C = 6$ row and the $E = 18$ column.

To further illustrate *CEQ* matrices, those for the six first-row transition metals vanadium through nickel, inclusive, are given in Tables II to VII.

Types of Reactions

Depending upon the effects on the discrete variables C, E, and Q, reactions of coordination complexes may be of seven basic types falling into four main categories.

A) Isoelectric Exchange. In this type of reaction, the values of all three discrete variables C, E, and Q are the same in both the starting material and the product. This is thus the case where a ligand is replaced by another ligand with the same charge. An example is the reaction of hexacarbonylmolybdenum with triphenylphosphine to give $(C_6H_5)_3PMo(CO)_5$, i.e.,

$$Mo(CO)_6 + (C_6H_5)_3P \rightarrow (C_6H_5)_3PMo(CO)_5 + CO.$$

B) Positive-moving Exchange / Negative-moving Exchange. In these types of reactions, the values of C and E are the same in both the starting material and the product, but the value of Q is different in the product than in the starting material. Depending on the direction of change of Q, two types of reactions are possible.

1. Positive-moving Exchange. Q is greater algebraically in the product than in the starting material. An example of this rather rare type is the reaction of ferrocyanide ion ($Q = -4$) with carbon monoxide to give the $[Fe(CN)_5CO]^{-3}$ ion ($Q = -3$), i.e.,

$$[Fe(CN)_6]^{-4} + CO \rightarrow [Fe(CN)_5CO]^{-3} + CN^-.$$

Table II. *CEQ* Matrix for Vanadium

Electronic Configuration, E

Coordination Number, C

C \ E	*13*	*14*	*15*	*16*	*17*	*18*	*19*
8							
7							
6		$[V^{III}L_6]^{+3}$ $[V^{III}X_6]^{-3}$ $V(bipy)^{+3}$ $V(CN)_6^{-3}$	$[V^{II}L_6]^{+2}$ $[V^{II}X_6]^{-4}$ $V(bipy)_3^{+2}$ $V(CN)_6^{-4}$		$V^{\circ}L_6$ $V(CO)_6$	$[V^{-I}L_6]^-$ $V(CO)_6^-$	
5							
4							

Table III. *CEQ Matrix for Chromium*

Electronic Configuration, E

Coordination Number, C	*13*	*14*	*15*	*16*	*17*	*18*	*19*
8							
7							
6	$Cr^{V}ZX_5]^{-2}$	$[Cr^{IV}X_6]^{-2}$	$[Cr^{III}L_6]^{+3}$ $[Cr^{III}X_6]^{-3}$	$[Cr^{II}X_6]^{-4}$	$[Cr^{I}L_6]^{+}$ $Cr^{I}L_5X$	$Cr^{0}L_6$ $[Cr^{0}X_6]^{-6}$	
	$[CrOCl_5^{-2}$	CrF_6^{-2}	$Cr(NH_3)_6^{+3}$ $Cr(CN)_6^{-3}$	$Cr(CN)_6^{-4}$	$Cr(bipy)_3^{+}$ $Cr(CO)_5I$	$Cr(CO)_6$ $Cr(CN)_6^{-6}$	
5						$[Cr^{-II}L_5]^{-2}$ $Cr(CO)_5^{-2}$	
4							

Table IV. *CEQ* Matrix for Manganese

Electronic Configuration, E

13	*14*	*15*	*16*	*17*	*18*	*19*	*Coordination Number, C*
							8
							7
		$[Mn^{IV}X_6]^{-2}$ MnF_6^{-2}	$[Mn^{III}X_6]^{-3}$ $Mn(CN)_6^{-3}$	$[Mn^{II}L_6]^{+2}$ $[Mn^{II}X_6]^{-4}$ $Mn(CNR)_6^{+2}$ $Mn(CN)_6^{-4}$	$[Mn^{I}L_6]^{+}$ $[Mn^{I}X_6]^{-5}$ $Mn(CO)_6^{+}$ $Mn(CN)_6^{-5}$		6
					$[Mn^{-I}L_5]^{-}$ $Mn^{-I}L_4T$ $Mn(CO)_5^{-}$ $Mn(CO)_4NO$		5
					$Mn^{-III}LT_3$ $MnCO(NO)_3$		4

Table V. *CEQ* Matrix for Iron

Electronic Configuration, E

13	14	15	16	17	18	19	*Coordination Number, C*
							8
							7
			$[Fe^{IV}L_4X_2]^{+2}$ $Fe(diars)_2Cl_2^{+2}$	$[Fe^{III}L_6]^{+3}$ $[Fe^{III}X_6]^{-3}$ $Fe(phen)_3^{+3}$ $Fe(CN)_6^{-3}$	$[Fe^{II}L_6]^{+2}$ $[Fe^{II}X_6]^{-4}$ $Fe(phen)_3^{+2}$ $Fe(CN)_6^{-4}$		6
				$Fe^{I}L_4X$ $Fe(CO)_4I$	$Fe^{0}L_5$ $Fe(CO)_5$		5
$[Fe^{III}X_4]^-$ $FeCl_4^-$					$[Fe^{-II}L_4]^{-2}$ $Fe^{-II}L_2T_2$ $Fe(CO)_4^{-}$ $Fe(CO)_2(NO)_2$		4

Table VI. *CEQ* Matrix for Cobalt

Electronic Configuration, E

Coordination Number, C	*14*	*15*	*16*	*17*	*18*	*19*	*20*
8							
7							
6				$[Co^{IV}X_6]^{-2}$ CoF_6^{-2}	$[Co^{III}L_6]^{+3}$ $[Co^{III}X_6]^{-3}$ $Co(NH_3)_6^{+3}$ $Co(CN)_6^{-3}$	$[Co^{II}L_6]^{+2}$ $Co(H_2O)_6^{+2}$	
5				$Co^{II}X_2L_3$ CoI_2(triars)	$[Co^{I}L_5]^{+}$ $Co(CNR)_5^{+}$		
4		$[Co^{II}L_4]^{+2}$ $[Co^{II}X_4]^{-2}$ $Co(diars)_2^{+2}$ $CoCl_4^{-2}$			$[Co^{-I}L_4]^{-}$ $Co^{-I}L_3T$ $Co(CO)_4^{-}$ $Co(CO)_3NO$		

Table VII. *CEQ* Matrix for Nickel

Electronic Configuration, E

14	*15*	*16*	*17*	*18*	*19*	*20*	*Coordination Number, C*
							7
				$[Ni^{IV}X_6]^{-2}$ NiF_6^{-2}	$[Ni^{III}X_6]^{-3}$ NiF_6^{-3}	$[Ni^{II}L_6]^{+2}$ $Ni(en)_3^{+2}$	6
			$Ni^{III}L_2X_3$ $(Et_3P)_2NiBr_3$	$Ni^{II}L_3X_2$ (triars)$NiBr_2$			5
		$[Ni^{II}L_4]^{+2}$ $[Ni^{II}X_4]^{-2}$ $Ni(CN)_4^{-2}$	$[Ni^{I}X_4]^{-3}$ $Ni(CN)_4^{-3}$	$Ni^{0}L_4$ $[Ni^{0}X_4]^{-4}$ $Ni(CO)_4$ $Ni(CN)_4^{-4}$			4
		$Ni^{0}L_3$ $C_{12}H_{18}Ni$					3

Gal. 6A — ALFRED WERNER 14470

(E = 18)

Coordination Number, C (π-C_5H_5 occupies three coordination positions)	Ti, Zr, Hf	V, Nb, Ta	Cr, Mo, W	Mn, Tc, Re	Fe, Ru, Os	Co, Rh, Ir	Ni, Pd, Pt	Cu, Ag, Au
8			$C_5H_5M^{IV}L_2X_3$ $C_5H_5Mo(CO)_2Br_3$					
7		$C_5H_5M^{I}L_4$ $C_5H_5V(CO)_4$	$C_5H_5M^{II}L_3X$ $[C_5H_5M^{II}L_4]^+$ $C_5H_5Mo(CO)_3Br$ $[C_5H_5Mo(CO)_4]^+$	$[C_5H_5M^{III}L_3X]^+$ $[C_5H_5Re(CO)_3Cl]^+$				
6		$[C_5H_5M^{-I}L_3]^{-2}$ $[C_5H_5V(CO)_3]^{-2}$	$C_5H_5M^{\circ}L_2T$ $[C_5H_5M^{\circ}L_3]^-$ $C_5H_5Cr(CO)_2NO$ $[C_5H_5Cr(CO)_3]^-$	$C_5H_5M^{I}L_3$ $C_5H_5Mn(CO)_3$	$C_5H_5M^{II}L_2X$ $[C_5H_5M^{II}L_3]^+$ $C_5H_5Fe(CO)_2I$ $[C_5H_5Fe(CO)_3]^+$	$C_5H_5M^{III}LX_2$ $C_5H_5CoCOI_2$	$C_5H_5M^{IV}X_3$ $C_5H_5Pt(CH_3)_3$	
5					$[C_5H_5M^{\circ}L_2]^-$ $[C_5H_5Fe(CO)_2]^-$	$C_5H_5M^{I}L_2$ $C_5H_5Co(CO)_2$	$C_5H_5M^{II}LX$ $CF_3Ni(CO)C_5H_5$	
4							$C_5H_5M^{\circ}T$ $[C_5H_5M^{\circ}L]^-$ C_5H_5NiNO $[C_5H_5NiCO]^-$	

Table IX. *AEQ* Matrix for Hexacyanometallates ($C = 6$)

Ti	*V*	*Cr*	*Mn*	*Fe*	*Co*	*Ni*	*Cu*	*Electronic Configuration, E*
		$Cr^{\circ}(CN)_6^{-6}$	$Mn^{I}(CN)_6^{-5}$	$Fe^{II}(CN)_6^{-4}$	$Co^{III}(CN)_6^{-3}$			*18*
			$Mn^{II}(CN)_6^{-4}$	$Fe^{III}(CN)_6^{-3}$				17
		$Cr^{II}(CN)_6^{-4}$	$Mn^{III}(CN)_6^{-3}$					16
	$V^{II}(CN)_6^{-4}$	$Cr^{III}(CN)_6^{-3}$						15
	$V^{III}(CN)_6^{-3}$							14
								13

Table X. *AEQ* Matrix for Bis-π-Cyclopentadienylmetal Compounds

Ti	*V*	*Cr*	*Mn*	*Fe*	*Co*	*Ni*	*Cu*	*Electronic Configuration, E*
						$(C_5H_5)_2Ni^{II}$		20
					$(C_5H_5)_2Co^{II}$	$[(C_5H_5)_2Ni^{III}]^+$		19
				$(C_5H_5)_2Fe^{II}$	$[(C_5H_5)_2Co^{III}]^+$			18
				$[(C_5H_5)_2Fe^{III}]^+$				17
		$(C_5H_5)_2Cr^{II}$						16
	$(C_5H_5)_2V^{II}$	$[(C_5H_5)_2Cr^{III}]^+$						15
$(C_5H_5)_2Ti^{II}$								14

2. NEGATIVE-MOVING EXCHANGE. Q is lesser algebraically in the product than in the starting material. An example of this type of reaction is the reaction between hexacarbonylmolybdenum ($Q = 0$) and iodide ion to give the $[Mo(CO)_5I]^-$ ion ($Q = -1$), i.e.,

$$Mo(CO)_6 + I^- \rightarrow [Mo(CO)_5I]^- + CO.$$

C) Reduction/Oxidation. In these types of reactions, the value of C is the same in both the starting material and the product, but the values of E and Q are different in the product than in the starting material. Depending on the directions of change of E and Q, two types of reactions are possible.

REDUCTION. E is greater and Q is less in the product than in the starting material. An example is the reduction of hexacarbonylvanadium ($E = 17$, $Q = 0$) with sodium to give sodium hexacarbonylvanadate ($E = 18$, $Q = -1$), i.e.,

$$V(CO)_6 + Na \rightarrow Na[V(CO)_6].$$

OXIDATION. E is less and Q is greater in the product than in the starting material. An example is the oxidation of ferrocyanide ion ($E = 18, Q = -4$) with chlorine to give ferricyanide ion ($E = 17, Q = -3$), i.e.,

$$Fe(CN)_6^{-4} + \tfrac{1}{2}Cl_2 \rightarrow Fe(CN)_6^{-3} + Cl^-.$$

D) Oxidative Addition / Reductive Elimination. In these types of reactions the value of E is the same in both the starting material and the product, but the values of C and Q are different in the product than in the starting material. Depending on the direction of change of C and Q two types of reactions are possible.

OXIDATIVE ADDITION. C and Q are both greater in the product than in the starting material. Reactions of metal carbonyl anions with organic halides to form σ-bonded alkyl derivatives fall into this category. Thus, the $Mn(CO)_5^-$ anion ($C = 5, Q = -1$) reacts with methyl iodide to form $CH_3Mn(CO)_5$ ($C = 6$, $Q = 0$) according to the following equation:

$$Mn(CO)_5^- + CH_3I \rightarrow CH_3Mn(CO)_5 + I^-.$$

REDUCTIVE ELIMINATION. C and Q are both less in the product than in the starting material. An example of this type of reaction is the reduction of $Mn(CO)_5Br$ ($C = 6$, $Q = 0$) with excess sodium to give the anion $Mn(CO)_5^-$ ($C = 5$, $Q = -1$), i.e

$$Mn(CO)_5Br + 2Na \rightarrow Na[Mn(CO)_5] + Br^- + Na^+.$$

The ACQ and AEQ Matrices

The *CEQ* matrix discussed above is useful for depicting the coordination chemistry of a given metal. In order to depict the chemistry of coordination compounds of a given type, the *ACQ* and *AEQ* matrices may be useful.

Ideally an *ACQ* matrix is three-dimensional with the dimensions corresponding to atomic number (*A*), coordination number (*C*), and ionic charge (*Q*). The electronic configuration (*E*) is constant for the listed series of complexes—generally the favored rare gas configuration $E = 18$.

Compounds of a specified type such as mono-π-cyclopentadienyl derivatives (Table VIII) may be listed in such an *ACQ* matrix. For the sake of convenience the following two special features are present in the *ACQ* matrix of Table VIII.

1) As in the *CEQ* matrices (Tables I to VII), the *Q* axis in the *ACQ* matrix has been eliminated. Instead, for each value of *A* and *C*, the extremes of different values of *Q* are given.

2) The atomic number *A* alternately may be regarded as representing a specific column of the periodic table. The same column in the *ACQ* matrix of Table VIII can represent a complex of either chromium, molybdenum, or tungsten, for example.

For compound types where the coordination number (*C*) tends to remain more constant than the electronic configuration (*E*), an *AEQ* matrix instead of an *ACQ* matrix can be used. Except for the substitution of an electronic configuration (*E*) axis for a coordination number (*C*) axis, an *AEQ* matrix is entirely analogous to an *ACQ* matrix. Tables IX and X illustrate *AEQ* matrices for the hexacyano complexes and the di-π-cyclopentadienyl complexes, respectively, of the first row transition metals.

Conclusion

This paper has pointed out the essential features of a formal structure to the chemistry of the coordination compounds. Preparation and inspection of *CEQ*, *ACQ*, and *AEQ* matrices for many systems of coordination compounds should clarify many aspects of coordination chemistry and suggest areas for future research. More detailed discussion on the application of the principles in this paper to specific systems appears more appropriate for papers devoted to these specific systems.

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Electron-Pair Repulsions and Molecular Shape

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According to the electron-pair repulsion theory, the general shape of a molecule AX_n *may be predicted from the total number of electron pairs in the valency shell of A. The extension of this simple theory to account for some of the finer details of molecular shape is considered. The results of recent structure determinations on* SF_4, PF_5, CH_3PF_4, $(CH_3)_2PF_3$, XeF_6, $TeBr_6^{-2}$, *and other molecules are discussed in terms of electron-pair repulsions. The apparently anomalous trigonal prism molecules, such as* $Re[S_2C_2(C_6H_5)_2]_3$, *are discussed.*

Werner postulated that 6-coordinate complexes have an octahedral structure. He demonstrated, by the classical method of determining the number of isomers of variously substituted complexes, that they were indeed octahedral and did not have the two other possible structures in which all six ligands are equivalent—namely the plane hexagon and the trigonal prism. Since then, the vast majority of 6-coordinated molecules has been bound to have an octahedral structure, although sometimes this is distorted, usually by elongation along a four-fold axis. Occasionally trigonal prism structures are found, and XeF_6 has a still less symmetrical structure. Four-coordinate molecules almost always have a tetrahedral structure. Sometimes, however, they are square planar, in addition to which a few molecules such as SF_4 and $(CH_3)_2TeCl_2$ have been found with less symmetrical structures.

Almost any theory correctly predicts the octahedral and tetrahedral structures of 6- and 4-coordinated molecules. Thus, a simple ionic model in which a central positive ion attracts a number of negative ions gives these structures because, for a given central atom to ligand distance, they maximize the distance between the ligands and hence minimize their repulsive interactions. For this reason, the octahedron is more stable than the trigonal prism, and the tetrahedron is more stable than the square plane. An extension of this model, namely crystal field theory, explains why some 6-coordinated molecules of transition elements have an octahedral structure distorted along a four-fold axis, and also why some 4-coordinated molecules are square planar. Alternatively, if we prefer a covalent model, we can assume that molecular geometry is determined by steric effects—i.e., by non-bonded interactions between the ligands. Again we arrive at the same conclusions, namely that 4-coordinated molecules should be tetrahedral and 6-coordinated molecules octahedral. Similarly, it is obvious that a 2-coordinated molecule would be predicted to be linear. However, many molecules do not have these shapes, thus Cl_2O is angular, SF_4 is not tetrahedral, and XeF_6 is not octahedral. The shapes of these molecules show that it is necessary to allow for the effects of the non-bonding or lone pairs of electrons on the molecular shape, and it is now well-known that the general shapes of a very large number of molecules can be predicted by simply considering the total numbers of electron pairs (bonding and nonbonding pairs) in the valency shells of each atom forming two or more bonds (*10*, *12*, *14*).

It is assumed that the operation of the Pauli exclusion principle and electrostatic repulsion determine the arrangement of the electron pairs in the valency shell of any atom. It can then be shown that the most probable arrangements for up to nine electron pairs are as follows (*10*):

two:	linear
three:	equilateral triangle
four:	tetrahedron
five:	trigonal bipyramid
six:	octahedron
seven:	1:3:3, 1:4:2 or 1:5:1
eight:	square antiprism
nine:	3:3:3

We thus obtain an immediate explanation for the angular shape of Cl_2O, which is based on a tetrahedral arrangement of four electron pairs in the valency shell of the oxygen atom and for the shape of SF_4, which is based on a trigonal bipyramidal arrangement of five electron pairs.

This simple theory can be extended to give a qualitative understanding of many of the finer details of molecular shapes by taking into account the fact that the electron pairs in a valency shell are generally not all equivalent; they may be binding different ligands, be unshared or lone-pairs, or be participating in multiple bonding. These differences can be allowed for by making the following reasonable assumptions: (1) the size of a bonding electron pair, or the space that it takes up on the surface of an atom, increases with decreasing electronegativity of the ligand; (2) a non-bonding or lone pair is larger and takes up more room on the surface of an atom than a bonding pair; and (3) the two electron pairs of a double bond take up more room than the one electron pair of a single bond (*12*).

Let us first consider the trigonal bipyramidal molecules PF_5, $(CH_3)PF_4$, and $(CH_3)_2PF_3$, the structures of which have been determined by Bartell and Hansen (*3*). The molecular parameters for these three molecules are given in Figure 1. The important features that need explanation are as follows: (1) the molecules are trigonal bipyramids or distorted trigonal bipyramids; (2) the axial bonds are longer than the corresponding equatorial bonds; (3) methyl groups occupy equatorial positions; (4) all the bond lengths increase and the ratio of the length of the axial bonds to the length of the equatorial bonds r_{ax}/r_{eq} increases as the number of CH_3 substituents increases; and (5) methyl substitution causes the P-F bonds to be bent away from the CH_3 groups.

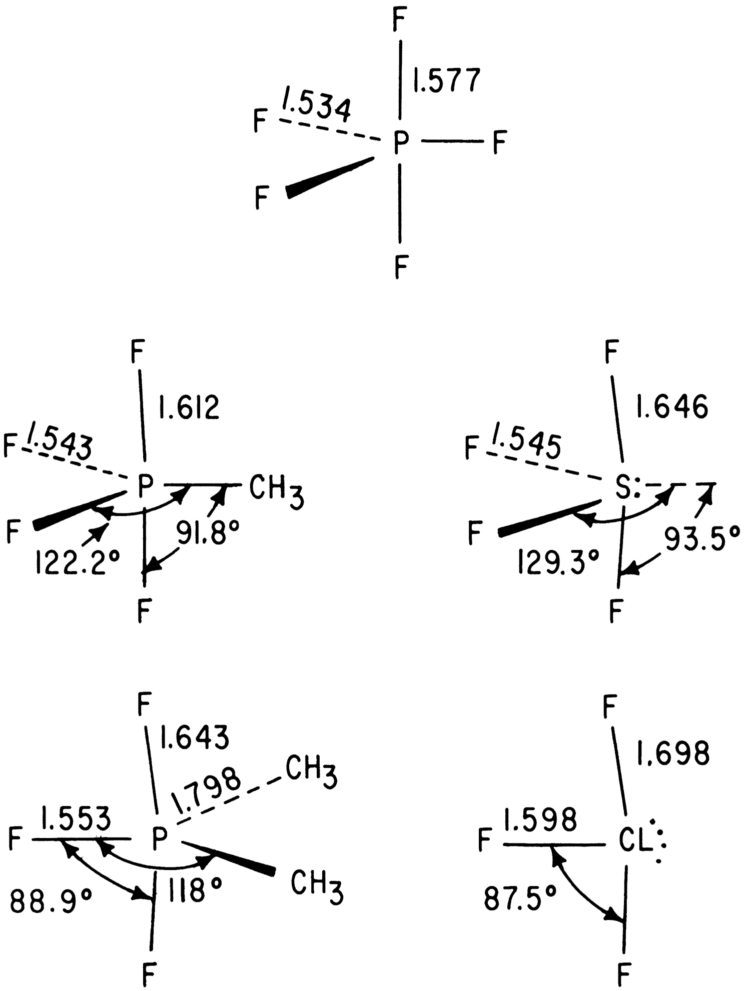


Figure 1. Molecular parameter for PF_5, $(CH_3)PF_4$, and $(CH_3)_2PF_3$

As the most probable arrangement of five equivalent electron pairs is the trigonal bipyramid, any molecule in which a central atom with spherical or completed inner shells has five electron pairs in its valency shell forming single bonds to five equivalent ligands is expected to be a trigonal bipyramid. The axial electron pairs in this arrangement are not equivalent to the equatorial pairs, and, in particular, because the former have three nearest neighbors at 90° while the latter have only two such neighboring pairs, equilibrium can only be attained if the axial pairs are at a greater distance from the nucleus than the equatorial pairs. Thus, in all such trigonal bipyramid molecules the axial bonds are longer than the equatorial bonds (*11, 13*). Moreover, the smallest electron pairs which have the smallest interactions with other electron pairs tend to go into the axial positions, and the larger electron pairs occupy the equatorial positions where there is more room for them. Thus, the most electronegative ligands, which have the smallest bonding electron pairs, always go into the axial positions and the less electronegative ligands—i.e., the methyl groups in the molecules we are considering, occupy the equatorial positions. This is a quite general rule, and there are a number of other examples—e.g., in PF_3Cl_2, $PFCl_4$, and $P(CF_3)Cl_4$ the more electronegative F or CF_3 groups occupy the axial positions (*18*). The substitution of a fluorine by a methyl group decreases the effective electronegativity of the phosphorus and allows all the bonding pairs to move away from the phosphorus slightly, thus increasing all the bond lengths. In addition, however, the axial fluorine bonds are closer to the large methyl group bond than the equatorial fluorine bonds, hence they suffer a greater repulsion and increase more in length than the equatorial bonds. They are also pushed away from the methyl group so that the axial FPF bond angle becomes less than 180°, in just the same way as the large, lone pairs cause the same angle in the SF_4 and ClF_3 molecules to be less than 180°. Indeed, the molecules that we are considering are closely related to SF_4 and ClF_3 in the sense that they are all derived from PF_5 by replacing one or more fluorines by either CH_3 groups or by unshared pairs of electrons. The molecular parameters then change in the manner expected as the very small electron pair binding a fluorine increases in size when it binds the less electronegative CH_3 group and increases in size again when it becomes a lone pair.

The theory of valence-shell, electron-pair repulsions assumes that the stereochemistry of a molecule is determined by the interactions between electron pairs in the valency shell, and that interactions between filled shells of ligands are in general of lesser importance. However, it is clear that for high coordination numbers and for sufficiently large ligands repulsions between the ligands could become important. It is interesting to ask, therefore, whether there are any structures that do show the importance of ligand interactions. This is particularly important at the present time because of the current interest in the structure of xenon hexafluoride.

Most theoretical methods that were applied to this molecule either predicted that it would not exist (*1*), or that it would have a regular octahedral structure (*6*, *17*, *21*). However, as there are seven electron pairs in the valency shell of the xenon, consideration of electron-pair repulsions shows that the structure would not be expected to be octahedral but that it should be based on an arrangement of seven electron pairs. The most probable arrangement of seven electron pairs cannot, unfortunately, be predicted with complete certainty as there are three arrangements of seven equivalent pairs that have rather similar energies and whose relative stability depends on the exact form of the interaction between the electron pairs (*10*). Hence, we cannot make any definite prediction except that the structure will not be octahedral. The most likely arrangement for six-bonding, and one nonbonding, electron pair would appear to be the 1:3:3 arrangement in which the lone pair occupies the unique position opposite the middle of one face of an octahedron, of which the corners are occupied by the six-bonding pairs (Figure 2). The octahedron is, of course, distorted by the presence of the seventh nonbonding pair so that the face occupied by the lone pair is enlarged and squashed down towards the opposite face. It now seems certain from recent electron diffraction work that xenon hexafluoride does not have a regular octahedral structure but a distorted structure of the type described (*2*, *15*). The possible molecule $XeOF_6$ could be predicted to have a very similar structure in which the oxygen replaces the lone pair of XeF_6. There are, however, similar molecules such as $TeCl_6^{+2}$, $TeBr_6^{+2}$, and $SbBr_6^{+3}$ which definitely have regular octahedral structures (*5*, *16*) and which, therefore, constitute exceptions to the predictions of elec-

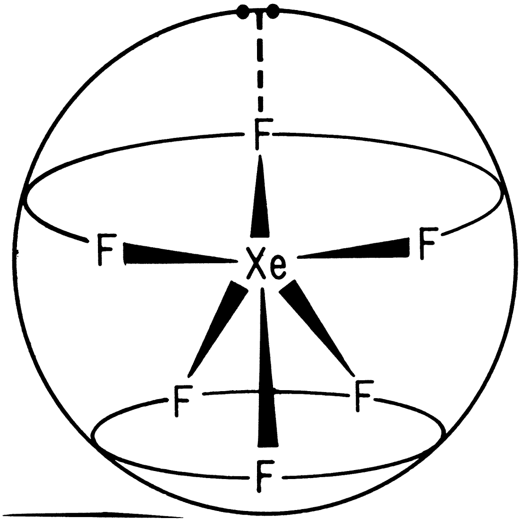


Figure 2. Probable structure of XeF_6

tron-pair repulsion theory. Here it is reasonable to assume that ligand-ligand interactions predominate. For example in the $TeBr_6^{+2}$ anion the six bromines take up all the space around the central tellurium. The bromine-bromine distance is 3.81 A., which may be compared with the normal van der Waal's distance of 3.9 A. We see that there is no room for the unshared pair. If the unshared pair is forced in, the bromine-bromine distances must be considerably reduced with a consequent large increase in the Pauli repulsion. In a pentagonal bipyramid arrangement, for example, some of the bromine-bromine separations would have to be reduced to 2.96 A. It seems, therefore, that the lone pair cannot be accommodated in the valency shell but must be forced inside—presumably into a spherical or *s*-type orbital. That this occurs is in fact borne out by the bond lengths in these ions which are unusually long. Thus the sum of the covalent radii for Te and Br gives an expected bond length of 2.51 A., whereas the observed bond length is 2.71 A. (*5*). Similarly, in the $TeCl_6^{-2}$ ion the observed bond length is 2.41 A., but the value calculated from the sum of the covalent radii is only 2.27 A. For the $SbBr_6^-$ ion, which does not have a lone pair, the observed bond length is 2.53 A., which is close to the value of 2.55 A. calculated from the covalent radii. In the $SbBr_6^{-3}$ ion, however, in which there is a nonbonding pair of electrons, the bond length is 2.78 A. (*16*). Our explanation of these anomalously long bond lengths is essentially the same as that given by Beach some time ago (*4*). He suggested that the nonbonding pair occupies the *s*-orbital in the valency shell and that the next highest *s*-orbital is used for bonding, the bonding orbitals being described as $p^3d^2\,s$ hybrids. The reason why the lone pair is not stereochemically inactive in xenon hexafluoride is that the smaller fluorine atoms do not take up all the space around the xenon, as is shown by the formation of the stable ions, XeF_7^- and XeF_8^{-2} (*19*). Thus, there is room for the nonbonding pair in the valency shell of xenon in XeF_6, and it is possible for it to exert its full stereochemical influence.

As there are some AX_6E molecules (E denotes an unshared pair of electrons) with an octahedral structure, it is natural to inquire if there are any AX_4E molecules with a tetrahedral structure instead of the SF_4 structure based on the trigonal bipyramidal arrangement of five electron pairs. As there are only four ligands, they would have to be quite large to take up all the space around a central atom so it is not surprising that no tetrahedral molecules of this kind are in fact known. However, there are a few molecules whose structures are distorted from the expected structures towards a tetrahedral structure. Thus, SF_4, $(CH_3)_2TeCl_2$, ClF_3, BrF_3, and $C_6H_5ICl_2$ all show the expected deviations from the ideal bond angles predicted by a trigonal bipyramid arrangement of five electron pairs (*11, 13*). However, in $(p\text{-}CH_3C_6H_4)_2SeBr_2$, $(p\text{-}CH_3C_6H_4)_2SeCl_2$, and $(C_6H_5)_2TeBr_2$ the halogens in the axial positions appear to be bent slightly towards the lone pair in the equatorial position

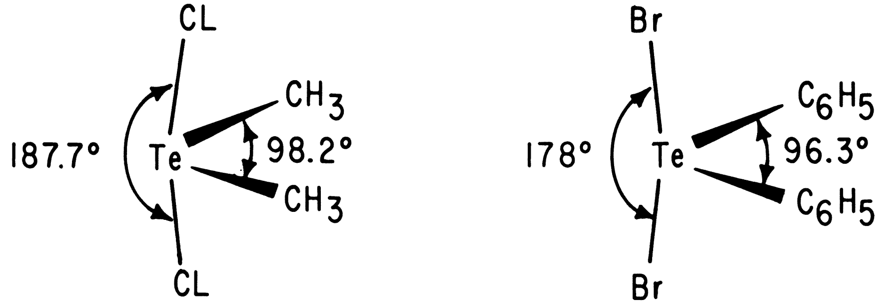
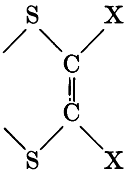


Figure 3. The structure of $(C_6H_5)_2TeBr_2$

rather than away from it (*11*) (Figure 3). It seems reasonable to suppose that because of the large size of the ligands in these cases there is some ligand-ligand interaction and hence some distortion towards the tetrahedral structure. In these cases, the nonbonding pair does not exert its full stereochemical influence but may be regarded as having moved slightly inside the bonding pair.

It has long been known that in the three-dimensional polymeric structures of MoS_2 and WS_2, the metal atom is 6-coordinated by sulfur and the sulfur atoms have a trigonal prism arrangement. Very recently the same stereochemistry has been found in some discrete complexes with bidentate ligands of the type:



in which the central metal may be V, Cr, Mn, W, Re, or Co. In some cases the metal has an incomplete (nonspherical) inner shell which might influence the stereochemistry, but in other cases the inner shells are complete and a regular octahedral structure would be predicted. In the two structures that have been determined by x-ray crystallography, the sulfur atoms have a trigonal prism arrangement and all the sulfur-sulfur distances are essentially equal and are considerably less than the normal van der Waal's distance. For example, in $Re[S_2C_2(C_6H_5)_2]_3$ the sulfur-sulfur distances are 3.02 A. (*8*), while in $Mo[(HCS)_2]_3$ they are 3.10 A. (*20*). These may be compared with the van der Waal's distance of 3.7 A. The same sulfur-sulfur distance is found in several square planar 4-coordinated complexes of these ligands (*7, 9*). It seems reasonable to suppose, therefore, that there are reasonably strong sulfur-sulfur interactions and that these play an important part in determining the trigonal prism and square planar geometry of these compounds.

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17

The Masking of Ligand Reactivity by Coordination

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A very large number of typical ligand reactions is retarded or suppressed completely when these ligands are present in complexes. Both steric and electronic factors can play important roles in this masking of reactivity. In many cases the specific nature of the metal in the complex is of considerable importance in determining the extent of such masking. Very often these changes in reactivity can be put to synthetic uses. In most cases it is possible to determine whether the reaction is completely suppressed or merely slowed down by determining the rate of the reaction at various ligand-to-metal ratios. In many of the cases examined where masking occurs, it is found that the complexed species reacts but at a much slower rate than when free. Some general principles governing these phenomena are suggested.

One of the earliest types of observation which was used to distinguish combinations of the sort which we now recognize as coordination compounds from looser aggregations was the absence of certain characteristic reactions of the constituent cations, anions, and neutral molecules. Indeed, this masking of normal ligand characteristics pervades the field in a very comprehensive manner, extending to physical as well as chemical characteristics (i.e., the electrical conductivity of complexes). Before passing on to more recent studies of masking, it is very instructive to consider some of the older ones which were so useful in the construction of the present edifice of coordination chemistry.

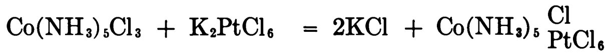
Perhaps the most striking and widespread of these earlier reports is the frequent absence of characteristic anion precipitation tests found for complexes containing anions. These are especially striking where the precipitate has a small solubility product and the complex has a large stability constant. A closely related observation is the essential absence of a basic reaction in freshly prepared solutions of stable ammines. Such solutions of stable complexes simply do not give most of the characteristic reactions of the ligands.

The difference in reactivity of the two types of chlorine in $[\mathrm{Co(NH_3)_5Cl]Cl_2}$ was noted by Werner (*74*) who compared the chloride in the coordination sphere to the chlorine in ethyl chloride. He adds the comment:

"This difference is especially characteristic and can be seen with exceptional clarity in those cases in which both types of function are present in the same compound."

Other reactions which he cited as of diagnostic use for this purpose are:

$$\mathrm{Co(NH_3)_6Cl_3 + 3K_2PtCl_6 = 6KCl + (Co(NH_3)_6)_2\,(PtCl_6)_3,}$$



$$\mathrm{Co(NH_3)_5Cl_3 + K_2PtCl_6 = 2KCl + Co(NH_3)_5\begin{matrix}Cl\\ PtCl_6\end{matrix}}$$

and the reaction with concentrated sulfuric acid in which the ionic chlorides are transformed into hydrogen chloride rather rapidly.

This "masking" of the typical ligand reactivity via coordination is a thread which runs throughout early work on these compounds and allowed the concept of the coordination sphere to be put on a definite basis as a result of chemical tests.

Subsequent work has shown that it is more common to have a *difference in rates* for typical ligand reactions, rather than a qualitative difference in reactivity. This is generally true of precipitation reactions as well as more involved reactions. It is therefore necessary to examine the general features of these reactions in considerably greater detail if we wish to appreciate the basic factors which govern the masking of ligand reactions.

Steric and Electronic Factors Involved in the Masking of Ligand Reactions

The masking of a ligand reaction by coordination may be defined as a situation in which a typical reaction of the free ligand is found to be retarded or stopped completely upon coordination of the ligand. As information accumulates, however, it has become apparent that it is quite difficult to predict all the circumstances under which masking will occur. The nature of the ligand, the attacking reagent, the electronic configuration of the metal ion, and the type of complex must be considered, as well as the nature of the accessible transition states. For reactions between large ungainly molecules, a transition state of very restricted geometry is often necessary. In such cases masking may often be effected by making use of a knowledge of the transition state. This is especially true of reactions which require contact between two or more atoms of each reactant. Where the availability of a ligand electron pair is necessary for the usual course of the reaction, one would also anticipate that coordination would hinder the progress of the reaction along its normal path. We can anticipate that the masking of a ligand reaction may have a steric or an electronic basis or one which is a combination of such factors.

The number of cases in which coordination has been reported to have a masking action is quite large. For purposes of summary these may be listed as arising from the following causes:

1) The donor atom, which is also the reactive site on the ligand, is held in such a manner that a reaction cannot follow its normal course. An example of this sort may be seen in the fact that the ammonia molecules of $Co(NH_3)_6^{+3}$ have lost their ability to neutralize protonic acids. Reactions which involve the lone pairs of trivalent nitrogen (in amines and their derivatives), trivalent phosphorus, trivalent arsenic, and trivalent antimony are generally masked when this lone pair is used to form a coordinate bond. For donor atoms which possess two or more unshared pairs, such as —O— or —S—, the involvement of one of the pairs in a coordinate bond will generally *not* result in complete masking. The same general kind of masking may be found in redox reactions which involve lone pairs which can also function as bonding pairs in coordinate bonds.

2) The coordination results in serious stereochemical restrictions on the accessible ligand conformations. One of the inescapable by-products of coordination is a change in the accessible ligand conformations. Thus, ethylenediamine, which is more or less free to rotate about the carbon-carbon bond in the free state, becomes fixed almost exclusively in the *gauche* conformation in its complexes. With larger ligands, the coordination process often introduces more obvious and more drastic restrictions upon the steric properties of parts of the molecule, especially the donor groups. Thus, coordination can be expected to have some effect on the steric factor in the rate constant of a given reaction. Unfortunately, it is very difficult to predict when the coordination of a reactive group in a molecule will result in an unfavorable conformation for a given reaction.

3) The coordination may alter the oxidation or reduction potential of a ligand sufficiently to render a given process thermodynamically unfavorable. This may result from a number of causes which include changes in the electronic density patterns of the reactive sites or changes in the characteristic redox reactions of the ligand (i.e., the *number* of electrons which can be easily lost or gained).

4) Coordination may result in a change in the electrical charge on a reactive site of the ligand. An example may be seen in the greatly increased acidity of the hydrogen atoms in a system of the sort M-Donor-H. If coordination changes the ligand into a strong acid, the resultant ioniza-

tion of the proton will leave a negatively charged site on the ligand. The attack of another negatively charged species should be seriously hindered by such a process.

5) In at least some instances, the coordination process will involve an electron transfer process, in addition to sharing. In some of the complexes of nitric oxide (NO), considerable evidence supports the claim that one electron is transferred completely to the metal ion (reducing it to a lower oxidation state) and that the ligand is present as complexed NO^+ (*27*). Here, the actual ligand is a species quite different in its electronic structure from its parent compound.

An appreciation of these conditions can best be seen by an examination of a number of specific reactions, including several in which masking is not found, though it might have been anticipated.

Some of the reactions of coordinated donor atoms are quite unexpected. Thus, coordinated thiol will react with alkyl bromides to form sulfonium salts. Here, there are lone pairs on the donor atom in addition to the one involved in forming the coordinate bond. Their qualitative reactivity is hardly affected by coordination. Ammonia which has been coordinated to platinum(IV) will form *N*-chloro derivatives when treated with hypochlorite. This reaction involves an N-H bond rather than the lone pair. Coordinated PCl_3 will undergo hydrolysis to give coordinated $P(OH)_3$, a reaction which involves the P-Cl bonds rather than the lone pair.

The areas in which masking has been examined in more detail will now be considered separately.

Masking of Ligand Oxidations

The action of many common inorganic oxidants can be formulated as proceeding through intermediate complexes. While such mechanisms are open to reinterpretation, in many cases prior coordination of the ligand is definitely found to exert a retarding action on the course of the oxidation. Unfortunately, this same retarding action has been found in some reactions where the formation of an intermediate complex by the oxidant is extremely unlikely. The nature of the coordination center used in the masking reaction is also of some importance. When the resulting complex is inert to substitution, the masking may be complete; if this complex is labile the rate of reaction will usually be reduced, but not very much below the rate of dissociation of the labile complex.

When oxidants are examined, there are found to be two principal classes. In the first group one finds species such as periodate, which must usually form an ester with the substrate prior to effecting its oxidation. In the second group one finds oxidants such as ferricyanide, which extract an electron without forming any kind of a chemical bond with the substrate. One would not expect coordination of the substrate to affect these two types of processes in the same manner. If, as often happens, the sites most susceptible to attack by oxidants are also the best donor sites toward coordination centers, these sites after coordination will be unavailable for the formation of an intermediate complex with oxidants such as periodate. This kind of masking is found in the tellurate esters of glycols.

One example of such a masking of an oxidation reaction is oxidation of EDTA by permanganate. The rate of this reaction is considerably reduced when the EDTA is complexed to either chromium(III) or bismuth(III) (*4*). Derivatives of EDTA, such as hydroxyethylethylenediaminetriacetic acid (HETA), are similarly masked against oxidation by acid vanadate(V) when coordinated to chromium(III) or cobalt(III) (*28*). In this latter case the more stable cobalt(III) complex was found to undergo oxidation at a slower rate than the chromium(III) complex. It was also found that the rates of oxidation of $[Co(HETA)Br]^{+}$ and $[Co(HETA)(OH_2)]^{+2}$ were similar. In systems containing labile complexes, the pH is very important in governing both the relative amounts of ligand which are complexed and the effectiveness of the oxidant. Because most common oxidants are used in strongly acidic media, experimental conditions must be adjusted very carefully to insure that coordination can occur, if masking is desired. In cases where an acidic medium is used, inert complexes, added as such, are most suitable for examining the occurrence of masking.

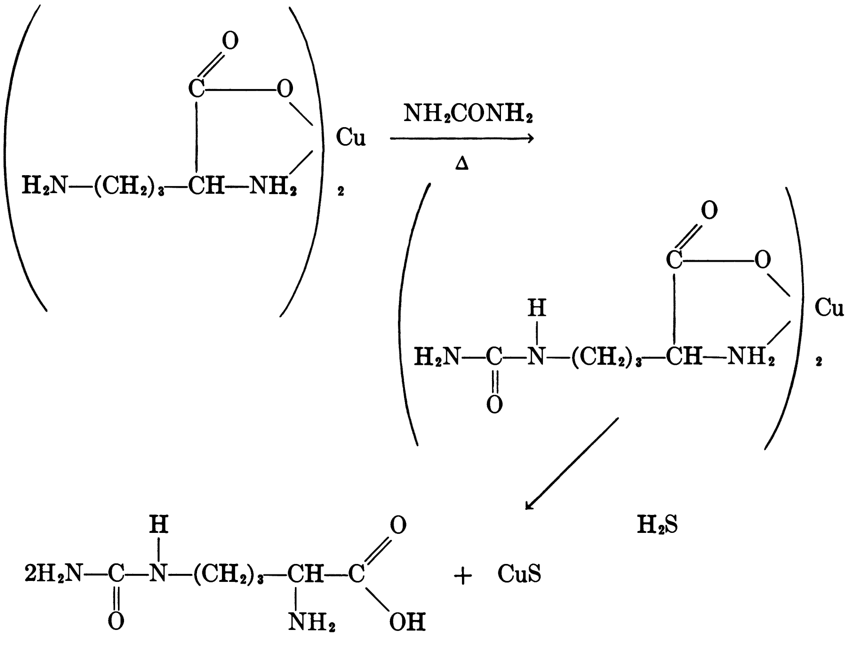
Masking can also be effected by coordination in situations where the oxidant is not likely to form stable, intermediate complexes with the ligand. Ferricyanide, $Fe(CN)_6^{-3}$, is such an oxidant, and it has been found that complexing of reducing sugars with borate masks them toward oxidation by basic solutions of ferricyanide (*28*, *50*). In this respect, ferricyanide is similar to a number of oxidants for reducing sugars, most reactions of which can be masked to a greater or less extent by complexing the reducing sugar with borate. Another example of masking toward an oxidant which does not form a stable intermediate complex is the masking of glycine toward nitrite or nitrous acid when the glycine is complexed to chromium(III) (*21*).

Our knowledge of the masking of ligand oxidations is limited in part by the limitations of our knowledge of the mechanisms of the normal oxidations. Until these are known in more detail, masking of oxidizing reactions may be treated only on the basis of the empirical results, and predictions of masking effectiveness must be based on analogy with known cases.

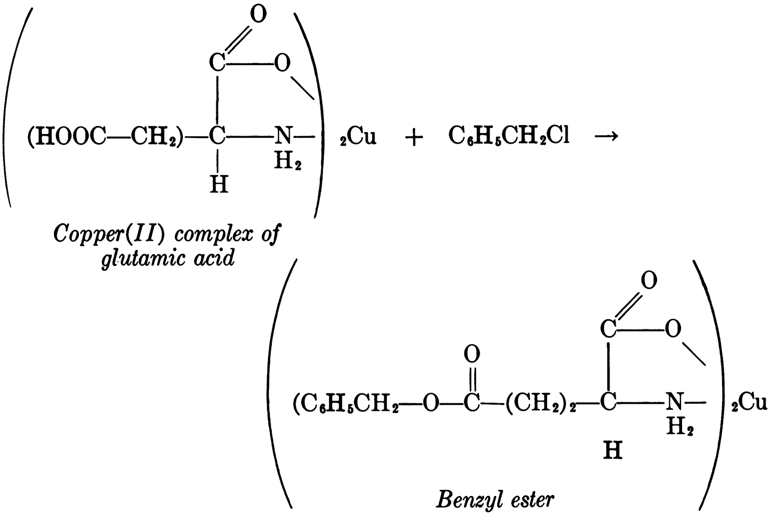
The masking of aromatic phenols against the oxidative side reactions possible in a medium used to effect diazo coupling can be achieved via coordination. For example, the reaction of 4-diazodimethylaniline with chromotropic acid (1,8 dihydroxynaphthalene-3,6-disulfonic acid) results in a 58% yield of the dye in which coupling has occurred at the 4-position of chromotropic acid. The dye is contaminated with by-products which arise from the concurrent oxidation of the ligand and, as a result, does not have a color of satisfactory purity. By using the calcium complex of chromotropic acid, the yield may be increased to 90%, producing a dye of a purer color. Here, coordination apparently suppresses oxidative side reactions (*49*).

Non-oxidative Amino Acid Reactions

The formation of copper(II) complexes with alpha amino acids can be used to mask either the amino group or the carboxyl group against the action of various reagents (*5*, *54*). This procedure is especially useful in carrying out reactions of alpha amino acids which contain additional functional groups of the sort tied up in the chelate ring. The conversion of citrulline to ornithine via the copper(II) complex is a good example (*45*, *46*, *47*):



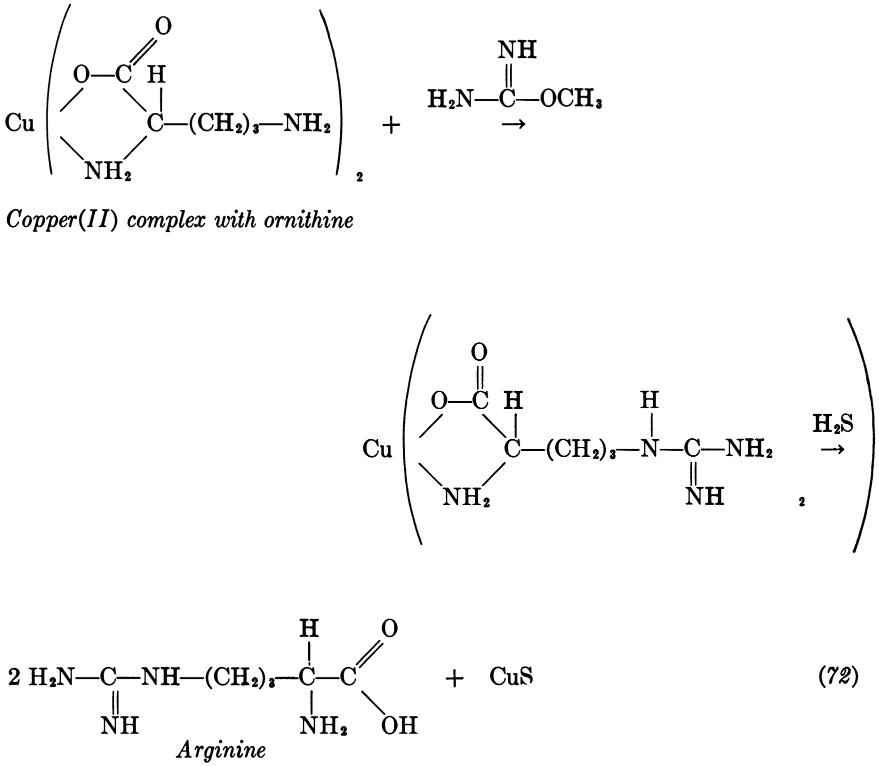
This screening of the alpha amino group and the carboxyl group is characteristic of the copper(II) complexes of such compounds. A number of uses of this which have appeared in the literature is listed below.



Copper(II) complex of glutamic acid

Benzyl ester

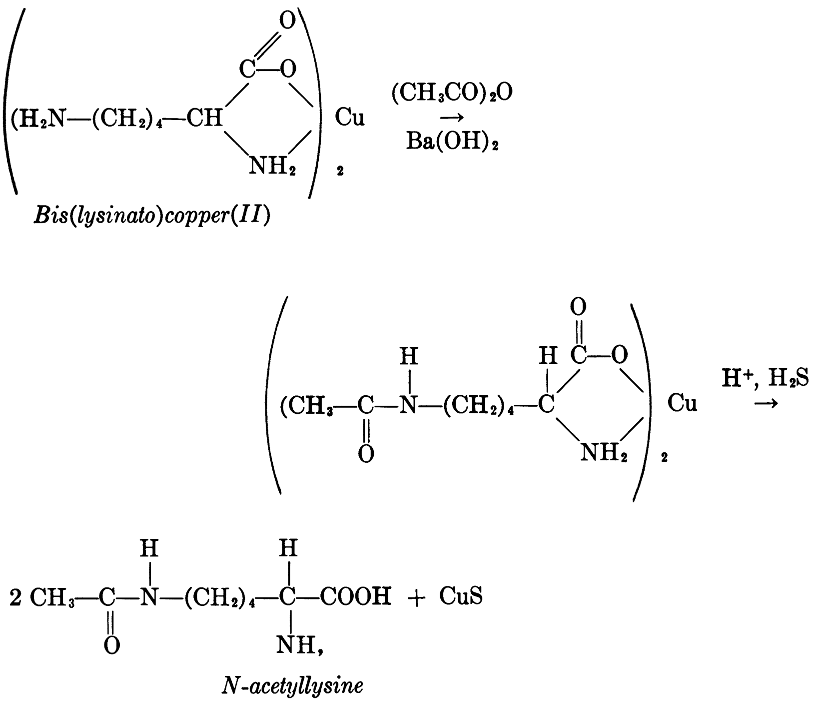
(24)



Copper(II) complex with ornithine

Arginine

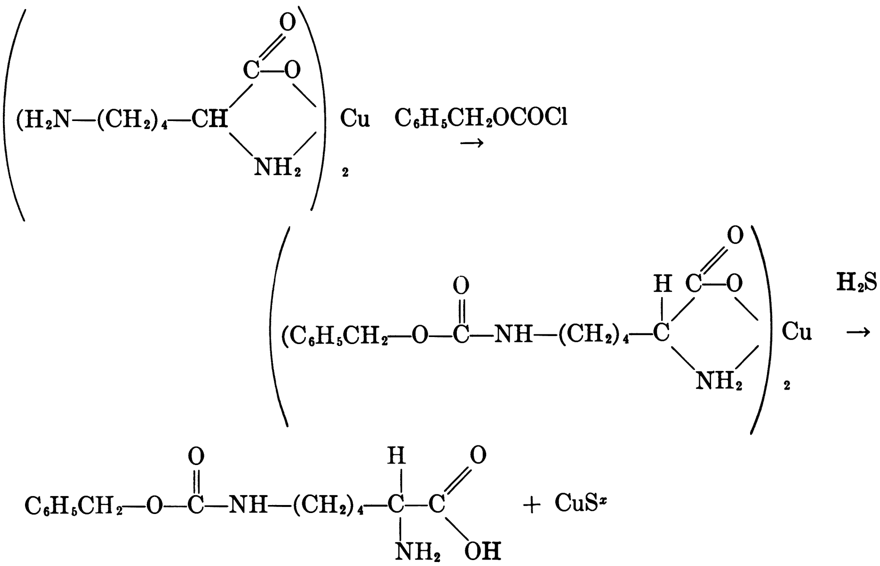
(72)



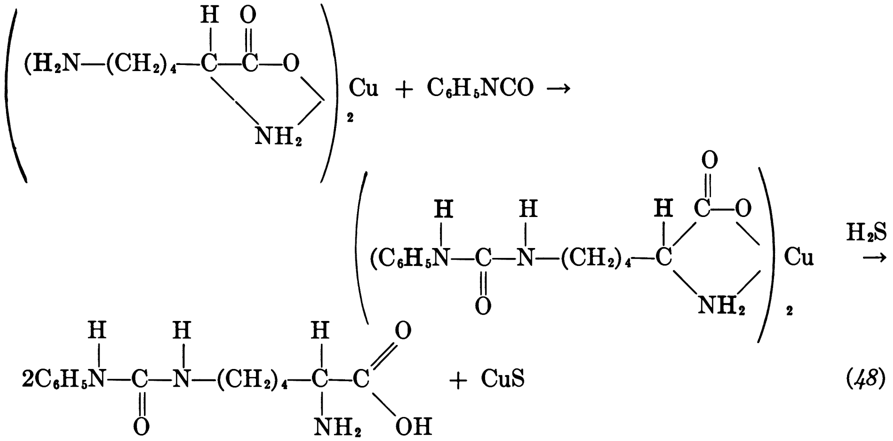
Bis(lysinato)copper(II)

N-acetyllysine

(56)

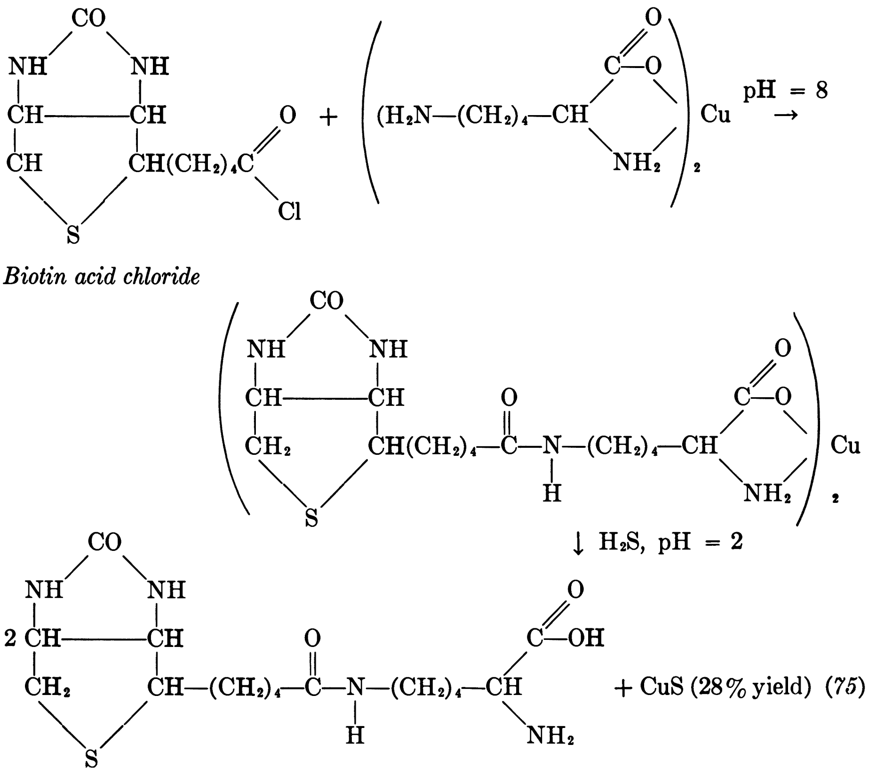


The ornithine complex with copper(II) undergoes this same reaction (*68*).



(*48*)

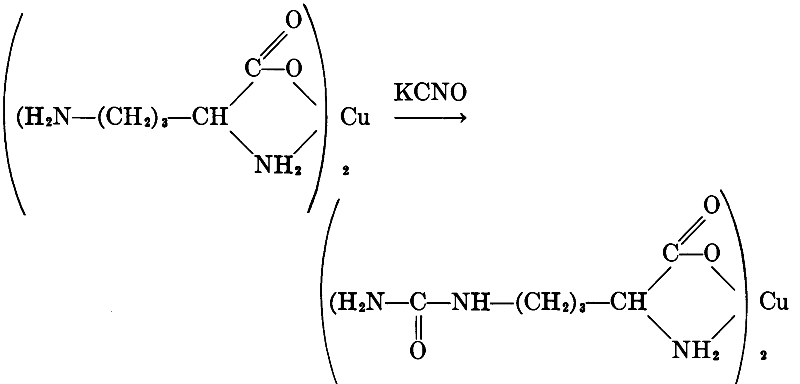
This report also describes reactions with acid chlorides (the Schotten-Baumann procedure), nitrourea, *o*-methylisouronium salts, and *S*-alkylisothiouronium salts. A more impressive example of the same general type is the following:

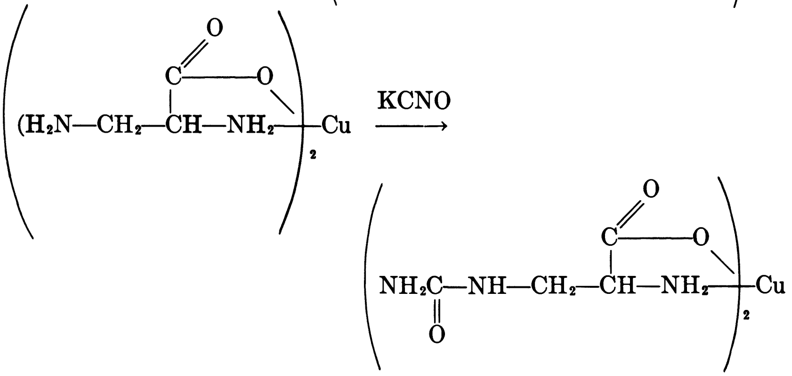


Biotin acid chloride

+ CuS (28% yield) (*75*)

The reaction of a terminal amino group with potassium cyanate also proceeds readily:


(66)


(33)

Here the 3-(or β-) amino group can coordinate to the copper, yet the reaction apparently goes via the complex in which this amino group is free. Two kinds of copper(II) complexes are formed by α-, β-amino acids such as this one (*51*). In a mildly acidic solution, the β-amino group will be protonated and hence accessible for reaction (*1*). In a more basic solution it will be coordinated to the copper(II).

The masking of the reactions of the amino groups of α-amino acids by forming the copper(II) complexes is found to be effective for a large number of other reagents, including fluorodinitrobenzene (*59*) and acetylation reagents (*34*, *56*).

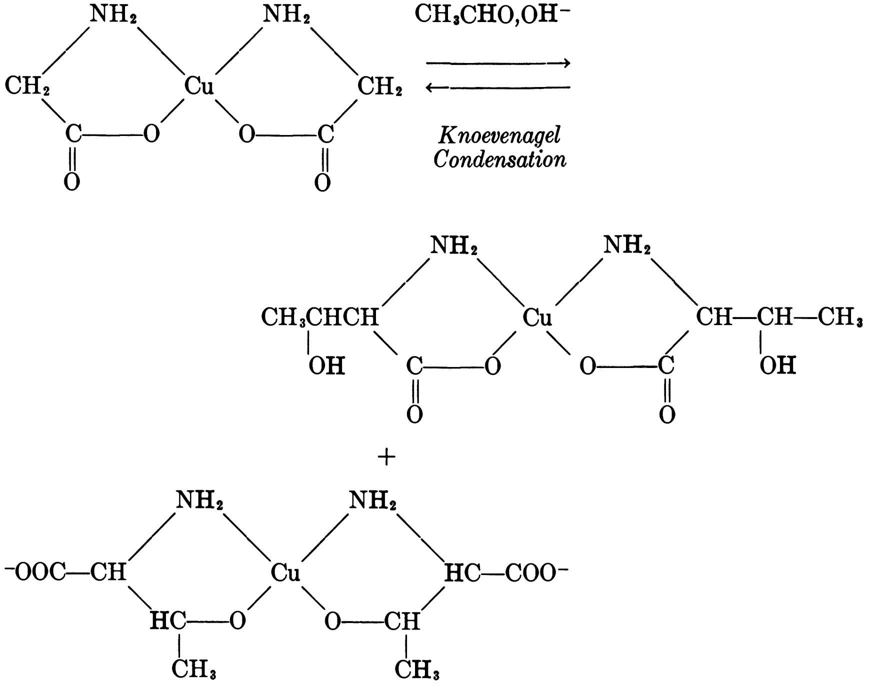
The reasons for the effectiveness of the masking in these cases appear to be:

1) The considerable stability of the complex with respect to both dissociation and exchange reactions of the ligand; and

2) The presence of a much more reactive, uncoordinated group on the ligand which consumes the added reagent before any appreciable amount can react with the momentarily dissociated alpha amino groups.

A difference in the rate constants of only about 30-fold for the free and the coordinated groups is sufficient to utilize successfully the masking action in these cases. There are presently no comparative data on the relative rates of the reaction of the two types of amino groups in complexes such as bis(ornithine)copper(II).

Another method of using masking is also dependent upon the concurrent polarization of the ligand. An example is seen in the reaction of copper glycinate with acetaldehyde in a basic solution to give copper threoninate by a Knoevenagel condensation (*57*, *62*). The threonine can subsequently be recovered by treating it with hydrogen sulfide:



Copper threoninate + Copper allothreoninate
(64% yield)

The yields obtained with tris(glycinato)cobalt(III) in this type of reaction were considerably lower (*25*). Copper glycinate and $(CH_3)_2CHCHO$, condensed under similar conditions, give β-hydroxyleucine in good yields (*26*). Serine and phenylserine can be prepared by the analogous reactions of copper glycinate with formaldehyde and benzaldehyde, respectively (*60*). Aldehydes add on to the copper complex of threonine to give 6-coordinate complexes, the low solubility of which allows such a method to be used to separate threonine from allothreonine (*69*).

The reaction of glycine in the optically active complex *levo*-glycinato-bis(ethylenediamine)cobalt(III) iodide with acetaldehyde in the presence of sodium carbonate resulted in a partially asymmetric synthesis of threonine (*55*). The asymmetric yield was estimated at 8% in this case. Glycinato-bis(*levo*-propylenediamine)cobalt(III) chloride, subject to the same reaction conditions, underwent this reaction with an asymmetric yield of only 1%. The different yields of the asymmetric product were tentatively ascribed to differences in the stabilities of the complex ions undergoing the reactions. Dwyer (*16*) ascribes the principal effect of the metal in these reactions to be one of providing masking by coordination, rather than activation by electronic polarization. Because direct comparison with the free ligand is difficult, this question has not yet received a direct answer in these systems. It seems unlikely that a direct comparison can be made because of the rapidity of reactions of the type $RCHO + H_2NQ \rightarrow RCH = NQ + H_2O$.

The masking of the alpha amino group in the copper complex of lysine is not always complete. Treatment of the aqueous solution of the copper complex of L- or DL-lysine with ethylene oxide, until the amino content fell to one-half of its original value, resulted in the formation of both $(HOCH_2CH_2\text{-})_2N\text{-}(CH_2)_4CH(NH_2)COOH$ and $H_2N(CH_2)_4CH(COOH)N\text{-}(C_2H_4OH)_2$ in the relative ratio of 3:1. This indicates that the complex was either partially dissociated (most likely) or that the ratio of the rates of attack of the two amino groups stands as 3:1 (*20*). This is one of the few reactions where the masking of the alpha amino group is incomplete in the complexes, and the mixture of products obtained here is atypical for such ligand reactions.

Esterifications of Hydroxy Groups in Ligands

A number of ligands bears hydroxy groups which are ostensibly capable of reaction with various esterification reagents. The studies of the reactions of amino alcohols which have been directed toward the detection of reactions of free donor groups have produced rather discordant results which make any generalization impossible.

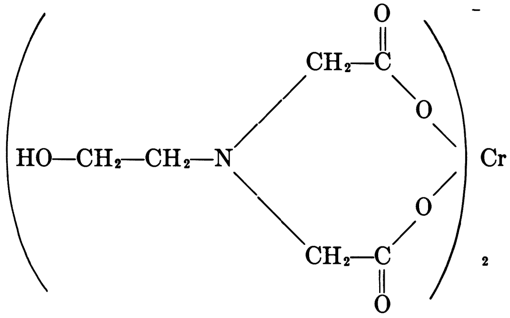
In the first study of this sort (*29*), Keller and Edwards sought to prepare tris(*N*-hydroxyethylethylenediamine)cobalt(III) and to examine the reactivity of the uncoordinated hydroxy group. They reported such groups to be completely inert in the material they prepared. A subsequent study (*15*) reported that the oxidation of a basic mixture of a cobalt(II) salt and *N*-hydroxyethylethylenediamine produced primarily tris(ethylenediamine)cobalt(III). In this latter study, a method for preparing complexes of *N*-hydroxyethylethylenediamine (hereafter abbreviated as etolen) was developed based upon reactions of the type:

$$[Co(NH_3)_6]Cl_3 + 3\ \text{etolen} \xrightarrow[\Delta]{H_2O} [Co(\text{etolen})_3]^{+3} + 6NH_3 + 3Cl^-$$

Complexes with the ligand *N*-hydroxyethyldiethylenetriamine (hereafter abbreviated as dietolen) were prepared in a similar manner:

$$[Co(NH_3)_6]Cl_3 + 2\ \text{dietolen} \xrightarrow[\Delta]{H_2O} [Co(\text{dietolen})_2]^{+3} + 6NH_3 + 3Cl^-$$

In both cases the cationic complexes so prepared had uncoordinated hydroxyl groups, and in both cases all attempts to combine these with nitric acid, thionyl chloride, benzoyl chloride, or acetyl chloride failed. Because these ions have large positive charges which might interfere with the reaction, it was also decided to prepare analogous complexes with a lower net charge on the cation. Accordingly, $[Co(\text{dietolen})(SCN)_3]$ and $[Co(\text{dietolen})(NO_3)_3]$ were prepared and investigated in a similar fashion. In both cases, the complexes decomposed in the presence of the reagents, so no conclusions could be drawn. In another study involving chromium(III) complexes (*36*), the complex ion bis(2-hydroxyethyliminodiacetato)chromium(III):

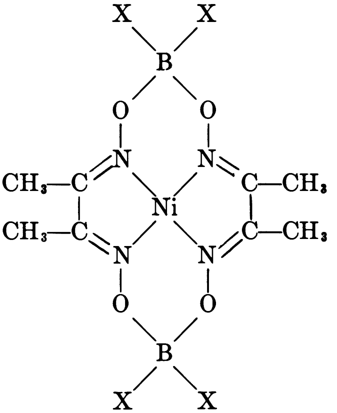


$= [Cr(HOA)_2]^-$

was subjected to several acetylating processes, most of which failed to acetylate the free hydroxyl groups. Refluxing in a mixture of acetic anhydride and glacial acetic acid resulted in considerable decomposition but did allow the isolation and characterization of $(H_3O)[Cr(AcOA)_2]$, the doubly acetylated complex which was obtained in about 25% yield. Because this ion has a negative charge, the arguments used to explain the lack of reactivity in the cobalt complexes are inadequate—at least here. Krause and Goldby discuss possible reasons for the sluggishness of these reactions. None of the proposed explanations is considered acceptable by these authors, and this phenomenon presently has no satisfactory explanation.

The masking of the hydroxyl reactions in complexes of vicinal dioximes (*71*) appears to be due to the formation of a very stable hydrogen bond. Tschugaeff reported that these hydroxy groups do not react with phenyl isocyanate. Barker (*2*) noted that 1,2,bis(butanediondioximato-

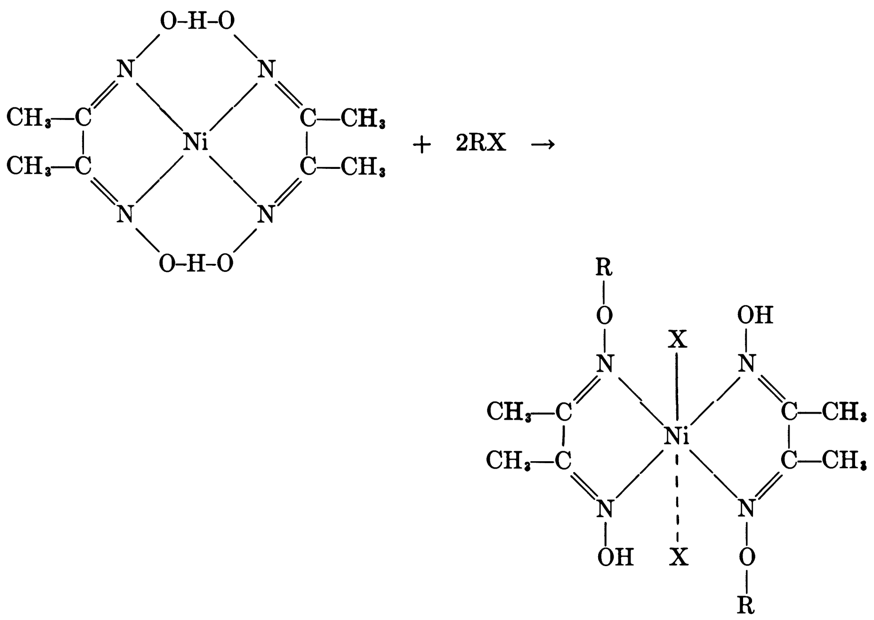
N,N′)nickel(II) did not undergo the acetylation reaction characteristic of the parent dioxime when it was treated with acetic anhydride. The hydroxyl group of this complex was also found not to undergo reaction with a solution of methyl magnesium iodide in amyl ether (*8*). The infrared spectra of these complexes have been interpreted in terms of an exceptionally short O—H—O, hydrogen-bonded system (*73*). The masking found for these reactions is not a general one, however, and is not found for all reactions of vicinal dioxime complexes. Thus, nickel dimethylglyoxime and some related complexes have been found to react with boron compounds of the type BX_3, where X = F, CH_3, nC_3H_7-, nC_4H_9-, and isobutyl (*63*). Schrauzer formulated these products as:



The compound $Ni(DMG)_2B_2F_4$ also formed adducts with bases such as pyridine, isonitriles, and triphenylphosphine. The bis-pyridine adduct is presumably octahedral and yet is diamagnetic—a rather unusual situation.

The reaction of nickel dimethylglyoxime with methyl iodide and methyl sulfate was first examined by Barker (*2*). More recent studies (*10*) indicate that the reaction pattern in these cases is essentially as shown on the following page. A related study of the reaction of the nickel(II), palladium(II), and platinum(II) complexes of dimethylglyoxime with acetyl chloride showed that the products of such a reaction were $M^{II}(HDMG)Cl_2$ and the free acetylated ligand (*35*). With 2-pyridinaldoxime, the palladium(II) complex can be monoacylated, while the platinum(II) complex gives a diacylated complex, $[Pt(POX\text{-}COCH_3)_2]Cl_2$, where POX is the monovalent anion derived from 2-pyridinaldoxime. The studies of Busch and his co-workers have considerably clarified the conflicting reports on the reactions of coordinated oximes (*64*, *65*, *70*).

There are many additional instances where coordination masks a ligand toward the action of normally effective reagents. In most of these cases the interference is based primarily upon steric restrictions intro-



duced by coordination. One such example is the masking of coordinated olefins toward the action of bromine, which is well-established in the case of $[PtCl_2(C_2H_4)]_2$ (*18*); this compound undergoes bromination of the double bond in the ethylene only at elevated temperatures which are capable of dissociating the olefin. The immediate product of the reaction with bromine is $PtCl_2Br_2(C_2H_4)_2$—possibly as the dimer. A similar initial product is found in the chlorination of $[PtCl_2(C_2H_4)]_2$, which gives $PtCl_4(C_2H_4)$ (*12*), and in the bromination of $[PtCl_2(\text{styrene})]_2$, which gives $PtCl_2Br_2(\text{styrene})$ (*30*). Other examples of a rather different sort, which are suppressed by coordination, include the basic hydrolysis of the cyanide ion, the rearrangement of cyanate to urea in the presence of ammonium ion, and the corresponding rearrangements of thiocyanate. All these reactions involve addition to a ligand double bond which, in turn, involves the donor atom in a very direct fashion.

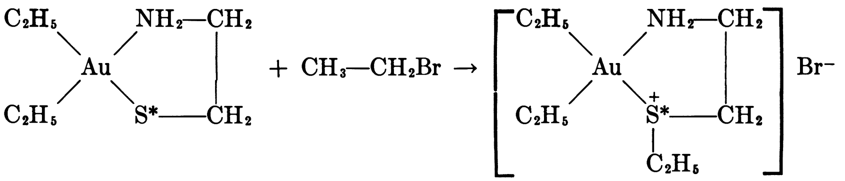
A masking action more directly related to the charge of the central cation is found in the changes in rates of aromatic halogenation reactions upon coordination. For both aniline and phenol and their derivatives, the usual explanations of reactivity toward electrophiles are closely tied up with the availability of the lone pair on the nitrogen or oxygen. Because these are also the lone pairs involved in forming coordinate bonds, one would anticipate that coordination should have some quantitative effect on the halogenation reactions of aromatic ligands as well as their other reactions with electrophiles. Such effects are almost exclusively changes in the rates of such reactions. Where quantitative data are available, it is found that the rates of such reactions *are less* than those of the literal ligand (which is R—NH_2 in the case of anilines and RO^- for phenols) (*6, 7, 13, 52*).

Quaternization Reactions

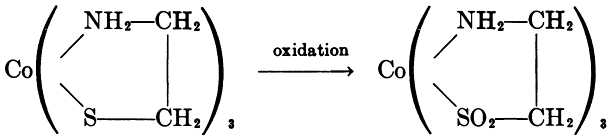
The ability of a donor atom to undergo a quaternization reaction with an alkyl halide or similar reagent is very strongly dependent upon the nature of the donor species and its attached groups.

The masking of coordinated arsine toward the quaternization reaction with methyl iodide has been used to demonstrate the coordination of all of the arsenic atoms of the ligand tris(orthodiphenylarsinophenyl)arsine (QAS) in its complex with platinum(II) (*9, 53*). This reaction is found with uncoordinated arsines.

The reactions of coordinated thiols have been examined in more detail. In one of the first reports on this subject (*17*), the alkylation of (2-aminoethylthio)diethylgold to give a complex sulfonium ion was found to occur quite readily:



The same complex reacts with chloramine T to give a complex in which a nitrogen has been attached to the coordinated sulfur. These authors concluded that the sulfur atom of the original complex "displays the reactivity typical of an organic sulfide." They also reported that the sulfur atom in the corresponding complex of cobalt(III) could be oxidized to the sulfone without disrupting the complex:



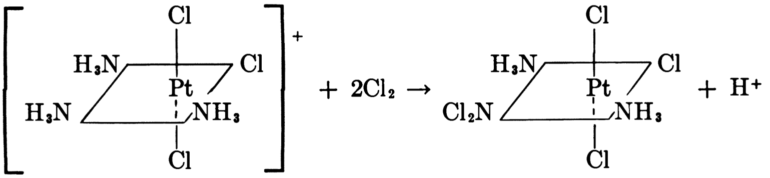
A kinetic study of the alkylation of coordinated thiol in NH_2CH_2-CH_2SH and related ligands revealed that the reaction proceeded without the breaking of the metal-sulfur bond (*11*). The nucleophilicity of the coordinated sulfur was found to depend on the central metal involved but was greater than that of the sulfur in a thiol. It was found that sulfur in such ligands did not react with alkyl halides when it occupied a bridging position between two metal atoms in a polynuclear complex.

For elements of Groups V and VI in low oxidation states (e.g., thiols, thioethers, amines, phosphines, arsines, and the like), the patterns of reaction masking are obviously dependent on the mechanism of the reactions. Where the reaction involves an unshared electron pair, such as is the case in quaternization, these will be masked when no pair of electrons is free and will often be masked for sulfur when only one pair of electrons is free. This is obviously true with amines, arsines, and phosphines which are coordinated to a single metal atom. With thiols, when the sulfur atoms act as bridging groups between two metal ions, or with thioethers present in chelate rings, such reactions do not seem to proceed even when there is a single electron pair ostensibly uninvolved in bonding. The two free electron pairs of the coordinated thiol group seem to be not equivalent. Perhaps some of this masking is due to steric hindrance. As a rule of thumb, a coordinated alkyl derivative of an element (Z), R_nZ will not undergo a quaternization reaction, though $R_{n-1}ZH$ which coordinates as $R_{n-1}Z^-$ will. For reactions which involve expansion of the octet of the donor atom, such as occurs in the halogenation of $C_6H_5PR_2$, coordination again provides extensive and effective masking.

Reactions of Coordinated Ammonia

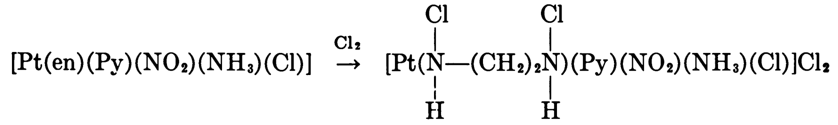
The change in the chemical properties of ammonia which results from coordination is due to the drawing of electronic density from the molecule toward the acceptor center. The most immediate consequence of this is an increase in the acid strength of the hydrogen atoms of the ammonia (*3*). This is most pronounced for complexes with platinum(IV), osmium(IV), gold(III), and other ions of heavy platinum metals.

The chemical exploitation of this change is seen in a very impressive manner in the work of Kukushkin on the reactions of coordinated ammonia with halogens (*37–44*). In the initial study it was established that the chlorination of $[Pt(NH_3)_3Cl_3]Cl$ in water proceeded as follows:



The compound containing coordinated chloramine is inclined to undergo a violent decomposition, so it should be prepared only in small quantities. A number of other reactions of this same type was demonstrated, including

$$[Pt(NH_3)_5Cl]Cl_3 \xrightarrow[H_2O]{Cl_2} [Pt(NH_3)_4(NCl_2)Cl]Cl_2$$

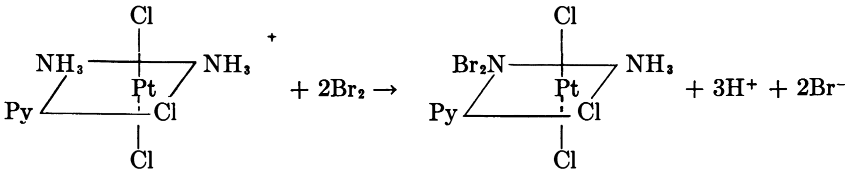


$$[Pt(en)(Py)(NO_2)(NH_3)(Cl)] \xrightarrow{Cl_2} [Pt(\underset{H}{\overset{Cl}{N}}-(CH_2)_2\underset{H}{\overset{Cl}{N}})(Py)(NO_2)(NH_3)(Cl)]Cl_2$$

and

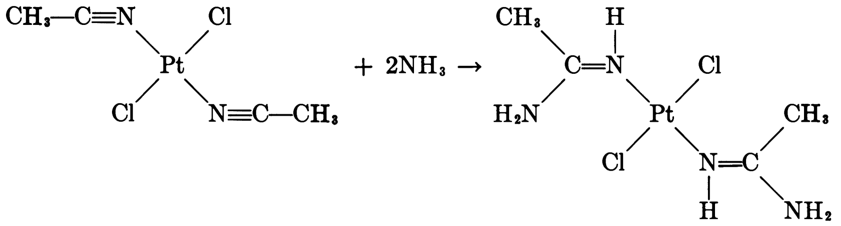
$$[Pt(NH_3)_5(OH)]Cl_3 \xrightarrow{Cl_2} [Pt(NH_3)_3(NCl_2)_2Cl]Cl$$

Here, there is no evidence that masking interferes in any way with these reactions. When the complexes of palladium(II) were examined for a similar reactivity, no complexes containing coordinated chloramines could be isolated (*43*, *44*). The reaction of ammines of platinum(IV) with bromine can be used to introduce bromoamine in the coordination sphere, but the products are somewhat less stable than those obtained with chlorine. The general nature of the processes is similar. One example of a bromination reaction established by Kukushkin is:

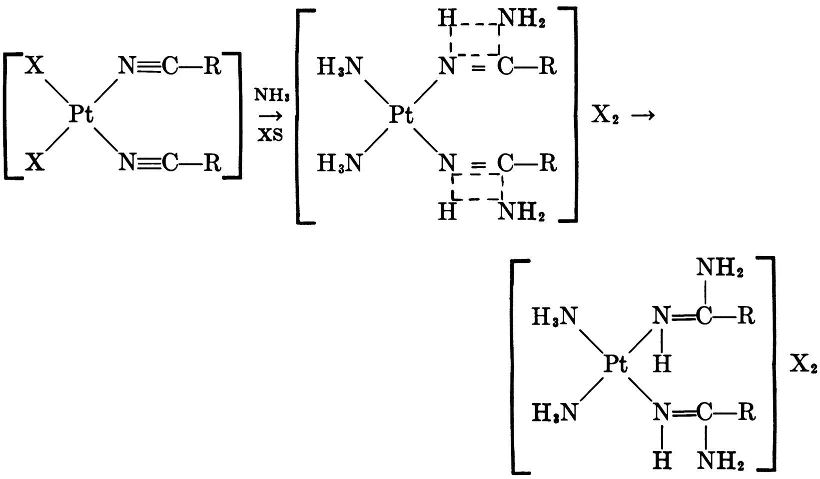


Kukushkin's work on reactions in the inner sphere of tetravalent platinum was preceded by earlier studies of I. I. Chernyaev (*14*) who showed that nitrite or hydroxylamine coordinated to platinum(II) could be reduced to coordinated ammonia. Grinberg and Gildengershel (*22*) reported that ethylamine (EtNH$_2$) in [Pt(NH$_2$Et)$_4$Cl$_2$]Cl$_2$ could be hydrolyzed to ethyl alcohol, leaving the nitrogen coordinated to the platinum. The failure of coordination to mask a typical ligand reaction is by no means uncommon.

Another example is found in the various platinum(II) ammines which "contain" acetonitrile. One such is formed by reaction of [Pt(CH$_3$CN)$_2$Cl$_2$] with ammonia. This gives a product with a formal composition corresponding to [Pt(CH$_3$CN)$_2$(Cl)$_2$(NH$_3$)$_2$]. For many years this was considered to be an unusual complex in which platinum(II) was 6-coordinated. There are very few instances (if any) in which platinum(II) exhibits a coordination number other than 4. It has been shown by x-ray studies (*67*) that the product of this reaction is [Pt(acetamidine)$_2$Cl$_2$] and that the reaction may be written as shown at the top of the next page. Here, the coordination act accentuates the electron drift from the nitrile carbon atom and makes it more susceptible to attack by nucleophiles—in this case, ammonia. This kind of process had been essentially substantiated by chemical studies carried out previously, and the formation of



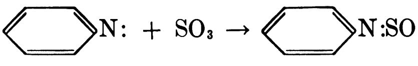
amidines in such reactions was suggested as early as 1951. A mechanism of this reaction which seems consistent with the known facts (*31*, *32*) is that of Kharitonov, Chia-chien, and Babaeva:



The displacement of the X groups from the platinum(II) does not always occur. This kind of a reaction, between a coordinated nitrile and an amine to give an amidine, is one of considerable generality for complexes of the type $[PtX_2(N{\equiv}C\text{-}R)_2]$.

The Moderation of Lewis Acid Strengths

Related to, but quite distinct in purpose from, the usual notions of masking is the use of coordination to moderate the action of a very vigorous Lewis acid. An example of this may be seen in the use of the pyridine and dioxane complexes of sulfur trioxide in place of the parent compound (*19*). Because the complexes used here must release sulfur trioxide to other reactants, it is imperative that no reaction beyond coordination occurs. Thus, pyridine reacts only to give the adduct below.



The use of tertiary amines, amides, ethers, and thioethers also gives this kind of adduct. Because the stability of the complex varies directly with the basic strength of the ligand, it is found that the reactivity (which is determined by the ease with which sulfur trioxide is released from the complex) is inversely related to the stability of the complex and hence the basic strength of the ligand. It is found that the typical reactions of sulfur trioxide (e.g., sulfonation, sulfation, and sulfamation) are also reactions of the sulfur trioxide adducts, but coordination moderates the reactivity of the sulfur trioxide and usually makes it easier to control the reaction.

Miscellaneous Aspects

There are a number of other reaction systems, the results of which bear on the topic of masking. These are either more specialized situations or ones where generalizations at the present time seem premature.

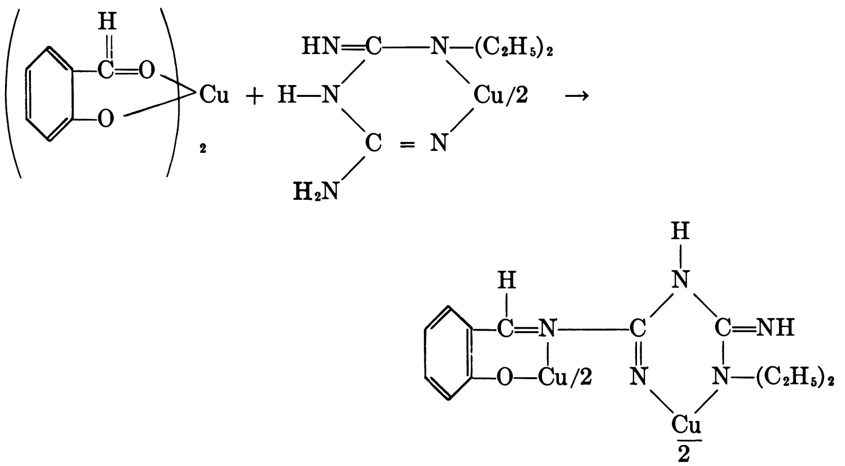
Coordination of arylalkyl ketones to aluminum chloride masks the normal reactions of the aliphatic alpha hydrogens toward bromine and chlorine and allows the halogenation reaction to occur on the aromatic nucleus, rather than on the aliphatic hydrogens, as is usually observed (*58*). The same procedure is also effective in aromatic halogenation of the corresponding aldehydes. Acetophenones and propiophenones normally give phenacyl or alpha halopropiophenones in the absence of such protection. As carried out, the reaction system contains a considerable excess of aluminum chloride, which also aids in the generation of a more effective halogenating agent.

Grinberg and Kats (*23*) studied the thermal decarboxylation of ortho-, meta-, and para-aminobenzoic acids and their complexes with platinum(II). The behavior found was similar for ligand and complex, except for the case of *p*-aminobenzoic acid. Here, the free ligand underwent the decarboxylation, but the complex did not.

A reaction similar, in some respects, to those of alpha-epsilon amino acids is shown at the top of the following page. This illustrates clearly that coordination does not mask the aldehyde oxygen toward amines (*60*, *61*).

Kinetic Behavior

A problem common to all studies of retarding ligand reactions is that of differentiation between the slow reaction of the ligand in the complex and the more rapid reaction of the ligand which is released from the com-



plex. Thus, the existence of the retardation can be determined by relatively simple studies on the reaction rates of systems with the same concentration of ligand and an increasing concentration of metal ion. The basis of the retardation can only be established from a much more thorough examination of the rate behavior in the system. Consider the reaction of a ligand L with a reagent R to give products P (which may or may not be complexed):

$$L + R \xrightarrow{k_2} P$$

In the presence of metal ions, one has the equilibrium

$$M + L \rightleftarrows ML;\ K_f = [ML]/[M][L]$$

and the possible reaction

$$ML + R \xrightarrow{k_{ML}} MP.$$

A situation of this sort, in which only one complex, the lowest, needs to be considered, can be approximated with large metal ion-to-ligand ratios.

If ML does not react at all, the variation of the observed rate constant, based on the total concentration of L, will follow a characteristic pattern as M is varied. Because

$$\text{Rate} = k_2[R][L],$$

if [R] is held constant and the rate measured for solutions in which [M] has progressively larger values, the experimentally observed rates will be given by

$$\text{Rate} = k_e[R][L]_t = k_2[R][L].$$

When only a single complex, ML, needs to be considered

$$[\mathrm{L}]_t = [\mathrm{L}] + [\mathrm{ML}] \text{ or}$$

$$[\mathrm{L}] = [\mathrm{L}]_t \left(\frac{1}{1 + K_f[\mathrm{M}]}\right)$$

and

$$\frac{k_e}{k_2} = \left(\frac{1}{1 + K_f[\mathrm{M}]}\right)$$

If k_e is plotted against $[\mathrm{M}]_t$, one will observe a monotonic decrease as the amount of metal ion present increases. This is for systems in which [ML] does not react at all. If it does react, but at a slower rate, then

$$k_e[\mathrm{R}][\mathrm{L}]_t = k_2[\mathrm{R}][\mathrm{L}] + k_{\mathrm{ML}}[\mathrm{R}][\mathrm{ML}].$$

In this case $k_e \rightarrow k_{\mathrm{ML}}$ as $[\mathrm{M}]_t$ increases, and an essentially constant k_e will be found as $[\mathrm{M}]_t$ increases beyond a certain range. These cases are shown in Figure 1.

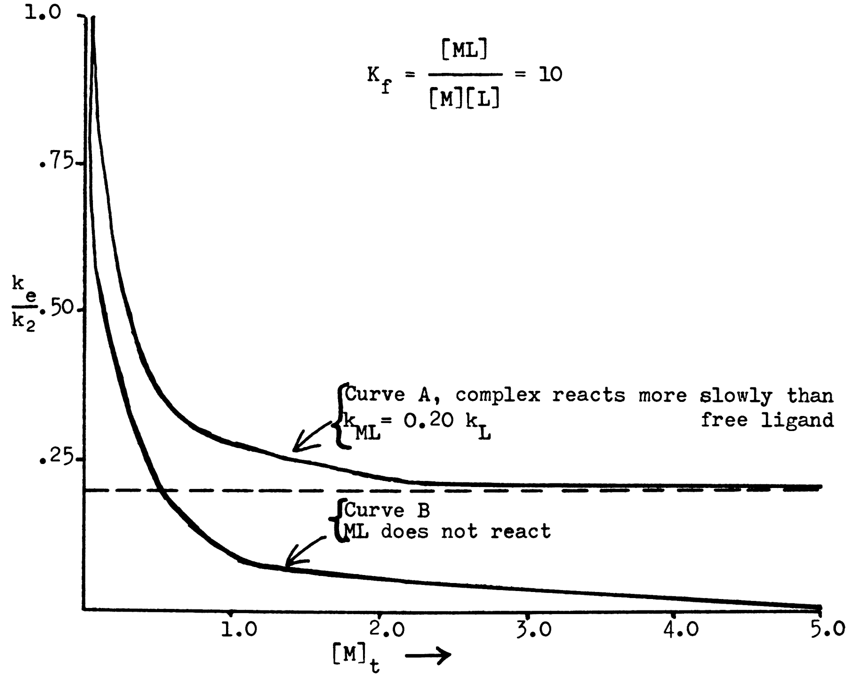


Figure 1. Variation of observed rate constants

Curves which are of the same form as curve B have been obtained for the diazo-coupling (*52*) and iodination (*6, 7, 13*) of 8-hydroxyquinoline-5-sulfonic acid and its metal complexes and for the oxidation of glucose and its boric acid complex with ferricyanide (*50*).

Acknowledgment

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18

Some Reactions of Coordinated Ligands

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Although coordination of a ligand about a metal ion may either suppress or enhance reactivity, the present discussion is limited to the latter. Evidence is cited for enhancement of reactivity resulting solely from coordination, including cases where the evidence is indirect and involves species that exist only in solution. The principal emphasis is placed upon species that can be isolated as pure compounds, fully characterized, and which participate in reactions not exhibited by the uncoordinated ligand. Most of these species result from deprotonation of ethylenediamine and a variety of other ligands by means of amide ion in liquid ammonia and other bases in other solvents. In addition to a review of the pertinent background literature, numerous unpublished results of current studies are included.

Until recently, reports of the effect of central metal ions in coordination compounds on the reactivity of ligands have been scattered throughout the chemical literature. One of the first such reports was the observation that oxalate ion coordinated with cobalt(III) did not undergo many of the typical reactions of uncoordinated oxalate with oxidizing agents (*30, 39*). Later, Werner (*13, 67–69*) employed ligand reactivity to demonstrate that the thiocyanate ion in the thiocyanatopentaaminecobalt(III) ion is bonded through nitrogen. Hydrolytic oxidation of this complex cation gave the hexamminecobalt(III) cation:

$$[Co(NH_3)_5(NCS)]^{2+} + H_2O \rightarrow [Co(NH_3)_6]^{3+} + \text{oxidation products}$$

Similarly, Chernyaev (*16*) reduced the nitro group in the nitroethylenediamineammineplatinum(II) cation, $[Pt(en)(NH_3)(NO_2)]^+$, with zinc and hydrochloric acid to the diammine cation, $[Pt(en)(NH_3)_2]^{2+}$, thus demonstrating that the nitro group was bonded to platinum through nitrogen.

Intensive efforts by various workers to study coordination compounds from the standpoint of ligand reactivity seem to have matured only during the last three decades. Different authors have divided ligand reactions into various classifications as to type (*8*, *39*, *42*). For the purposes of the present discussion, ligand reactions are divided into the following types:

a) Those reactions occurring at the coordinated atom.

b) Those reactions occurring at an atom adjacent to the coordinated atom.

c) Those reactions occurring in the chelate ring not considered in *a* or *b* above.

d) Reactions occurring outside the chelate ring.

Abbreviations used in this paper are: en, ethylenediamine; (en-*x*H), an en ligand from which *x* protons have been removed; pn, propylenediamine; men, *N*-methylethylenediamine; sdmen, *N*,*N*′-dimethylethylenediamine; tetmen, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine; dien, diethylenetriamine; (dien-*x*H), a dien ligand from which *x* protons have been removed; DMGO, dimethylglyoxime; and Az, ethylenimine.

Reactions of Type a

A central metal ion usually has a pronounced effect on the reactivity of a coordinated ligand at the coordinated atom or atoms. An important reaction of this type which has synthetic value is the reaction of alkenes and alkynes with hydrogen and carbon monoxide in the presence of a metal carbonyl. This is actually the catalytic process of hydroformylation and, although catalysis is beyond the scope of this work, it is nevertheless of interest from the standpoint of ligand reactivity. The reaction of ethylene with hydrogen and carbon monoxide in the presence of $HCo(CO)_4$ as a catalyst is proposed to proceed (at least formally) through the steps shown (*11*, *13*):

$$H_2C{=}CH_2 + HCo(CO)_4 \rightarrow (CO)_3HCo(C_2H_4) + CO$$

$$(CO)_3HCo(C_2H_4) \rightarrow (CO)_3Co(C_2H_5)$$

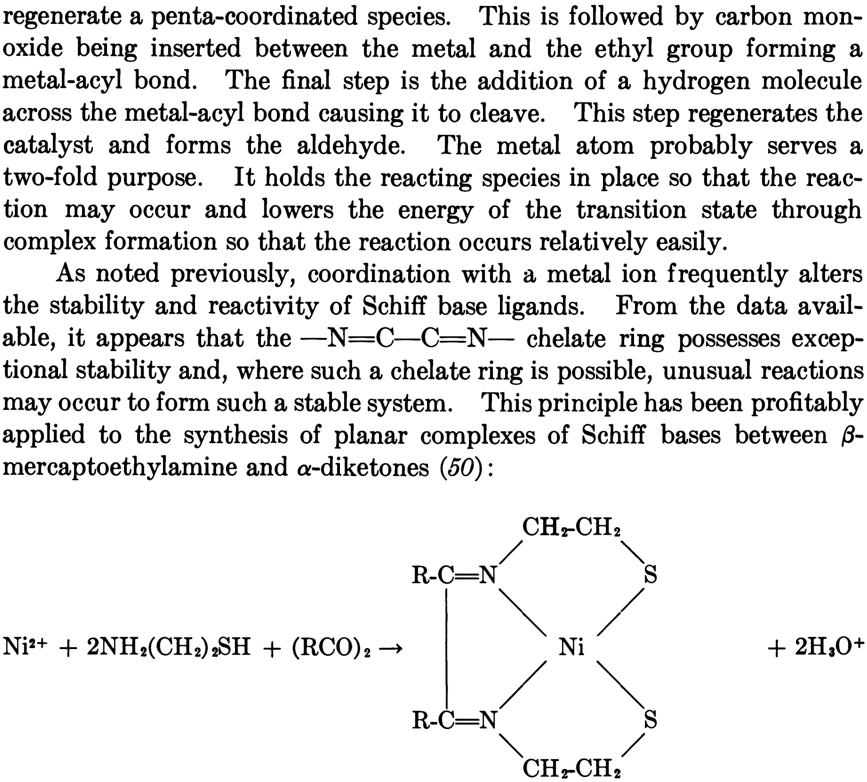
$$(CO)_3Co(C_2H_5) + CO \rightarrow (CO)_4Co(C_2H_5)$$

$$(CO)_4Co(C_2H_5) + CO \rightarrow (CO)_4Co(\text{-}COCH_2CH_3)$$

$$(CO)_4Co(\text{-}COCH_2CH_3) + H_2 \rightarrow HCo(CO)_4 + CH_3CH_2CHO$$

The initial reaction is thought to be the π-coordination of an ethylene molecule to the cobalt carbonyl compound accompanied by the displacement of a carbonyl group. The migration of the hydrogen from the cobalt atom to the ethylene group results in an ethyl group attached to cobalt via a sigma bond. The third step is adding carbon monoxide to the metal to regenerate a penta-coordinated species. This is followed by carbon monoxide being inserted between the metal and the ethyl group forming a metal-acyl bond. The final step is the addition of a hydrogen molecule across the metal-acyl bond causing it to cleave. This step regenerates the catalyst and forms the aldehyde. The metal atom probably serves a two-fold purpose. It holds the reacting species in place so that the reaction may occur and lowers the energy of the transition state through complex formation so that the reaction occurs relatively easily.

As noted previously, coordination with a metal ion frequently alters the stability and reactivity of Schiff base ligands. From the data available, it appears that the —N=C—C=N— chelate ring possesses exceptional stability and, where such a chelate ring is possible, unusual reactions may occur to form such a stable system. This principle has been profitably applied to the synthesis of planar complexes of Schiff bases between β-mercaptoethylamine and α-diketones (*50*):



When a metal ion such as nickel(II) is absent, thiazoles and mercaptals are formed. Such reactions have been carried out in which the diketone was biacetyl, 2,3-pentanedione, 2,3-octanedione, 1-phenyl-1,2-propanedione, and 1,2-cyclohexanedione (*51*). In like manner, the tris complexes of *N*,*N*′-dimethyl-2,3-butane diimine with iron(II), cobalt(II), and nickel(II) may be prepared from methylamine and biacetyl when the appropriate metal ion (*27*, *28*, *41*) is present. Replacing methylamine with hydroxylamine causes the formation of α-dioximes (*13*).

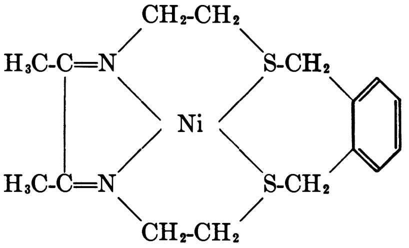
Ewens and Gibson reported that a coordinated sulfur atom such as that in a coordinated mercaptide commonly behaves as a nucleophile (*26*). For example, they found that β-mercaptoethylaminediethylgold reacts with methyl iodide to form the corresponding thioether. Such reactions have been extended to complexes of other metals, especially nickel and palladium, with ligands of a similar nature. Reactions of this type represent an energy transfer process. Upon methylation of a mercapto complex of a metal ion such as nickel, the Ni-S-R bond, which is quite strong, is replaced by the relatively weak, nickel-thioether bond. This fact is quite strikingly emphasized by transforming the square planar diamagnetic nickel mercapto complex to the paramagnetic octahedral thioether complex. In the case of the palladium(II) mercapto complexes, the impaired complexing ability of the thioether resulting from methylation causes one ligand to be lost, producing $[Pd(NH_2CH_2CH_2SR)X_2]$. Thus, methyl iodide yields the product $[Pd(NH_2CH_2CH_2SCH_3)I_2]$. However, when benzyl bromide replaces methyl iodide, a mixture of seemingly $[Pd(NH_2CH_2CH_2SCH_2C_6H_5)_2]Br_2$ and $[Pd(NH_2CH_2CH_2SCH_2C_6H_5)Br_2]$ is produced. Such behavior is in accord with the lesser coordinating ability of bromide toward palladium(II), as compared with the iodide.

Studies of the reactivity of coordinated mercaptide groups show that terminal groups exhibit a greater tendency to act as nucleophiles than do bridging groups (*14*). Kinetic investigations suggest that there may be a pre-equilibrium coordination of the alkyl halide to the central metal ion

$$[Ni_2L_2] + RX \overset{\text{fast}}{\rightleftharpoons} [Ni_2L_2 \cdot RX] \xrightarrow{\text{slow}} [Ni_2(L)(LR)]X$$

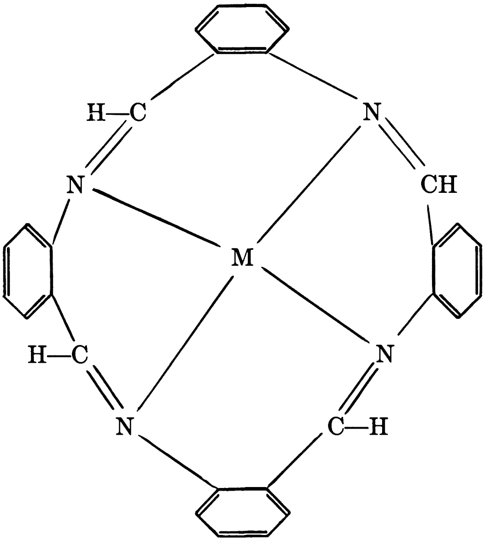
above (or below) the plane of the complex ion, resulting in the low activation energies and frequency factors observed for such reactions. The nucleophilic power of a sulfide group is greatly impaired by replacing nickel(II) with palladium(II), an ion which has little tendency to become penta-coordinated.

Reactions of this type have been successfully employed to prepare complexes containing macrocyclic rings. The product of the reaction between bis-(β-mercaptoethylamine)nickel(II) and biacetyl—i.e., 2,2′-dimethyl(ethanediylidenedinitrilo)-diethanethiolnickel(II) (*see* above), reacts with one mole of α,α′-dibromo-*o*-xylene to give a product in which the nickel ion is completely enclosed by chelate rings. Efforts to demonstrate similar reactions with trimethylene diodide and ethylene dibromide have

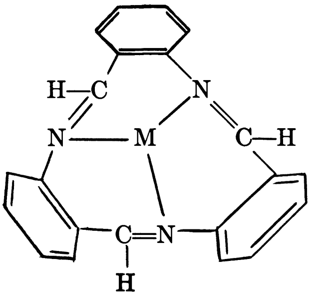


not met with equal success. The suggestion has been made that the ethylene dibromide may be too short to span the distance between the sulfur atoms. Much of the work involving mercapto complexes has been summarized in a recent review by Busch *et al.* (*14*). The term "template hypothesis" has been coined to describe reactions of this type in which the central metal ion, through coordination, serves as a "template" to hold the reactive sites in place while the reaction proceeds (*52*).

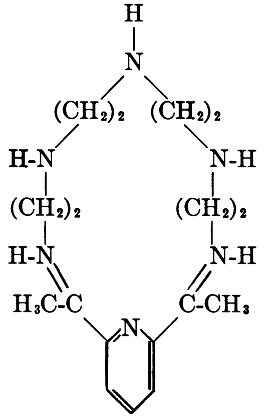
Exploitation of the "template" hypothesis by Busch and Melson (*43–45*) resulted in the self-condensation of *o*-aminobenzaldehyde in the presence of copper(II) or nickel(II). One of the products of this reaction is the tetradentate ligand tetrabenzo[b,f,j,n][1.5.9.13] tetrazacyclohexadecine, in which the four donor nitrogen atoms are coordinated in a planar manner around the metal ion.

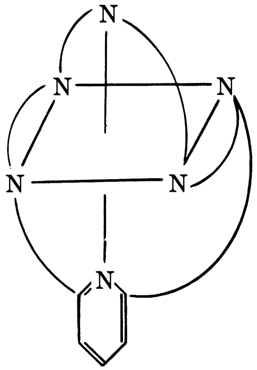


In the presence of nickel(II) a second, tridentate ligand was formed in addition to the tetradentate ligand shown above. The complexes of this ligand, tribenzo[b,f,j][1.5.9]triazacycloduodecine, are octahedral, and the three donor nitrogen atoms occupy one face. The remaining three positions are occupied by two unidentate anions and one water molecule or, in the case of bulky or weakly coordinating anions, by three water molecules.



Curry and Busch (*20*) have further demonstrated the success of this technique by first treating iron(II) chloride 4-hydrate with one molar equivalent of 2,6-acetylpyridine followed by addition of one molar equivalent of tetraethylenepentamine. Conversion to the iodide gives the compound (2,16-dimethyl-3,6,9,12,15,21-hexaazabicyclo[15.3.1]heneicosa-1(21),2,15,17,19-pentaene-9-ato)iron(III) diiodide. The ligand and its presumed mode of coordination are shown below.





The iron is oxidized to the trivalent state, yet the complex is obtained as the diiodide. The proposed explanation is that the ligand is coordinated as a univalent anion; a proton is removed from the amine nitrogen trans to the pyridine ring to relieve strain in the chelate ring.

Similar results were obtained when tetraethylenepentamine was replaced with triethylenetetramine. However, in this case the ligand does not deprotonate. The sixth octahedral position was occupied by hydroxide, and the complex was isolated as the perchlorate, $[FeL(OH)](ClO_4)_2$. Somewhat related reactions have been carried out in which triethylenetetramine complexes of copper(II) or nickel(II) were treated with acetone (*37*, *38*).

Ligands in which phosphorus is the coordinating atom undergo a variety of reactions at the coordinated atom, and some of these have recently been discussed by Schmutzler (*48*). Platinum(II) complexes of trichlorophosphine solvolyze in water and alcohols to form phosphorous acid or stable orthophosphite esters. The gold compound, $AuCl(PCl_3)$, forms similar stable solvolysis products from alcohols but is reduced in water (*13*).

$$[PtCl_2(PCl_3)_2] + 6ROH \rightarrow PtCl_2[P(OR)_3]_2 + 6HCl$$

In contrast to this behavior, the corresponding iridium compound $[IrCl_3(PCl_3)_3]$ does not solvolyze in alcohols. These reactivities reflect the effect of the metal ion on the electron density at the phosphorus atom. Some studies of the effect of coordination on the ethylenimine molecule have recently been reported by Edwards *et al.* (*47*). Although the ring in uncoordinated ethylenimine is easily broken by mineral acids, organic acids, and acids in the presence of strong nucleophiles, this ring, when coordinated to rhodium in trichlorotris(ethylenimine)rhodium(III), $[Rh(Az)_3Cl_3]$, remains intact when treated with reagents such as hydrochloric acid or hydriodic acid. The ring stability of the coordinated ethylenimine in these complexes is thought to result from the coordinate saturation of the nitrogen atom, which prevents a proton from being added to the imino nitrogen. It is also quite apparent that the labilizing effect of the metal ion on ring opening is much less than that of an attached proton.

Probably the best known and most investigated reaction of a ligand at the coordinated atom is the acidic nature of various coordinated ligands. This concept of proton dissociation from a coordinated ligand is not a recent one, for very early in this century Bjerrum determined the pK_a of $[Cr(H_2O)_6]^{3+}$ to be 4.05 at 25°C. (*4*), a value later refined by Lamb and Fonda to 3.8. Of greater interest, however, is the acidic behavior of protons on coordinated atoms other than oxygen.

In their attempts to prepare bis-ethylenediaminegold(III) bromide, Block and Bailar (*12*) obtained instead the *N*-deprotonated complex $[Au(en)(en\text{-}H)]Br_2$. This complex is sufficiently basic to be titrated to $[Au(en)_2]^{3+}$ with aqueous solutions of strong acids. Similarly, $[Au(en)_2]^{3+}$ can be deprotonated by aqueous solutions of strong base. Also, Dwyer and Hogarth (*21*) reported that the reaction of $(NH_4)_2OsBr_6$ with anhydrous ethylenediamine at 10°C. gives $[Os(en\text{-}H)_2(en)]Br_2$. Titration data show this compound to behave as a weak monoacidic base, and $[Os(en\text{-}H)(en)_2]Br_3 \cdot 3H_2O$ can be isolated from this compound in 5*N* hydrobromic acid. Reduction of the dibromide followed by addition of iodide ion precipitates the fully protonated osmium(III) complex, $[Os(en)_3]I_3$. This behavior emphasizes the effect of nuclear charge of the metal ion on the acidity of the protons at the coordinated atom. This point is further emphasized by considering the series of octa-coordinated osmium complexes (*22*). As the oxidation state of osmium increases in this series of compounds, so does the extent of deprotonation:

$$[Os^{IV}(en\text{-}H)_2(en)_2]I_2, \quad [Os^{V}(en\text{-}H)_3(en)]I_2 \cdot 4H_2O, \quad [Os^{VI}(en\text{-}H)_4]I_2.$$

The dissociation constants for ionizing a proton from one or more coordinated ammine groups have been determined fairly accurately in a number of cases. A representative sampling is shown in Table I. The field strength of the platinum(II) ion is too small to render its ammine complexes sufficiently acidic for the dissociation constant to be determined in aqueous solution. Likewise, the complex ions $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Ir(en)_3]^{3+}$, and $[Rh(en)_3]^{3+}$ all have pK_a values less than 10^{-12}. The pK_a for $[Rh(NH_3)_6]^{3+}$ has been estimated to be approximately

Table I. Acid Dissociation Constants of Complexes in Aqueous Solution

Complex	pK_{a1}	pK_{a2}	pK_{a3}	*Ref.*
$[Pt(pn)_3]^{4+}$	5.4	9.6	10.7	*33*
$[Pt(en)_3{}^{4+}$	5.5	9.8	10.7	*33*
$TetmenH_2{}^{2+}$	5.85	8.97	—	*49*
$[Pten(NH_3)_4]^{4+}$	6.2	10	—	*4*
s-$DmenH_2{}^{2+}$	7.47	10.3	—	*7*
$enH_2{}^{2+}$	7.47	10.2	—	*6*
$menH_2{}^{2+}$	7.56	10.4	—	*5*
$[Pt(NH_3)_6]^{4+}$	7.9	10.1	—	*4*
$[Pt(NH_3)_5Cl]^{3+}$	8.1	10.5	—	*4*
$[Pt(NH_3)_5Br]^{3+}$	8.2	10.4	—	*4*
cis-$[Pt(pn)_2Cl_2]^{2+}$	8.3	10.4	—	*33*
$NH_4{}^+$	9.25	—	—	—
$[Pt(NH_3)_5(OH)]^{3+}$	9.5	10.7	—	*4*
trans-$[Pten_2Cl_2]^{2+}$	10.4	—	—	*33*
trans-$[Pt(pn)_2Cl_2]^{2+}$	10.7	—	—	*33*

11.1 (*33*). The data in Table I show the general effect of the charge of a complex cation on its relative acidity, as well as the relative effect of platinum(IV) compared with a proton on the acid-strengthening effect of an amine (e.g., compare pK_{a1} of $[Pt(en)_3]^{4+}$ with that of $enH_2{}^{2+}$).

Recent work by Watt and co-workers has shown that by working in solvents more basic than water, ammine complexes which exhibit no apparent acidic properties in water become acidic in these solvents. Consequently, although $[Pt(NH_3)_4]^{2+}$ is stable and shows no tendency to deprotonate in alkaline aqueous solutions, treatment with two molar equivalents of potassium amide in liquid ammonia results in diamidodiammineplatinum(II) (*66*).

$$[Pt(NH_3)_4]Br_2 + 2\ KNH_2 \rightarrow [Pt(NH_3)_2(NH_2)_2] + 2\ KBr$$

Deammoniation of this product at 130°C. gives platinum(II) amide. Similar reactions have been carried out with the ethylenediamine complex of platinum(II), and both the singly deprotonated product, [Pt(en)(en-H)]I, and the doubly deprotonated product, $[Pt(en\text{-}H)_2]$, were isolated as solid products and characterized (*60*). Later work showed that under proper conditions a white solid could be obtained which behaved as K[Pt(en-H)(en-2H)] (*57*). Each of these deprotonated species behaves as a strong base in aqueous solution, and the original material, $[Pt(en)_2]^{2+}$, is regenerated.

Similar studies have been made with bis-ethylenediaminepalladium(II) iodide, from which [Pd(en)(en-H)]I and $[Pd(en\text{-}H_2]$ have been isolated and characterized (*59*). An interesting feature in the case of the palladium compounds is that the deprotonated species, although apparently stable in an atmosphere of dry air, decompose upon standing in an atmosphere of dry helium. Furthermore, although the $[Pd(en)_2]^{2+}$ ion apparently shows no acidic behavior in water, the deprotonated ion, $[Pd(en)(en\text{-}H)]^+$, behaves as a weak base in water. The doubly deprotonated complex, $[Pd(en\text{-}H)_2]$, behaves as a strong base and shows no indication of the intermediate, $[Pd(en)(en\text{-}H)]^+$, when titrated with acid in aqueous solution. This behavior has been explained by the consideration of π-bond formation between the vacant $5p_z$ orbital on the palladium ion and the electron pair on the deprotonated nitrogen atom in the complex $[Pd(en)(en\text{-}H)]I$. This would render the electron pair on nitrogen less available for electrophilic attack by a proton, resulting in its weakly basic behavior.

In only one case, to be noted later, has it been possible to obtain unequivocal proof, by isolating a product, that deprotonation of a complex beyond the formation of a monovalent anion occurs with potassium amide in liquid ammonia. Potentiometric titration of $[Rh(en)_3]^{3+}$ with potassium amide in liquid ammonia at −35°C. gave evidence for stepwise deprotonation through the formation of $[Rh(en\text{-}H)_2(en\text{-}2H)]^-$ (*55*), with some evidence for a possible further step. The products which could be isolated and identified were $[Rh(en)_2(en\text{-}H)]I_2$, $[Rh(en)(en\text{-}H)_2]I$, $[Rh(en\text{-}H)_3]$, and $K[Rh(en\text{-}H)_2(en\text{-}2H)]$ (*55, 56*).

Similar behavior has been observed for $[Ir(en)_3]I_3$ (*62*). Two solid products were isolated from reactions involving this compound and potassium amide in liquid ammonia—$[Ir(en)(en\text{-}H)_2]I$ and $K_2[Ir(en\text{-}H)(en\text{-}2H)_2]$. This appears to be the only case in which the divalent anion of a deprotonated ammine complex has been proved by isolation of the product. Although only one of the intermediate deprotonated species has been isolated, those remaining, $[Ir(en)_2(en\text{-}H)]I_2$, $[Ir(en\text{-}H)]$, and $K[Ir(en\text{-}H)_2(en\text{-}2H)]$, probably exist in solution.

A limited amount of work has been done with complexes of diethylenetriamine (*61*). Treatment of bis-diethylenetriaminerhodium(III) iodide with potassium amide in liquid ammonia resulted in the isolation of solid $[Rh(dien\text{-}H)_2]I$ and $[Rh(dien\text{-}H)(dien\text{-}2H)]$. For the corresponding iridium complex, similar treatment resulted in the isolation of $[Ir(dien\text{-}H)(dien\text{-}2H)]$. Further deprotonation presumably occurs, at least in the case of the rhodium complex, as evidenced by the fact that the solid $[Rh(dien\text{-}H)(dien\text{-}2H)]$, which precipitates upon adding slightly more than three molar equivalents of potassium amide, dissolves completely when a total of six molar equivalents of potassium amide is added.

Other bases have been employed to deprotonate these complexes (*63*). The singly deprotonated complex $[Os(en\text{-}H)(en)_2]I_2$ can be obtained by reaction of $[Os(en)_3]I_3$ with one molar equivalent of potassium or potassium amide in liquid ammonia, with a six-fold molar excess of KOC_2H_5 in ethanol, or with a four-fold molar excess of KOH in ethanol. However, further deprotonation to form [Os(en-H)$_2$(en)]I and [Os(en-H$_3$] required ammonia solutions of KNH_2; neither KOC_2H_5 nor KOH in ethanol were sufficiently basic to effect these deprotonation steps. [Attention is called elsewhere to deprotonations effected with ethylenediamine (*21*, *22*), hydroxide ion (*12*), and solutions of potassium in ammonia (*62*)].

Practically all of the research into the acidic behavior of these ammine complexes to date has been concerned primarily with determining the maximum number of protons removable from these complexes. Such information should provide some insight into the ability of a metal ion to polarize the nitrogen atom and thus weaken the remaining nitrogen bonds; the greater the polarizing power of the metal ion is, the more acidic is the complex. However, two important questions remain to be answered: (a) From which positions are succeeding protons removed? (b) Can a second proton be removed from a coordinated amino group?

In considering the first question, for a doubly deprotonated octahedral tris-ethylenediamine complex, the possibilities are:

(1) *cis*-[M(en)(en-H)$_2$]
(2) *trans*-[M(en)(en-H)$_2$]
(3) [M(en)$_2$(sen-2H)]
(4) [M(en)$_2$(uen-2H)]

In these formulas, en-H has its usual significance, with sen-2H representing the symmetrically deprotonated ligand $^-HNCH_2CH_2NH^-$, uen-2H representing the unsymmetrically deprotonated ligand $H_2NCH_2CH_2N^{2-}$, and cis or trans representing the sites of deprotonation relative to each other. The same possibilities exist for a square planar complex also. From an electrostatic point of view it would seem appropriate to dismiss Formula 4 immediately. There is a dearth of information, however, definitely distinguishing between the three remaining possibilities or establishing if, in fact, all systems even behave similarly in this respect. Likewise, the second question above cannot be answered on the basis of the foregoing information. Accordingly, studies have been carried out to resolve these uncertainties.

Assuming that rearrangement of the deprotonated ligands does not occur, use of the complex [Pt(bipy)(en)]$^{2+}$ permits study of a single en ligand in the presence of a bidentate ligand that is not subject to deprotonation. This should permit establishment of both the maximum extent and site of deprotonation. It has been found (*65*) that the π-bonding bipyridyl ligand so enhances the acidity of the coordinated ethylenediamine that partial deprotonation results simply from exposure to the relatively weakly basic ammonia molecule; the product of equilibration with liquid ammonia at −33.5°C. is [Pt(bipy)(en-H)]I·[Pt(bipy)(en)]I$_2$. The deprotonation is completed with the amide ion in liquid ammonia to provide successively [Pt(bipy)(en-H)]I and [Pt(bipy)(en-2H)], both of which are methylated

(*64*) by reaction with methyl halides at room temperature to form *N*-methyl- and *N,N'*-dimethylethylenediamine, respectively. The latter compound is further deprotonated stepwise with amide ion in ammonia and subsequently methylated to provide the *N,N,N',N'*-tetramethylethylenediamine ligand. It is significant, of course, that under the same conditions, coordinated en is not methylated.

In view of the foregoing results and earlier and unsuccessful efforts to methylate species such as [M(en-H)(en)]X and $[M(en\text{-}H)_2]$, where M = Pt^{2+}, Pd^{2+}, these cases either have been or are being re-examined (*54*). In the case of palladium, it has been found that the bipyridyl ligand is not critical; both [Pd(en-H)(en)]I and $[Pd(en\text{-}H)_2]$ have been methylated.

Deprotonation of octahedral complexes also has been demonstrated (*53*). Thus, when $[Rh(en)_3]I_3$ reacts with amide ion in ammonia, $[Rh(en\text{-}H)_2(en)]$ and $[Rh(en\text{-}H)_3]$ are formed. Both are methylated with CH_3I at room temperature, but in the latter case the methylation product is not identical with the complex synthesized independently using *N*-methylethylenediamine. This suggests that the deprotonated species may be [Rh(en-2H)(en-H)(en)]. Similarly, deprotonation of $[Co(en)]I_3$ leads to the isolation of $[Co(en\text{-}H)_2(en)]I$, which has also been methylated. Both $[Rh(en\text{-}H)_2(en)]I$ and $[Co(en\text{-}H)_2(en)]I$ react with $SOCl_2$ at room temperature to form dichloroiodides, in which there is one $=S=O$ group per mole of complex; this has been confirmed both by analysis and the characteristic $\nu_{S=O}$ at 1265 cm.$^{-1}$ The structure of these species has not been resolved.

The deprotonation of numerous other ligands and reactions of the deprotonated species are also in progress (*58*). Specific cases studied thus far include glycine and *β*-alanine complexes of nickel(II), the nickel(II) complexes with both *o*-aminophenol, *o*-aminothiophenol, and *o*-phenylenediamine.

Reactions of Type b

The type of reaction that a ligand may undergo, or the position at which a reaction may occur, can often be altered by masking one or more positions through coordination. The classical synthesis of isonitriles from silver cyanide and an organic halogen compound is an example of this type of ligand reaction. The corresponding reaction with sodium cyanide provides the nitrile (*29, 34*). Similar reactions have been used to prepare isonitrile complexes (*13*), as shown on the following page. Many reactions of this type have been summarized recently in a rather comprehensive review (*36*).

A different reaction of this type, which has been the subject of considerable investigation, is the hydrolysis of amino acid esters in the presence of divalent metal ions which enhance the rate of hydrolysis (*9, 10, 40, 70*). Kroll (*40*) was the first to demonstrate that the rate of hydrolysis of ethyl

$$Ag_4Fe(CN)_6 + 4C_2H_5I \rightarrow [Fe(CNC_2H_5)_4(CN)_2] + 4AgI$$

$$K_4Fe(CN)_6 + 3(CH_3)_2SO_4 \rightarrow [Fe(CHCH_3)_6] + 3SO_4^{2-} + 4K^+$$

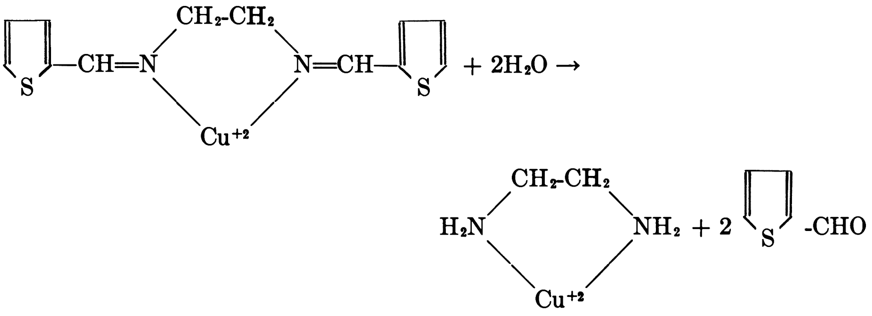
$$[Fe(CNCH_3)_6]Cl_2 + (130\text{-}150^\circ\ \text{C., } \textit{in vacuo}) \rightarrow$$
$$2CH_3Cl + [Fe(CNCH_3)_4(CN)_2]\ (\alpha \text{ and } \beta \text{ forms})$$

$$(\alpha \text{ or } \beta \text{ form}) + CH_3I \rightarrow [Fe(CNCH_3)_6]I_2$$

$$(\alpha + \beta) + C_2H_5I \rightarrow (\alpha \text{ and } \beta)\ [Fe(CNCH_3)_4(CNC_2H_5)_2]I_2$$

glycinate was accelerated by adding copper(II) ion. This system was further studied from the standpoint of kinetics and mechanism by Jones and co-workers (*17*). Their proposed mechanism involves initial coordination of the glycine about the metal ion (through the amine nitrogen and keto-oxygen atoms to form a chelate), followed by coordination of an hydroxide ion with the copper ion. This second step, which is most likely due to the loss of a proton from a water molecule coordinated with the copper(II) ion, is proposed to explain that the kinetics of the reaction is second order in hydroxide ion. The third step in the hydrolysis is the nucleophilic attack of hydroxide ion on the carboxyl carbon atom, resulting in the ethoxide ion being replaced. This leads to the product glycine, either uncombined or coordinated about the copper ion. This type of mechanism, in which a chelate ring is formed, is strongly supported by investigations of Alexander and Busch (*1*) on the hydrolysis of glycine esters complexed through the nitrogen atom only in the coordination cation, *cis*-$[Co(en)_2(NH_2CH_2CO_2R)X]X_2$. Such compounds can be maintained in aqueous solution, even at low pH, for several hours with no appreciable hydrolysis of the ester. However, in the presence of the mercury(II) cation, hydrolysis of the coordinated ester is extremely rapid compared with the rate of hydrolysis of the ligand coordinated through the amino group alone. The mercury(II) cation reacts with the complex in aqueous solution to remove the coordinated halide—producing a highly reactive penta-coordinated complex. The resulting vacant position is taken by the carbonyl oxygen of the ester to form the chelated ester. As in the case of copper(II), the cobalt(III) ion polarizes the carbonyl bond, thus rendering the carbon atom positive. This position is then attacked by water (in the absence of a stronger nucleophile), leading to hydrolysis. Studies of this nature demonstrate the strong effect coordination may have in altering ligand reactivity.

Reactions of Schiff bases coordinated with metal ions have been examined from the standpoint of stability and reactivity. Eichhorn (*23*, *25*) examined the complex formed between bis-(thiaphenal)ethylene-diimine and copper(II). It was found that, when complexed to copper(II), the ligand becomes unstable and hydrolysis occurs; this leads to the aldehyde and the copper-ethylenediamine complex.



The proposed explanation for this behavior is that the —S—C—C=N— chelate ring either forms very feebly or it does not form at all. Without this stabilizing chelate effect, the electron withdrawing power of the metal ion facilitates nucleophilic attack by water at the imine carbon atom leading to the observed hydrolysis. Similar observations have been made with bis-(2-pyridinal)ethylenediamine (*11*). It is of interest that the Schiff base formed between salicylaldehyde and glycine is stabilized by chelate formation at pH values where the uncombined ligand is readily hydrolyzed (*24*, *46*). In this case, however, chelation through the phenolic hydroxy group is very likely and probably leads to the observed stability.

Bis(dimethylglyoxime)nickel(II) reacts with both methyl iodide and methyl sulfate to give a complex in which the anionic oxygen sites are methylated (*13*). Similar reactions

$$[\mathrm{Ni(DMGO^-)_2}] + 2\mathrm{RX} \rightarrow [\mathrm{Ni(DMGOR)_2X_2}]$$

occur when nickel is replaced by palladium(II) or platinum(II). Similar behavior is observed with 2-pyridinaldoxime and these metal ions. In the case of each ligand, however, one molecule of ligand tends to be displaced by halide when the metal ion is palladium(II) or platinum(II).

Reactions of Type c

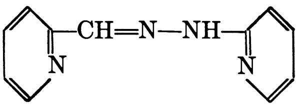
This reaction type considers those reactions which occur at a position somewhat remote from the metal ion as compared with the previous types of reactions. Nuclear magnetic resonance studies of the complexes $[\mathrm{Co(en)_2(alanine)}](\mathrm{NO_3})_2$ and the corresponding glycine complex by Busch and Williams (*71*) have shown that the methylene hydrogen atoms in the coordinated amino acids are labile. These hydrogen atoms exchange for deuterium atoms in deuterium oxide, as do also the amino hydrogens. None of the protons on ethylenediamine is exchanged. This behavior agrees with the earlier reported observation that the copper(II) glycine complex reacts with aldehydes and ketones to form β-hydroxyamino acids (*13*).

Green and co-workers (*31*, *32*) have studied the effect of coordination on the acidity of the imino proton in pyridine-2-aldehyde-2-pyridylhydrazone and related compounds. The structures, names, and acid dissociation constants for these ligands are shown in Table II.

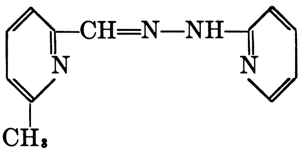
Table II. Acid Dissociation Constants of Hydrazone Ligands

	Ligand[a]	pK_{a1}	pK_{a2}	pK_{a3}
I	pyridine-2-aldehyde-2′-pyridylhydrazone	2.87	5.71	ca. 14.5
II	6-methylpyridine-2-aldehyde-2′-pyridylhydrazone	3.65	6.06	>14
III	pyridine-2-aldehyde-2′-pyrimidylhydrazone	1.1	4.48	13.3
IV	pyridine-2-aldehyde-3′-methyl-2′-pyrazinylhydrazone	1.4	4.52	12.9

[a]



I



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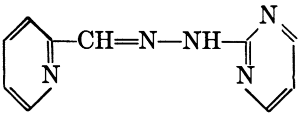

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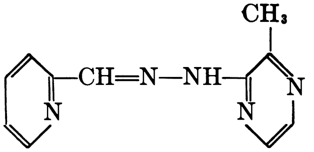


IV

The third acid dissociation constant, pK_{a3}, represents the removal of the imino proton. The bis complexes of these ligands have been examined and found to behave as dibasic acids; the acidity arises from the dissociation of the imino proton from each ligand. The acid dissociation constants for the iron(II) complexes of these ligands are shown in Table III.

Upon coordination with a metal ion, the acidity of the imino group is greatly increased. Although changes in the ligand outside the chelate ring have a small effect on the magnitude of the dissociation constant of the imino group (i.e., note the slight variation in pK'_{a1}), the magnitude of the acid-strengthening effect of the coordinated metal ion on this group is not changed, as can be seen from the essentially constant values of (pK_{a3}-pK'_{a1}).

Table III. Acid Dissociation Constants of Fe(II) Complexes of Hydrazone Ligands

Complex	pK'_{a_1}	pK'_{a_2}	$(pK_{a_3}\text{-}pK'_{a_4})$
$[\mathrm{Fe(I)_2}]^{2+}$	5.68	6.57	8.8
$[\mathrm{Fe(II)_2}]^{2+}$	6.28	7.95	>7.7
$[\mathrm{Fe(III)_2}]^{2+}$	4.56	6.09	8.7
$[\mathrm{Fe(IV)_2}]^{2+}$	4.12	5.61	8.8

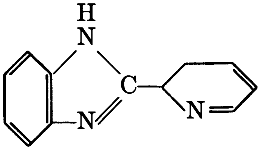
The relative acid-strengthening effect of various divalent metal ions was also investigated using Ligand I above. The relative order of this effect is (pK'_{a_1} and pK'_{a_2} are given in parentheses) as follows:

Fe(5.68,6.57) > Cu(5.96,8.74) > Ni(7.37,8.50) > Zn(7.94,8.85) > Cd(8.93,10.22)

This order is based upon the first acid dissociation constant; on the basis of the second acid dissociation constant, the position of copper and nickel is reversed.

Reactions of Type d

Freiser and co-workers have investigated the acid-strengthening effect of chelation on a ligand at a position outside of the chelate ring. One of the earlier studies involved divalent metal complexes of 2-(2-pyridyl)-benzimidazole (*35*),



V

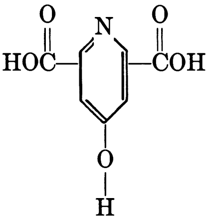
Titration of metal complexes of this ligand shows that the imino proton is probably removed. The relative effect of the metal ions studied to promote this behavior — with the pH at half-neutralization given in parentheses — appears to be

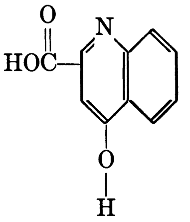
$\mathrm{Cu^{2+}}(6.4) > \mathrm{Co^{2+}}(7.1) > \mathrm{Zn^{2+}}(7.3) > \mathrm{Ni^{2+}}(7.4) > \mathrm{Mn^{2+}}(8.4)$

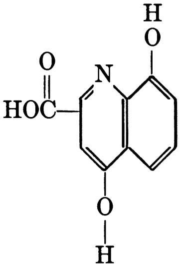
Nickel and cobalt form tris complexes, whereas the other metal ions form bis complexes.

Similar studies have been made to determine the acid-strengthening effect of a metal ion on the *p*-hydroxy group attached to a pyridine-type ligand (*2*, *3*). The ligands used in this study were 2,6-dicarboxy-4-

hydroxypyridine (VI), 4-hydroxyquinaldinic acid (VII), and 4,8-dihydroxyquinaldinic acid (VIII).


VI


VII

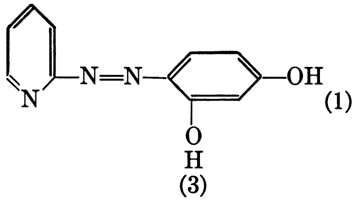

VIII

Metal chelation was found to have an acid-strengthening effect on the 4-hydroxy group of these ligands far in excess of that which could be attributed to a shift in the keto-enol equilibrium involving this group. Ligands VI and VII form chelates in the same manner through the nitrogen atom and carboxyl group, whereas Ligand VIII coordinates through the nitrogen atom and the 8-hydroxy group. As will be seen, this difference in chelate ring affects the acid-strengthening ability of the coordinated metal ion. For each ligand, the metal ions are arranged below in decreasing order of their acid-strengthening ability, followed in parentheses by the difference in the acid dissociation constant of the 4-hydroxy group in the ligand and in the complex.

Ligand VI: Cu(6.4) > Co(5.9) > Zn(5.7) = Ni(5.7)
Ligand VII: Cu(6.7) > Zn(5.9) > Ni(5.7) > Co(5.6)
Ligand VIII: Cu(5.0) > Zn(4.8) > Co(4.6) > Ni(4.5) > Mn(3.8)

The magnitude of the acid-strengthening effect is quite similar with Ligands VI and VII, whereas this effect is generally smaller with Ligand VIII. This difference supposedly reflects the effect of the position of the chelate ring in labilizing the proton on the 4-hydroxy group. With Ligand VIII, however, the 2-carboxy group is not coordinated so that the ligand behaves as a 2-substituted 8-hydroxyquinoline. This steric effect may account for at least a part of the decreased effect on the acidity.

The effect of metal chelation on the acidity of 4-(2-pyridylazo)-resorcinol (IX) has also been investigated by Freiser (*18*, *19*). The acid dissociation constants for the ligand were found to be: $pK_{a_1} = 7.0$, $pK_{a_3} = 12.4$. Upon coordination to a metal ion, the proton on the 3-hydroxy group is displaced so that chelation may occur. The remaining 1-hydroxy group is acidic, and the acid dissociation constants for complexes of some divalent metal ions are shown in Table IV.



IX

The copper complex coordinates with only one molecule of ligand and, as a result, the complex carries a positive charge. In forming the cobalt(II) chelate, only one proton is released instead of the expected two, although the complex is apparently a bis complex. Two protons can be titrated in the resulting complex. It has been suggested (*15, 18*) that oxidation may occur upon chelate formation and that this may consume one proton. For this reason, the cobalt complex in the above list is shown with a positive charge.

Table IV. Acid Dissociation Constants of Metal Complexes of 4-(2-Pyridylazo) Resorcinol

Complex	pK'_{a1}	pK'_{a2}
$[CoL_2]^+$	4.7	6.0
$[CuL]^+$	5.5	—
$[NiL_2]^+$	7.7	9.2
$[ZnL_2]^+$	7.7	9.3
$[MnL_2]^+$	8.8	10.3

Although Freiser has interpreted the above data as indicating an acid-strengthening effect of the metal ion on the 1-hydroxy group, this appears to be true only for the cobalt and copper complexes. The nickel, zinc, and manganese complexes show acid dissociation constants for the 1-hydroxy group which are, in fact, smaller than that for the ligand alone. One may conclude that in the complexes of nickel, zinc, and manganese with this ligand, these metal ions are less electron-withdrawing than a proton. The cobalt(III) and copper(II) ions are more electron withdrawing than a proton, possibly owing to the higher metal ion charge to ligand ratio in their complexes.

Acknowledgments

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19

The Chelate Effect

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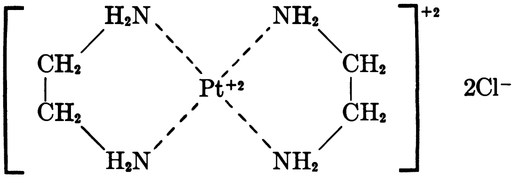
Modern concepts of the nature of chelate compounds and interpretations of their high stability are considered in detail. The translational entropy contribution to stability, originally described by Schwarzenbach and Adamson, is broadened to include entropy increases resulting from displacement of solvated water molecules from cation and anion through charge neutralization effects. A favorable chelate enthalpy effect results from more positive heats of formation of chelating ligands. A detailed, general analysis of the constitutional factors controlling the stabilities of chelate compounds reveals five enthalpy effects and six entropy effects as significant. Principles are illustrated with thermodynamic data taken from the literature on metal chelates of polyamines and amino-polycarboxylic acids.

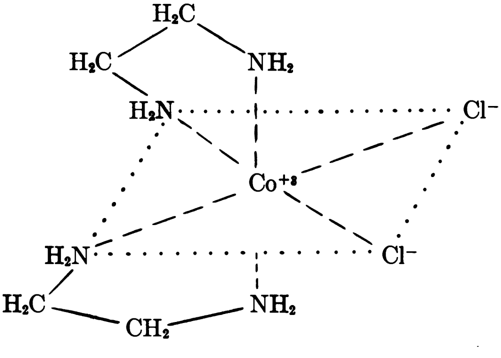
A discussion of the chelate effect is especially appropriate for this symposium because Werner was the first to synthesize and recognize the significance of metal chelate compounds. The application of Werner's coordination theory to complexes made it possible to identify chelate rings and to indicate their significance with respect to the stereochemistry of coordination compounds. Although the high stability of metal chelate compounds became qualitatively known, and many chelates were subsequently synthesized, theories and concepts of chelate ring formation did not develop beyond the level attained by Werner for many decades. Only during the past 15 years have quantitative equilibrium measurements been made, and only during the past five years has a significant amount of data on heats and entropies of metal chelate formation become available. On the basis of this recent work, it is now possible to understand more thoroughly the nature of metal chelate rings and the constitutional factors which determine their special properties. It is these properties, which differ from those of analogous complexes having no metal chelate rings, which are included in the concept called "the chelate effect." Since some interesting kinetic effects involving special properties of metal chelates have recently become known, it is convenient to distinguish between the terms "equilibrium chelate effect" and "kinetic chelate effect." This paper deals with the "equilibrium chelate effect."

Werner's Discovery of Chelate Compounds

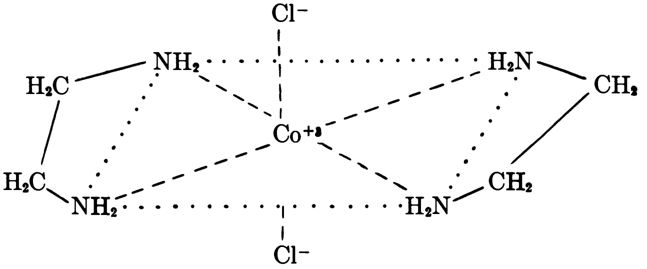
In 1893 Werner (*19*) clearly recognized the cyclic nature of the coordinate bonding in bisethylenediamineplatinum(II) chloride (I) and suggested that the 4-coordinate bonds between Pt(II) and the amino groups of the chelating ligand are co-planar. On the basis of his coordination theory, he suggested that the two chloride and four amino groups of the two isomeric forms of dichlorobisethylenediaminecobalt(III) chloride



I. *Bisethylenediamineplatinum(II) chloride*



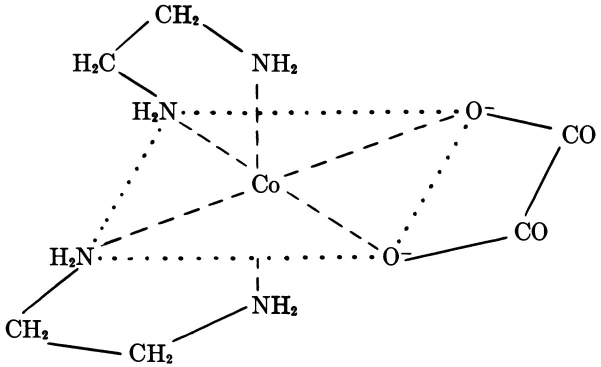
II. *Cisdichlorobisethylenediaminecobalt(III) ion*



III. *Transdichlorobisethylenediaminecobalt(III) ion*

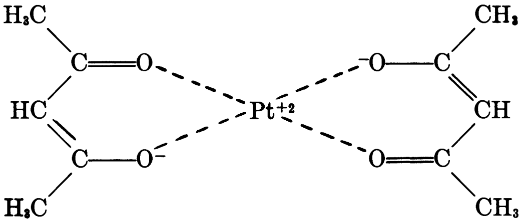
(II and III), prepared by Jorgensen (*9*), were arranged octahedrally about the cobalt(III) ion, existed as cis and trans forms, and involved metal coordination to amino groups at both ends of the ethylenediamine ligand to form two metal chelate rings.

Later, Werner and Vilmos (*20*) took advantage of metal chelate ring formation in determining the stereochemistry of the dichloroethylenediaminecobalt(III) chlorides. The isomer which was found to react readily with oxalate to give oxalatobisethylenediaminecobalt(III) chloride (IV) was considered to be the cis form because the steric requirements of the oxalato chelate ring are such that the oxalate oxygens must occupy cis positions in the coordination sphere of the cobalt(III) ion.



IV. *Oxalatobisethylenediaminecobalt(III) ion*

Shortly afterward Werner (*18*) reported the preparation of bisacetylacetonoplatinum(II) (V), a complex carrying zero charge and having two six-membered metal chelate rings.



V. *Bisacetylacetonoplatinum(II)*

Recent Developments

After Werner's time, many investigators described the special properties of metal chelates and explained them on the basis of qualitative principles. In his systematic review, Diehl (*7*) pointed out that a chelating ligand is more firmly bound than the corresponding monodentate ligands because of the presence of two or more coordinate bonds. If one bond is broken, the remaining bonds still remain and, effectively, the metal chelate is still not dissociated. This idea is strikingly close to later semiquantitative concepts of the nature of the (equilibrium) chelate effect.

Later, Martell and Calvin (*11*) noted the high stabilities of the alkaline earth-EDTA chelates and suggested that the heats of coordinate bond formation in solution (i.e., relative to the aquo metal ion) must be negligible, and that the stabilities of the aquo chelates must be due to a favorable entropy change associated with formation of the metal chelate compound. The stabilizing effect of the chelate ring was therefore concluded to be an entropy effect.

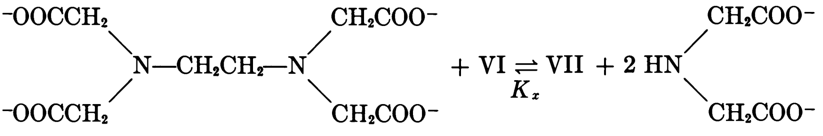
The term chelate effect was first used in 1952 by Schwarzenbach (*15*). To demonstrate the nature of the chelate effect he used as models a bidentate ligand and two unidentate ligands which form coordinate bonds of equivalent strength with a metal ion. He predicted increased stability for the metal chelate on the basis of statistical considerations. The model required a zero heat of reaction in the replacement of two unidentate ligands by one bidentate chelating ligand, so that the stabilizing chelate effect must be an entropy effect.

Recently a large amount of experimental data on stability constants (*17*) of metal chelates and associated heats and entropies of formation has revealed that many factors enhance the stabilities of metal chelates in solution. This paper examines each of these factors and discusses their significance.

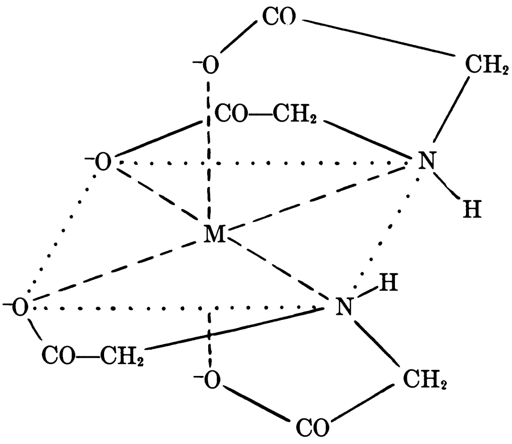
The Schwarzenbach Model

In 1952 Schwarzenbach (*15*) reviewed the stabilities of analogous complexes and chelates that differ in the number of metal chelate rings but resemble each other quite closely in all other respects. In the replacement of two iminodiacetate ligands by one ethylenediaminetetraacetate ligand, for example, the equilibrium constant for the replacement reaction, given below, varied from $10^{2.4}$ to $10^{5.2}$, depending on the metal ion. Formulas VI and VII show that the main difference between the two chelates is the formation of an additional chelate ring involving both nitrogen donors in Formula VII. Structural Formula VI is arranged to emphasize the analogy between these metal chelate compounds and is shown in the less stable (and probably non-existent) cis form. The equilibrium constant of the above reaction, K_x, would therefore be even greater than the values found experimentally.

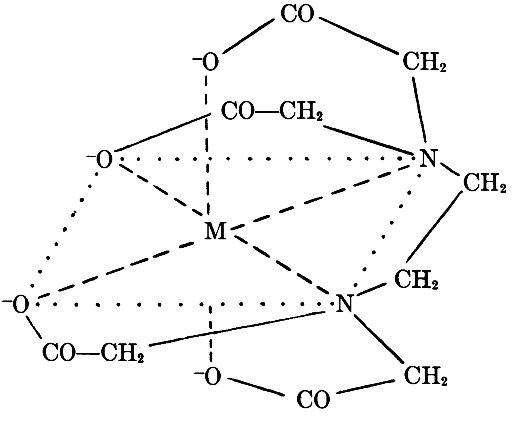
To explain the chelate effect, Schwarzenbach used the following model, in which two unidentate ligands, L, are displaced from the coordination



$(K_x \sim 10^{2.4} - 10^{5.2})$



VI. *Metal chelate of iminodiacetate ligand*



VII. *Metal chelate of ethylenediaminetetraacetate ligand*

sphere of the metal ion by a bidentate ligand, L—L. It was assumed that the affinities of the individual donor groups of both ligands for the metal ion are equivalent, so that the enthalpy of the replacement reaction is zero. If the intrinsic stability constant for the combination of the unidentate ligand with a metal ion is K (i.e., for a metal ion of coordination number of unity), then the stability constant for the formation of the metal complex ML is nK. Thus, for the complex ML_2, we have:

$$\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML} \qquad K_{\mathrm{ML}} = nK \tag{1a}$$

$$\mathrm{ML} + \mathrm{L} \rightleftharpoons \mathrm{ML_2} \qquad K_{\mathrm{ML_2}} = \frac{n-1}{2}K \tag{1b}$$

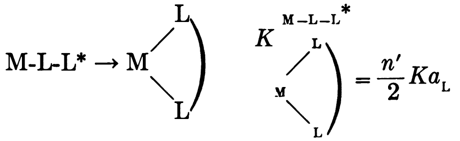
The overall formation constant is:

$$\mathrm{M} + 2\mathrm{L} \rightleftharpoons \mathrm{ML_2} \qquad \beta_{\mathrm{ML_2}} = \frac{n(n-1)}{2}K^2$$

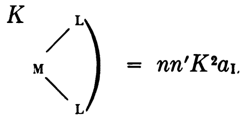
The chelate compound may be considered to be formed by the combination of a single donor group with the metal ion:

$$\mathrm{M} + \mathrm{L\text{-}L} \rightleftharpoons \mathrm{M\text{-}L\text{-}L^*} \qquad K_{\mathrm{M\text{-}L\text{-}L^*}} = 2nK \tag{2a}$$

The unattached group has a high effective concentration, indicated by the activity term a_L, which is much greater than unity. Thus:

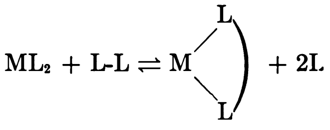


$$\mathrm{M\text{-}L\text{-}L^*} \rightarrow \mathrm{M}\left\langle\begin{matrix}\mathrm{L}\\ \mathrm{L}\end{matrix}\right) \qquad \frac{K_{\mathrm{M}\left\langle\begin{smallmatrix}\mathrm{L}\\ \mathrm{L}\end{smallmatrix}\right)}}{K_{\mathrm{M\text{-}L\text{-}L^*}}} = \frac{n'}{2}Ka_{\mathrm{L}} \tag{2b}$$

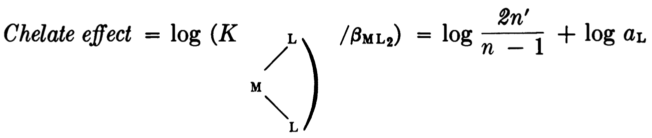


$$K_{\mathrm{M}\left\langle\begin{smallmatrix}\mathrm{L}\\ \mathrm{L}\end{smallmatrix}\right)} = nn'K^2a_{\mathrm{L}}$$

where n' is smaller than $n-1$ since not all uncoordinated positions on the metal ion are available to the second group of the ligand. For the displacement reaction, we have



$$\mathrm{ML_2} + \mathrm{L\text{-}L} \rightleftharpoons \mathrm{M}\left\langle\begin{matrix}\mathrm{L}\\ \mathrm{L}\end{matrix}\right) + 2\mathrm{L}$$



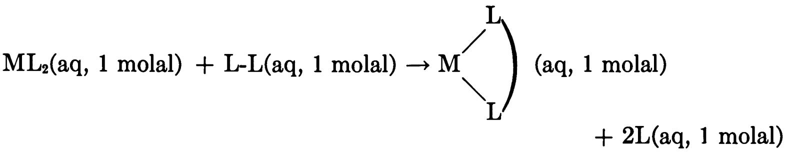
$$\textit{Chelate effect} = \log\left(K_{\mathrm{M}\left\langle\begin{smallmatrix}\mathrm{L}\\ \mathrm{L}\end{smallmatrix}\right)}/\beta_{\mathrm{ML_2}}\right) = \log\frac{2n'}{n-1} + \log a_{\mathrm{L}} \tag{3}$$

This model therefore predicts that forming a single chelate ring in solution will produce an increment of stability which is expressed by a relatively unimportant statistical factor, $\log(2n'/(n-1))$, and by the term $\log a_L$. This quantity is considerably greater than unity and was approximated by estimating the free volume of the uncoordinated ligand donor group with the aid of molecular models.

The same approach led to estimating the effect the size of the chelate ring has because the free volume would be greater as the distance between the two donor groups increases, and its effective concentration would decrease. The extreme case would involve a large distance between the donor groups so that the second group would be entirely free, and the chelate effect disappears completely.

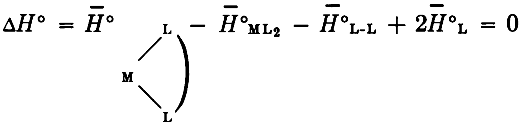
Translational Entropy Considerations

The above explanation of the chelate effect depends on the fact that a unit molal standard state is employed for all solute species. The heat and entropy of the replacement reaction correspond to those that would result from converting the reactants to products in their standard states:

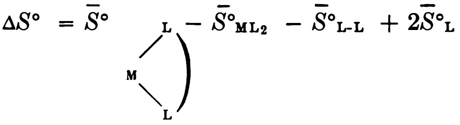


$$\mathrm{ML_2(aq,\ 1\ molal)} + \mathrm{L\text{-}L(aq,\ 1\ molal)} \rightarrow \mathrm{M}\!\left\langle\begin{matrix}\mathrm{L}\\ \mathrm{L}\end{matrix}\right) \mathrm{(aq,\ 1\ molal)} + \mathrm{2L(aq,\ 1\ molal)} \qquad (4)$$

The heat and entropy of this reaction can then be expressed in terms of the differences in partial molal heats and entropies of the individual species in solution:



$$\Delta H^\circ = \bar{H}^\circ_{\mathrm{M}\left\langle\begin{smallmatrix}\mathrm{L}\\ \mathrm{L}\end{smallmatrix}\right)} - \bar{H}^\circ_{\mathrm{ML_2}} - \bar{H}^\circ_{\mathrm{L\text{-}L}} + 2\bar{H}^\circ_{\mathrm{L}} = 0 \qquad (5)$$



$$\Delta S^\circ = \bar{S}^\circ_{\mathrm{M}\left\langle\begin{smallmatrix}\mathrm{L}\\ \mathrm{L}\end{smallmatrix}\right)} - \bar{S}^\circ_{\mathrm{ML_2}} - \bar{S}^\circ_{\mathrm{L\text{-}L}} + 2\bar{S}^\circ_{\mathrm{L}} \qquad (6)$$

If the differences in the internal and solvation entropies of these substances are neglected, the only remaining entropy would be the translational entropy, and ΔS° becomes the entropy of formation of one mole of solute at unit molality, corresponding to the formation of one metal chelate ring. For the formation of x chelate rings the translational entropy increase is given by:

$$\Delta S^\circ = xR\ell n\ 55.5 = 7.9x \qquad (7)$$

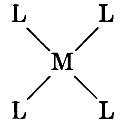
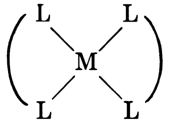
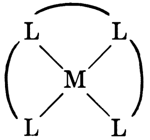
Thus, it is seen that the effect described by Schwarzenbach has precise thermodynamic meaning—the change in the entropy of translation that accompanies metal chelate ring formation. The entropy effects estimated by Schwarzenbach, up to 2.0 log K units, agree quite well with the value obtained with the thermodynamic approximation. Experimentally, one would expect wide deviations from this value (7.9 entropy units per chelate ring) because of the variations in solvation and internal entropies of complexes and ligands that occur in the displacement reaction.

The importance of translational entropies was first pointed out by Adamson (*1*) who recalculated the formation constants of a number of mono- and poly-amine complexes for a unit mole fraction standard state. This calculation showed that the chelates are no more stable than analogous complexes with fewer chelate rings. Thus, for the pure substances (having the same properties as the dilute solute species), there would be no stabilizing entropy of translation for each mole of product formed, and reactions in which the number of moles of product is greater than the number of moles of reactant would not be favored. Thus, it is seen that the chelate effect due to translational entropy applies only to reactions in solution, and that for pure substances (i.e., for the solid state) chelates are not favored over simple complexes.

Rather than consider reactions at unit mole fraction, standard states can be conceived at much lower concentrations than the usual one molal concentration. For example, if a standard state of 0.0010 molal were employed, the chelate effect would be quite large, 21.7 entropy units per mole of solute formed in solution or per metal chelate ring formed in the displacement reaction.

The fact that the translational entropy chelate effect is eliminated by changing the standard state from unit molal to unit mole fraction does not, of course, nullify the experimental reality of greater solution stabilities attendant to metal chelate ring formation. Whatever the standard state, the equilibrium constant itself shows the increasing disparity between chelate and complex stabilities as the compounds become more dilute. This effect, which is well known to everyone who has used equilibrium constants to calculate degrees of dissociation, is probably greater than one would ordinarily realize for dilute solutions. The effect of dilution on degree of dissociation, resulting from translational entropy effects, is illustrated in Table I. The examples given assume that $\Delta H°$ does not vary with the reactions shown, and that no steric effects prevent coordination. For purposes of comparison, if an arbitrary value of 10^{24} is selected for the stability constant of the metal chelate formed from the quadridentate ligand, the translational entropy chelate effect predicts approximately 10^{22} for the complex with one less chelate ring, and $\sim 10^{18}$ for the complex with no chelate rings, as is indicated in Table I.

Table I. Comparison of Degrees of Dissociation

Ligand	*Complex*	*No. of Chelate Rings*	*Quotient*
L		0	$\frac{[ML_4]}{[M][L]}$
L—L		2	$\frac{[M(L—L)_2]}{[M][L—L]^2}$
L—L—L—L		4	$\frac{[M(L—L—L—L)]}{[M][L—L—L—L]}$

Effect of Size of Chelate Ring

The Schwarzenbach model illustrated above, and a more sophisticated model described by Cotton and Harris (*6*), clearly show that the enhanced stability of a metal chelate compound due to the translational entropy effect should decrease as the distance between the two donor groups of a bidentate ligand increases. This conclusion is readily visualized with the aid of the proposed intermediate in the formation of the bidentate chelate, M—L—L*, described above. As the length of the chain between the bound donor group, L, and the uncoordinated donor group L* of the ligand increases, there is progressively less probability that the donor group L* will become coordinated with the metal ion. As the chain length increases, therefore, the translational freedom of L* (that eventually becomes restricted in chelate ring formation) becomes greater, so that the entropy decrease in the second step of the chelate formation reaction becomes progressively greater. Thus, the overall translational entropy increase in the displacement reaction decreases with increasing distance of separation of the two donor groups, until the effect of the second step finally cancels out the first, and the effective entropy increase finally drops to zero.

Although application of the Schwarzenbach and Cotton models to real systems generally failed to give agreement with experiment, there are many examples in the literature of the influence of ring size on stability. On the basis of the formation constants of the alkaline earth chelates of the EDTA homologs, represented by Formula VIII, Schwarzenbach and Ackerman (*16*) demonstrated as early as 1948 the remarkable influence ring size has

of Complexes and Chelates in Dilute Solution

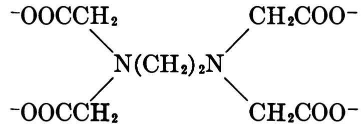
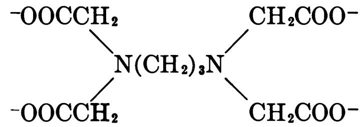
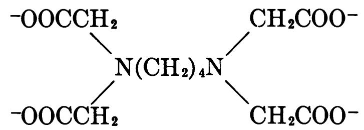
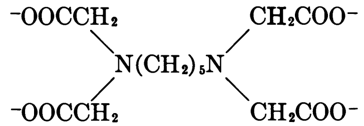
	1.0 M Complexes		*1.0 × 10^{-3} M Complexes*	
Value	*Free [M]*	*% Dissociation*	*Free [M]*	*% Dissociation*
10^{18}	1×10^{-5}	1×10^{-3}	1×10^{-4}	10
10^{22}	3×10^{-8}	3×10^{-8}	5×10^{-9}	5×10^{-4}
10^{24}	1×10^{-12}	10^{-10}	3×10^{-14}	3×10^{-9}

on stability. Their data were quite similar to the stability constants reported recently by Anderegg (*2*), given in Table II, and indicated a remarkable decrease in stability constant (e.g., ~10^6 for the Ca(II) chelate) as one goes from a five- to an eight-membered ring. The data in Table II, however, show that the stability decrease associated with increase in size of the chelate ring formed between the two nitrogen donor atoms (Formula VIII) is mainly an enthalpy effect, and that the entropy increase generally remains about the same as n varies from 2 to 4 (as the chelate rings increase from five- to seven-membered rings). However, these reactions are not analogous to the replacement reactions used for the models described above to illustrate the translational entropy effect. This is because they involve replacing water molecules by a ligand, rather than replacing one ligand by another.

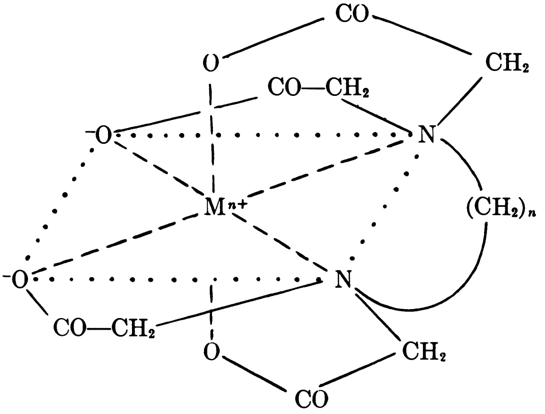
Enthalpy Changes Associated with Chelate Ring Formation

Williams (*22*) was the first to point out that decrease in enthalpy usually accounts for a considerable part of the stability increase associated with metal chelate formation. The thermodynamic data in Table III illustrate this effect for a series of ethylenediamine chelates relative to the corresponding metal ammines. The data show that in nearly all cases the increased stability of the metal diamine chelate over that of the amine is due largely to a more favorable heat of formation. This effect is considered due, at least in part, to a more positive heat of formation of the ligand

Table II. Thermodynamics of Formation

Ligand	*Log K,* *Mg*$^{+2}$
	8.8 3.5 51
	6.3 9.1 59
	6.3 8.5 54
	4.8

having the larger number of donor groups. Furthermore, it results from the overcoming of the mutual repulsions of the polar coordinating groups in the synthesis of the multidentate ligand. This situation produces a more favorable enthalpy change in coordinating the metal ion by the chelating ligand because formation of the complex with monodentate ligands will involve overcoming greater mutual repulsive forces between the donor



VIII. *Metal chelates of EDTA homologs*

of Metal Chelates of EDTA Homologs

ΔH° (*kcal./mole*) and ΔS° (*cal./degree·mole*)				
Ca^{+2}	La^{+2}	Ni^{+2}	Cu^{+2}	Zn^{+2}
10.8	15.6	18.7	18.6	16.3
−6.6	−2.8	−7.6	−8.2	−4.8
27	61	59	58	59
7.4	11.3	18.3	19.1	15.3
−1.7	3.8	−6.8	−7.7	−2.3
27	64	60	60	62
5.8	9.2	17.5	17.5	15.2
0.9	0.1	−7.0	−6.5	−3.5
30	42	56	57	57
4.6	—	13.6	—	12.8
		−8.5	—	−4.0
		34	—	44

groups. This "built-in" enthalpy effect which stabilizes metal chelates relative to analogous complexes should be an important part of the chelate effect and should increase with increasing polarity or charge on the donor groups of the multidentate ligand.

The operation of this enthalpy chelate effect may be seen in the variation of chelate ring size with stability illustrated in Table II. In all the examples given in this table, the decrease in stability, as the length of the chain between the iminodiacetate groups is increased from 2 to 4, is due mainly to changes in the enthalpy of reaction rather than changes in the entropy. Assuming that all the donor groups become coordinated to the metal ion, the main difference between the complex formation reactions involving different values of x is the difference in the distances between the charged donor groups of the free ligand in solution. As n increases, it is necessary to bring these groups together from greater distances to form the complex so that the coulombic repulsive forces that must be overcome become greater, and the formation of these complexes becomes less exothermic as the chain length increases. Therefore, it is seen that in a more compact ligand such as EDTA the internal mutual repulsive forces of the ligand donor groups are already partially overcome, and a more favorable enthalpy of chelate formation is "built-in" to the chelating ligand which forms the smallest (five-membered) rings.

Table III. Heats and Entropies of Formation of Ethylenediamine Chelates from Metal-ammines

Reaction	$-\Delta H°$ *kcal./mole*	$T\Delta S°$ *kcal./mole*
$Cu(NH_3)_2^{+2} + en \rightarrow Cuen^{+2} + 2NH_3$	1.3	−0.6
$Cu(NH_3)_4^{+2} + 2en \rightarrow Cu(en)_2^{+2} + 4NH_3$	5.1	−2.9
$Ni(NH_3)_2^{+2} + en \rightarrow Nien^{+2} + 2NH_3$	1.9	+1.2
$Ni(NH_3)_4^{+2} + 2en \rightarrow Ni(en)_2 + 4NH_3$	3.3	+5.6
$Ni(NH_3)_6^{+2} + 3en \rightarrow Ni(en)_3 + 6NH_3$	4.7	+6.3
$Cd(NH_3)_2^{+2} + en \rightarrow Cden^{+2} + 2NH_3$	−0.9	0
$Cd(NH_3)_4^{+2} + 2en \rightarrow Cd(en)_2^{+2} + 4NH_3$	1.0	+3.2

Entropy Effects Associated with the Combination of Positive and Negative Ions

Although the arguments given above indicate that a metal chelate compound should be more stable than the corresponding complex having fewer chelate rings, they do not predict that metal chelates will have exceptionally high solution stability. While high stability can be easily achieved through favorable enthalpy changes resulting from the formation of coordinate bonds with high covalent character, such is generally not the case for the more basic metal ions, such as the alkaline earths, that do not form strong coordinate bonds with donor groups in aqueous solution (i.e., that do not form significantly more stable complexes with aqueous bases than they do with water). For such metal ions, high chelate stabilities must be achieved, if at all, through entropy effects.

Williams (*22*) pointed out that favorable entropy increases occur whenever positive and negative ions combine in aqueous solution. This effect actually arises from the release of solvated water molecules that occurs in charge neutralization because the product is always much less hydrated than the reactants. Thus, in the reaction shown below $x + y - z$ is always considerably greater than unity.

$$M(H_2O)_x^{m+} + L(H_2O)_y^{n-} \rightleftharpoons ML(H_2O)_z^{(m-n)+} + (x + y - z)H_2O$$

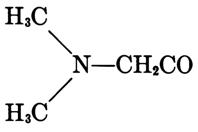
While it might seem that effects of this type should not influence the equilibrium constant, because solvent molecules are involved at about unit activity, the above reaction certainly involves an entropy increase because the number of particles on the right hand side of the equation is greater than that on the left. The effect shows up thermodynamically through the negative partial molal entropies assigned to both positive and negative ions. The entropies of aqueous ions become more negative as charge increases and as the size of the ion decreases, because both effects increase the polarization and orientation of water molecules about the ion. The larger complex ions have much higher entropies because of the neutralization of charge and reduction of solvation that occur on complex formation; therefore the combination of a positive metal ion with a negative ligand, both with low partial molal entropies, is accompanied by a stabilizing entropy increase.

An empirical relationship has been proposed by Powell and Latimer (*13*) for the partial molal entropies, $\bar{S}^\circ$, of aqueous ions:

$$\bar{S}^\circ = 3/2\, R\ln M + 37 - 270\, z/r_e^2 \qquad (8)$$

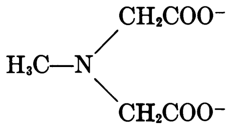
where M is molecular weight, z is charge of the ion, and r_e is the effective radius in Angstroms, equivalent to the crystal radius +2A. for cations, and crystal radius +1A. for anions. The direct consequence of this relationship is that with charge neutralization the negative entropy contributions of both metal ions and ligands disappear and that the effect increases as the sizes of the positive and negative ions decrease.

The entropies of formation of the 1:1 bivalent metal complexes of the structurally related ligands, Formulas IX–XIII, reported by Martell (*10*) show a linear correlation with the square of the reciprocal of the effective ionic radius of the metal ions, r_e, in Equation 8, and with the number of negative carboxylate groups of the ligand that combine with the metal ion.



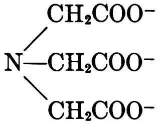
$\mathrm{(H_3C)_2N{-}CH_2CO}$

IX. *N,N-dimethylglycinate ion* L^-



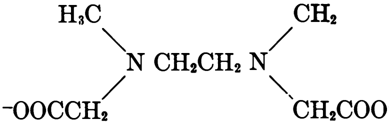
$\mathrm{H_3C{-}N(CH_2COO^-)_2}$

X. *N-methyliminodiacetate ion* L^{-2}



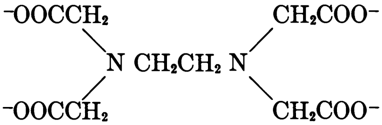
$\mathrm{N(CH_2COO^-)_3}$

XI. *Nitrilotriacetate ion-* L^{-3}



$\mathrm{(H_3C)(^-OOCCH_2)N\ CH_2CH_2\ N(CH_2)(CH_2COO^-)}$

XII. *N,N′-dimethylethylenediaminediacetate ion,* L^{-2}



$\mathrm{(^-OOCCH_2)_2N\ CH_2CH_2\ N(CH_2COO^-)_2}$

XIII. *Ethylenediaminetetraacetate anion,* L^{-4}

The radius of the ligand donor group does not enter into the correlation since only one type of donor, the carboxylate group, is involved in charge neutralization with the metal ion (i.e., the value of r_e for the carboxylate group remains constant). The agreement between the coordination entropies, effective metal ion radii, assuming reasonable numbers of metal-carboxylate bonds form, is indicated in Table IV and illustrated graphically in Figure 1. The correlation shown is remarkable in that it is the first correlation of this type in which the variation of several ligands and many metal ions are included in the same linear relationship. The success of the correlation provides support for the coordination numbers

Table IV. Correlation of Entropy of Chelate Formation with Radius of Metal Ion and Effective Charge of Ligand[a]

Ligand Anion	*Divalent Metal Ion*	ΔS *(e.u.)*	*r, A.*	*Ligand Coord. Number*	*Ze*	Ze/r_e^2
EDTA	Mg	52	0.65	6	4	1.47
(XIII)	Ca	29	0.99	5	3	0.76
	Sr	26	1.13	5	3	0.66
	Ba	22	1.35	5	3	0.54
	Mn	48	0.80	6	4	1.23
	Fe	51	0.75	6	4	1.31
	Co	58	0.72	6	4	1.35
	Ni	57	0.69	6	4	1.40
	Cu	56	0.65	6	4	1.47
	Zn	57	0.74	6	4	
	Cd	41	0.97	6	4	1.03
	Hg	36	1.10	6	4	0.91
	Pb	35	1.21	6	4	0.82
NTA	Mg	44	0.65	4	3	1.10
(XL)	Ca	32	0.99	4	3	0.76
	Ba	24	1.35	4	3	0.54
MIMDA	Mg	25	0.65	3	2	0.73
(X)	Sr	21	1.13	3	2	0.44
	Mn	26	0.80	3	2	0.62
DMEDDA (XII)	Mg	31	0.65	4	2	0.73
DMG (IX)	Mg	16	0.65	2	1	0.36

[a] r = Pauling ionic radii, A.; r_e = ionic radius + 1.0 A.; Ze = number of coordinated negative carboxylate groups of ligand.

assumed in Table IV, and for the concept that the entropy increase associated with positive and negative ion combinations is a major factor in determining the stabilities of complexes.

It should be pointed out that this entropy may be much greater, especially for highly charged ions, than that associated with the entropy

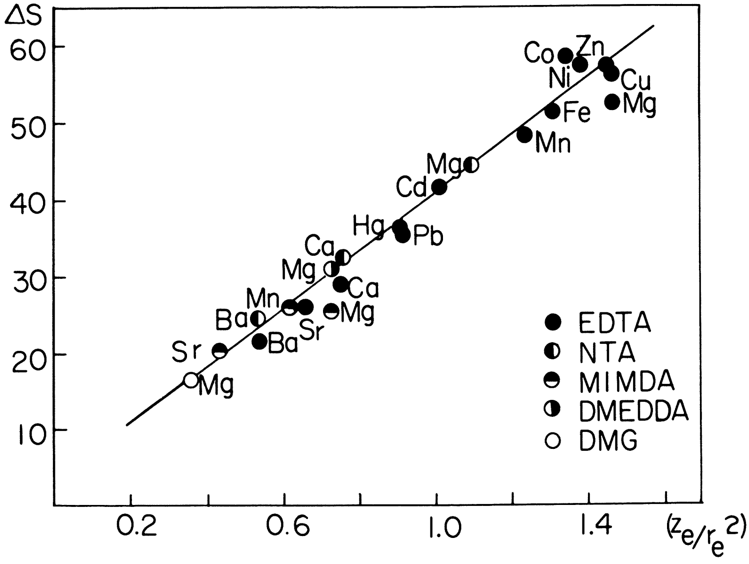


Figure 1. Correlation of entropies of formation of aminopolycarboxylic acid chelates in aqueous solution with effective radius of the metal ion, r_e, and number of negative carboxylate groups of the ligand, Z_e, that become coordinated with the metal ion; r_e = crystal (Pauling) radius + 1.0 A.; EDTA = ethylenediaminetetraacetic acid; NTA = nitrilotriacetic acid; MIMDA = N-methyliminodiacetic acid; DMEDDA = N,N'-dimethylethylenediaminediacetic acid; DMG = N,N-dimethylglycine

of dilution described above. In the relationship given in Equation 4, the number of water molecules displaced in the process of charge neutralization and coordination is usually more and can be very much more than one would predict if water were merely an unidentate ligand that is replaced by the ligand under consideration. This effect is due to the fact that highly charged ions may have more than one layer of solvated, highly oriented water molecules displaced by coordination. This factor, which results from rapidly increasing solvation with ionic charge, is taken into account in the empirical entropy relationship, Equation 8, through the appearance of an additional factor, the reciprocal of the effective ionic radius, r_e, which increases rapidly with ionic charge.

Although ligands are usually less strongly solvated than metal ions, ligand solvation may also contribute significantly to the entropy increase that occurs through the loss of water on coordination. This effect would be expected to be greatest for small, relatively compact ligands having high negative charge.

The entropy increase associated with the coordination of metal ions by negative ligands, of the type illustrated in Figure 1 and Table IV, may be used to indicate the number of coordinate bonds formed, provided that comparisons are made between similar coordinating groups. As the length of the carbon chain between the iminodiacetate groups in Formula VIII increases, it is inevitable that the tendency for both iminodiacetate groups to combine with the metal ion eventually decreases, giving a less favorable entropy effect and making the ligand terdentate rather than sexadentate. Formerly, when only stability data were known for such substances (*16*), it was thought that this structural change was the reason for the drop in stability observed (e.g., for the Ca^{+2} ion) as the number of carbon atoms in the bridge increases from 2 to 4. Now, however, because of the availability of heats and entropies of reaction (*2*), it is seen that the observed drop in stability is an enthalpy effect and, that for all metal ions listed, the entropy increase is maintained quite constant as the number of bridging carbon atoms increases from 2 to 4 (i.e., as one goes from five- to seven-membered chelate rings). Only when the chelate ring increases to eight members does a drop in the entropy of complex formation occur. Thus, the data in Table II may indicate that sexadentate complexes of similar structure are formed for all metal ions and for all ligands illustrated, regardless of whether five-, six-, or seven-membered chelate rings are formed by the two nitrogen atoms. Only for the highest homolog shown is there any serious doubt about the structure of the aqueous chelate and the possibility that not all donor groups of the ligand become coordinated to the metal ion.

This discussion of the data in Table II demonstrates the importance of obtaining enthalpies and entropies of reaction to gain an understanding of the nature of chelate ring formation in aqueous solution. In the absence of absolute structural proofs, the number of chelate rings formed in solution can only be inferred from thermodynamic data. The examples in Table II show that the ideas resulting from stability data alone may be misleading and can lead to different conclusions than one would draw on the basis of more complete thermodynamic data.

Entropy and Enthalpy Changes Associated with Steric Effects

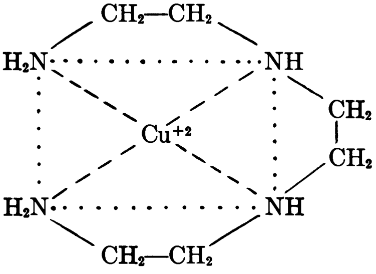
Steric influences on the heats and entropies of chelate formation may arise from the difficulty encountered by the ligand in assuming the conformation most suitable for effective coordination of a metal ion. Examples of this effect may be seen in the data given in Table V for tetracoordination of Cu^{+2}, Ni^{+2}, and Zn^{+2} by polyamines (*12, 14*). Probable structures of these complexes are represented by Formulas XIV–XVII. It is interesting that the main differences between the stabilities of the tren and trien complexes are due to differences in enthalpies, rather than in entropies, of reaction. Of the two sets of chelate compounds, those of Zn(II) represent the more nearly "normal" situation because all four donor groups of each ligand can coordinate to the metal ion with little strain. The remarkable difference between the enthalpies of formation of Chelates

XVI and XVII must be due to the more compact structure of the uncoordinated ligand, triaminotriethylamine, "tren," and the fact that forming corresponding Chelate Compound XVII requires that lower mutual repulsive forces between the donor groups of the ligand be overcome, which is not the case for the formation of XVI. For the latter compound, the uncoordinated ligand must exist in an extended form in solution, with the donor groups much farther apart on the average.

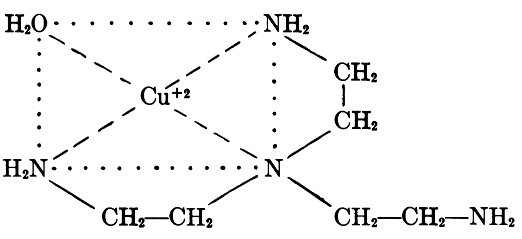
Table V. Molar Heats and Entropies of Formation of Metal Chelates of Triethylenetetramine (Trien) and β,β′,β″-Triaminotriethylamine (Tren)

Reaction	$-\Delta H°$, *kcal./mole*	$T\Delta S°$, *kcal./mole*
Cu^{+2} + trien	21.6	5.8
Cu^{+2} + tren	20.4	5.4
Zn^{+2} + trien	8.9	7.5
Zn^{+2} + tren	13.8	5.8

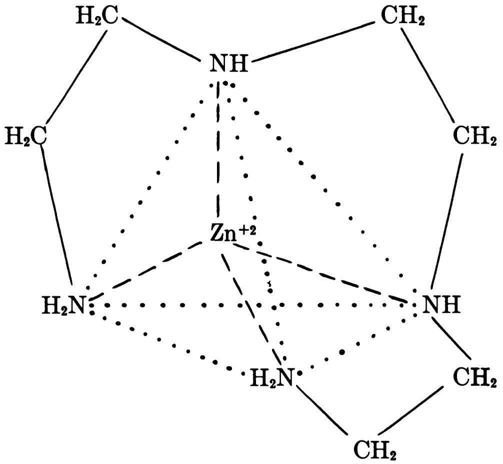
A similar enthalpy difference must exist for the copper(II) chelates, XIV and XV, if one considers the fact that only three donor groups can be strongly bound to Cu(II) in XV. (The fourth amino group may be weakly bound in one of the octahedral positions at right angles to the plane of strong coordination containing three nitrogens and one oxygen.) Thus, it is seen that the enthalpy of coordination per nitrogen atom is again much greater for the tren chelate and is probably due to a greater enthalpy



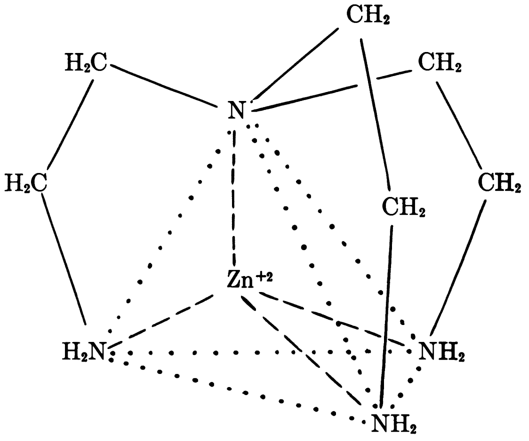
XIV. *Cu(II)-trien chelate*



XV. *Cu(II)-tren chelate*



XVI. *Zn(II)-trien chelate*



XVII. *Zn(II)-tren chelate*

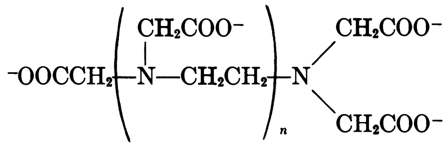
chelate effect of the type described above for the Zn(II) tetramine chelates, as well as for the ethylenediamine homologs in Table II.

The entropy changes observed for the formation of Chelates XIV-XVII are not so easily rationalized. Certainly the entropy increase per ligand donor group for XV is greater, as one would expect, than that of XIV, because the formation of the former compound would require less change in the conformation of the ligand in the course of coordination. The reason for the lower value of $\Delta S°$ for the formation of Formula XVII is not apparent and may be considered anomalous. It is possible, however, that the much tighter coordinate bonding in this complex may reduce the internal vibrational and rotational freedom of the coordinate ligand to the point where the overall entropy change becomes unfavorable. In fact, this type of reciprocal relationship between entropies and enthalpies of coordination is emerging as a general phenomenon as more thermodynamic data become available. Tight bonding, resulting in a favorable heat of reaction, produces an unfavorable entropy change by virtue of reducing the configurational entropy that strong coordinate bonding produces. On the other hand, a less favorable heat of complex formation resulting from the presence of weak coordinate bonds allows that considerable configurational entropy be retained in the complex, thus producing a more favorable entropy change for the coordination reaction.

Many other examples of steric effects are compiled in recent equilibrium data (*17*), and many of the observed effects are apparently due to enthalpies and entropies of formation of the free ligand in solution. For this reason, more reliable data on heats and entropies of chelate formation and on heats and entropies of formation of metal ions and ligands in solution should be accumulated for developing further understanding of the chelate effect.

Stabilities of NTA and EDTA Analogs

Recently new data have become available on the stabilities of metal chelates formed from NTA and EDTA analogs, represented by XVIII, through the publication of equilibrium data on the chelates of two higher members of the series, triethylenetetraminehexaacetic acid (TTHA) and tetraethylenepentamineheptaacetic acid (TPHA) (*3*, *4*). The stabilities of some representative metal chelates of the series of ligands represented by Formula XVIII are listed in Table VI.

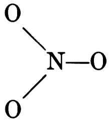
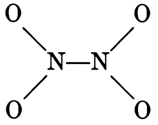
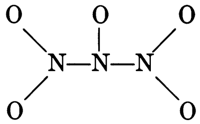
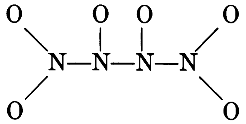
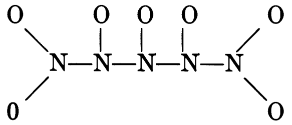


XVIII. *Analogs of NTA and EDTA*

Analysis of the data in Table VI shows that for divalent metal ions of coordination number ~6, the maximum stability is reached with the third member of the series, and that the metal ion affinity of the ligand as a whole decreases somewhat beyond that point. Since the enthalpy and entropy factors described above should favor higher stability as the number of donor groups and ionic charge of the ligand increases, the decrease in stability for values of *n* of 3 and 4 must be due to unfavorable enthalpy, and perhaps entropy, factors required to overcome mutual repulsions of the

Table VI. Structural Analogs of NTA and EDTA

(t = 25°C.; μ = 0.10)

			Log Formation Constants of 1:1 Chelates			
n^a		*Ligand*	*Ca*$^{+2}$	*Cu*$^{+2}$	*La*$^{+3}$	*Th*$^{+4}$
0	NTA		6.57	12.96	10.47	12.4
1	EDTA		10.4	18.7	15.2	23.2
2	DTPA		10.7	21.1	19.5	≳27
3	TTHA		9.9	20.3	23.1	≫27
4	TPHA		~9.0	~20	>27	≫27

[a] n corresponds to n in Formula XVIII.

ligand donor groups in forming the chelate. Since only a fraction of the donor groups of the higher members of the ligand series is employed in coordinating divalent metal ions, the change in conformation on coordination must alter the energetically more favorable positions that all the donor groups of the free ligand occupy in solution. Determining the heats and entropies of formation of these complexes would be helpful in obtaining a more detailed picture of the nature of the stability variations observed.

It is interesting to note that for metal ions having high coordination numbers (i.e., for tri- and tetravalent metal ions), the stabilities continue to increase for all ligands in the series. Apparently the increased enthalpy and entropy effects resulting from additional coordination more than compensate for the mutual repulsions of the ligand donor groups and the additional strain of forming a large number of chelate rings from a single ligand.

Conclusions

A more complete analysis of the entropies and enthalpies of ligand donor group orientation, ring closure, internal repulsions resulting from ring formation, and vibrational rotational freedom is beyond the scope of this paper. Although these effects have been discussed (*5*, *8*, *21*), the precise application of these concepts to metal chelate ring formation in solution is not yet possible because of their inherent complexity and present uncertainties about the partial molal enthalpies and entropies of complex organic ligands in solution.

Table VII. Factors Influencing Solution Stabilities of Complexes

Enthalpy Effects	*Entropy Effects*
Variation of bond strength with electronegativities of metal ions and ligand donor atoms.	Number of chelate rings.[b]
Ligand field effects.	Size of the chelate ring.[b]
Steric and electrostatic[b] repulsions between ligand donor groups in the complex.	Changes of solvation on complex[b] formation.
Enthalpy effects related to the[a] conformation of the uncoordinated ligand.	Arrangement of chelate rings.[b]
Other coulombic forces involved in chelate ring formation.	Entropy variations in uncoordinated ligands.
	Effects resulting from differences in configurational entropies of the ligand in complex compounds.

[a,b] Effects are either unique for metal chelate ring formation, as contrasted to coordination by unidentate ligands, or are factors which are considerably different when chelation is involved.

[b] Factors considered most important in view of this paper. For further information, refer to text.

The above table contains a relatively complete list of the factors involved in determining enthalpies and entropies of metal chelate formation in aqueous solution. Of these, the effects designated by footnote *a* are either unique for metal chelate ring formation, as contrasted to coordination by unidentate ligands, or are factors which are considerably different when chelation is involved.

These factors may now be considered the basis for the differences in solution stabilities of metal complexes and chelate compounds and account for the chemical phenomena summarized in the term "chelate effect." Those factors that emerge as the most important in light of this paper are designated in Table VII as footnote *b*.

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20

Linkage Isomerism

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A ligand which contains more than one coordinating group can bond to metal ions in more than one way; however, if only one of the coordinating groups can combine with a particular metal at one time, the ligand is called "ambidentate" and may form linkage isomers, differing only in the point of ligand attachment. The first mononuclear pair (the xantho and isoxantho ions $[Co(NH_3)_5,NO_2{}^{+2}]$*) was prepared in 1857. The second was characterized in 1962. Since then, 10 or so pairs of complexes exhibiting the phenomenon called by Werner "salt isomerism" have been found by reinvestigating older literature preparations, by applying synthesis concepts based on mechanism studies, or by examining series of complexes containing related ligands differing in their class a or class b affinities.*

A ligand which contains two different donor groups, only one of which can coordinate to a particular metal ion at one time, is termed "ambidentate." Such ligands give rise to complexes exhibiting linkage isomerism. The complexes have the same geometric configuration, and their only difference lies in the point of attachment of the ligand; hence, the isomerism is quite distinct from flexidentate chelation (*11*), which involves multidentate ligands using varying numbers of coordinating groups. Linkage isomerism involving chelating ligands is extremely uncommon but not unknown (*15*).

Historical

Although the xantho and isoxantho complexes of cobalt(III) having the composition $(NH_3)_5CoNO_2.X_2$ (where X = Cl or $\frac{1}{2}SO_4$) had been known for some time (*17, 21, 22*), Werner was the first to recognize that the pair constituted one example of a more general phenomenon and, accordingly, included salt isomerism (*43*) in his seven-fold complex classification. Early assignments of structure were based on color and relative stabilities, and more recent infrared studies have confirmed (*26*, *30*) that the xantho complex contains the nitrite group bonded through the nitrogen, while the isoxantho complex contains the nitrite bonded through one oxygen. An investigation (*28*) of the mechanism of formation of the nitrito (isoxantho) complex and its subsequent isomerization to the more stable nitro isomer led to the conclusion that the reaction involves attack by dinitrogen trioxide (the anhydride of nitrous acid) on hydroxypentaamminecobalt(III).

$$(NH_3)_5CoH_2O^{+3} + H_2O \rightleftharpoons (NH_3)_5CoOH^{+2} + H_3O^+$$

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O$$

$$(NH_3)_5CoOH^{+2} + N_2O_3 \rightarrow (NH_3)_5CoONO^{+2} + HNO_2$$

Oxygen tracer experiments (*25*) confirmed that the cobalt-oxygen bond remained intact throughout the reaction. The nitrito complexes of pentaamminerhodium(III), pentaammineiridium(III), and pentaammineplatinum(IV) have been obtained by the same method (*5*). In a similar way, adding sulfur dioxide or sodium sulfite to solutions of aquopentaamminecobalt (III) ion at low temperatures and low pH yields the unstable pink oxygen-bonded sulfito complex rather than the stable yellow-brown sulfur-bonded isomer.

A second approach has been developed for preparing linkage isomers—that of deliberately modifying the bonding characteristics of the central metal ion through coordination with ligands such as triphenylarsine; in this way the palladium(II) complexes of nitrogen- and sulfur-bonded thiocyanate have been obtained (*8*).

In some cases the synthesis has yielded a mixture of the two linkage isomers; this is certainly the case with thiosulfatopentaamminecobalt (III) chloride (*32*) and possibly with hydrogen thiosulfatopentacyanocobaltate (III) also (*34*). It has also been found that an equilibrium between the two isomers is sometimes established in the solid (*6*) or in solution (*19*, *40*, *44*); in the latter the position of equilibrium depends greatly on the solvent.

Constituent Parts of Linkage Isomers

Metal Ions. Metal ions may be divided into two groups: (a) those that form their most stable complexes with ligands bonding through the first atom of any group in the periodic table and (b) those which form their most stable complexes with ligands bonding through subsequent atoms of any periodic group (*3*). The transition between a and b type behavior is more or less gradual, and b metals are found clustered in the later stages of each transition series, occupying a triangular area (the

Chatt-Leden triangle (*23*)) in the periodic table, with the most pronounced class b behavior shown by elements in its center:

		Cu	
Rh	Pd	Ag	
Ir	Pt	Au	Hg

Some elements (for example, Mn, Fe, Co, Ni; Mo, Tc, Ru, Cd; W, Re, Os, Tl, Pb, Bi, Po) show varying degrees of a and b character and fall in a borderline region of rather diffuse boundary. Factors influencing metal behavior in this region seem to be oxidation number (*20*), the resulting electronic configuration (copper(I) shows class b tendencies while copper(II) is borderline), or the other ligands associated with the metal in its complexes. The most numerous examples of linkage isomerism are expected among complexes of metals of this borderline group or of metals showing weak class a or class b behavior, with the further requirement that at least for pure preparations of the individual isomers, the complexes must be inert (d_3, low-spin d^6, d^8 systems). It is not surprising then that the isomerism has been observed for complexes of cobalt(III), rhodium(III), iridium(III), platinum(IV), and manganese (I) (all d^6) and of palladium(II) and platinum(II) (d^8) in the solid state, but not for complexes of chromium(III) or iron(III), and for cadmium(II) only in solution.

The Ligands. In general, the coordinating centers of an ambidentate ligand will not possess the same affinity for a particular metal ion; the more polarizable and larger the coordinating atom or group and the more empty orbitals it possesses, the greater its affinity for class b metals, while the smaller the atom or the more π electrons available for donation to the metal, the greater its affinity for class a metals. Class a affinity increases from left to right in the periodic table and from bottom to top, so that thiocyanate bonds to class a metal ions through the nitrogen atom but to class b metal ions through the sulfur; the point of attachment of this ligand has, in fact, been used to establish the class behavior of a number of metal ions. Table I lists the ligands that have been found in linkage isomers, and Table II lists some other common ambidentate ligands and representative complexes. It may be seen that (with the exception of the selenocyanate ion) all the anions use one of the adjacent atom pairs in bonding.

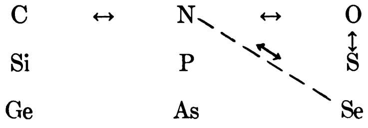


Table I. Ligands Known to Form Linkage Isomers

Ligand		*Complex*	*Metal*	*Reference*
Nitrite	M—N, M—O	$(NH_3)_5MX^{+2}$	Co	*21, 22, 30, 43*
			Rh, Ir, Pt	*5*
	M—N, M—O	$en_2MX'X^+$	Co	*4*
Thiocyanate	M—N, M—S	$(bipy)MX_2$	Pd	*8*
	M—N, M—S	$(As(C_6H_5)_3)_2MX_2$	Pd	*8*
	M—N, M—S	MX_4^{-2}	Cd	*19, 40*
	M—N, M—S	$(CO)_5MX$	Mn	*44*
Sulfite	M—S	$(NH_3)_5MX^+$	Co	*27*
	M—O	$(NH_3)_5MX^+$	Co	*39*
Thiosulfate	M—S, M—O	$(NH_3)_5MX^+$	Co	*32, 33*
Cyanide	M—C	MX_6^{-3}	Co, Cr, Fe, Mn	*7, 13, 18*
	M—C, M—N	$MX_5'X^{-3}$	Co	

Clearly, the smaller the differences in affinities of the coordinating groups, the more probable the formation of linkage isomers. Examining the two tables also suggests that anions containing nitrogen and phosphorus or sulfur and selenium atoms might well participate in linkage isomerism.

Table II. Other Ligands Exhibiting Ambidentate Behavior

Ligand		*Complex*	*Metal*	*Reference*
Urea	M—O	MCl_2X_2	Cu, Zn	*31*
	M—N	MCl_2X_2	Pd, Pt	*31*
	M—O	MCl_4X_2	Sn, Ti	*12*
	M—N	MBr_4X_2	Sn	*12*
	M—O	MX_6^{+3}	Cr, Fe	*31*
Thiourea	M—N	MCl_4X_2	Ti	*35*
	M—S	MCl_2X_2	Pt, Zn	*45*
	M—S	MCl_4X_2	Sn	*12*
	M—S	MX_4^{+2}	Pd, Pt	*45*
Selenocyanate	M—N	$(NH_3)_5MX^{+2}$	Co	*9*
	M—Se	$(bipy)MX_2$	Pd, Pt	*9*
	M—N	MX_4^{-2}	Co, Fe, Zn	*10, 42*
	M—Se	MX_4^{-2}	Hg, Pd, Pt	*10, 42*
	M—N	MX_6^{-n}	Cr(III), Y(III), Ni(II)	*10*
	M—Se	MX_6^{-n}	Rh(III), Pt(IV)	*10, 42*
Dimethyl sulfoxide	M—O	MCl_2X_3	Co, Ni	*16, 37*
	M—O	MCl_2X	Cd, Hg	*16, 37*
	M—S	MCl_2X_2	Pd, Pt	*16, 37*
	M—O	MCl_2X_2	Cu	*16, 37*

The other ligands present in the complex can affect the isomerism in two ways: they can modify the class behavior of the metal, and they can impose steric restrictions on the coordination site of the ambidentate ligand.

Of the two, the steric effect is easier to understand—i.e., the closer that bulky ligands can come to the metal the less space left for the ambidentate ion and the more favorable a less branched configuration for the ligand becomes (*8*, *44*). Sulfur-bonded thiocyanate, because of its angular M—S—CN structure, has larger steric requirements than the nitrogen-bonded, with linear M—N—CS. Thus, while platinum(II) (because of its class b tendencies) shows the expected sulfur bonding to thiocyanate in $(NH_3)_2Pt(SCN)_2$, this changes to nitrogen bonding when the ammonia groups are replaced by the larger triphenylphosphines. In contrast, replacing the latter by triphenylstibines once more permits sulfur bonding because the phenyl groups are further away from the central metal, and steric hindrance is decreased.

It is more difficult to account for the electronic effect, partly because it is not easy to investigate without accompanying changes in steric effects. It has been suggested (*20*) that the more ligands of high class b affinity that are associated with a particular metal the more b-like the metal becomes and the greater its affinity for still more ligands of this type; for example, the fluoro complex is the most stable of the pentaamminecobalt (III) halides and the iodo the least stable, while the iodo is the most stable of the pentacyanocobalt(III) halides, and the fluoro complex is not known. By itself this idea of "inorganic symbiosis" is of limited applicability because the stable form of the selenocyanatopentacyanocobaltate(III) ion is the nitrogen-bonded form and not the selenium-bonded isomer as would be predicted (*9*). Another suggestion is that (*44*) an increase in negative charge at the metal increases the class a character—an idea that is in apparent conflict with the "hard-soft" concept (*29*), and while it does explain the bonding in the selenocyanatopentacyanocobaltate(III) ion, it does not explain the bonding in thiocyanatopentacyanocobaltate (III). The third hypothesis (*41*) is that π-electron acceptor ligands in the complexes tend to reduce the electron density about the central metal, enhancing its class a behavior; support for this is found in the thiocyanato complexes of platinum(II) and palladium(II). There is no one theory at present which will adequately cover all the experimental observations, but in spite of this a preliminary survey of series of complexes containing ligands varied in some systematic way appears to be a powerful tool in preparing linkage isomers.

Structure Determination and Rates of Isomerism

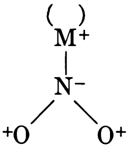
Most structures have been assigned on the basis of the infrared absorption spectra of the complexes, taking into account both the symmetry of the ligands involved and the spectra of related ions. Table III lists the various peaks which have been used in the determinations, together with their (tentative) assignments. Frequencies have been used in the past

Table III. Infrared Assignments

Ligand	*Vibration and Frequency, cm.*$^{-1}$			*Example*	*Reference*
Nitrite		$\nu_s(NO_2)$			
		1375		CH_3-NO_2	
		1310		RCo-NO_2^{+2a}	*26*
		1420		RRh-NO_2^{+2}	*5*
		1410		RIr-NO_2^{+2}	*5*
		1330		RPt-NO_2^{+3}	*5*
		1065		RCo-ONO^{+2}	*26*
		1048		RCr-ONO^{+2}	*26*
		1060		RRh-ONO^{+2}	*5*
		1065		RIr-ONO^{+2}	*5*
		995		RPt-ONO^{+3}	*5*
		1250		$NaNO_2$	
		814		*trans*-CH_3-ONO	
		794		*trans*-H-ONO	
Thiocyanate	$\nu(C\text{-}N)$	$\nu(C\text{-}S)$	$\delta(N\text{-}C\text{-}S)$		
	2072	837	482	$Zn(NCS)_4^{-2}$	*36*
	2065	844	481	$Co(NCS)_4^{-2}$	*36*
	2089	844	—	$PdY_2(NCS)_2^a$	*8*
	2100	842	—	Pd(bipy)$(NCS)_2$	*8*
	2119	—	—	$PdY_2(SCN)_2$	*8*
	2117	700	—	Pd(bipy)$(SCN)_2$	*8*
	2109	698	429	$Pd(SCN)_4^{-2}$	*36*
	2100	697	427	$Pt(SCN)_4^{-2}$	*36*
	2127	695	427	$Au(SCN)_4^{-2}$	*36*
Sulfite	δ_{as}(O-S-O)	ν_s(S-O)	δ_s(O-S-O)		
	970	970	498		
	983^b	947^b		Na_2SO_3	*27*
	1050–1150	960	519	RCo-SO_3^+	*27*
	(902, 862)	(989)	(460)	RCo-OSO_2^+	*27*
Thiosulfate	ν_s(S-O)	ν(S-S)			
	995	446		$NA_2S_2O_3$	
	997	424		RCo-$OS_2O_2^+$	*32*
	1010	415		RCo-SSO_3^+	*32*
	1030	412		CH_3-SSO_3^-	*38*

[a] R = $(NH_3)_5$; Y = $As(C_6H_5)_3$.
[b] Raman spectrum.

as a measure of the bond order M—X; in general, the higher the frequency, the greater the bond order. In the nitro complexes, for example, the symmetric and antisymmetric —NO_2 stretching, the —NO_2 wagging, and the M—N stretching bands all show the same trends (*26*), giving increased bond order along the sequence Ni(II), Co(III), Pt(II). The NO_2 stretching frequencies are considerably different in the nitrito and nitro complexes, and further, the nitrito lack the wagging vibration, ν_6, as shown below.



The infrared spectra of thiocyanates have been used for some time to determine M—S or M—N bonding and, thus, the class behavior of the metal ions; in a number of cases the assignments have been confirmed by x-ray analysis. The C—S stretching absorption occurs around 830 cm.$^{-1}$ in nitrogen-bonded complexes, considerably higher than in the sulfur-bonded (*ca.* 700 cm.$^{-1}$), reflecting the greater double bond character of C—S in M—N=C=S than in M—S—C≡N. Unfortunately, a number of organic ligands (particularly those with a pyridine system) also absorb in the region, and recent work suggests (*36*) that the N—C—S bending vibration may be more useful in structure assignment; one band is found near 475 cm.$^{-1}$ in *N*-thiocyanato complexes, whereas there are three or four bands in the spectra of sulfur-bonded complexes, with the most intense lying near 420 cm.$^{-1}$ Presumably, the greater number of peaks in the latter is caused by the nonlinear M—S—CN structure.

The absorption spectrum of $(NH_3)_5CoOSO_2^+$ has not yet been recorded in the literature, but it is likely to be similar to the spectrum of $Cu(SO_3)_2^{-2}$. The values listed for the absorption frequencies under $RCoOSO_2^+$ in Table III are those for the copper(II) complex (*27*). Sulfite ion possesses C_{3v} symmetry, and this is retained in the sulfur-bonded complexes—i.e., coordination through oxygen should lower the symmetry to C_3 and so remove the degeneracy of the ν_3 (asymmetric) stretching of the SO_2 group. Accordingly, the spectrum of the *S*-sulfitopentaamminecobalt(III) ion should (and does) show only two S—O stretching peaks while that of the *O*-sulfitopentaamminecobalt(III) ion should show three.

A pure sample of the sulfur-bonded thiosulfatopentaamminecobalt(III) ion has not yet been obtained. The usual method of preparation yields a mixture of the isomers, with the oxygen-bonded in nine-fold excess. Differential electron transfer experiments have shown that the ratio can be decreased to 2:1, and the assignment of structure has been based on these experiments and the changes observed in the infrared spectrum at 1000 and 420 cm.$^{-1}$

The rates of isomerization have been determined for complexes in solution by following changes in the visible absorption spectra (*2*), and in the solid state by following the disappearance of infrared absorption bands or by dissolving samples of the complex at various times in water and measuring the visible spectra. Some of the specific rates are listed in Table IV; in general, rates of isomerization are greater in solution than in the solid state (*1*) and appear to be independent of the nature of the anion

Table IV. Specific Rates of Isomerization

Metal	*Anion*	*State*	*Temp., °C.*	*Specific Rate, 10^5k, sec.$^{-1}$*	*Reference*
		$-ONO \rightarrow -NO_2$			
Co(III)	NO_3	solid	25	0.80	*1*[a]
	Cl	solid	25	0.19	*1*[a]
			50	3.5	*6*[a]
	Cl	soln.	25	3.2	*2*[a]
	NO_3	soln.	25	7.7	*28*
Rh(III)	Cl	solid	25	7.5	*5*[a]
	Cl	soln.	25	96	*5*
Ir(III)	Cl	solid	50	33	*5*
	Cl	soln.	25	4.4	*5*
			50	67	*5*
Pt(IV)	Cl	solid	50	8.4	*5*[a]
	Cl	soln.	25	5.6	*5*
		$-NO_2 \rightarrow -ONO$			
Co(III)	Cl	solid	50	7.4	6[a]
		$-SCN \rightarrow -NCS$			
Pd(II)	—	solid	125	3.3	*8*[a]
			150	8.6	*8*[a]

[a] Calculated from data in paper.

unless this is also the ambidentate ligand (*28*). The rates are first order, and over a fairly wide range they are not affected by acid concentration or by changes in ionic strength. Isomerization of nitritopentaammine-rhodium(III) is more rapid than might be expected (the reason for this is not known), and conversion to the nitro complex proceeds to completion.

This contrasts with the corresponding cobalt(III) complex—i.e., in the solid state the two isomers are in equilibrium, and the specific rates for the forward and reverse processes (*see* below) measured (*6*) at a number of different temperatures suggest that earlier values (*2*) give ($k_1 + k_2$) rather than k_1 alone.

$$(NH_3)_5CoONO^{+2} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (NH_3)_5CoNO_2^{+2}$$

The rate of isomerization of the sulfur-bonded dithiocyanatobis(triphenylarsine)palladium(II) takes place so rapidly in solution that a visible absorption spectrum cannot be obtained. In the solid state the rearrangement is much slower (30 minutes at 156°C.) and is even slower when the solid is incorporated at low concentration in a potassium bromide disc, with a half-life of 130 minutes at 150°C. This decrease on going from the

Table V. Specific Rates of Electron Transfer

Complex	*Reductant*	*Temp., °C.*	*k, M^{-1} sec.$^{-1}$*	*Reference*
$(NH_3)_5CoOSO_3^+$	Cr(II)	25	18	*32*
$(NH_3)_5CoSO_3^+$	Cr(II)	25	18.6	*32*
$(NH_3)_5CoOS_2O_2^+$	Cr(II)	25	13.3	*32*
$(NH_3)_5CoSSO_3^+$	Cr(II)	25	0.18	*32*
$(NH_3)_5CoONO_2^{+2}$	Eu(II)	25	160	*24*
$(NH_3)_5CoNO_2^{+2}$	Eu(II)	25	100	*24*
$(NH_3)_5CoONO^{+2}$	Eu(II)	25	75	*24*

pure solid to the diluted solid does not occur with the nitrite complexes· Specific rates are listed in Table IV.

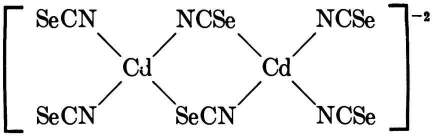
The sulfur-bonded thiocyanatopentacarbonylmanganese(I) rearranges to the nitrogen-bonded isomer in five minutes when dissolved in acetonitrile at 25°C. Adding petroleum ether will precipitate this latter complex as a yellow powder; if this is suspended in Nujol at 25°C., conversion back to the sulfur-bonded complex takes place within five hours (*44*).

Reactions

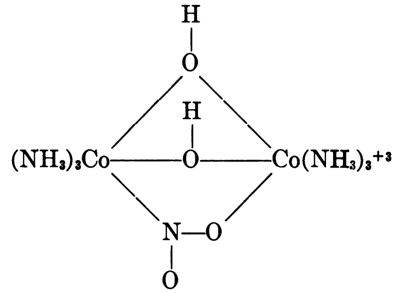
As yet, little has been done to study the reactions of the coordinated ambidentate ligands, partly because of the instability of one of the linkage isomers. The rates of electron transfer between chromium(II) and cobalt(III) through $—OSSO_2$ and $—SSO_3$ have been measured, as have those between europium(II) and cobalt(III) through $—NO_2$ and —ONO. Specific rates are listed in Table V. The activation parameters for the chromium(II) reduction of cobalt(III) through $—SO_3$ and $—OSO_3$ are similar. Two rate constants differing by a factor of 74 are obtained for the reduction through the thiosulfate group, and partial reduction of the mixture of linkage isomers followed by separation on an ion exchange column shows that the oxygen-bonded complex is reduced more rapidly than the sulfur-bonded complex. The cobalt(III) center is always reduced before the bridging ligand in the europium(II) reductions of complexes containing oxyanions of nitrogen, although the kinetics are more difficult to follow because the liberated nitrous acid oxidizes the europium more rapidly than does the remaining cobalt(III) complex.

Bridged Complexes

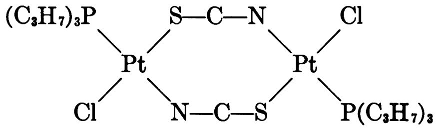
Since an ambidentate ligand possesses at least two groups capable of coordinating to metal ions, polynuclear complexes may also exhibit linkage isomerism. The selenocyanate complex of cadmium[10], $[(C_4H_9)_4N]_2[Cd_2(CNSe)_6]$, contains the dimeric anion on the next page,



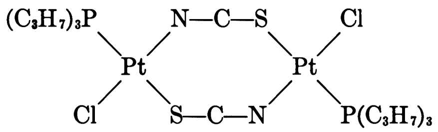
and the nitro group acts (*26*) as an unsymmetric bridge in di-μ-hydroxy-μ-nitrobis[triamminecobalt(III)],



but few pairs of linkage isomers are known. One example is (*14*) di-μ-thiocyanatobis[chlorotripropylphosphineplatinum(II)], which exists in α and β forms:



α; yellow



β; greenish-yellow

The isomers are obtained by treating di-μ-chlorobis[chlorotripropylphosphineplatinum(II)] with two equivalents of potassium thiocyanate—i.e., in cold acetone the α isomer forms; in boiling acetone, the β isomer. There do not appear to be any examples of bridged linkage isomers where the ambidentate ligand is not involved in the bridge.

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21

Coordination Chemistry of the Lanthanide Elements — One Hundred Years of Development and Understanding

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Coordination compounds of the lanthanide elements are distinguished by profound property differences from the derivatives of the d-transition elements and similarities to those of the alkaline-earth elements. Predominantly ionic bonding and lack of interactions of the 4f orbitals are significant in establishing these differences and similarities. Coordination numbers of at least six through 12 are observed. Irregularities in thermodynamic stability in aqueous solution are traceable to changes in coordination number or differences in degree of penetration of the primary hydration sphere. Complexation alters to a limited degree properties dependent upon the 4f electrons but changes significantly and quite regularly properties dependent upon ion concentrations and useful in separations. Absorption of energy by aromatic ligands leads to important fluorescent or line-like emission with certain cations.

At the time of Alfred Werner's birth, the only lanthanide elements that had been identified positively were lanthanum and cerium. Yttrium, a lanthanide element by all criteria except electronic configuration, was known also. However, in 1891 when Werner proposed the substance of the coordination theory, all of the elements of the lanthanide series except promethium, europium, and lutetium had been clearly identified and quite well characterized. Only promethium remained undiscovered at the time of Werner's demise.

Although it might be assumed quite reasonably that the coordination chemistry of the some 15 elements known during Werner's lifetime would have developed significantly during that period, the literature contains only a few accounts of synthesis and characterization. Indeed, the 1920 edition of Werner's classic monograph (*50*) records essentially the same information as the 1908 edition, namely the compositions of a limited number of double nitrates, sulfates, and oxalates. Both Spencer (*45*) and Little (*28*), in their comprehensive compilations of data at about the same time, describe only certain lanthanide double salts and adducts, but not within the framework of complex compounds or coordination chemistry.

Subsequent developments prior to the 1940's were meager, and even as late as 1953 the significant aspects of this area were reviewed in terms of only 60 literature citations (*33*). Yet a 1965 review covering published information only through 1962 required in excess of 500 references (*36*), and the current literature contains literally a flood of accounts of various aspects of the coordination chemistry of the lanthanide elements.

Certainly the problems involved in separation and purification limited severely most early attempts to prepare and study the complex species that would have permitted logical extensions of Werner's ideas to this series of elements. Paradoxically, it was the utilization of differences in the properties of certain complex species, in the 1940's and subsequently, that permitted the development of the large-scale fractionation procedures that have made the lanthanide elements available in sizeable quantities and high purities at not unreasonable prices and have thus permitted more extensive and comprehensive investigations of their compounds. However, lack of availability cannot account completely for the paucity of data in the early literature. Significant also is the general reluctance of the lanthanide ions to form complex species of substantial thermodynamic stability and the profound differences between the properties of those species that do form and the corresponding derivatives of the *d*-type transition metals. The synthesis of new and strongly complexing ligands, in particular those of the chelating type, has done much to prompt more recent studies in this broad area.

Coordination Chemistry of the Lanthanide Elements—General Survey

The formation and properties of the lanthanide complex species can be best understood by summarizing first some of the pertinent general characteristics of these elements. In their ground states, the lanthanide atoms have the characteristic valence-shell electronic configurations $4f^n5d^16s^2$ or $4f^{n+1}6s^2$, where $n = 0$ for lanthanum and 14 for lutetium, overlying the closed-shell xenon arrangement. The atoms are large and readily oxidized. In both aqueous or nonaqueous systems and the solid state, oxidation yields the tripositive ions (Ln^{+3}) preferentially, probably as a consequence of a fortuitous balance between ionization energy and solvation or lattice energy, respectively (*10*). Only a limited number of strongly reducing dipositive (Sm^{+2}, Eu^{+2}, Yb^{+2}), or strongly oxidizing tetrapositive (Ce^{+4}) ions, can be distinguished in solution. All of the cations are fundamentally of the noble-gas type, the distinguishing $4f$ electrons being essentially completely shielded from direct environmental and chemical effects. As a consequence of the increase in nuclear charge without the compensating effect of adding balancing electrons to higher energy levels, crystal radius in a given oxidation state decreases with increasing atomic number (the *lanthanide contraction*). Among the tripositive ions, this decrease in size accounts for the differences in the degree to which any property that permits fractional separation is exhibited. That the size of the yttrium(III) ion is duplicated in the general dysprosium-erbium region accounts for the lanthanide-like properties that are responsible both for the natural occurrence of yttrium with and for the experimental difficulties encountered in separating yttrium from the heavier lanthanide elements. Such unusual properties (e.g., paramagnetism, radiant energy absorption, and emission), as are characteristic of certain of the lanthanide ions, can be traced to the presence of unpaired $4f$ electrons. In most other respects, these ions are remarkably similar to the alkaline-earth metal ions.

A comparison of the coordination chemistry of the lanthanide elements with that of the *d*-type transition metals shows some striking differences in thermodynamic stability, magnetic and spectral properties, and bonding. Appreciably stable species, other than the hydrated cations, can be obtained only with the most strongly chelating ligands and, in particular, only when these ligands contain in their molecular structures highly electronegative donor atoms (e.g., oxygen). Commonly, the magnetic properties, the color, and the light absorption and emission characteristics of the lanthanide complex species differ little or not at all from those of either the hydrated cations or the stripped cations in ionic crystals. Isomerism and slow substitution reactions are uncommon and poorly characterized.

Both the ground-state electronic configurations of the lanthanide cations and the radial extension of the $4f$ orbitals are important in accounting for differences between the properties of these complex species and those of the *d* transition-metal ions and for the general properties of the lanthanide species themselves. Among the *d* transition-metal ions, the *d* orbitals are in the valence-shell arrangements and are thus both involved in bonding and affected in their energy distributions by the nature of the ligands present. Shielding of the $4f$ orbitals is sufficient, however, that there is little likelihood of electrons in them participating in bonding through hybridization or other type of orbital interaction. It is probable, therefore, that cation-ligand interactions among the lanthanide complex species are largely electrostatic with a minimum of crystal- or ligand-field stabilization (*22, 34, 36, 40, 47*). The expected resemblances between these species and the corresponding ones derived from the ions Ca^{+2}, Sr^{+2}, and Ba^{+2} are observed in practice. Experimental evidences, largely in terms of magnetic and spectral data, and very rapid substitution reactions supporting this point of view, are multiple (*36*). By contrast, although there are some evidences for covalent interaction (*22–25*), this type of interaction is much less extensive.

In terms of this model, both cation size and differences in the sizes of the various cations are important. In any state of oxidation, a lanthanide ion is comparatively large. Strong electrostatic attractions between such an ion and a ligand must, therefore, be limited. These attractions may be expected to increase in magnitude for a given oxidation state, as the cationic radius decreases, and for a given lanthanide element, as the cationic charge increases. Both of these variations are well established (*36*).

Although several factors appear to mitigate against their formation, many complex species derived from the lanthanide ions have been described (*36*). Some of these appear to exist only as ion pairs in solution and do not have sufficient stability to permit them to carry through series of reactions without concomitant dissociation. Others exist only in the solid state and dissociate or decompose upon dissolution. Still others are of sufficient stability to exist as such, both in solution and as isolable solids. Essentially all of the species described are derived from the tripositive ions, and essentially no information is available relative to complex species in nonaqueous systems. A broad classification of typical species is given in Table I (*36*).

Some Topics of Current Investigative and Practical Interest

Interest in the lanthanide complex species is centered currently largely in coordination number and stereochemistry, in thermodynamic stability and its interpretation, in the effects of the ligand on the properties of the lanthanide ion, and in practical applications.

Coordination Number and Stereochemistry

Although many of the compositions summarized in Table I appear to be consistent with an assignment of coordination number 6 to each of the lanthanide ions in its complex species, an increasingly impressive array of evidence supporting coordination numbers of 7, 8, 9, and even 10 and 12 (*36*) has appeared recently. Included among the experimental evidences are ionic compositions such as $[Ln(H_2O)_9]^{+3}$, $[Ln(H_2O)_6Cl_2]^{+}$, $[Ln(DTPA)]^{-2}$, $[Ln(NTA)_2]^{-3}$, $[Ln(HEDTA)(IMDA)]^{-2}$, and $[LnF_7]^{-3}$, each of which suggests operating a coordination number larger than 6.

Table I. A Classification of Typical Complex Species

Class	*Oxidation State of Ln*	*Examples*[a, b]
Ion-pair associations (in solution)	+3	$[LnX]^{+2}$ (X = Cl, Br, I, NO_3, SCN, ClO_4)
	+4	$[Ce(OH)]^{+3}$
Isolable adducts	+3	$LnCl_3 \cdot xNH_3$ ($x = 1 - 8$) $LnX_3 \cdot 6$ ap (X = SCN, I, ClO_4) $Ln(NO_3)_3 \cdot 3$ TBP $Ln(ClO_4)_3 \cdot 4$ DMA $LnX_3 \cdot x$ phen (X = Cl, SCN, NO_3, $C_2H_3O_2$; $x = 2,3$)
Chelates (in solution or isolable)	+2	$[Eu(EDTA)]^{-2}$
	+3	$[Ln(on)_3]$ $[Ln(diket)_3 \cdot xH_2O]$ ($x = 1 - 3$) $(BH)[Ln(diket)_4]$ $[Ln(EDTA)(H_2O)_3]^-$ $[Ln(NTA)_x]^{3-3x}$ ($x = 1,2$) $[Ln(HEDTA)(IMDA)]^{-2}$
	+4	$[Ce(on)_4]$ $[Ce(diket)_4]$
Miscellaneous (halo)	+3	$M^I[LnF_4]$, $M_3{}^I[LnF_6]$
	+4	$M_2{}^I[LnF_6]$ (Ln = Ce, Pr) $M_3{}^I[LnF_7]$ (Ln = Ce, Pr, Nd, Tb, Dy) $(BH)_3[LnCl_6]$

[a] Abbreviations: ap, antipyrine; TBP, tri-(*n*-butyl)phosphate; DMA, *N*,*N*-dimethylacetamide; phen, 1,10-phenanthroline; EDTA, ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate; on, 8-quinolinolate; diket, 1,3-diketonate; B, organic amine; NTA, nitrilotriacetate; HEDTA, *N*′-(2-hydroxyethyl)ethylenediamine-*N*,*N*,*N*′-triacetate; IMDA, iminodiacetate.

[b] Water molecules often present also but not always indicated.

(DTPA = diethylenetriamine-*N*,*N*,*N*′,*N*′,*N*″-pentaacetate; T = tropolonate). Similar evidence is afforded by the syntheses of compounds such as $[Ln(diket)_3 \cdot 3H_2O]$, $(BH)[Ln(diket)_4]$, $[HLa(EDTA)(H_2O)_4]$, $M^I[LnT_4]$ (*37*), and many others (*17*, *32*, *36*, *42*, *43*).

Appropriate stoichiometric composition does not in itself positively indicate a coordination number. However, the ions $[Ln(H_2O)_9]^{+3}$ and $[Gd(H_2O)_6Cl_2]^+$ have been detected and described quantitatively in crystals (*36*). Crystal-structure determinations have established 10-coordination in the molecular species $[HLa(EDTA)(H_2O)_4]$ and 9-coordination in the ionic species $[Ln(EDTA)(H_2O)_3]^-$ [Ln = La, Tb), with the 10-coordinate anionic species persisting for Ln = La-Sm and the 9-coordinate species for Ln = Tb-Lu (*19*, *26*, *27*). Among these ions, the transition from 10- to 9-coordination appears in the vicinity of Ln = Eu, Gd as a consequence of cationic size being decreased (*26*). Eight-coordination has been suggested for the 1,3-diketone chelates of the type $(BH)[Ln(diket)_4]$ on the basis of spectroscopic data (*1, 2*) and for the tropolonate ions $[LnT_4]^-$ on the basis of proton nuclear magnetic resonance data (*37*).

An ion of the type $[Ln(H_2O)_9]^{+3}$ has trigonal prismatic geometry, with a water molecule opposite each rectangular face (*18*). In crystals of the salt $La_2(SO_4)_3 \cdot 9H_2O$, some of the La^{+3} ions are surrounded icosahedrally by 12 oxygen atoms from sulfate ions, whereas other La^{+3} ions are 9-coordinate (*20, 31*). The ion $[Gd(H_2O)_6Cl_2]^+$ is probably a hybrid of a square antiprism and a triangular dodecahedron, with coordination number 8 (*30*). In the molecule $[HLa(EDTA)\ (H_2O)_4]$, the four carboxylate oxygen atoms, the two ethylenediamine nitrogen atoms, and one of the water oxygen atoms lie very nearly at seven of the eight vertices of a *quasi*-D_{2d} dodecahedron surrounding the La^{+3} ion (*26, 27*). The mean of the positions of the other three water molecules defines the eighth dodecahedral position. The entire arrangement is that of two hemispheres—one containing the four water molecules and the other the ethylenediaminetetraacetate donor sites. Removing the acidic proton effects a general shrinkage which results in a single water molecule being ejected and the formation of the geometrically similar ion $[La(EDTA)\ (H_2O)_3]^-$ (*26, 27*). Eight-coordination in the $[Ln(diket)_4]^-$ ions also gives a dodecahedral array of donors about the central Ln^{+3} ion (*2*).

Geometrical isomerism is potentially possible among many of the lanthanide chelates. The 1,3-diketone chelates, the species derived from the aminepolycarboxylic acids, the tropolonates, and many other complex derivatives are asymmetric and, thus, potentially capable of exhibiting optical isomerism. That the only resolutions reported have been limited to some tris(diketone) compounds (*35*) may reflect more the tendency of these ionically-bonded species to racemize rapidly in polar environments than in the absence of asymmetry. The existence of more than a single modification of each of several tetrakis(di-keto)europium(III) compounds may reflect asymmetry also (*1*).

Thermodynamic Stability

Properly speaking, the thermodynamic stability of a complex species is measured by the free-energy change (ΔG) that occurs in its formation from its components. Both the enthalpy (ΔH) and the entropy (ΔS) changes are reflected in the free-energy change and may be significant in determining its numerical magnitude. Indeed, when complex species are based upon chelating ligands, the entropy change is often the more significant of the two (*36*). The free-energy change is, of course, directly related to the thermodynamic formation constant (K) of the species in question. Few, if any, thermodynamic formation-constant data are available for the lanthanide complex species at a standard state of infinite dilution, but many concentration-based values have been determined experimentally (*36*, *41*), often under conditions of constant ionic strength (μ)—i.e., constancy of activity coefficients. Typical of some of the more recent data are those listed in Table II. Enthalpy and, ultimately, entropy changes have been obtained for a number of systems in terms of the temperature dependence of the formation-constant values, but only in a few instances have the enthalpy changes been determined calorimetrically (*12–15*, *29*, *38*, *47*). Some typical thermodynamic data are given in Table III.

Table II. Some Formation-Constant Data for 1:1 Complex Species at 25°C.

	log K			*K*
Cation	*PDTA(21)*[a]	*IB(5)*[b]	*HIB(46)*[c]	NO_3^-*(6)*
La^{+3}	16.42	1.57	2.22	—
Ce^{+3}	16.79	1.62	2.37	1.63
Pr^{+3}	17.17	1.80	2.48	—
Nd^{+3}	17.54	1.91	2.54	—
Pm^{+3}	—	—	—	2.48
Sm^{+3}	17.97	2.00	2.63	2.04
Eu^{+3}	18.26	1.98	2.71	—
Gd^{+3}	18.21	1.86	2.71	—
Tb^{+3}	18.64	1.73	2.87	1.13
Dy^{+3}	19.05	1.65	2.95	—
Ho^{+3}	19.30	1.63	2.98	—
Er^{+3}	19.61	1.61	3.03	—
Tm^{+3}	20.08	1.61	3.13	0.56
Yb^{+3}	20.25	1.62	3.18	—
Lu^{+3}	20.56	1.65	3.21	—
Y^{+3}	18.78	1.64	2.88	—

[a] PDTA, propylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate (μ = 0.1 *M*, 20°C.).
[b] IB, isobutyrate (μ = 2.00 *M*).
[c] HIB, α-hydroxyisobutyrate.

Formation-constant or free-energy data indicate that for a given ligand a lanthanide ion gives a generally less stable complex species than does a *d* transition-metal ion (*41*). Exact comparisons among the lanthanide ions as a whole are restricted by the limited number of ligands for which data for the entire series are available. Predictions, in terms of the electrostatic concept of bonding, that thermodynamic stability should increase with decreasing crystal radius of the Ln^{+3} ion, or with increasing nuclear charge, for a given ligand are in overall accord with observation for the lighter cations (La^{+3}-Sm^{+3} or Eu^{+3}), but not necessarily for the heavier cations (Eu^{+3}-Lu^{+3}). For the ions above Gd^{+3}, trends in stabilities

Table III. Enthalpy and Entropy Changes for the Formation of Some Typical 1:1 Complex Species at 25°C.[a]

	EDTA(29)		*NTA(38)*[b]		*Dipic(12, 14)*[c]		*IB(5)*	
Ion	$\Delta H°$	$\Delta S°$	ΔH	$\Delta S°$	$\Delta H°$	$\Delta S°$	ΔH	ΔS
La^{+3}	−2.926	59.7	0.320	48.8	−3.125	25.8	3.47	18.8
Ce^{+3}	−2.938	60.8	−0.215	48.8	−3.547	26.1	3.33	18.6
Pr^{+3}	−3.198	61.4	−0.502	48.9	−3.913	26.1	3.02	18.4
Nd^{+3}	−3.623	61.3	−0.803	48.8	−4.012	26.5	2.84	18.3
Pm^{+3}	—	—	—	—	—	—	—	—
Sm^{+3}	−3.349	64.4	−1.047	49.1	−4.283	25.9	2.66	18.1
Eu^{+3}	−2.558	67.6	−1.029	49.1	−4.073	26.6	2.91	18.8
Gd^{+3}	−1.730	71.2	−0.626	50.7	−3.582	27.8	3.45	20.1
Tb^{+3}	−1.114	75.5	−0.61	52.8	−2.689	30.5	4.38	22.6
Dy^{+3}	−1.211	77.3	0.350	54.8	−2.169	32.4	5.04	24.5
Ho^{+3}	−1.356	78.0	0.543	56.1	−1.946	33.2	5.31	25.3
Er^{+3}	−1.708	78.3	0.593	56.9	−1.850	33.8	5.49	25.8
Tm^{+3}	−1.870	79.1	0.585	57.8	−1.834	34.2	5.39	25.5
Yb^{+3}	−2.310	79.2	0.400	58.0	−1.925	34.0	5.35	25.4
Lu^{+3}	−2.512	79.1	0.180	57.7	−2.191	33.9	5.35	25.5
Y^{+3}	−0.588	77.5	1.027	56.0	−1.438	33.8	5.36	25.5

[a] All ΔH values in kcal./mole; all ΔS values in cal./mole-deg. Consult original papers for significance of ΔH *vs.* $\Delta H°$, ΔS *vs.* $\Delta S°$.

[b] At 20°C.

[c] Dipic, dipicolinate.

are qualitatively of three types: increase with increasing nuclear charge, little or no change with increasing nuclear charge, and maximum stability with some cation in the series (*36*). Detailed examination of formation-constant data commonly show discontinuities in stability at the Eu^{+3} or Gd^{+3} ion, which suggest that in the middle of the series stability is less than would be predicted on the basis of the purely electrostatic model. It is significant also that the Y^{+3} ion, which on the basis of electrostatic interaction alone should position itself with the Dy^{+3}-Er^{+3} ions, does so only where trends of the first type are observed (*36*). For the other two cases, this ion appears with the lighter lanthanide ions, specifically, close to the Nd^{+3} ion.

No completely adequate explanation has yet been offered to account for observed trends in thermodynamic stability, the *gadolinium break*, and the migratory behavior of the yttrium ion (*36*). To the crystal-field, stereochemical, and thermodynamic arguments previously presented (*36*) may be added both variants and some new approaches. Structural studies in the EDTA series suggest strongly that change in the coordination number of the central Ln^{+3} ion does indeed occur in the general Gd^{+3}-ion region (*26*). Choppin and co-workers (*6–8*, *48*) have shown by stability-constant, enthalpy, and entropy data that ions of the type LnX^{+2} (X = Cl, SCN, NO_3) are outer-sphere ion pairs, in which the primary hydration sphere of the lanthanide ion is largely retained, and for which the enthalpy change favors and the entropy change opposes their formation. The thermodynamic stabilities of these species reflect only changes in ionic attraction and vary linearly with properties such as ionic conductance that are proportional to the radii of the hydrated cations. Carboxylate and monofluoro complex ions, on the other hand, appear to be of the inner-sphere type (*5*, *14*, *38*, *48*), in which the primary hydration sphere of the Ln^{+3} ion has been broken to greater or lesser degree, and for which enthalpy change opposes and entropy change favors their formation. The stabilities of these species indicate that three hydration regions exist, namely La^{+3}-Nd^{+3}, Pm^{+3}-Tb^{+3}, and Dy^{+3}-Lu^{+3}, for the first and last of which the hydration sphere increases slowly in size with increasing atomic number and for the second of which the increase is rapid. Variation in stability thus reflects the effects of opposing enthalpy and entropy contributions. The same type of explanation appears to be reasonable for the aminepolycarboxylate chelates (*36*, *47*). Although most reported enthalpy and entropy values show wide and unsystematic variations, eliminating the complicating effects of changing effective hydration number of the uncomplexed lanthanide ion near the middle of the series has shown that the enthalpy of reaction of the diglycollate or dipicolinate ion with the crystalline ethylsulfates varies nearly monotonically with atomic number (*47*). Stabilization of the complex species with respect to those of lanthanum, gadolinium, and lutetium is of the order of only a few hundred calories per mole (*47*). The gadolinium break and the position of yttrium are consequences of fortuitous combinations of effects. Certainly attempts to correlate these variations directly with crystal radii are impractical because the variations in crystal radii may well be smoothed out or altered in the hydration process.

Bonding

Little can be added to or taken from the wealth of information supporting the concept of electrostatic interaction between ligand and lanthanide ion (*36*). That thermodynamic stability data do not agree completely with the predictions of the simple ionic model can be associated with changes in the sizes of and degrees of penetration into the hydration spheres of the cations without obviating the general concept. Asymmetry, bond-length data, and change in coordination number with increasing atomic number among the ethylenediaminetetraacetate chelates are all in complete accord with the concept of electrostatic interaction (*26*).

Effects of Complexation on the Properties of Ln^{+3} Ions

As may be expected, complexation has all of the effects attendant upon reducing the concentrations of the lanthanide ions in solution. Furthermore, by shielding the cations themselves from external influences and chemical attack, complexation often enhances the solubilities of the lanthanide species in non-aqueous solvents and their extractability into such media. Volatility may be enhanced also and even selectively, as is evidenced by the successful gas chromatographic separation of the lanthanide ions as their tris(dipivaloylmethane) chelates (*11*). The effects upon color and light absorption and upon magnetic properties are strikingly less with the lanthanide ions than with the *d* transition-metal ions, as a consequence of course of the fact that the electrons that are responsible for these properties in the lanthanide species are not in the valency shell.

Of particular current interest are the fluorescence and laser properties of certain chelates of specific lanthanide ions (*1, 3, 4, 9, 32, 39, 44*). That a number of the cations have characteristic fluorescence spectra has been well-known for many years. However, present interest and development can be traced to Weissman's observation (*49*) that certain europium(III) chelates, either as crystals or in benzene solution, fluoresce via a mechanism involving the broad absorption of energy by the aromatic portions of the ligands and reemission of a portion of this energy as narrow and highly characteristic spectral lines. Subsequent investigation has shown that initial absorption of energy raises the chelate to a vibrational level in the first excited singlet state (S_1). Deactivation via internal conversion to lower levels follows this process, and the energy released often appears as molecular fluorescence or phosphorescence. Not the least significant pattern for energy release may involve successively an internal conversion to a triplet state, a radiationless transition to a lower-lying lanthanide ion state, and a radiative transition to a still lower ionic state. The last of these processes gives line-like, coherent radiation and is responsible for laser-type behavior. Line spectra result in particular with chelates of the ions Sm^{+3}, Eu^{+3}, Tb^{+3}, and Dy^{+3}, ions that are close in configuration to the half-filled $4f^7$ arrangement. The red emission from europium(III) and the green emission from terbium(III) are particularly characteristic. Of the chelating agents studied, certain of the 1,3-diketones (e.g., dibenzoylmethane, benzoylacetone) have shown particular promise, especially in the tetrakis compounds.

Applications

Improvement in fractional separations in terms of the varying stabilities of lanthanide complex species is a well-known and highly important area of applied chemistry (*34, 36*). The complex species are often useful in analytical determinations. Certain of them possibly can be applied in constructing amorphous transparent or liquid laser devices.

Conclusion

Were Werner alive today, he would be gratified to know of the developments in the chemistry of the lanthanide complex species that, although not implicit in his original concepts, have nevertheless done much to supplement and add to an understanding of these concepts.

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22

Chemistry of Zerovalent Nickel, Palladium, and Platinum Derivatives

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The chemistry of the zerovalent state in nickel, palladium, and platinum compounds is reviewed. After a historical introduction in which the development of this chemistry is analyzed in terms of the current theory of the stabilization of low valency states, the most interesting classes of zerovalent compounds are described. The stability and properties of these compounds are discussed and related to the nature of the ligands and the coordinated metal. The catalytic properties of these zerovalent derivatives toward olefins, diolefins, and acetylenes are considered in connection with the facility of ligands exchange, the variation of coordination number, and the stereochemistry. A discussion of the π bond is reported.

The first coordination compound with a low oxidation number, tetracarbonylnickel (*141*), was discovered in 1890. Despite extensive efforts, however, very few substances of this type were synthesized in the next 50 years.

The lack of any knowledge on the structure and bonds of these compounds was responsible for the poor results. In fact, when tetracarbonylnickel was first prepared, Werner's theory had not as yet been postulated, and even later the theory was not extended to the carbonyls because they were considered anomalous compounds, owing to their chemical and physical properties.

The studies on coordination compounds with the central metal in a low oxidation state began to fluorish just prior to World War II. Nickel, palladium, and platinum were particularly investigated for the following reasons:

1) Tetracarbonylnickel had been recognized as having the tetrahedral coordination (*8*, *31*, *63*) with a metal-to-carbon bond of unexpected length (1.82 A. instead of about 2.1 A.).

2) The new definition of formal oxidation number given by Pauling (*154*) defined the new class of coordination compounds as having a zero oxidation number.

3) At the same time, Reppe (*158*) discovered the catalytic properties of tetracarbonylnickel and its derivatives in the carbonylation reactions and in the cyclization of alkynes, and this gave a tremendous thrust forward to the experimental research on the chemistry of carbonylnickel derivatives. In the beginning the development of the chemistry of low oxidation states proceeded concomitantly with the chemistry of zerovalent d^{10} metals and, particularly, with the chemistry of nickel(0).

In 1942-43, $K_4[Ni(CN)_4]$ (*66*) and $K_4[Pd(CN)_4]$ (*32*) were obtained and the zerovalent oxidation state was thus stabilized for the first time with a ligand different from that of carbon monoxide and for a metal in a complex anion.

The stability of these zerovalent compounds was explained by Pauling for the nickel carbonyl (*154*) as having been brought about by a resonance between tetrahedral structures with simple and double bonds between carbon and nickel. This was then extended by Deasy (*65*) to the complex cyanides. This hypothesis had been advanced (*154*) to explain the low value of the nickel-to-carbon bond (1.82 A.), in comparison with the calculated distance for a single bond (2–2.2 A.). The consequence of the double bond character of the bond was that the electronic density on the metal was lowered so that the effective charge had a value very close to zero. This interpretation was appropriate to Pauling's electroneutrality principle (*153*). Considering the electronegativity of carbon in CO and CN^-, a charge zero on the metal corresponded to a double bond percentage of 75–78% for $Ni(CO)_4$ and about 67% for $K_4[Ni(CN)_4]$ (*6*, *84*).

Although the possibility of assigning the order of the bond from bond distances was much criticized (*196*), the partial double bond hypothesis offered a semiquantitative interpretation of the formation of zerovalent derivatives. Above all, it supplied the researchers with qualitative rules about the nature of those ligands apt to stabilize the low oxidation states. It appeared then for the first time that ligands having unsaturated donor atoms of low electronegativity could behave similarly to carbon monoxide, and it was foreseen (*126*) that isocyanides should be able to give stable zerovalent nickel compounds. These compounds were, in fact, isolated soon after by three groups of researchers (*91*, *116*, *132*).

Almost simultaneously nickel(0) compounds with PCl_3 (*107*, *202*), PF_3 (*52*), and PR_3 (*160*) were obtained as well. These ligands fit the classifications reported for the low electronegativity, which could be qualitatively deduced from their basicity, but they were not isostructural with carbon monoxide, as were the isocyanides, and had vacant *d* orbitals instead of vacant *p* orbitals.

These experimental facts required a clearer interpretation of the mechanism of double bond formation. This was achieved by the so-called "back donation" hypothesis which explained the previous "double bond" hypothesis in terms of molecular orbitals.

By extending the hypothesis originally designed for other systems to the transition metal, it was shown that ligands apt to stabilize the low oxidation states must have donor atoms with low σ-donor capacity and with vacant low-energy orbitals of proper symmetry for overlapping with the filled non-bonding *d* orbitals of the metal in order to form a π bond (*41*, *201*). By this mechanism the negative charge is not localized on the high energy atomic orbitals; the nonbonding *d* electrons of the metal are stabilized, which easily explains why d^{10} systems such as the Ni(0), Pd(0), and Pt(0) derivatives are stable.

As a matter of fact, even now the "back donation theory" bases itself mostly on chemical evidence, while the physicochemical data are at least controversial. However, it appears to be fully plausible, also from a quanto-mechanical point of view, because the value of the overlap integrals confirmed an interaction between the filled *d* orbitals of the metal and the vacant *p* or *d* orbital of the ligand in different types of coordination (*62*). In conclusion, this was the leading hypothesis for all subsequent research work on the chemistry of low oxidation numbers—and especially on nickel(0), palladium(0), and platinum(0). The results obtained in the years following 1951 were numerous, important, and often completely unexpected.

Methods of Synthesis

There are different methods for preparation of the zerovalent nickel, palladium, and platinum derivatives. Generally, these methods are similar to those usually employed in the chemistry of the low oxidation states. The more commonly used are the following:

Direct Synthesis from the Metals. The first zerovalent compound prepared, namely $Ni(CO)_4$, was first obtained by this method—i.e., from active nickel and carbon monoxide at ordinary temperature and pressure (*141*). Though not largely applicable, this method can be used in some other cases. $K_4[Ni(CN)_4]$ could be prepared from metallic nickel and potassium cyanide (*205*), while some chloro- (*156*), bromo- (*125*), and fluorophosphine (*118*) and some tertiary diphosphine (*44*) could react with metallic nickel to give the tetracoordinated nickel(0) derivatives.

Exchange Reactions. The substitution reaction of $Ni(CO)_4$ with other ligands was the first method used to obtain other Ni(0) derivatives from the carbonyl (*160*).

From the palladium(0) di-isocyanides a complete replacement could easily be obtained (*129*) with tertiary phosphines and phosphites.

An analogous substitution could be obtained from π-allyl (*200*) and π-cyclopentadienylnickel compounds (*151*) and from π-allyl π-cyclopentadienylpalladium (*80*) with phosphines, phosphites, and isocyanides.

Reduction by Alkali Metals. This was the first reduction method successfully used; it is particularly useful for reducing in liquid ammonia cyanides (*66*), alkynyls (*146*), ammines (*193*), and ethylendiammines (*192*). The same reaction on phosphine compounds gives low yields because the reagents are insoluble in liquid ammonia (*45*). The zerovalent nickel compounds with phosphites are obtained in good yield with the potassium graphite compound KC_8 (*110*).

Reduction by Sodium Tetrahydridoborate or Naphthalenide. These methods were applied to the reduction of nickel(II), palladium(II), and platinum(II) derivatives with tertiary diphosphines and diarsines (*45*, *47*).

Reduction by Hydrazine. This was a very successful method for preparing the palladium(0) and platinum(0) derivatives with tertiary phosphines, phosphites, and arsines (*4*, *129*, *130*, *133*). Also, the tetraisocyanidenickel(0) compounds can be obtained at high yield in this way (*132*). In the case of platinum this reduction can give place either to zerovalent derivatives (*130*) or to platinum(II) hydrides (*49*), according to the reaction conditions, the nature of the ligands, and the halogen atoms bound to the metal. This reduction is a very complicated reaction (*186*) in any case.

Reduction by Ethanolic Potassium Hydroxide. This reaction gives about the same results as hydrazine and sodium tetrahydridoborate. It gives excellent results in the preparation of the zerovalent complex isocyanides (*127*), phosphines, and phosphites (*130*).

Spontaneous Reduction. With ligands having reducing properties, as isocyanides (*127*), phosphines (*129*), and phosphites (*106*, *189*), the reduction can be brought about by the ligand itself—usually in ethanolic solution.

Analogous reactions are the synthesis of $Ni(CO)_4$ from NiS (*12*) and carbon monoxide, while the synthesis from dimethyldioxymatonickel or from $Ni(S_2CPh)_2$ appears to be a disproportionation reaction (*97*, *98*).

Other Reducing Agents. The trifluophosphine metal(0) derivatives have been obtained by reduction with copper (*117*, *118*). Tetracarbonylnickel was obtained from nickel(II) salts in solution by reduction with dithionite (*100*, *101*) or analogous compounds (*76*). Some olefin complexes have been obtained by reduction with alkylaluminum (*197*, *198*).

Survey of Reported Carbonyl Compounds

Only one pure carbonyl has been isolated so far, namely tetracarbonylnickel, which can be obtained in many ways with very high yields (*46*). A polymeric platinum carbonyl having the stoichiometry $Pt(CO)_2$ has been recently reported (*28*) but not fully characterized. On the contrary, many substituted carbonyl compounds, with ligands having P^{III}, As^{III}, Sb^{III}, Bi^{III} as donor atoms, are known—especially in combination with nickel. These can be obtained in many ways, as follows.

By Direct Replacement on Tetracarbonylnickel. This was the first way by which nickel(0) carbonyl derivatives, different from $Ni(CO)_4$, were obtained with tertiary phosphines, arsines, stibines (*160*), and bismutines (*17*), and with triarylphosphites (*131*) and arsenites (*17*).

The monosubstituted replacement compounds are always easily obtained at room temperature and the disubstituted at higher temperatures (*138, 159, 160*).

However, it was not generally possible to obtain trisubstituted compounds from phosphines (except for trimethylphosphine (*19*)), while the phosphites give the trisubstituted derivatives (*131*) easily. Later Bigorgne (*19*) described all the possible substitution derivatives of carbonyl nickel with trimethylphosphite and triethylphosphite.

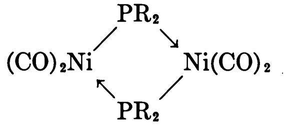
With cyclic phosphites offering no steric hindrance, as $P(OCH_2)_3C\text{-}CH_3$ (*188*) and $P(OCH_2)_3(CH_2)_3$ (*90*), all the substitution derivatives were isolated and characterized. The first of these ligands gives monosubstitution at room temperature, disubstitution in boiling chloroform (4 hrs.), trisubstitution in boiling ethylbenzene (6 hrs.), while the tetrasubstitution could only be achieved by refluxing for 16 hrs. in chlorobenzene. This shows that the activation energy for replacement of the first and second CO is low, and then it rapidly increases.

The chelating tertiary diphosphines (*43*) and arsines (*43, 149*) give dicarbonyl compounds easily. Analogous to this is the behavior of the tetraphosphine, $C(CH_2\text{-}PR_2)_4$, which gives the disubstitution compound and forms two chelate rings giving a carbonylated spiro nickel(0) derivative (*69*).

The tetrasubstituted diphosphines $R_2P\text{-}PR_2$ (where R = Me, Ph (*88*), or cyclohexyl Et(*108*)), which cannot chelate, give dinuclear monosubstituted derivatives at low temperatures.

$$(CO)_3Ni \leftarrow PR_2—PR_2 \rightarrow Ni(CO)_3$$

On heating, they give the bridged disubstituted phosphides (*88*) shown below. With some chelating diphosphines, such as $o\text{-}C_6H_4(PEt_2)_2$, $o\text{-}C_6H_4(PPh_2)_2$, and $Ph_2PCH_2CH_2PPh_2$ (*43*), the complete substitution of carbon monoxide can be obtained under drastic conditions.



Finally, some chelating triphosphines (*42*), such as $C_6H_5P[o\text{-}C_6H_4P(C_2H_5)_2]_2$ and $CH_3P[CH_2P(C_6H_5)_2]_2$, yield very easily the trisubstituted compounds so difficult to obtain with tertiary monophosphines.

From Complexes of Nickel(II) and Zinc(II) with Phosphines and Tetracarbonylnickel. This method is especially convenient for preparing the disubstituted derivatives by the reactions (*58*, *175*):

$$NiBr_2(PPh_3)_2 + Ni(CO_4) = NiBr_2 + 2CO + Ni(CO)_2(PPh_3)_2$$

$$ZnCl_2(PPh_3)_2 + Ni(CO)_4 = ZnCl_2 + 2CO + Ni(CO)_2(PPh_3)_2$$

By Interaction with the Metal and CO. Tertiary phosphines react with metallic nickel and carbon monoxide at high pressure to give good yields of the disubstituted compounds (*208*, *209*).

By Reduction of Nickel(II) Complexes with Carbon Monoxide. Monosubstituted tricarbonylnickel compounds can be obtained by reaction of carbon monoxide with $NiBr_2(PR_3)_2$ at a temperature from 70°C. (*26*) to 150°C. (*207*) and a pressure of from 75 (*26*) to 150 (*207*) atm. From $Ni(NO_3)_2(PPh_3)_2$ at 65°C. and 70 atm., $Ni(CO)_2(PPh_3)_2$ is obtained (*26*).

From Phosphine Platinum(0) Derivatives and Carbon Monoxide. From the compounds $Pt(PAr_3)_4$ or $Pt(PAr_3)_3$ with carbon monoxide at high pressure, the carbonyl derivatives, $Pt(CO)_2(PAr_3)_2$ and $Pt(CO)(PAr_3)_3$, are obtained (*130*). The carbonylation reaction of $Pt(PPh_3)_4$, $Pt(PPh_3)_3$, and $Pt(PPh_3)_2$ at atmospheric pressure has been recently reinvestigated (*38*), and $Pt(CO)(PPh_3)_2$, $Pt(CO)_2(PPh_3)_2$, and $Pt(CO)(PPh_3)_3$ have been fully characterized. The solution of the latter compound, as opposed to the corresponding nickel (0) derivative, is completely dissociated:

$$Pt(CO)(PPh_3)_3 \rightleftharpoons Pt(CO)(PPh_3)_2 + PPh_3,$$

and releases carbon monoxide on heating:

$$PtCO(PPh_3)_3 \rightleftharpoons Pt(PPh_3)_3 + CO.$$

These compounds with an excess of phosphine give the tetrakisphosphine platinum(0) derivatives with displacement of all carbon monoxide.

By Carbonylation of Platinum(II) Derivatives in Presence of Reducing Agents. Recently, some polymeric platinum(0) derivatives of the type, $Pt_3(CO)_3L_4$, $Pt_3(CO)_4L_3$ (where L is triphenylphosphine or an alkylaryl tertiary phosphine) and $Pt_3(CO)_3L_3$ (where L is benzyldiphenylphosphine), have been obtained by carbonylation of a hydroalcoholic solution of K_2PtCl_4 in the presence of the ligand, potassium hydroxide, and hydrazine (*28*), and by carbonylation of $PtR_2(PR_3)_2$ (*27*). These are probably cluster compounds with bridging carbonyl groups only (as shown by their IR spectra). The same compounds could be obtained from the polymeric $Pt(CO)_2$ with the calculated amount of tertiary phosphine, from $Pt(PPh_3)_3$ and $PtCO(PPh_3)_2$ by refluxing in ethanolic potassium hydroxide, and finally from $Pt(CO)_2(PPh_3)_2$ by refluxing in ethanol (*38*). On the other hand, these polynuclear compounds treated with the required amount of phosphine give $Pt(CO)(PR_3)_3$, which can also be obtained directly from K_2PtCl_4, hydrazine, and CO in the presence of three moles of phosphine (*53*).

Halogenophosphine Derivatives

These compounds are important because they were the first examples of complete substitution of $Ni(CO)_4$ by phosphines and because, from both chemical and physical points of view, they are similar to carbonyl derivatives. The methods by which they can be prepared are as follows:

Direct Synthesis. Some chlorophosphines and arsines react directly with metallic nickel in the same way as carbon monoxide to form the tetrasubstituted derivatives. This reaction was described initially for PCl_2Me and PCl_2Ph by Quinn (*156*); soon afterwards Maier (*125*) obtained analogous reactions with $AsBr_2Me$ and PBr_2Me.

Recently, Kruck (*118*) succeeded in preparing $Ni(PF_3)_4$ from metallic nickel and phosphorus trifluoride under drastic conditions (350 atm., 100°C.), as did Street and Burg under mild conditions (*181*), even though Wilkinson and Chatt (*52*, *202*) had previously reported that no reaction occurs between these reagents.

By Replacement of Carbon Monoxide on Tetracarbonylnickel. This reaction is much easier than that with tertiary phosphines. In fact, PCl_3 (*107*), $C_6H_5PCl_2$, and $(C_6H_5O)PCl_2$ (*131*) give completely substituted compounds.

Antimony trichloride, on the contrary, gave only $Ni(CO)_3(SbCl_3)$ (*203*). The direct reaction between $Ni(CO)_4$ and PF_3 has been investigated extensively. Chatt (*52*) obtained a complex mixture from which he could isolate the nearly pure $NiCO(PF_3)_3$. Bigorgne (*19*) studied the same reaction by IR spectroscopy, recognizing that even at 0° C. all four substitution compounds are present together. He isolated and characterized the tetrasubstituted $Ni(PF_3)_4$ obtained in this way.

Later, the same author (*123*) could obtain all the products: $Ni(CO)_3PF_3$ at 0° C., impure with some $Ni(CO)_4$ and $Ni(CO)_2(PF_3)_2$; $Ni(CO)_2(PF_3)_2$ almost in pure state at 25° C.; $NiCO(PF_3)_3$ at 45–55° C.; and finally $Ni(PF_3)_4$, still very impure with carbonylated derivatives, by heating the reagents at 70° C. for many days.

Quite recently, Kruck (*118*) obtained 80% yields of tetrakistrifluorophosphine nickel by reaction at 100° C. and 350 atm. Clark and co-worker (*56*) studied the reaction mixture of $Ni(CO)_4$ and PF_3 by gas chromatography and NMR, determining the physical constants (density, vapor pressure) of all the substitution products, and showing that in first approximation the equilibrium composition of the mixture can be calculated if there was a statistical equilibrium between the ligands: CO and PF_3. This means that the metal-to-ligand bonds are of the same strength.

With $C_6H_5PF_2$, the substitution of carbon monoxide was complete (*162*). On the contrary, $P(CF_3)_3$ (*70*) and $P[N(CH_3)]_2Cl$ (*148*) gave only mono- and disubstitution.

The chelating diphosphine $(CF_3)_2PCH_2CH_2P(CF_3)_2$ gave a very volatile dicarbonyl compound (*35*). The nonchelating diphosphines $(CF_3)_2P\text{-}P(CF_3)_2$ (*34*) and $Cl_2P\text{-}PCl_2$ (*122*) gave complicated products from which the bridged monosubstituted dinuclear compounds could be isolated, as:

$$(CO)_3Ni \leftarrow (CF_3)_2P - P(CF_3)_2 \rightarrow Ni(CO)_3$$

and

$$(CO)_3Ni \leftarrow Cl_2P - PCl_2 \rightarrow Ni(CO)_3$$

Finally, cyclotetrakis(fluoromethylphosphine) $[CF_3P]_4$ acted as a nonchelating tetradentate (*34*) ligand giving derivatives of the type:

$$(CF_3P)_4[Ni(CO)_3]_n \qquad (n = 1, 2, 3)$$

From these data it appears that, when at least two halogen atoms are bound to phosphorus, the substitution is completed unless particular experimental conditions are used. However, if the halogens are bound to the alkyl substituents, the halogenophosphines behave in much the same way as the tertiary alkyl- or arylphosphines, giving mono- and disubstitution.

Exchange Reactions. We are considering here the reactions by which the phosphines bound to the metal can be replaced by a different ligand and those by which halogen atoms, belonging to the phosphine, can be exchanged.

The trichlorophosphine can be exchanged completely (*119, 202*) by the trifluoro- and tribromophosphine as a result of the reaction:

$$Ni(PCl_3)_4 + 4PY_3 = Ni(PY_3)_4 + 4PCl_3 \qquad (Y = F, Br)$$

On the other hand, the fluoro derivative can be obtained from $Ni(PCl_3)_4$ by fluorination with reagents as SbF_3 (with catalytic amounts of SbF_5 (*202*) or KSO_2F (*176*)).

From Metal Halides, Phosphine and Halogen Acceptors. This method was set up by Kruck and co-workers to isolate nickel(0) (*118*), palladium(0), and platinum(0) (*117*) tetrakisfluorophosphine derivatives. The halogen acceptor was copper, and the reaction conditions were rather mild for nickel (100° C., 135 atm.) and more drastic for palladium and platinum (100° C., 350 atm.). The physical (melting and boiling points) and chemical (decomposition, temperature) properties of these compounds are reported below:

	m.p., °C.	*b.p., °C.*	*dec., °C.*
$Ni(PF_3)_4$	−55	70	> +70
$Pd(PF_3)_4$	−41	—	−20
$Pt(PF_3)_4$	−15	86	+90

The physical properties have the expected trend, while the thermal instability of the palladium derivative appears anomalous and can perhaps be attributed to a combination of kinetic and thermodynamic factors. (Platinum should be thermodynamically more unstable but kinetically stable.) In any case, it appears that $Ni(PF_3)_4$ is more stable than nickel carbonyl, and this confirms that the palladium and platinum tetratrifluorophosphine derivatives could be prepared.

Miscellaneous Methods. $Ni(PF_3)_4$ was obtained recently (*147*) from $(\pi\text{-}C_5H_5)_2Ni$ and PF_3 in a sealed tube, and $Pd(PF_3)_4$ (*182*) was obtained from $PdCl_2(CO)_2$ and PF_3.

Compounds with Tertiary Phosphines, Arsines, and Phosphites

The compounds with tertiary phosphines are interesting because they have been prepared for all the three metals. Their stability to oxidation has the trend: Pt > Pd > Ni. The compounds with tertiary di- and polyphosphines, which are even more stable, show the same increase in stability with the atomic number. The compounds with the phosphites are the more stable; they have been obtained for all three metals and are not oxidized by air.

All the compounds with nonchelating ligands display a variable stoichiometry, having four, three, and, in a few cases, even two ligands (*184, 199*). There are numerous preparation methods as follows:

From Tetracarbonylnickel or Tetracyanonickelate(0) by Substitution. We have already discussed this method for $Ni(CO)_4$. It completely replaces carbon monoxide only with some diphosphines (*43*) and with unhindered phosphites (*90, 188*). The substitution of $K_4[Ni(CN)_4]$ is easier and produces tetrasubstituted nickel(0) derivatives also with tertiary phosphines, arsines, and stibines (*13*).

By Replacement of Zerovalent Isocyanide Derivatives. This method was described for preparing the tris and tetrakis palladium(0) derivatives with tertiary aromatic phosphines and phosphites (*129*). It might be extended to nickel.

By Reduction. The first reducing agents used to prepare the platinum(0) (*130, 133*) and palladium(0) (*129*) derivatives with tertiary phosphines and phosphites were hydrazine and ethanolic potassium hydroxide.

With the latter, an excess of the phosphine had to be used to obtain the tetracoordinated derivatives, while hydrazine without any excess of ligand gave the tricoordinated derivatives (*130*). Chatt and co-workers (*45, 47, 51*) obtained the nickel(0), palladium(0), and platinum(0) derivatives with the chelating diphosphines, diarsines, and triphosphines by reduction with sodium tetrahydridoborate or naphthanelide.

The nature of platinum zerovalent derivatives was questioned by Chopoorian *et al.* (*55*) who considered them platinum(II) dihydrides. A new careful investigation (*47, 133*), however, has confirmed that they are certainly zerovalent compounds. The nickel(0) derivatives with tertiary monophosphines can be obtained as well from $NiBr_2L_2$ and sodium tetrahydridoborate or ethanolic potassium hydroxide in the presence of an excess of the ligand (*185*), while those with phosphites were prepared using potassium graphite (*110*) (C_8K) as the reducing agent. By reduction with alkylmetals (*199*), zerovalent tetrasubstituted nickel(0) compounds with tertiary phosphine, arsines, and stibines have been obtained.

By Reduction of the Ligand. This method was used to prepare the tetrakisphosphitenickel(0) derivatives from nickel(II) salts with an excess of the phosphite and a tertiary amine (*106, 189*). Also, $(\pi\text{-}C_5H_5)_2Ni$ with a phosphite gave $Ni[P(OR)_3]_4$ (*151*). $Ni(PEt_3)_4$ was prepared from di-π-allyl nickel and PEt_3 (*200*) and, analogously, $Pd(PPh_3)_4$ from $Pd(\pi\text{-}C_5H_5)(C_6H_9)$ with PPh_3 (*80*).

By Synthesis from the Metal and the Phosphine. Some nickel(0) derivatives with tertiary aromatic chelating diphosphines have been obtained by reaction of metallic nickel with these ligands (*43*) and, similarly, the palladium(0) derivative of $o\text{-}C_6H_4(PEt_2)_2$ was obtained from the metal (*44*).

Cyano and Alkynyl Compounds

The cyanometallates(0), such as $K_4[M(CN)_4]$ (M = Ni, Pd), have been obtained as pure compounds by reducing in liquid ammonia with potassium the corresponding divalent derivatives (*32*, *66*), while the platinum compound was not isolated (*32*). Watt and co-workers (*191*) studied the potassium reduction mechanism by a potentiometric technique. They found the mechanism proceeded in two steps. The reduction to Ni(I) was fast, while that to Ni(0) was a very slow reaction. The nickel(0) compound was also obtained from metallic nickel, KCN, and $Hg(CN)_2$ in 1:5:2 ratio at 500° C. (*205*). In this case, too, the reaction mechanism was investigated in detail. $K_4[Ni_2(CN)_6]$ is first formed, and then it disproportionates as follows:

$$2KCN + K_4[Ni_2(CN)_6] = K_4[Ni(CN)_4] + K_2[Ni(CN)_4]$$

$K_4[Ni(CN)_4]$ could not be obtained from $K_2[Ni(CN)_4]$ and metallic nickel, but it could be prepared with a 20% yield from the following reaction.

$$2KCN + K_2[Ni(CN)_4] \xrightarrow{480^\circ\ C} (CN)_2 + K_4[Ni(CN)_4]$$

The zerovalent cyanometallates are compounds with strong reducing properties, and they are known to reduce water. The stability of these complex cyanides decreases with increasing atomic number. The nickel compound is stable (*in vacuo*) up to 160° C.; the palladium compound decomposes slowly (*in vacuo*) at ordinary temperatures, while the platinum derivative could not be isolated at all.

These cyanides exchange rapidly with many ligands. Nast (*145*) described a carbonylcyanonickelate which he obtained by the following reaction:

$$K_4[Ni(CN)_4] + 2CO = K_2[Ni(CN)_2(CO)_2] + 2KCN,$$

and a nitrosylcyanonickelate obtained from tricyanocarbonylnickelate(I):

$$K_2[Ni^{I}(CN)_3CO] + NO = K_2[Ni(CN)_3NO] + CO.$$

Compounds of this type have been previously obtained by reaction of nickel carbonyl with potassium cyanide (*33*), which gives a mixture of:

$$K_2[Ni(CN)_2(CO)_2] \quad \text{and} \quad K[NiCN(CO)_3]$$

The latter was recently prepared with this most interesting reaction (*190*):

$$Ni(CO)_4 + [(CH_3)_3Si]_2NNa = Na[NiCN(CO)_3] + [(CH_3)_3Si]_2O$$

These carbonylcyanonickelates are rather unstable compounds which disporportionate into $K_4[Ni(CN)_4]$ and $Ni(CO)_4$. Behrens and co-workers (*13*) have recently described very rapid exchange reactions between

$K_4[Ni(CN)_4]$ and ligands having P^{III}, As^{III}, Sb^{III}, and heterocyclic nitrogen as donor atoms. It appears that the cyanide ion is more easily replaced than carbon monoxide in tetracarbonylnickel. The reactions are as follows:

$$K_4[Ni(CN)_4] + 4L = NiL_4 + 4KCN$$

$$K_4[Ni(CN)_4] + 2D = NiD_2 + 4KCN$$

(L = PPh_3, $AsPh_3$, and $SbPh_3$; D = α, α'-dipyridyl, 1,10-phenanthroline and chelating tertiary diphosphines and diarsines).

Only with a trichelating triphosphine (T) could the intermediate K[Ni(CN)T] (*14*) be isolated.

The structural analogies between the C-donor atoms of the cyanides and the alkynes led Nast to prepare the alkynylnickelate(0) (*146*), the alkynylpalladate(0) (*144*), and the alkynylplatinate(0) (*143*). The nickel(0) derivatives were obtained from the tetrakisalkynylnickelate(II) by reduction with potassium in liquid ammonia. They correspond to the stoichiometry $K_4[Ni(C{\equiv}CR)_4]$ and are probably tetrahedral. The palladium(0) and platinum(0) derivatives on the contrary, though prepared quite similarly, have the stoichiometry $K_2M\ (C{\equiv}CR)_2$—i.e., the metal is formally only dicovalent. All these compounds have strong reducing properties, but the nickel derivatives are more stable than the pyrophoric platinum and palladium compounds.

Isocyanide Derivatives

Nickel(0) and palladium(0) derivatives of this class are known. The nickel derivatives were first obtained by complete replacement of the carbon monoxide of $Ni(CO)_4$ by aromatic isocyanides (*91*, *96*, *115*, *116*). With aliphatic isocyanides the reaction is more difficult. Hieber (*91*, *96*) obtained the only trisubstituted methylisocyanide derivative, $NiCO(CNCH_3)_3$, but recently Bigorgne (*18*, *21*), who studied the reaction

$$Ni(CO)_4 + n\,CNR = Ni(CO)_{4-n}(CNR)_n + n\,CO$$

(with R = Me, Et, Ph), showed that all possible replacement products can be isolated up to the tetraalkylisocyanide derivatives with convenient techniques.

The tetrakisisocyanide nickel(0) compounds can be obtained (*132*) both with aliphatic and aromatic isocyanides, starting from nickel(II) salts using hydrazine, ethanolic potassium hydroxide, hydroxostannate(II), or dithionite as reducing agents. Organic nickel(II) salts such as acetate, dimethylgloximate, alkylxantogenate, and dialkyldithiocarbamate were preferred for this reaction. All these compounds have the stoichiometry $Ni(CNR)_4$ and are probably tetrahedral; the aromatic derivatives are yellow, stable compounds, monomeric in solution; the analogous aliphatic derivatives are more unstable.

The palladium(0) derivatives were obtained (*127*) by reducing $PdI_2(CNR)_2$ (R is aromatic) with ethanolic potassium hydroxide and an excess of aromatic isocyanide; they correspond to the stoichiometry $Pd(CNR)_2$, but their molecular weight could not be determined on account of their very low solubility. They are dark brown crystals (a red form was also obtained in some preparations) (*127*) and dissolve in an excess of isocyanide, giving a clear solution from which unstable yellow needles can be obtained (*128*)—probably $Pd(CNR)_3$ or $Pd(CNR)_4$. Fischer (*80*) prepared the analogous aliphatic isocyanides from $Pd(\pi\text{-}C_5H_5)\cdot(C_6H_9)$. He too observed two forms: a clear, unstable form, and a dark, stable one. He could measure the molecular weight of $Pd(CNC_6H_{11})_2$ and found that polymerization increased with time up to the tetrameric form (found 1195; calc. 1300). By reaction of aromatic phosphites with diisocyanidepalladium(0), a partial replacement of the isocyanide takes place, giving tetracoordinated palladium derivatives, $PdCNR[P(OR)_3]_3$, corresponding to $Ni(CO)\,[P(OR)_3]_3$ (*129*).

Nitrosyl Compounds

The oxidation numbers of the metals in the nitrosyl compounds depend on whether this ligand is considered NO^-, NO, or NO^+. However, it is generally assumed that, at least in the diamagnetic nitrosyl compounds which show N—O stretching frequencies above 1700 cm.$^{-1}$, the nitrosyl group is to be considered as NO^+ (*75*). Therefore, the nitrosyl compounds reported below are to be considered as nickel(0), palladium(0), and platinum(0) derivatives.

These compounds are divided into three classes as follows:

Halonitrosyl Compounds. The nickel derivatives have been known for a long time (*92, 104*) and have the stoichiometry $[NiNOX]_n$ (X = Br, I, OR).

According to Hieber (*103*), *n* is 4, and therefore these compounds can be considered to have a tetrahedral coordination around the metal, with halogen bridges much the same as $[Cu(AsR_3)I]_4$ (*135*). They can be obtained with the reactions as follows:

$$2n\,NiX_2 + 2n\,NO + n\,Zn = 2[Ni(NO)X]_n + n\,ZnX_2$$

$$4n\,Ni(CO)_4 + 6n\,NO + 4n\,ROH = 4[Ni(OR)(NO)]_n + n\,N_2 + 16n\,(CO) + n\,H_2O$$

The analogous palladium derivatives were obtained later by Smidt and Irne (*178*) in this interesting way:

$$2PdCl_2 + 2NO + H_2O = Pd(NO)Cl + [PdCl_3NO_2]^{-2} + 2H^+$$

$$[PdCl_3NO_2]^{-2} + R{-}CH{=}CH_2 = Pd(NO)Cl + 2Cl^- + RCOCH_3$$

The nickel compounds have the NO stretching frequencies at *ca.* 1800 cm.$^{-1}$ in ethanol solution and *ca.* 1860–1870 cm.$^{-1}$ in the solid state (*109*). This shift might be due either to the polarity of the solvent or to the opening of the halogen bridge with depolymerization and coordination of the ethanol. A probably monomeric palladium nitrosyl compound, $Pd(NO)_2Cl_2$, has been described since 1926 by Manchot and Waldmuller (*134*) and was recently confirmed (*86*). It was obtained from the reaction of nitrogen oxide on the methanol solution of palladium dichloride and proved very unstable. It shows two strong N—O stretching bands at 1833 and 1818 cm.$^{-1}$, as expected from a tetrahedral structure.

The reaction of tetracarbonylnickel with nitrogen oxide has undergone much investigation (*86*) and is probably very complicated. The blue compound which can be obtained, according to Griffith and co-workers (*86*), is paramagnetic and derives from tetrahedral nickel(II).

More recently Feltham and Carriel (*73*) pointed out that if the reaction takes place under high pressure for a very short time, it gives a blue nickel(0) derivative corresponding to $[Ni(NO)NO_2]_n$, which is very similar to the compound, $Ni(NO)_2$, previously obtained by Mond and Wallis (*142*). This compound shows a strong band in the IR spectra at 1845 cm.$^{-1}$, assigned to NO^+ stretching, and the bands typical for the bridging NO_2 groups at lower wavelengths. By adding triphenylphosphine or cyclopentadiene, the corresponding monomeric nickel(0) derivatives were obtained (*73*):

$$Ni(NO_2)(NO)(PPh_3)_2 \qquad (\pi\text{-}C_5H_5)Ni(NO)$$

Therefore, it can reasonably be assumed that this nitrosylnitrite has a tetrameric structure like that of $[NiNOX]_4$ (X = Br, I, OR), and that in the presence of water or air it is rapidly decomposed to a nickel(II) derivative.

Cyclopentadienyl Derivatives. The compound $(\pi\text{-}C_5H_5)Ni(NO)$ was obtained by Piper, Cotton, and Wilkinson (*155*) from dicyclopentadienylnickel and nitrogen oxide. The palladium and platinum derivatives have recently been obtained by Fischer and co-workers (*77, 78*) in the following ways:

$$1/n[Pd(NO)Cl]_n + NaC_5H_5 = (\pi\text{-}C_5H_5)Pd(NO) + NaCl$$

$$PdCl_2 + 2NO + NaC_5H_5 = (\pi\text{-}C_5H_5)Pd(NO) + NaCl + NOCl$$

$$1/2\ Pt_2Cl_2(CO)_4 + NO + NaC_5H_5 = (\pi\text{-}C_5H_5)Pt(NO) + 2CO + NaCl$$

The structure of these compounds was inferred from their rotational (*61*) and vibrational (*74*) spectra. Because the molecule has C_{5v} symmetry with a fivefold axis, the most probable structure has the NO group on the fivefold axis—normal to the C_5H_5 plane (Figure 1). It is interesting that palladium and platinum have the same structure as nickel, as shown by the similarity of IR spectra, while the NO stretching decreases with increasing atomic number:

$$\nu\text{NO} = (\text{Ni})\ 1802;\ (\text{Pd})\ 1789;\ (\text{Pt})\ 1739\ \text{cm.}^{-1}$$

as if the back donation to the cyclopentadienyl ring were stronger with nickel than with platinum.

This effect is unusual and, for instance, in the carbonyl and nitrosyl derivatives of chromium, molybdenum, and tungsten there is no shift of the CO or NO stretching bands in the isostructural derivatives with an increasing atomic number.

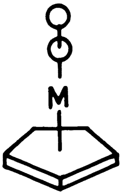


Figure 1

Compounds with Donor Atoms Belonging to V B Group. The compounds of the type $NiX(NO)L_2$ or $[NiX(NO)L]_2$ can be obtained in many ways.

Hieber and co-workers (*93*, *94*) studied the reaction $[Ni(NO)X]_4 + 4L = 2\ [NiX(NO)L]_2$ and $[Ni(NO)X]_4 + 8L = 4\ NiX(NO)L_2$ (where X is Br and I, and $L = PR_3$, $P(OR)_3$, AsR_3, SbR_3, and NHR_2). The dimeric derivatives generally have the trans structure, but the one with tricyclohexylphosphine was obtained in both cis and trans form. The two isomers can be recognized (*10*) from the number of NO stretching bands in the IR spectrum: the trans isomer with C_{2v} symmetry has only one active band, while the cis isomer with C_{2h} symmetry has two bands.

Also studied were the derivatives of the type $NiX(NO)L_2$, $[NiX(NO)L]_2$, and $NiX(NO)L_2$, with X = SCN, SEt, SPh (*104*), or $C\text{-}(CN)_3$ (*11*). The thiocyanato compounds are the most interesting (*10*). In $Ni(NCS)(NO)L_2$ the NCS group is considered bound through nitrogen because ν_{CS} is at 809–820 cm.$^{-1}$; in $[Ni(CNS)(NO)L]_2$, the thiocyanate is considered bridging two different nickel atoms because ν_{CN} is 2125 cm.$^{-1}$ and ν_{CS} is 774 cm.$^{-1}$ ($L = P(C_6H_{13})_3$), and the same should apply to $[Ni(NO)CNS]_2$, for which ν_{CN} is 2189 cm.$^{-1}$ and ν_{CS} is 762 cm.$^{-1}$

Booth and Chatt (*26*) have obtained the compounds of the type $NiX(NO)(PR_3)_2$ [$X = NO_2, NO_3$; R = Et, Ph] by reaction of carbon monoxide with $Ni(NO_3)_2(PR_3)_2$. By exchange with NaX (X = Cl, Br, I), they isolated the corresponding halogeno derivatives. These are red, brown, or violet, diamagnetic compound shaving ν_{NO} = 1750–1770 cm.$^{-1}$ and electric moments of about 7 *D*, in accordance with a tetrahedral structure.

The same compounds, with R = Ph, have been obtained by Feltham (*72*) in different ways. At first, he reinvestigated the product of the reaction between $Ni(CO)_2(PPh_3)_2$ and NO, which had been formulated as $Ni(PPh_3)_2(NO)_2$ (*87*). The diamagnetism of this compound, and the fact that it showed only one IR band in the region of the NO^+ stretching (at 1745 cm.$^{-1}$), had been explained by the presence of an NO^- group which was considered to show an IR band at *ca.* 1200 cm.$^{-1}$ (*121*). Feltham proved, to the contrary, that the compound was a nitrosylnitrite, $Ni(NO_2)(NO)(PPh_3)_2$, that is formed by traces of nitrogen dioxide. With pure NO, the blue $Ni(OH)(NO)(PPh_3)_2$ forms through an intermediate hyponitrite as follows:

$$2Ni(CO)_2(PPh_3)_2 + 4NO =]NiNO(PPh_3)_2]_2\,N_2O_2 + 4\,CO$$

$$[Ni(NO)(PPh_3)_2]_2N_2O_2 + H_2O = 2Ni(OH)(NO)(PPh_3)_2 + N_2O$$

An analogous reaction carried out on $Ni(CO)_3PPh_3$ in methanol gives:

$$Ni(OCH_3)(NO)(PPh_3)2CH_3OH$$

The same compounds were also obtained (*71*) when $NiX_2(PPh_3)_2$ reacted with sodium nitrite in the presence of an excess of ligand as a reducing agent:

$$NiX_2(PPh_3)_2 + NaNO_2 + PPh_3 = NiX(NO)(PPh_3)_2 + PPh_3O + NaX$$

From these compounds many others, among which is the hyponitrite which decomposes as shown above, giving $Ni(OCH_3)(NO)(PPh_3)_2$, could be obtained by a double exchange with silver salts. With $P(But)_3$, the reaction is different and produces the nickel(II) compound, $Ni(NO_2)_2(PBut_3)_2$.

Finally, $NiCl(NO)(PPh_3)_2$ also was obtained by Addison and Johnson (*1*) by adding triphenylphosphine to the reaction product of tetracarbonylnickel with nitrosylchloride.

Compounds with N-Donor Ligands

These may be divided in two classes, namely the nickel(0) derivatives of heterocyclic nitrogen bases which can form bonds with some π character and the platinum(0) amine and ethylenediamine compounds.

The nickel compounds with α,α'-dipyridyl and 1,10-phenanthroline could be obtained by Behrens (*13*) by exchange from $K_4[Ni(CN)_4]$. Using the nickel carbonyl as a starting material, the reaction with amines is complicated by disproportionation so that it could only be proved that the primary reaction product in solution was $Ni(CO)_3Am$ (Am = pyridine or picolin) (*99*). With ammonia too, the reaction is very fast, and the primary products are $Ni(CO)_3NH_3$ and $Ni(CO)_2(NH_3)_2$ (*15*) which disproportionate above $-60°C$. Only with chelating ligands L-L having more π character, such as 1,10-phenanthroline, α,α'-dipyridyl (*99*), and 1,4-diazobutadiene (*24*), could stable disubstitution products of the type $Ni(CO)_2(L\text{-}L)$ be isolated, as Hieber has shown since 1932 (*102*).

The analogous palladium and platinum compounds were not described, but it appears that they might be stable enough to be isolated.

The platinum(0) derivatives with ammonia and ethylenediammine (en) were obtained by reduction of $[Pt(NH_3)_4]Br_2$ (*193*) and $[Pten_2]I_2$ (*192*) with potassium in liquid ammonia. These interesting compounds have a very low stability; the ammonia derivatives dissociate slowly yielding the metal, while the ethylenediammine derivatives slowly evolve hydrogen, giving the amido derivative of platinum(II):

$$[Pt\ en_2]\ (\text{pink}) \rightarrow [Pt(en\text{-}H)_2]\ (\text{yellow}) + H_2$$

The latter can be directly prepared using potassium amide instead of potassium metal. Also, these compounds do not go along with the general rule that zerovalent metal atoms have to be stabilized by back donation, because neither ammonia nor ethylendiamine have vacant low energy *p* or *d* orbitals. Besides, in this case, the metal atom having a d^{10} configuration cannot be stabilized by the ligand field.

π *Complexes with Olefins and Alkynes*

These compounds, many of which have been isolated and characterized quite recently, are very interesting because they are connected with many catalytic processes. From this point of view the most important of them derive from nickel, but the more stable platinum compounds without any catalytic properties have often been studied to isolate the intermediates and to understand the catalysis mechanism.

Compounds with Mono-olefins. Compounds with mono-olefins are obtained from tetracarbonylnickel and olefins having electronegative groups in the molecule, such as acrylonitrile (*168*), fumaronitrile, cinnamic nitrile (*166*), acrolein (*166*), and maleic anhydride (*194, 195*). They have the general formula $Ni(\text{olefin})_2$, are insoluble, and therefore probably polymeric. The olefin is directly bound to the metal, as it can be deduced from the lowering or disappearance of the $\nu_{C=C}$ band in the IR spectrum (*82, 194*), while the electronegative groups do not generally take part in the coordination (*194*). In the compound with maleic anhydride, the shift of the C=O stretching is 40–50 cm.$^{-1}$, while in the compound with acrolein it is 150 cm.$^{-1}$ The C—N stretching mode is also lowered about 30 cm.$^{-1}$ in nitrile complexes. This means that the electronegative groups are polarized as a result of the strong back donation; in the case of acrolein the CO group can be considered attached directly to the bond.

Diolefin Compounds. The first of these compounds was described as the result of the reaction of cyclopentadiene with tetracarbonylnickel (*79*), but later it was proved that this diamagnetic compound having an electric moment of 1.16*D* was instead a nickel(II) derivative (*81*). A Ni zero compound important for its catalytic properties was prepared by Wilke (*197*) by reducing bispentan(2,4)dionatonickel with alkylaluminum in presence of cycloocta-1,5-diene. It has the stoichiometry $Ni(C_8H_{14})_2$ and its IR and Raman spectra were consistent with a molecule having no center of symmetry. It was very unstable, probably because the diene does not have orbitals of enough low energy to give back donation. It exchanges rapidly with ligands having more π-acceptor properties, as carbon monoxide (giving $Ni(CO)_4$) and acrylonitrile (giving $Ni(CH_2{=}CHCN)_2$). With the same reduction method, other complexes with diolefins (cyclooctatetraene) and triolefins (cyclododecatriene) have been obtained (*200*). The latter compound is coordinately unsaturated and gives addition compounds with carbon monoxide and triphenylphosphine (Figure 2).

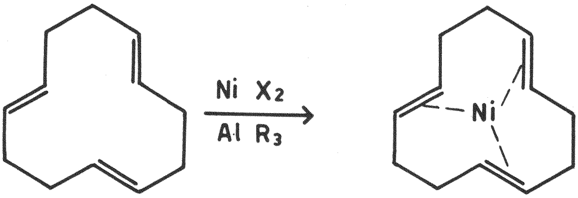


Figure 2

The cyclooctatetraene (COT) nickel derivative could be isolated as $Ni(COT)_2$, which rapidly polymerizes to $[Ni(COT)]_n$. We consider that the nickel derivatives of quinones belong to this class of compounds. These, because of the nature of the ligand, can in some cases be nickel(II) derivatives. By reaction of tetracarbonylnickel with duroquinone (D) (tetramethyl-1,4-benzoquinone), the diamagnetic compound NiD_2 has been obtained, while benzoquinone gives an analogous, but paramagnetic, compound (*172*). The different behavior can be ascribed to the fact that the duroquinone compound is a nickel(0) derivative stabilized by a strong back donation from the 3*d* electrons of the metal in the lower vacant molecular orbital of the ligand, while the benzoquinone compound is a nickel(II) derivative. Benzoquinone, in fact, has a higher electron affinity and, instead of accepting some negative charge by back donation, it receives two electrons from the metal, forming an ionic compound. This agrees with the fact that the nickel(0) derivatives have a strong charge transfer band with an energy of *ca.* 5,5 *eV* (*173*), and that the CO stretching band is lowered by about 50 cm.$^{-1}$

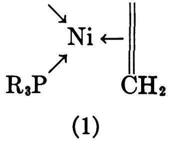
Mixed diolefin quinone complexes of the type Ni(diolefin)D have been obtained by reaction of tetracarbonylnickel with the quinone and the olefin, by reaction of bisduroquinone nickel with the olefin (*174*), or finally by reaction of bis(cycloocta-1,5-diene)nickel with duroquinone (*165*). These compounds have a high electric moment, are very soluble in polar solvents, show a strong nickel-to-quinone charge transfer band, and have the carbonyl stretching band even more strongly shifted than the bisquinone complexes. This is in accordance with a tetrahedral structure having a strong back donation from the nickel to the quinone, while the olefin acts apparently only as a donor. The tetrahedral arrangement has been confirmed for cycloocta-1,5-dieneduroquinone-nickel (*163*), which showed a structure having the metal symmetrically bound to both ligands.

These compounds exchange the olefin only under drastic conditions (80–120°C.) (*174*) and react with carbon monoxide to give the carbonyl only at 60°C. and 100 atm. (*171*).

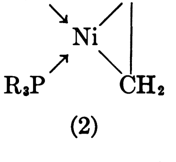
Bis(tetracyclone)nickel was obtained by reaction of tolane or of tetracyclone with $Ni(CO)_4$ (*5*).

Phosphine Compounds with Olefins or Alkynes. These compounds generally have the stoichiometry $M(PR_3)_2(Alk)$ (M = Ni, Pt; Alk = mono-olefin, diolefin, or alkyne). The derivatives with duroquinone have been obtained both from nickel bisduroquinone and tributylphosphine or tetracarbonylnickel, duroquinone, and the phosphine (*164*).

The derivatives with triethylphosphine and ethylene, styrene, stilbene, and methylstyrene have been prepared from bispentan-2,4-dionatonickel and alkylaluminum compounds in the presence of the phosphine and the olefin (*200*). The oxidation number of nickel in these compounds is controversial because the compounds can be considered to be either tricoordinated nickel(0) derivatives (1) or square planar nickel(II) derivatives (2).



(1)



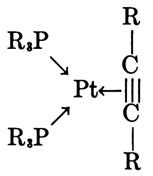
(2)

Analogous compounds with olefins having stronger π-acceptor properties, such as tetrafluoroethylene (*152*) or tricyanophenylethylene (*169*), have been isolated and studied. They are diamagnetic and stable in air; from IR and fluorine NMR spectra evidence, Parshall (*152*) considers the structure of $Ni(PPh_3)_2(C_2F_4)$ more apt to be Formula 2.

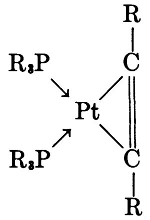
$Ni(CH_2{=}CH\text{-}CN)_2(PPh_3)$ and $Ni(CH_2{=}CH\text{-}CN)_2(PPh_3)_2$ were obtained from bisacrylonitrilenickel and triphenylphosphine (*166*). Platinum compounds have been obtained by reducing *cis*-$PtCl_2(PR_3)_2$ with hydrazine in the presence of an olefin (*50*). The olefins were *trans*-stilbene derivatives. The compounds obtained were stable to oxidation.

Compounds with aliphatic olefins or with diolefins have been easily obtained by reaction of $Pt(PPh_3)_2$ with the olefins, octene, *n*-pentene, butadiene, and cycloocta-1,5-diene (*187*). They are white, stable to oxidation, and exchange the olefin with other ligands easily. Tetracyanoethylene (C_6N_4) derivatives of the type $Pt(PR_3)_2(C_6N_4)$ (R = Et, Ph) have been obtained recently (*7*) by different reactions—i.e., from tetrakis(triphenylphosphine)-platinum(0) or *trans*-$PtHCl(PR_3)_2$ and tetracyanoethylene, or from $Pt(PPh_3)_2$(alkyne) and tetracyanoethylene. The compounds with the latter ligand are always more stable than the compounds with other olefins.

Some alkyne compounds have been isolated with platinum and nickel. The first were obtained from *cis*-$PtCl_2(PR_3)_2$ with hydrazine in the presence of the alkyne (*48*) or from bis(triphenylphosphine)-platinum(0) and the alkyne (*184*). They correspond to $Pt(PR_3)_2$(alkyne) and, like the corresponding nickel derivatives, can be considered tricovalent platinum(0) derivatives or square planar platinum(II) derivatives.



(3)



(4)

The spectroscopic evidence favors Structure 4 because the —C≡C— stretching band is shifted to 1700 cm.$^{-1}$, i.e., to a value corresponding to the —C=C— stretching. The same frequency shift was found in $Pt(PPh_3)_2CF_3C{\equiv}CCF_3$ (*29*), as compared with the value of 1820 cm.$^{-1}$ found for the cycloalkene (*124*) (Figure 3).

Some nickel derivatives with a formula $Ni(PR_3)_2$(alkyne) have been reported (*200*) (alkyne = tolane and butyne; R = Et) but not described in detail.

Miscellaneous Compounds

Some nickel(0) derivatives which could not be classified in a distinct class are reported here.

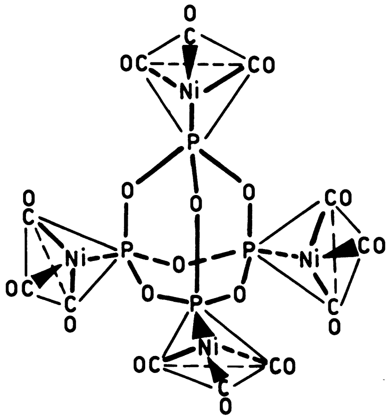


Figure 3

Compounds with Phosphorus(III)oxide. By reacting tetraphosphorus hexaoxide with tetracarbonylnickel, Riess *et al.* (*161*) obtained a compound which they considered to be Figure 4—i.e., a P_4O_6 molecule in which the four tricovalent phosphorus atoms are bound to four $Ni(CO)_3$ groups. The authors followed the reaction with phosphorus NMR spectroscopy and observed that the tricarbonylnickel groups are coordinated one after the other. Unfortunately, the compounds with less than four coordinated groups give way to further substitution and form polymeric substances.

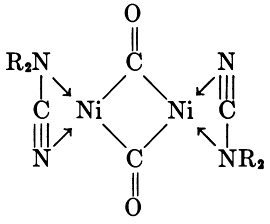
Substitution Compounds of $Ni(CO)_4$ by Aminophosphines, Cyanatophosphine, Thiocyanatophosphine. In the reaction of tetracarbonylnickel or bis(cyclopentadienylcarbonylnickel) with trisdimethylaminophosphine(L), the disubstitution compound, $Ni(CO)_2L_2$, was obtained (*114*, *148*).

$$C_5H_5NiCO_2 + 2L = Ni(CO)_2L_2 + Ni(C_5H_5)_2$$

The ligand $P[N(CH_3)_2]_3$ is a strong base with poor π-acceptor properties. This would be expected owing to the presence of the lone pairs on the nitrogen.

Tris(cyanato)phosphine, $P(NCO)_3$, and tris(thiocyanatophosphine), $P(SCN)_3$, give, on the contrary, tetrasubstitution (*204*), as would be expected for a strong π acceptor and yield white, diamagnetic compounds stable in air but which decompose in light.

Other Substitution Compounds of $Ni(CO)_4$. The dialkylcyanamide, R_2NCN (R = CH_3, $(CH_2)_5$), probably (*25*) yields:



Triphenylcyclopropane chloride and bromide give diamagnetic dimeric compounds considered in Figure 5 (*85*):

The nature of the compounds obtained from Ni(CO)$_4$ and the dimethylamides of Subgroup IV A metals (*30*) is, however, not yet well understood.

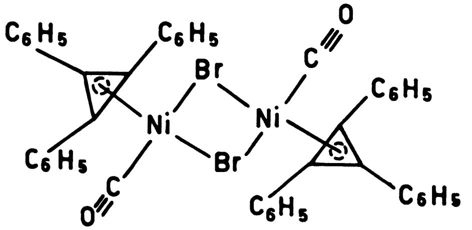


Figure 4

Catalytic Properties of Zerovalent Compounds

The catalytic properties of the nickel(0) derivatives have been studied extensively and have many industrial applications. We will briefly survey this field and will discuss some of the possible catalysis mechanisms proposed.

Carbonylation Reactions (*105,163*). Reppe (*160*) allowed acetylene, carbon monoxide, and tetracarbonylnickel to react in the presence of acids

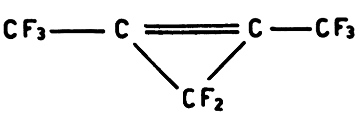
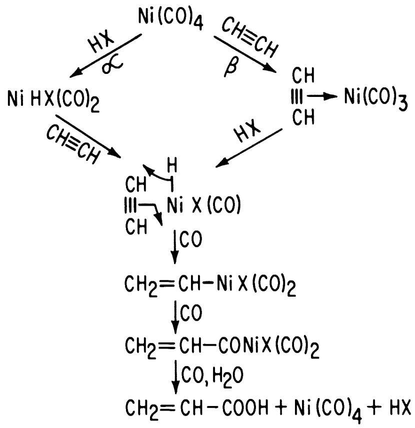


Figure 5

and obtained acrylic acid. This so-called carbonylation reaction in the presence of alcohols, thioalcohols, and amines gives esters, thioesters, and amides. The stoichiometry and the mechanism of this reaction have been greatly investigated (*163*), and it was found that water is essential to the reaction and that the reaction has an induction period. The most probable mechanism among the many proposed is shown below.



The induction period can be explained as the result of reactions α or β. The first, proposed by Heck (*89*), requires that tetracarbonylnickel have basic properties, but this could not be proved. In fact, the protonation reaction of carbonyls and carbonyl derivatives has been studied by Wilkinson and co-workers (*64*): $\mathrm{Ni(CO)_4}$ does react with acids but, contrary to $\mathrm{Fe(CO)_5}$, gives no NMR signal—indicating the formation of a hydride. However, the basic properties of some d^{10} systems have been recently shown in complexes with phosphines and arsines. The platinum(0) (*39*, *40*) derivatives yield stable hydrides according to the following equilibria:

$$\mathrm{Pt(PPh_3)_4} \rightleftharpoons \mathrm{Pt(PPh_3)_3} \underset{\mathrm{KOH}}{\overset{\mathrm{HX}}{\rightleftharpoons}} \mathrm{[PtH(PPh_3)_3]X} \underset{+\mathrm{PPh_3}}{\overset{-\mathrm{PPh_3}}{\rightleftharpoons}} \mathrm{PtHX(PPh_3)_2}$$

The nickel(0) and palladium(0) derivatives probably form unstable hydrides which react further with acids so that finally hydrogen (*40*) is released.

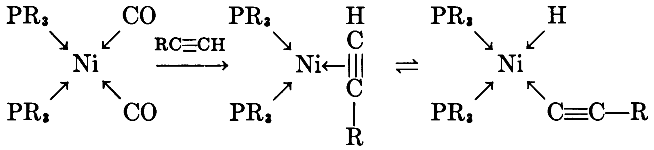
$$\mathrm{M(PPh_3)_4} \xrightarrow{\mathrm{HX}} \mathrm{MHX(PPh_3)_2} \xrightarrow{\mathrm{HX}} \mathrm{MX_2(PPh_3)_2} + \mathrm{H_2} \qquad (\mathrm{M} = \mathrm{Ni, Pd})$$

Also, the platinum(0) carbonyl derivatives, when reacting with acids, release the carbon monoxide and give hydrides (*38*):

$$\mathrm{Pt(CO)}_n\mathrm{(PPh_3)}_{4-n} + \mathrm{HX} = \mathrm{PtHX(PPh_3)_2} + n\mathrm{CO} + (2\text{-}n)\mathrm{PPh_3}$$

Therefore, the reaction of the carbonyls with acids to form hydrides seems probable. These reactions are very rapid and take place more easily if some carbon monoxide is replaced by a ligand with weaker π-acceptor properties (*40*). The induction period could be better explained by the reaction β, in which a CO molecule is replaced by acetylene. This reaction would probably proceed slowly and give a alkynyl carbonyl which should react better with acids than with $Ni(CO)_4$ because acetylene has a weaker π-acceptor character than carbon monoxide. The olefins can be carbonylated only under more drastic conditions (*163*).

Polymerization and Cyclization of Alkynes (*163*). In 1940 Reppe and Schweckendieck (*163*) discovered that the substitution derivatives of tetracarbonylnickel with phosphines, and particularly those of the type $Ni(CO)_2(PR_3)_2$, catalyze the linear polymerization and the cyclization to benzene derivatives of alkynes. Schrauzer (*167*) more recently showed that stoichiometric amounts of bisacrylonitrilenickel give the cyclization reaction. The reaction becomes, on the contrary, catalytic in the presence of a tertiary phosphine. Meriwether and co-workers (*57*, *136*, *137*, *140*) studied the possible mechanism of Reppe's reaction. They showed that both the polymerization and the cyclization reactions are particularly effective with monosubstituted acetylenes, and that the cyclization reaction is influenced by steric and electronic effects. They then proposed a mechanism by which the induction time is ascribed to this rather slow reaction:



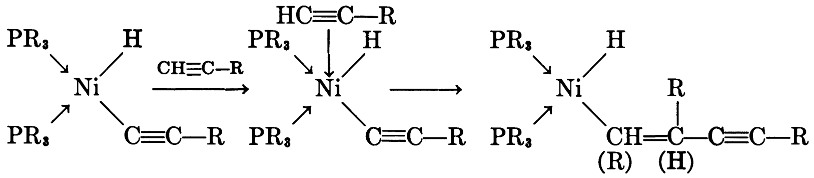
To prove this course, they carried out some investigations with D(1)-heptyne(1). The cyclization reaction is slower with the deuterated acetylene and, in the presence of $Ni(CO)_2(PPh_3)_2$, there is deuterium exchange between D(1)heptyne(1) and pentyne(1). This apparently indicates that the catalysis initiates with the breaking of the $\equiv C—H$ bond. Recent studies with platinum support this hypothesis even if, as in this case, the π compound is more stable than the hydride. In fact, $Pt(PPh_3)_2(HC\equiv CPh)$ can also be obtained by the following ways (*38*, *83*):

$$Pt(CO)_2(PPh_3)_2 + HC_2Ph = Pt(PPh_3)_2(HC_2Ph)$$

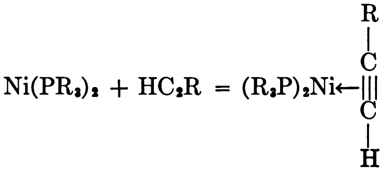
$$trans\text{-}PtHCl(PPh_3)_2 \xrightarrow{LiC_2Ph} PtH(C_2Ph)(PPh_3)_2 \rightarrow Pt(PPh_3)_2(HC_2Ph)$$

The subsequent polymerization mechanism should be analogous to that accepted for Ziegler-Natta reactions shown at the top of the following page.

The final step should consist of the hydrogen shifting to the polymerized hydrocarbon which would leave the coordination center, while the



coordinatively unsaturated $Ni(PPh_3)_2$ would rapidly add another alkyne molecule.



$$Ni(PR_3)_2 + HC_2R = (R_3P)_2Ni \leftarrow \begin{array}{c} R \\ | \\ C \\ ||| \\ C \\ | \\ H \end{array}$$

The fact that $Pt(PPh_3)_2$, which has been recently isolated, gives the over-reported reaction (*184*) is in accordance with this catalytic mechanism.

However, it is not yet well-understood why adding the alkyne to the nickel-hydrogen bond:

$$Ni\text{-}H + HC_2Ph = Ni\text{-}CH = CHPh$$

is not preferred to the insertion reaction which yields the linear polymer.

The trimerization reaction with benzene derivatives could sometimes follow a similar path but, since it also occurs with disubstituted acetylenes such as $HOCH_2C \equiv CCH_2OH$, some other mechanism must also be operating. Schrauzer explained the cyclization of tolane with a catalyst based on bisacrylonitrilenickel and triphenylphosphine by the so-called "π-complex, multicenter processes." With this process, three alkyne molecules would successively coordinate with nickel and then the ring closure would take place (*See* Figure 6).

The ligand L, which can be a triphenylphosphine molecule, hinders the fourth molecule of the acetylene from coordinating and, by preventing the formation of metallic nickel, makes the process catalytic. In fact, the same Schrauzer (*163*) obtained the polymerization of acetylene to cyclooctatetraene by a stoichiometric reaction with bisacrylonitrilenickel without any phosphine. He interpreted the reaction course as the formation of the intermediate, $Ni(C_2H_2)_4$, which then gives metallic nickel and the tetramer:

$$Ni(C_2H_2)_4 \rightarrow Ni + (C_8H_8)$$

However, some nickel(0) derivatives catalyze the cyclotetramerization. Leto and Leto (*120*), in fact, in the polymerization of propiolic esters $HC{\equiv}C{-}COOR$ by $Ni(PX_3)_4$ ($X = F, Cl$) obtained both the foreseen benzene derivatives and some cyclooctatetraene derivatives. Chini (*54*), on the other hand, from $HC{\equiv}CCH_2OH$ or $HC{\equiv}C\text{-}C(OH)(CH_3)_2$ recently obtained cyclooctatetraene derivatives with tetracarbonylnickel as the catalyst. With tricarbonylnitrosylcobalt, however, he obtained only benzene derivatives.

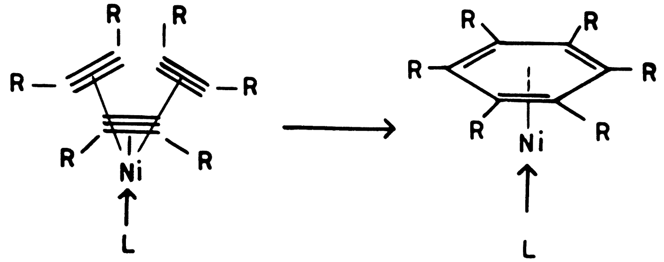


Figure 6

One can conclude that with some alkynes, if strong π acceptors are present in the catalyst, as CO or PX_3, a catalytic multicenter process can take place in which as many as four alkyne molecules are bound to nickel(0). However, when a coordination site is blocked by a ligand difficult to replace, the four-center process changes to a three-center.

The reason why the tetramerization reaction takes place catalytically in these cases without any separation of metallic nickel is not yet understood. This could be ascribed to the nature of the ligands, however, which can react with the nickel "*in statu nascendi.*" These results are interesting because they show that the tetramerization of the alkynes can be induced catalytically not only with nickel(II) compounds but sometimes also with tetrahedral nickel(0) derivatives (*170*).

Diene Cyclization. In 1952 Reed (*157*) discovered the catalytic dimerization of butadiene with Reppe catalyst in the presence of acetylene. Important results were obtained by Wilke (*200*) in the cyclization of butadiene with a nickel(0) catalyst. With bis-π-allylnickel, biscyclo-1,5-octadienenickel, or cyclododecatrienenickel, he obtained the trimerization of butadiene to cyclododecatetraene while, with a catalyst of the type $Ni(PR_3)_4$, in which perhaps one coordination site cannot be replaced, he obtained the dimerization to cycloocta-1,5-diene. The mechanism of these reactions, in which π-allyl systems can be in equilibrium with σ-π-allyl systems (Figure 7), have been proved by Wilke and co-workers who isolated the intermediate compounds. It is worth noting that all these catalysts have ligands of weak π-acceptor character which are labile and do not prevent butadiene from coordinating. The presence of weak π acceptors on the nickel tends to favor the structure of the diene, as was emphasized by Mason (*112*).

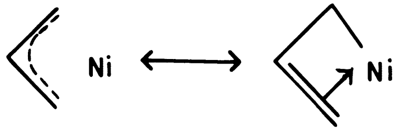


Figure 7

In fact, in this case the population of the lowest antibonding level in the diene increases as a consequence of the back donation mechanism. This corresponds, in valence bond terms, to a structure with two σ and one π bond instead of the structure with two π bonds (Figure 8). This strongly increases the reactivity of the 1,4-positions of the diene.

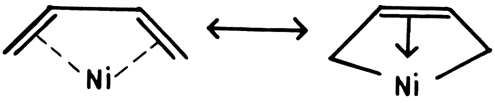


Figure 8

Discussion

From this survey some general features can be emphasized.

a) The stability of the compounds with good π-acceptor ligands, such as CO, PF_3, CNR, $C{\equiv}N$, and $HC{\equiv}C$, decreases with increasing atomic number, while the stability to oxidation of compounds with weak π-acceptor ligands (as tertiary phosphines, arsines) increases. The compounds with the ligands ammonia and ethylenediammine, having no π character at all, are anomalous and could be prepared only with platinum.

b) The number of ligands bound to the metal is generally four, sometimes three, and in a few cases two. The stability of the compounds with three and two ligands increases with increasing atomic number. Therefore, compounds of the type ML_3 have been obtained with palladium and platinum (where L is PR_3 or $P(OR)_3$), and compounds of the type ML_2 have been obtained with palladium (where L is CNR) and with platinum (where L is PPh_3). On the other hand, no similar nickel derivatives have ever been isolated for certain. Analogously, the complex acetylides are $K_4[Ni(C_2H)_4]$, $K_2Pd(C_2H)_2$, and $K_2Pt(C_2H)_2$.

c) The reaction rates of the zerovalent compounds of this group are high in comparison with the penta- and hexacoordinated zerovalent compounds of the other groups and decrease in the order Ni $\gg$ Pd $>$ Pt.

The interpretation of these facts is not easy, as the stability of the zerovalent state depends, among other things, on the interaction of the d electrons of the metal with the vacant low energy orbitals of the ligands.

The amount of π back donation in a symmetric electronic system, as a d^{10} atom, is still controversial. The d^{10} configuration, which in the gaseous state has spherical symmetry, is very stable. As a consequence, the ionization potential in the d^{10} configuration is much higher than in the spin-paired d^6 or d^8 configuration (*150*).

However, nickel has an ionization potential of 5.81 ev, not much higher than chromium (4.01 ev) and iron (3.9 ev) (always considering the spin-paired configuration), while palladium and platinum have 8.33 and 8.20 ev, respectively. Therefore, if the process of giving a π bond is compared with that of taking a d electron away from the metal, then the d^6 Cr^0 and the d^8 Fe^0 should give back bonding more easily than Ni^0, and the latter much more easily than Pd^0 or Pt^0.

This is in accordance with the facts—e.g., $Cr(CO)_6$ and $Fe(CO)_5$ are more stable to dissociation than $Ni(CO)_4$, and nickel(0) derivatives with strong π-acceptor ligands are more stable than palladium(0) and platinum(0) derivatives. Nyholm (*150*) considers that palladium and platinum carbonyls are not stable on account of their high ionization potentials $d^{10} \rightarrow d^9$, but other factors as the atomization heat and the spin-coupling energy should also respond to the ΔG of the formation reaction:

$$M_{(gas)} + nCO = M(CO)_{n(gas)}$$

However, as the atomization heat and the spin-coupling energy favor $Pd(CO)_4$, in comparison with $Ni(CO)_4$ and $Pt(CO)_4$, the influence of the back donation mechanism must be operative. Besides, the IR C–O stretching bands of the isoelectronic systems $Ni(CO)_4$, $[Co(CO)_4]^-$, and $[Fe(CO)_4]^{-2}$ show a downward shift of about 100 cm.$^{-1}$, with an increasing negative charge (*68*) which can only be explained by an increased back donation. Analogous is the case of the IR C–N stretching band of $[Ni(CN)_4]^{-4}$ (1985 cm.$^{-1}$), in comparison with $[Ni(CN)_4]^{-2}$ (2127 cm.$^{-1}$) (*6*).

All this could be taken as evidence for the π bonding in d^{10} tetrahedral configuration. On the other hand, the force constant of Ni-C in tetracarbonylnickel (2.1-2.5 mdyne/A.) (*111*, *179*) was found to be similar to the M-C force constant in $Ge(CH_3)_4$, $Sn(CH_3)_4$, and $Zn(CH_3)_2$, which is about 2.5 mdyne/A. (*36*). Taking three as the bond order in pure carbon monoxide, the C-O bond order in tetracarbonylnickel is 2.64 and that of Ni-C bond only 1.33—much less than it is usually considered (*179*). The thermochemical data show too, apparently, that the M-C bond order in $Ni(CO)_4$ is less than in $Fe(CO)_5$ and $Cr(CO)_6$. In fact, the bond energies, calculated with respect to the spin-coupled valence states, are CrC:55, FeC:58, and NiC:46 kcal./mole (*177*).

It is not easy to get an exact idea of the amount of π bonding. Kimball (*113*) considered that in a *Td* symmetry only two strong π bonds can be formed—through the d_{z^2} and $d_{x^2-y^2}$ orbitals. Cotton (*60*), on the contrary, pointed out that the four ligand σ orbitals span the representations A_1 and T_2, and that the set of eight π orbitals of the ligands spans the representation E, T_1, and T_2. Therefore, from simple symmetry considerations, five π bonds result. These can be of the same strength (using the five d orbitals), or two can be strong (using the d_{z^2} and $d_{x^2-y^2}$ orbitals) and three weak (using the three p orbitals). In effect, the situation is intermediate, and the d_{z^2} and $d_{x^2-y^2}$ should form stronger bonds. This is in accordance with the easy substitution of the first two CO molecules in $Ni(CO)_4$.

The amount of Ni–C π bond seems to increase with the replacement of CO by suitable ligands. The study of the IR spectra of the series of compounds $Ni(CO)_{4-n}L_n$ (where $n = 1, 2, 3,$ and 4 and $L = PR_3$, $P(OR)_3$, PX_3, and RNC) appears to confirm that Ni–C force constants are complementary to C–O force constants. This means that the negative charge density in the metal is partially distributed on carbonyl groups.

Many of these studies have been carried out by Bigorgne (*19*), who has found in $Ni(CO)_4$ by a simplified calculation of the force constants, an Ni–C bond order not higher than 1.25. The force constants Ni–C in $Ni(CO)_{4-n}L_n$ increase with the substitution and basicity of the ligand, as shown in Table I.

If we compare the force constants (*180*) for the three isoelectronic compounds $Ni(CO)_4$, $[Co(CO)_4]^-$, and $[Fe(CO)_4]^{-2}$ and for the triad $NiCO_3(PMe_3)$, $Ni(CO)_2(PMe_3)_2$, and $Ni(CO)(PMe_3)_3$ (*19*) we find that, in $Ni(CO)(PMe_3)_3$, the C-O bond order is about the same as that in $[Co(CO)_4]^-$, and the M–C bond order is the same as that in $[Fe(CO)_4]^{-2}$. On the other hand, $Ni(CO)_4$ and $Ni(CO)_3(PMe_3)$ have about the same M–C bond order, which rapidly increases in $Ni(CO)_2(PMe_3)_2$, as if a strong stabilization occurred in the disubstituted derivative. Bigorgne (*18*, *21*) also studied the series $Ni(CO)_{4-n}(NCR)_n$ (where $n = 1, 2, 3,$ and 4 and $R = Me$ and Ph), as shown in Table II.

The CO force constants decrease with decreasing number of CO ligands, while the CN force constants increase with decreasing number of MeNC ligands. The variations, however, are very small indeed. This explains why all four CO molecules of $Ni(CO)_4$ can be easily replaced

Table I. Force Constants

	$Ni(CO)_4$	$Co(CO)_4$	$Fe(CO)_4^{-2}$
$K_{M\text{-}C}$ (mdyne/A.)	2.49	3.55	4.06
$K_{C\text{-}O}$ (mdyne/A.)	16.28	13.22	11.40

Table II. Force Constants in Nickel Complexes

	$Ni(CO)_4$	$Ni(CO)_3L$	$Ni(CO)_2L_2$	$NiCOL_3$	NiL_4 ($L = CNMe$)
$K_{C\text{-}O}$ (mdyne/A.)	17.3	16.45	15.45	14.35	—
$K_{C\text{-}N}$ (mdyne/A.)	—	16.3	15.85	15.50	15.20

by isocyanides; in fact, in the substitution compounds the M-C bond energies are about the same as those in the carbonyl itself.

The attempts to assign the order of the bonds from the electric moments had very little success in that a very improbable bond order of 1.6–1.7 was found for Ni–P and Ni–As bonds (*43*). More interesting seems to be the estimate of the charge densities on the ligands from the electric moments (*22*, *23*). The results of the series $Ni(CO)_{4-n}P(OMe)_{3n}$ (n = 1, 2, and 3) are listed in Table III.

Table III. Charge on the Ligand in Nickel Compounds

	$Ni(CO)_3\,P(OMe)_3$	$Ni(CO)_2\,P(OMe)_3$	$NiCO\ P(OMe)_3$
π% Ni-C	0.21	0.44	0.71
(charge on the ligand)	0.24 e^-	0.14 e^-	0.08 e^-

This is in accordance with the results of IR spectroscopy which give the same bond order in $[Co(CO)_4]^-$ and in $Ni(CO)(P(OMe)_3)_3$. In fact, the decrease in the force constant from $Co_2(CO)_8$ to $[Co(CO)_4]^-$ is due to an increase of charge of 0.25 electron on each CO, analogous to the decrease in the force constant from $Ni(CO)_4$ to $Ni(CO)(P(OR)_3)_3$ which was brought about by 0.08 × 3 = 0.24 electron on the unique CO group. Also the ^{31}P NMR spectroscopy confirms an electronic flux when carbon monoxide is replaced by ligands which have strong σ-donor and weak π-acceptor properties (*139*) (*See* Table IV.).

It appears that with weak σ donors and strong π acceptor, such as PCl_3 or $P(OEt)_3$, the δ_P has rather little variation with increasing substitution,

in Carbonyls

$Ni(CO)_3PMe_3$	$Ni(CO)_2(PMe_3)_2$	$Ni(CO)(PMe_3)_3$
2.06	3.25	4.1
16.15	14.9	13.65

Table IV. Chemical Shifts

	Free Ligand δ_P	*Ni(CO)$_3$L* δ_P	$\Delta\delta_P$
PCl_3	−215	−185	+30
$P(OEt)_3$	−140	−157	−17
PPh_3	+ 6.6	− 42.9	−49.5
PEt_3	+ 19.1	− 47	−66.1

[a] The ^{31}P chemical shift is in ppm, with H_3PO_4 as standard.

while a stronger effect takes place with better σ donors and weaker π acceptors as PPh_3 and PEt_3. The negative value of δ_P is associated with the formation of a good σ bond, P → Ni.

The positive value found for PCl_3 (and for other halogenophosphines) can be understood as an inductive effect or as a very strong π bond which deshields the phosphorus atom. Many authors prefer the first explanation. In fact, in the case of PF_3 the Ni-P force constant was 2.7 (*206*) or 2.37 mdyne/A. (*123*)—a rather low value which does not indicate the presence of a double bond. On the other hand, the examination of the force constants in the series $Ni(CO)_{4-n}(PF_3)_n$ (n = 0, 1, 2, 3, and 4) indicates that PF_3 has about the same properties as CO (*59*, *123*). This is supported also by the statistical distribution of the products in the exchange reaction between $Ni(CO)_4$ and PF_3 and by the little variation of ^{31}P NMR chemical shift on these products (*56*). Loutellier and Bigorgne (*123*) prefer to consider trifluorophosphine as a weak σ donor and weak π acceptor for the following reasons.

The P-F force constant is about the same in both the free and complexed ligand, and this could not happen if the electronic density of phosphorus were perturbed by π back donation. Besides, the correlation of Taft's σ constants, with the CO stretching in the compounds $Ni(CO)_{4-n}(PX_3)_n$ (X = Et, Ph, OR, F, C≡CPh, CF_3), shows that the decrease of CO with a different X is fundamentally of an inductive nature (*20*).

This explains why $Pt(PF_3)_4$ and $Pd(PF_3)_4$ are stable, while the corresponding carbonyls have not yet been prepared. The negative charge on the central atoms of these compounds should, in fact, be quite negligible, so that a back-donation mechanism should not be necessary to stabilize the zerovalent state. We pointed out before that with palladium and platinum the back donation would be difficult because of the high ionization potential of the metals.

What we would like to emphasize here is that the nickel(0) compounds have a very high polarization and can easily give place to electronic exchanges, both by inductive and mesomeric mechanism (back donation), and that they are therefore very sensitive, even to little structural variations of the ligands.

of Nickel Complexes[a]

$Ni(CO)_2L_2$		$NiCOL_3$		NiL_4	
δ_P	$\Delta\delta_P$	δ_P	$\Delta\delta_P$	δ_P	$\Delta\delta_P$
−181	+34	−177	+ 38	−170	+45
−160	−20	−163	−160	−160	−20
− 32.6	−39.2	—	—	—	
− 20.7	−39.8	—	—	—	

We have pointed out also that the mesomeric mechanism in some carbonyl compounds can be important. In fact, the increase of the bond order by substitution with good σ donors can be ascribed to a better interaction of the *d* metal orbitals with the π-antibonding orbitals of carbon monoxide, owing to the destabilization of the *d* orbitals by increasing the charge on the metal (*67*). This could explain the stability of compounds such as $Pt(CO)_2(PAr_3)_2$ and $Pt(CO)(PAr_3)_3$, in comparison with the instability of $Pt(CO)_4$ (*150*). Besides, the influence of the π bonding is very apparent in the complexes with olefins. In fact, the olefins with electronegative groups, such as CN in $CH_2{=}CH{-}CN$, have a low energy antibonding orbital which can be used for the back donation and form the most stable compounds of this class.

The higher stability of palladium(0) and platinum(0) phosphine and arsine derivatives, in comparison with the corresponding nickel(0) derivatives, is not easy to understand. Probably the negative charge on the metals is rather high, and this makes nickel, which is the most electropositive of the triad, more unstable. Besides, if we consider "stability" as stability to oxidation, this will increase with increasing ionization potentials—i.e., in the order $Ni \ll Pd < Pt$. The presence of negative charge on the metal, in compounds ML_4 ($L =$ tertiary phosphine or phosphite), is proved by their easy dissociation to give tricoordinated compounds (*129*, *130*) and by their basic properties (*40*).

The stability of tricoordinated derivatives with weak π acceptors has been ascribed to the fact that it is much easier to form a π bond in a sp^2 hybrid than in a sp^3 hybrid (*113*). In fact, in the latter case, only two strong π bonds could form, while in a sp^2 hybrid the strong π bonds could be three (*2*). A structural investigation in progress (*16*) on $Pt(PPh_3)_3$ has confirmed the sp^2 hybridization with bond distances Pt-P slightly lower than the sum of the covalent radii. The platinum atom is 0.1 A. above the plane of the three phosphorus atoms, and this could be ascribed to the presence of a weak charge density on one side of the *z* axis. These results will aid in interpreting the kinetics of the substitution reactions of nickel(0) and platinum(0) derivatives.

Basolo and Wojcicky (*9*) studied the exchange reaction of CO in $Ni(CO)_4$ and found that the exchange does not depend on the concentration of CO. This means that the exchange follows a S_{N1} mechanism, and that the initial step is a dissociation reaction:

$$Ni(CO)_4 \rightleftharpoons Ni(CO)_3 + CO$$

The activation energy in toluene solution is 13 kcal./mole—much less than the energy of a Ni-C bond, which is 46 kcal./mole. This difference can be explained by the different sp^2 and sp^3 hybridizations and the consequential different amount of π bonding. This was confirmed by kinetic studies on the substitution reaction between $Ni(CO)_{4-n}L_n$ and L (L = tertiary phosphine), (*138*) which follow a S_{N1} mechanism. In the reaction

$$Ni(CO)_3L + L^* = Ni(CO)_2LL^* + CO$$

the initial step is the dissociation:

$$NiCO_3L \rightleftharpoons Ni(CO)_2L + CO$$

With different L (L = PPh_3, $P(n\text{But})_3$, $P(OEt)_3$) the rates are very similar, as though all the double bonds were concentrated on the CO moiety of $Ni(CO)_2L$. In the reaction:

$$Ni(CO)_2L_2 + 2L^* = Ni(CO)_2L_2^* + 2L$$

the initial step is:

$$Ni(CO)_2L_2 \rightleftharpoons Ni(CO)_2L + L$$

because, in this case, the carbon monoxide has been strongly stabilized.

No kinetic studies have been made on platinum carbonyl compounds; however, the carbonylation reaction of the tetrasubstituted phosphine derivatives of platinum(0) is slow enough for the tricoordinated compounds to isolate. The following steps have been proposed (*38*).

$$PL_4 \xrightarrow[\text{rapid}]{} PL_3 \xrightarrow[\text{slow}]{CO} Pt(CO)L_3 \xrightarrow[\text{rapid}]{} PtCOL_2 \xrightarrow[\text{very slow}]{CO} Pt(CO)_2L_2(L = PPh_3)$$

The reaction with carbon monoxide is slow on account of the very high stability of tricoordinated platinum derivatives. An S_{N1} kinetic mechanism has been found for other formally tricoordinated platinum derivatives (*3*)—e.g., in the reaction:

$$PtL_2(\text{alkyne}) + \text{alkyne}^* = PtL_2(\text{alkyne}^*) + \text{alkyne}$$

the dissociated step is:

$$\mathrm{PtL_2alkyne} \rightleftharpoons \mathrm{PtL_2} + \mathrm{alkyne}$$
$$(\mathrm{L} = \mathrm{PPh_3},\ \mathrm{alkyne} = \mathrm{RC_6H_4C{\equiv}CH})$$

It was found that the reaction rate decreases as the electron-withdrawing power of the R groups increases, and this fact is in accordance with a back donation from the platinum(0) to the alkyne.

It appears, therefore, that while in other d^n systems the possibility of nondissociative mechanisms increases for the heavier numbers, this is not the case for d^{10} zerovalent metals. The high stabilities of the coordinatively unsaturated states are probably ascribed to the poor π-bonding aptitude of higher coordinations.

Very little is known about the formally dicoordinated $\mathrm{Pd(CNR)_2}$ and $\mathrm{Pt(PPh_3)_2}$. The isocyanide palladium compounds can exist in two forms—the brown one probably being polymeric through metal-metal bonds. In fact, the IR C-N stretching band is at 2099 cm.$^{-1}$ in comparison with 2145 cm.$^{-1}$ (*37*) in the free ligand, showing that the isocyanide is not bridging. The clearer form, which is more stable with alkylisocyanides, has ν_{CN} at 1757 cm.$^{-1}$ (*79*), in comparison with 2150 cm.$^{-1}$ in the ligand. This may indicate a polymeric structure with bridging isocyanide groups (Figure 9).

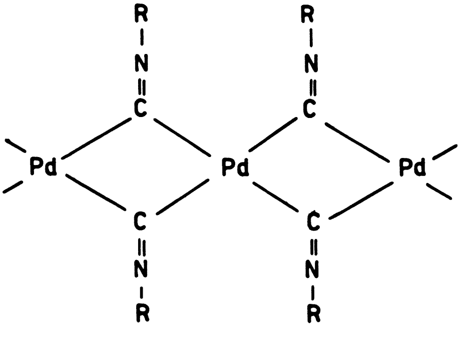


Figure 9

These compounds are very reactive, probably for the same reasons that $\mathrm{Fe_3(CO)_{12}}$ is more reactive than $\mathrm{Fe(CO)_5}$.

The compound $\mathrm{Pt(PPh_3)_2}$ which, in its yellowish form, is perhaps monomeric, gives a red polymeric form which is very reactive (*183*). The rapid reactions of this compound with hydrogen chloride, ethylene, butadiene, and hydrogen peroxide (*183*) confirm that some of the catalytic properties of these systems, particularly of nickel(0) derivatives, are ascribed to the presence of these highly reactive, coordinatively unsaturated species.

Conclusions

In conclusion, the zerovalent nickel, palladium, and platinum derivatives still offer a fertile field for new and extensive researches.

In particular, more structural data, more kinetic studies, a more thorough investigation of the platinum and palladium chemistry, the use of new techniques, such as ^{31}P NMR spectroscopy, and the determination of bond energies could increase our understanding of the bond nature and reactivity and make the interpretation of important catalytic mechanisms of these compounds easier.

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23

The Role of Optical Activity in the Development of Coordination Chemistry

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Werner relied on classical techniques involving the synthesis and separation of geometrical and optical isomers in establishing his intuitive coordination theory. To refute the belief that the optical activity might arise from the presence of carbon, Werner prepared and resolved $[Co((OH)_2Co(NH_3)_4)_3]X_6$. *Mills and Quibell resolved a Pt(II) complex which would be dissymmetric if planar, but not if tetrahedral. Bailar established the Walden type inversion for some substitution reactions of Co(III) complexes using optical rotatory dispersion (ORD) data. Recent studies of optical activity have concerned ORD and circular dichroism (CD) measurements which have been used for assigning absolute configurations. The CD studies are particularly useful in determining the stereochemistry of complexes from the splitting patterns determined by the molecular symmetry.*

Alfred Werner's coordination theory was intuitive. The substantiation of his flash of genius required many years of work. In the absence of physical methods on which we rely, he had to devise compounds which would permit one to distinguish among the various geometrical and binding situations which were considered. Werner had to consider all reasonable geometries, as well as a number of proposed descriptions which we would now dismiss as unreasonable, but which had to be refuted.

The general approach used was to prepare complexes which could exist in isomeric forms, the number of isomers expected depending upon the assumed model. So great was Werner's ingenuity and skill that many of the isomeric complexes now known can be considered to be some variation of those isolated by him. It is significant that optical activity played an important role in establishing the configurations of octahedral, tetrahedral, and even planar complexes before modern structural methods were used to settle the issues more directly.

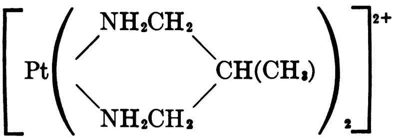
Although the term "chelate" was introduced later, it is apparent that Werner recognized and used chelation to great advantage. All of the optically active complexes prepared involved chelation. The relative stabilities of five- and six-membered chelate rings were studied later by Mann using the optical activity produced in a ligand when coordinated. He resolved the octahedral $[Pt(tap)Cl_4]$ (*41*) and planar $[Pt(tap)Cl_2]\cdot HX$ (*42*) (tap = α, β, γ-triaminopropane) to demonstrate that tap formed a five-membered ring giving an asymmetric carbon atom rather than a symmetrical six-membered ring.

Octahedral Complexes. Werner had shown for many examples that the number of geometrical isomers which could be isolated for complexes with coordination number 6 was that expected for an octahedron. However, the most powerful approach was reported in 1911 when he showed that complexes of the type *cis*-$[Co(en)_2X_2]^{n+}$ could be resolved into optical isomers (*68*). He reported the isolation of several more isomers of this type within a few months and the next year (*69*) reported the resolution of $[Co(en)_3]^{3+}$.

Werner must have felt satisfied that the octahedral arrangement of ligands in 6-coordinate complexes was firmly established, but some critics objected because the resolved complexes contained carbon, and optically active carbon compounds were well known. Werner silenced this objection by preparing and resolving a completely inorganic complex (*71*), $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$, in which the chelate ligands around the central Co(III) are the complex ions *cis*-$[Co(NH_3)_4(OH)_2]^+$. With this accomplishment, the major points of Werner's coordination theory for 6-coordinate complexes were firmly established long before modern structural methods were available.

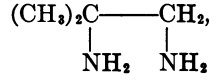
Tetrahedral and Planar Complexes. Two isomers of $[Pt(NH_3)_2Cl_2]$ were known, and Werner (*67*) proposed that they were cis and trans isomers with a planar configuration about Pt(II). Study of the reactions of this and other Pt(II) compounds led Werner to introduce the concept we now call the trans effect. Because isomerism of the type expected for a planar configuration was known only for complexes of Pt(II) and a few examples for Pd(II), the existence of anything other than a tetrahedral configuration for 4-coordinate species was questioned.

Mann (*43*) attempted to prove the configuration of



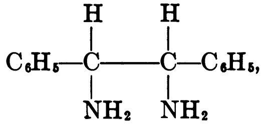
by looking for evidence of isomerism, but the attempt was unsuccessful. He found no cis-trans isomerism as expected for a planar complex, although we might expect the differences in physical properties to be too small to permit separating the isomers if they formed. If the complex ion were tetrahedral, it would be dissymmetric, but attempts to resolve it were unsuccessful. An unsuccessful resolution is never conclusive.

Mills and Quibell (*50*) ruled out a tetrahedral arrangement and provided evidence favoring a planar arrangement for the Pt(II) complex containing one molecule of isobutylenediamine,



$$(CH_3)_2\underset{NH_2}{\underset{|}{C}}\text{———}\underset{NH_2}{\underset{|}{CH_2}},$$

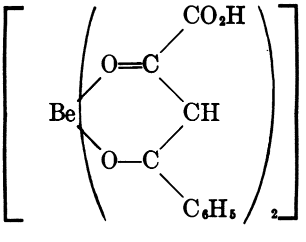
and one molecule of *meso*-stilbenediamine,



$$C_6H_5\text{—}\underset{NH_2}{\underset{|}{\overset{H}{\overset{|}{C}}}}\text{———}\underset{NH_2}{\underset{|}{\overset{H}{\overset{|}{C}}}}\text{—}C_6H_5,$$

by resolving the complex into optical isomers. The ion would contain a plane of symmetry if the N atoms are arranged tetrahedrally about the metal ion, but it is asymmetric for a planar configuration. The corresponding Pd(II) complex was also resolved, and the resolving agents were removed completely. Although these results eliminated a tetrahedral configuration, a pyramidal configuration about the metal ion could also account for the optical activity. It remained for structural methods to remove this uncertainty.

The burden of proof for planar 4-coordinate complexes was on Werner and those who supported this view for Pt(II) and Pd(II) complexes. In other cases chemists hardly needed to be convinced that the complexes should be tetrahedral. Tetrahedral complexes containing unsymmetrical bidentate ligands are dissymmetric, and this was demonstrated by the resolution of the Be(II) complex of benzoylpyruvic acid (*49*),



Optical activity was also demonstrated for the corresponding complexes of Zn(II) and Cu(II), although in these cases coordination numbers higher than 4 are more likely than for Be. In all three cases the resolving agent could not be removed in less time than required for complete racemization of the complexes. The complex bis(benzoylacetonato)beryllium(II) has been resolved on quartz, so that the active complex was obtained free from any resolving agent (*6*). The complex racemizes in a matter of hours.

Modern Developments

Reaction Mechanisms. Bailar (*2*, *3*) studied the formation of $[Co(en)_2CO_3]^+$ from optically active *cis*-$[Co(en)_2Cl_2]^+$ and found that products of opposite configurations were obtained under different conditions. He proposed a Walden type inversion for the substitution process. The configurations of the original complex and the products were related using optical rotatory dispersion curves. Dwyer (*19*) studied these reactions in detail and concluded that the inversion occurs through a trans displacement process involving both Ag^+ and OH^-

Measurements of optical rotations have been used to follow the course of other substitution reactions (*5*, *45*, *48*, *70*, *72*). The loss or retention of optical activity or inversion during a substitution process gives useful information concerning the mode of attack and the symmetry of intermediates or activated complexes. Studies of racemization and isomerization have led to elucidating the mechanism of stereochemical rearrangements in the fine work of Fay and Piper (*20*) with metal complexes of unsymmetrical 1,3-diketones.

Taube's review article (*64*), which provided the first basis for classifying inert and labile complexes, made use of all available observations of rates of formation or substitution reactions. Most of the observations were qualitative, but for the purpose of the classification it was sufficient to know whether the reaction was complete within a couple of minutes or whether a complex was sufficiently inert for geometrical or optical isomers to be isolated. Important qualitative observations came from attempts to resolve complexes, and much of the quantitative data came from studies of rates of racemization or isomerization.

There has long been dispute as to whether reduction processes such as in electroplating require the complex ion to dissociate first. Dissociation undoubtedly occurs in some cases, but Dwyer provided the most direct proof that oxidation and reduction processes can occur without dissociation (*15*). The optically active complex ion $[Ru(dipy)_3]^{2+}$ (dipy = dipyridyl) was oxidized to $[Ru(dipy)_3]^{3+}$ with Ce(IV) and then reduced back to the original complex ion with $FeSO_4$ without loss in rotation.

Stereospecific Effects. Early studies of Co(III) complexes of optically active propylenediamine (*62*, *65*, *66*), 1,2-cyclopentanediamine (*28*, *29*, *30*, *31*), and 1,2-cyclohexanediamine (*32*) indicated that one did not get all combinations of (+) and (−) ligand configurations with the two configurations of chelate rings in the tris complexes. The composition of the cyclopentanediamine complexes reported by Jaeger have been found to be incorrect (*53*) so the results are questionable. It was believed that for an optically active ligand one isomer, Λ[+++] or Δ[− − −], was formed exclusively. Later studies have shown that such stereospecific effects are generally not complete except for cases such as the sexadentate ligands propylenediaminetetraacetate ion and cyclohexanediaminetetraacetate ion.

Lifschitz (*39*) isolated both optical isomers of α-[Co(L-alaninate)$_3$] (meridional), and recently both optical isomers of the β (facial) isomer have been isolated in four laboratories. Bailar (*3*) isolated both isomers of [Co(−)pn$_2$CO$_3$]$^+$. He and several of his students have used the selective substitution in such optically active complexes of pn and en by a racemic mixture of a ligand to resolve partially the ligand. Dwyer studied the tris(propylenediamine) complexes of Co(III) (*16*) and Pt(IV) (*17*) and found that their formation is not absolutely stereospecific, as previously believed.

A classic paper by Corey and Bailar (*7*) provided the basis of understanding stereospecific effects in chelate complexes through conformational analysis of the chelate rings. Dwyer (*18, 58*) obtained all of the mixed en-(−)pn complexes with Co(III). The energy differences proved consistent with predictions from the Corey-Bailar treatment. Contributions to the optical activity from the vicinal effect of the pn and from the spiral of the chelate rings have been studied and found to be additive (*10*). Conformational aspects of chelate rings have been reviewed recently (*23*).

Spectroscopic Work. Early studies of optically active complexes used optical rotations at one or two wavelengths to characterize the compounds and to check for complete resolution. Later, optical rotatory dispersion (ORD) curves were used to relate configurations and establish whether they were retained or inverted during substitution reactions. Extensive ORD studies were made by Mathieu, Sargeson, Bürer, Hidaka, Shimura, Tsuchida, and several other Japanese workers. Kirschner (*1*) has studied the effects of inactive ions on ORD curves, and Woldbye (*73*) has studied the effects of ring size. Woldbye's excellent chapter (*74*) on ORD gives a comprehensive compilation of work on optically active complexes.

Mathieu (*44, 46, 47*) first combined studies of ORD, circular dichroism (CD), and absorption spectra of extensive series of complexes. During the same period Kuhn (*34*) was also interested in ORD and CD of complexes. Then for many years there was almost no active interest in CD studies. The renewal of interest in CD came about because of the surge in ORD work which was stimulated by improvements in instrumentation and by realizing the importance of Mathieu's and Kuhn's earlier work. Shortly after the reawakened interest in CD, the first recording instrument was developed (*24*) and was soon available.

Several CD papers have been concerned with assigning chirality to complexes. In most cases CD curves provide a more reliable basis for these assignments than do ORD curves because the components for individual electronic transitions are more easily separated for CD. An unequivocal assignment of chirality requires a definite assignment of a CD peak to an electronic transition, for which the sign can be predicted reliably.

The shapes of CD peaks are similar to those of absorption bands, but the CD peaks can be either positive ($\epsilon_l > \epsilon_r$) or negative ($\epsilon_l < \epsilon_r$) and, for transition metal complexes, the CD peaks are more narrow. The extent of overlap of CD peaks is far less serious than for ORD curves of more complex shape. Mason and co-workers (*4*) found that $(+)_D$-$[Co(en)_3]^{3+}$ gives two CD peaks of opposite sign in the region of the first absorption band. Only the positive CD peak is observed for light directed along the trigonal axis of the complex ion in a crystal. On this basis the long wavelength positive CD peak was assigned to the transition of E symmetry. The interpretation of the crystal CD spectrum has been questioned by Dingle (*9*), but Mason's assignment has been used as the basis for assigning many other complexes. The presence of two CD peaks in the first band region for the complex in solution reveals the true D_3 symmetry rather than the O_h symmetry suggested by the absorption spectrum, where the small trigonal splitting is not evident.

The absorption spectrum of K[Co(EDTA)] shows two intense symmetrical bands in the visible region (*33*, *60*), suggesting effectively cubic symmetry for the complex ion. However, the ORD curve reveals two Cotton effects in the long wavelength band region (*25*). The ion $[Co(en)(malonate)_2]^-$ was studied as a model, *cis*-$[CoN_2O_4]^-$, of $[Co(EDTA)]^-$, and the CD spectrum clearly revealed three peaks in each band region (*11*). This is the splitting expected for the true symmetry, C_2. Gaussian analysis of the CD curves for $[Co(en)(C_2O_4)_2]^-$ and $[Co(EDTA)]^-$ also gave three CD peaks in each band region. Gillard (*21*, *22*) looked at the CD spectrum of $[Co(EDTA)]^-$ without reference to the model compounds and concluded that only two CD peaks were present in each band region.

The absorption spectra of $[Fe(dipy)_3]^{2+}$, $[Fe(phen)_3]^{2+}$ (phen = 1,10-phenanthroline), and some related complexes are characterized by very intense and rather featureless charge transfer bands, which obscure the *d-d* transitions. Many papers have dealt with the solution spectra, and a recent paper reports polarized crystal spectra (*52*). The CD spectra reveal well-resolved peaks which have been assigned as *d-d* transitions (*26*). The ligand CD bands have been used to assign (*40*) the same configurations to $(+)$-$[Fe(dipy)_3]^{2+}$ and $(-)$-$[Fe(phen)_3]^{2+}$, even though the CD curves appear enantiomorphic throughout. This was done because of the differing symmetry of the π orbitals of the two ligands. It would not seem reasonable to expect the π bonding to reverse the signs of the CD peaks for the *d-d* transitions also, and the latter were used to assign the opposite configurations to these complexes (*26*). Mason *et al.* cited the solubilities of diastereoisomers as being consistent with their assignment, but the solubility rule is probably unreliable when the diastereoisomers differ in composition, as in this case (*26*). The CD spectra have also been used for metal complexes of dithiooxalate ion to observe the *d-d* transitions obscured in the absorption spectra by the intense charge transfer bands (*27*).

The stereochemistry of complexes containing multidentate ligands can be studied using CD spectra which often reveal the molecular symmetry rather than the higher effective symmetry suggested by the absorption spectra. Sargeson and Searle (*59*) studied the complexes of triethylenetetraamine of the type $[Co(trien)XY]^{n+}$. With X and Y in cis positions there are two isomers, one (α) with the terminal nitrogens trans to one another, and another (β) with them cis. The complexes were characterized and their absolute configurations assigned using CD spectra and knowledge of reaction mechanisms for the formation and reactions of the complexes.

Four isomers of $[Co(L\text{-alaninate})_3]$ have been prepared and studied by CD (*8, 12, 14, 36*). Denning and Piper used NMR spectra to support their assignments of the configurations of the isomers. Their assignments for the α and α' isomers (meridional) have been confirmed by an x-ray structure investigation of the α isomer (*13*).

Studies of ORD and CD spectra have been particularly important in developing the understanding of coordination chemistry because they give more detailed information about electronic transitions than is available from absorption spectra. Such information is of paramount importance in advancing bonding theories. Contributions to the theory of optical activity of complexes necessarily advance the bonding theories as well. Kuhn (*34, 35*) was an early contributor to the theory of optical activity of metal complexes. Moffitt (*51*) made important contributions in more modern terms. The recent theoretical work of Liehr (*37, 38*), Sugano (*63*), and Shinada (*61*) are of particular importance. Mason has been a major contributor to the experimental work in recent years with significant theoretical contributions also. Further advancement from the exceptionally fine experimental work and imaginative theoretical developments of the late Piper (*54, 55, 56, 57*) will be missed.

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24

Optical Activity and the Pfeiffer Effect in Coordination Compounds

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Since Werner's pioneering work on optical activity in complex inorganic compounds, there have been many important developments in the field. One of the more interesting of these is known as the "Pfeiffer effect," which is a change in the optical rotation of a solution of an optically active substance (e.g., ammonium d-α-bromocamphor-π-sulfonate) upon the addition of solutions of racemic mixtures of certain coordination compounds (e.g., D,L-*$[Zn(o\text{-}phen)_3](NO_3)_2$, where o-phen = ortho-phenanthroline). Not all combinations of complexes, optically active "environments," and solvents show the effect, however, and this work attempts to apply optical rotatory dispersion techniques to the problem, as well as to determine whether solvents other than water may be used without quenching the effect. Further, the question of whether systems containing metal ions, ligands, and optically active environments other than those already used will show the effect has been studied also.*

Since Werner's early paper (*19, 20*) on the optical activity he postulated and discovered in coordination compounds, there have been several discoveries closely related to this work. One of these is the observation by Pfeiffer and Quehl (*15*) that the optical rotation of an aqueous solution containing an optically active substance (e.g., ammonium *d*-α-bromocamphor-π-sulfonate, later referred to as the optically active "environment") may be changed by adding solutions of racemic mixtures of certain coordination compounds (e.g., D,L-$[Zn(o\text{-phen})_3](NO_3)_2$, where *o*-phen = *ortho*-phenanthroline). This effect has been referred to as the "Pfeiffer effect" in honor of its discoverer (*3, 4*) who first observed it during an attempted resolution of the racemic complex mentioned above (*15*).

Further studies of the effect were carried out by Pfeiffer and his co-workers (*14*, *16*), Brasted (*5*), Dwyer and co-workers (*7*), Kirschner (*9*), and others (*10*, *11*). Table I shows the systems which exhibited the Pfeiffer effect.

In this work the authors have attempted to expand the scope of the Pfeiffer effect to other systems and solvents and to determine unambiguously the source of the effect. To this end they applied optical rotatory dispersion techniques as a tool in their study.

Table I. Systems Exhibiting the Pfeiffer Effect

Complex[a]	*Optically Active Compound or Ion*	*Solvent*	*Reference*
$[Zn(o\text{-phen})_3](NO_3)_2$	*d*-camphorsulfonate	Water	(*15*)
$[Zn(o\text{-phen})_3]^{++}$	*d*-bromocamphorsulfonate	Water	(*15*)
"	*d*-cinchonine hydrochloride	Water	(*15*)
"	*l*-strychnine sulfate	Water	(*15*)
"	*d*-cinchonine monochloromethylate	Water	(*16*)
"	*d*-quinic acid	Water	(*16*)
"	*l*-nicotine	Water	(*16*)
$[Zn(dipy)_3]^{++}$	*d*-camphorsulfonate	Water	(*15*)
"	*d*-bromocamphorsulfonate	Water	(*16*)
$[Zn(8\text{-amq})_2]^{++}$	*d*-bromocamphorsulfonate	Water	(*11*)
$[Cd(o\text{-phen})_3]SO_4$	*d*-camphorsulfonate	Water	(*16*)
$[Cd(dipy)_3]^{++}$	*d*-bromocamphorsulfonate	Water	(*16*)
$[Cd(o\text{-phen})_3](NO_3)_2$	*d*-bromocamphorsulfonate	Water	(*16*)
$[Ni(o\text{-phen})_3]SO_4$	*d*-bromocamphorsulfonate	Water	(*14*)
$[Cd(o\text{-phen})_3]^{++}$	*l*-nicotine	Water	(*16*)
$[Ni(o\text{-phen})_3]^{++}$	*d*-camphorsulfonate	Water	(*14*)
"	*l*-nicotine	Water	(*14*)
$[Ni(dipy)_3]SO_4$	*d*-bromocamphorsulfonate	Water	(*14*)
$[Co(o\text{-phen})_3]SO_4$	*d*-bromocamphorsulfonate	Water	(*14*)
$[Co(o\text{-phen})_3]^{+++}$	*d*-bromocamphorsulfonate	Water	(*5*)
$[Mn(o\text{-phen})_3]^{++}$	*d*-camphorsulfonate	Water	(*16*)
$[Cu(edta)]^{-2}$	*l*-quinine hydrobromide	Water	(*9*)

[a] Abbreviations: *o*-phen = *ortho*-phenanthroline; edta = ethylenediaminetetraacetate; 8-amq = 8-aminoquinoline; and dipy = 2,2′-dipyridyl.

Experimental

All solutions were prepared from reagent grade chemicals and solvents without further purification. Two of the new ligands which were tested for the Pfeiffer effect, 2-(2-pyridyl)-benzimidazoline and 2-(2-pyridyl)-imidazoline, were prepared by the method of Walter and Freiser (*18*). The other ligand which had to be synthesized, (ethanediylidenetetrathio)tetraacetate (ETTA), was prepared by the method of Longo *et al.* (*12*). Tris(ethylenediamine)nickel(II) chloride was prepared by the method of State (*17*). Bis(salicylidene)triethylenetetramine aluminum(III) iodide $[Al(TS_2)]I$ was prepared by the method of Das Sarma and Bailar (*6*).

Necessary spectra were determined on a Cary Recording Spectrophotometer, Model 14. Optical rotations were determined with a Perkin-

Elmer Photoelectric Polarimeter, Model 141. Optical rotatory dispersion measurements were made either with the Perkin-Elmer instrument equipped with a Bausch and Lomb High Intensity Grating Monochromator, or with a manual spectropolarimeter constructed by Kirschner and co-workers (*1*) at Wayne State University. This instrument has been modified by replacing the calcite polarizing and analyzing prisms with quartz prisms and changing light source to a 500-watt Hanovia Xenon Arc Lamp.

Discussion and Results

The Pfeiffer Effect in Nonaqueous Solvents. ALCOHOLS. Because inner complexes are usually not soluble in water, and because the Pfeiffer effect has not yet been demonstrated to occur with an inner complex, the effect was studied in solvents other than water. One obvious choice is the lower alcohols because these solvents will dissolve most inner complexes and are suitable for polarimetric studies. However, Landis (*11*) has reported that the Pfeiffer effect does not take place in methanol with tris(1,10-phenanthroline)zinc(II) ion and *d*-α-bromocamphor-π-sulfonate (BCS) as the optically active environment. He reports that the final solutions were cloudy; therefore, their optical rotatory properties would be difficult to study, and the question was still open.

During the course of this work the authors were not able to observe the Pfeiffer effect in ethanolic solution. The optically active environments employed were *d*-camphor or 3-*d*-bromocamphor, and the complexes which

Table II. Systems Found Not to Exhibit the Pfeiffer Effect

Complex[a]	*Optically Active Environment*	*Solvent*
$Zn(bzac)_2$	*d*-camphor	Ethanol
$Ni(en)_3Cl_2$	*d*-α-bromocamphor-π-sulfonate	Water
$Zn(TTA)_2$	*d*-camphor	Ethanol
$Ni(dipy)_3Cl_2$	3-*d*-bromocamphor	Ethanol
$Ni(dipy)_3Cl_2$	*d*-(–)-camphoric acid	Ethanol
1 $NiCl_2$:3 dipyam	3-*d*-bromocamphor	Ethanol
1 $Zn(NO_3)_2$:2 terpy	*d*-α-bromocamphor-π-sulfonate	Water
Fe(*o*-phen)$_3$(ClO$_4$)$_2$	*d*-SbOtart	Water
$Zn(Bzac)_2$	3-*d*-bromocamphor	Ethanol
Cu:ETTA	*d*-α-bromocamphor-π-sulfonate	Water
Ni:3 pybim	*d*-(–)-camphoric acid	Ethanol-Water
$Cu(terpy)_2$	*d*-α-bromocamphor-π-sulfonate	Water
$Al(TS_2)$ I	*d*-α-bromocamphor-π-sulfonate	Water

[a] Abbreviations: Bzac = benzoylacetonate; en = ethylenediamine; TTA = thenoyltrifluoroacetonate; dipy = 2,2′-dipyridyl; dipyam = 2,2′-dipyridylamine; terpy = 2,2′,2″-terpyridyl; *o*-phen = 1,10-phenanthroline; ETTA = (ethanediylidenetetrathio)tetracetate; pybim = 2-(2-pyridyl)-benzimidazoline; *d*-SbOtart = *d*-antimonyltartrate; and TS_2 = bis(salicylidene)triethylene-tetramine.

were used are listed in Table II. The fact that the substances utilized for optically active environments are essentially nonionic may have been the reason for not observing the effect. Of course, it is possible that the effect does occur, but that the magnitude of the change in rotation is not large enough to be observed with the present instrumentation.

AMIDES AND ACIDS. The authors also found that the Pfeiffer effect can be observed in both *N,N*-dimethylformamide and glacial acetic acid. Figures 1 and 2 show the effect of changing the solvent composition from pure water to either glacial acetic acid or *N,N*-dimethylformamide. These figures show that the magnitude of the effect is greatly reduced in both solvents compared with water and that the sign of the effect changes in the acetic acid-water system.

Once these solvents had been established as suitable, they were applied to other systems besides the $[Zn(o\text{-phen})_3](NO_3)_2$-BCS system. One of the ligands of interest is 2-(2-pyridyl)-benzimidazoline, and preliminary work showed that the ligand would not form stable aqueous solutions with zinc(II) ion. However, ligand and zinc nitrate were successfully dissolved in glacial acetic acid. Several solutions, each containing both zinc nitrate and ammonium *d*-bromocamphorsulfonate, were prepared and were treated with the following ligands (one to each solution): *ortho*-phenanthroline, 2,2′-dipyridyl, and 2-(2-pyridyl)benzimidazoline. The resulting solutions were 0.01*M*. in zinc(II) ion and 0.03*M*. in ligand. Polarimetric measurements on the solutions both with and without the ligands showed that *ortho*-phananthroline produced the largest Pfeiffer effect and 2,2′-dipyridyl the smallest, with 2-(2-pyridyl)-benzimidazoline being between the two.

The Pfeiffer Effect in Aqueous Solution. During this work several additional systems which do not display the Pfeiffer effect in water were observed. These systems are reported in Table II. The ligands involved in these systems are: ethylenediamine, (ethanediylidenetetrathio)tetraacetate, bis(salicylidene)triethylenetetramine, and 2,2′,2″-terpyridyl.

Another ligand, 2-(2-pyridyl)-imidazoline, exhibited the Pfeiffer effect in water. The effect was observed with zinc(II) as the central metal ion and *d*-α-bromocamphor-π-sulfonate as the optically active environment. However, the effect was not observed for this ligand and nickel(II) in water, but the evidence for complex formation was not conclusive in this case.

Because the Pfeiffer effect is exhibited by tris(1,10-phenanthroline)-nickel(II) ion and *d*-α-bromocamphor-π-sulfonate and, because the complex has an absorption band in the visible region, this system was studied using optical rotatory dispersion techniques. The study revealed that the optical rotatory dispersion curves showing Pfeiffer rotation *vs.* wavelength were very similar to that of the resolved complex (Figures 3 and 4) (*8*).

The observed Pfeiffer rotation, $P_{obs.}$, is defined as:

$$P_{obs.} = \pm(\alpha_{s+c} - \alpha_s) \quad (1)$$

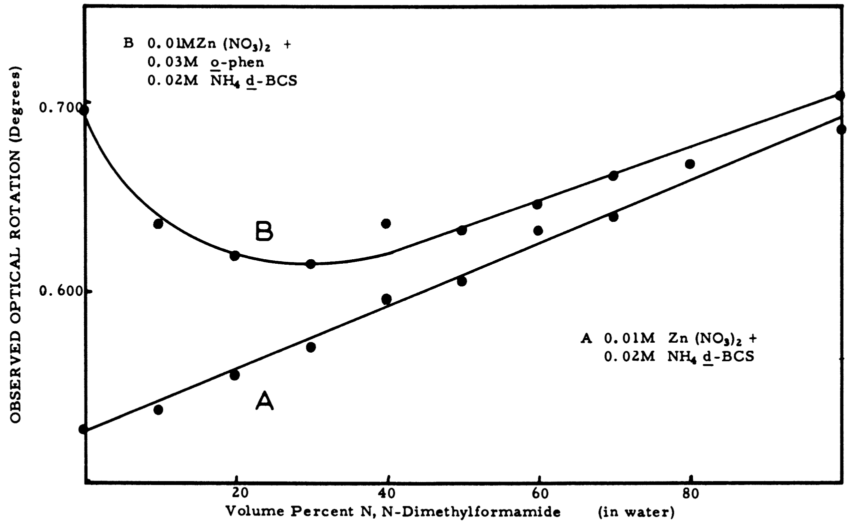

Figure 1. The Pfeiffer effect in N,N-dimethylformamide

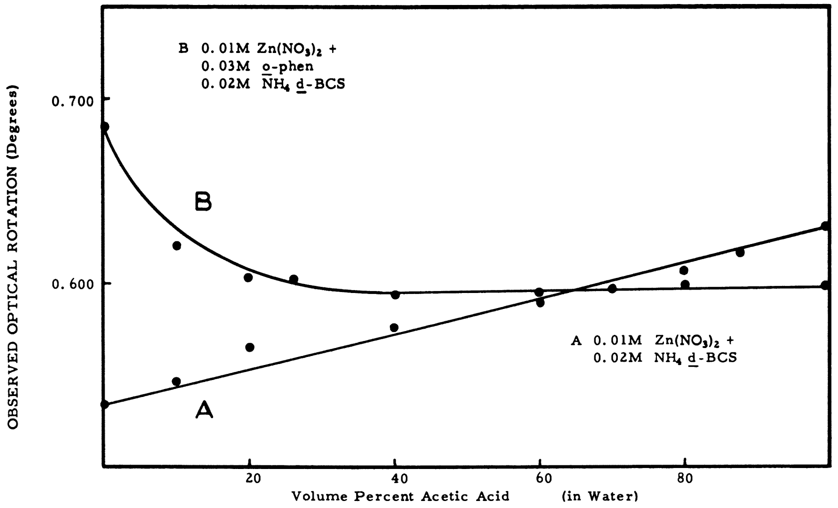

Figure 2. The Pfeiffer effect in acetic acid

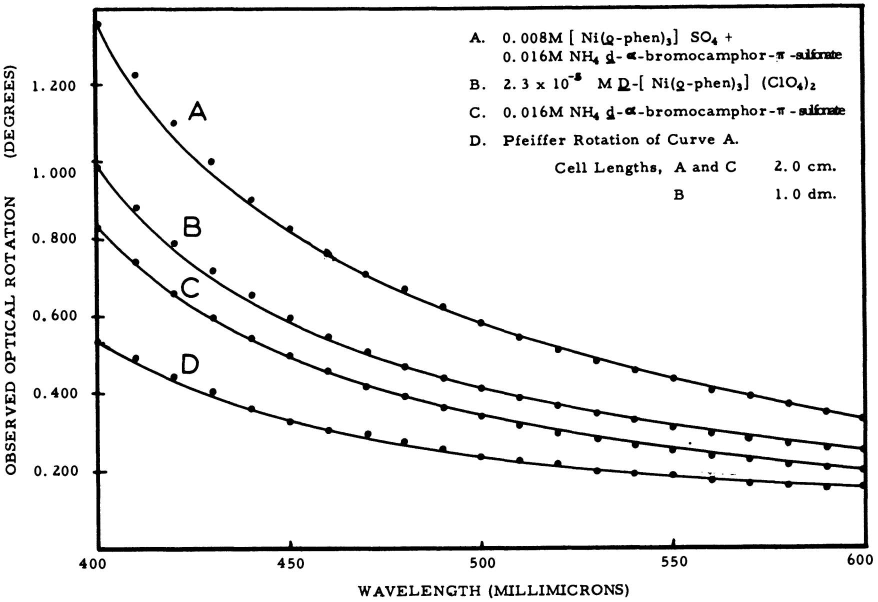

Figure 3. Comparison of the optical rotatory dispersion and the Pfeiffer rotation of $[Ni(o\text{-}phen)_3]^{++}$

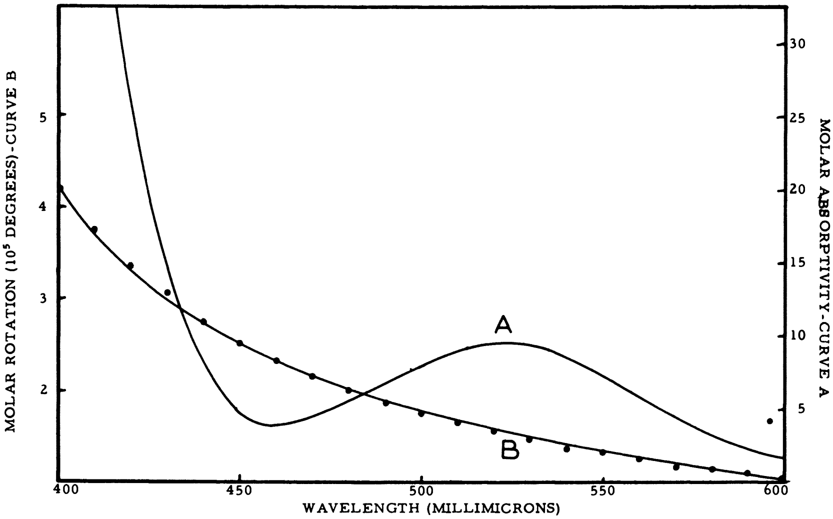

Fig. 4--- Optical Rotatory Dispersion and Absorption of $[Ni(o\text{-}phen)_3]^{++}$

Figure 4. Optical rotatory dispersion and absorption of $[Ni(o\text{-}phen)_3]^{++}$

where α_{e+c} is the observed rotation of the solution containing both the environment and complex, and α_e is the observed rotation of the solution containing the optically active environment compound alone. The sign to use in front of the parentheses is the same as the sign of rotation of α_e. Calculations involving the molar rotation of the resolved complex and the observed Pfeiffer rotation showed that the equilibrium between the optical antipodes is shifted by only about two and one-half per cent (*7*). This indicates that the effect may not be observed in some cases where it would be expected because of very small changes in the optical rotations.

The Pfeiffer Effect with Different Metal Ions. The Pfeiffer effect has been reported for complexes of zinc(II) and cadmium(II) (see Table I) but not for mercury(II). It was found during the course of this work that the effect also occurs with mercury(II). Solutions which were $0.005M$ in metal nitrate and $0.010M$ in ammonium *d*-α-bromocamphor-π-sulfonate were studied for the Pfeiffer effect upon adding sufficient *ortho*-phenanthroline to make the solutions $0.015M$ in ligand. It was found that the Pfeiffer effect was largest with mercury(II) and smallest with zinc(II). Increasing the ligand:metal ratio to six increased the Pfeiffer effect with mercury(II) the most. The behavior is not unexpected when the stability constants of the three complexes are examined, $\log K_3 = 5.20$, 4.10, and 3.7 for Zn(II), Cd(II), and Hg(II), respectively, with 1,10-phenanthroline (*2*). Table III shows the results of the experiments. From this table and Figure 5 it can be seen that changing the metal ion of the complex from Zn(II) to Cd(II) to Hg(II) enhances the observed Pfeiffer rotation.

Table III. Observed Pfeiffer Rotation (Degrees) for Systems with Different Ligand: Metal Ratios at 546 Millimicrons[a]

Metal Ion	*L/M = 3*	*L/M = 6*
Zn(II)	0.045	0.056
Cd(II)	0.074	0.075
Hg(II)	0.081	0.109

[a] Ligand is 1,10-phenanthroline.

Quantitative Aspects of the Pfeiffer Effect. Kuhajek (*10*) formulated an equation for calculating the magnitude of the Pfeiffer effect. In practice this equation is difficult to handle because some of the terms are difficult to define.

In order to test Kuhajek's relationship, two series of solutions were examined for the magnitude of the Pfeiffer effect. These solutions were composed of zinc(II) nitrate, 1,10-phenanthroline, and ammonium *d*-α-bromocamphor-π-sulfonate. The first of these series had the concentration of the optically active environment held constant, while the concentration of the complex (i.e., the tris-(*ortho*-phenanthroline) zinc(II) ion) was varied. In the second series the concentration of the complex was held constant, while that of the environment was varied. An experiment was

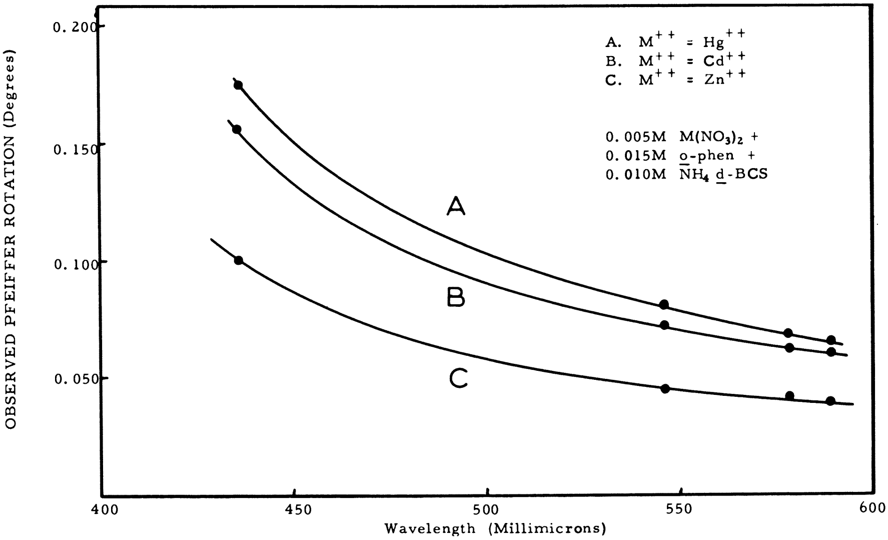

Figure 5. A comparison of the Pfeiffer effect with zinc (II), cadmium(II), and mercury (II)

also performed using a series similar to the first one mentioned above, but using 2,2′-dipyridyl as the ligand. The results of these are shown in Table IV.

It was found that the Pfeiffer rotation is nearly linear with regard to the concentration of either of two of the major constituents of the system (the complex or the environment) if the other is held constant. This linearity holds best at low concentrations of the solutes.

Since the Pfeiffer rotation is linear with respect to the concentration of each of the major constituents, it follows that it would be linear with respect to the product of the concentrations of these constituents. Figure 6 shows a plot of the Pfeiffer rotation *vs.* the product of the molar concentration of tris(1,10-phenanthroline)zinc(II) ion and the molar concentration of ammonium *d*-α-bromocamphor-π-sulfonate. As can be seen, the deviation from linearity is very slight. It should be also noted that at that high end of the curve, the relationship between the concentration of the two constituents is not so favorable as at other parts of the curve. The linearity of this plot suggests that an equation of the type utilized for the calculation of molar rotation might apply to this phenomenon also. Rewriting the specific rotation equation in standard form results in the following:

$$\alpha = [\alpha]\cdot c\cdot d \tag{2}$$

where α = observed optical rotation; $[\alpha]$ = specific rotation; c = concentration of optically active (environment) in g./ml.; and d = path length in decimeters.

Table IV. Variation of Pfeiffer Rotation ($P_{obs.}$) with Concentration

A. $[Zn(o\text{-}phen)_3]^{++}$ *and d-BCS*

$[c]^a$	$[e]$	α_e	α_{e+c}	P_λ	$[P_M]_\lambda$
0.005	0.010	0.281	0.321	0.039	7800
0.010	0.019	0.532	0.686	0.154	8100
0.010	0.019	0.528	0.695	0.167	8800
0.010	0.010	0.276	0.369	0.093	9300
0.010	0.020	0.564	0.743	0.179	8950
0.010	0.030	0.846	1.099	0.253	8450
0.010	0.040	1.125	1.449	0.324	8100
0.005	0.010	0.257	0.300	0.043	8600
0.010	0.010	0.280	0.367	0.087	8700
0.020	0.010	0.280	0.421	0.141	7050
0.030	0.010	0.280	0.461	0.181	6050

B. $[Zn(dipy)_3]^{++}$ *and d-BCS*

$[c]^a$	$[e]$	α_e	α_{e+c}	P_λ	$[P_M]_\lambda$
0.010	0.010	0.284	0.294	0.010	1000
0.010	0.020	0.565	0.593	0.018	900
0.010	0.030	0.847	0.874	0.027	900
0.010	0.040	1.122	1.158	0.036	900

[a] $[c]$ = molar concentration of complex; $[e]$ = molar concentration of environment; α_e = observed optical rotation of environment (in degrees); α_{e+c} = observed optical rotation of environment plus complex (in degrees); and $[P_M]$ = molar Pfeiffer rotation (in degrees).

The usual expression for molar optical rotation is:

$$[M]_\lambda^t = \frac{[\alpha](\text{mol. wt.})}{100} \tag{3}$$

This can be rewritten as:

$$[M]_\lambda^t = \frac{\alpha_{\text{obs.}}}{[c]\cdot d_m} \tag{4}$$

where $[c]$ = molar concentration and d_m = path length in meters. Since Pfeiffer rotation is also a linear function of concentration, a similar equation can be written to express it:

$$[P]_\lambda^t = \frac{P_{\text{obs.}}}{c\cdot e\cdot d} \tag{5}$$

where $[P]_\lambda^t$ = specific Pfeiffer rotation at a given wavelength, λ, and temperature, t; c = concentration of complex ion in g./ml.; e = concentration of environment in g./ml.; and d = cell path length in decimeters. The equation for "molar Pfeiffer rotation" ($[P_M]_\lambda^t$) can now be developed analogously as follows:

$$[P_M]_\lambda^t = \frac{P_{\text{obs.}}}{[e]\cdot[c]\cdot d_m} \tag{6}$$

where $P_{obs.}$ = observed Pfeiffer rotation at a wavelength, λ, and temperature, t; $[c]$ = molar concentration of complex ion; $[e]$ = molar concentration of environment; and d_m = cell path length in meters. The use of the molar Pfeiffer rotation expression permits a comparison of the Pfeiffer effect in different systems.

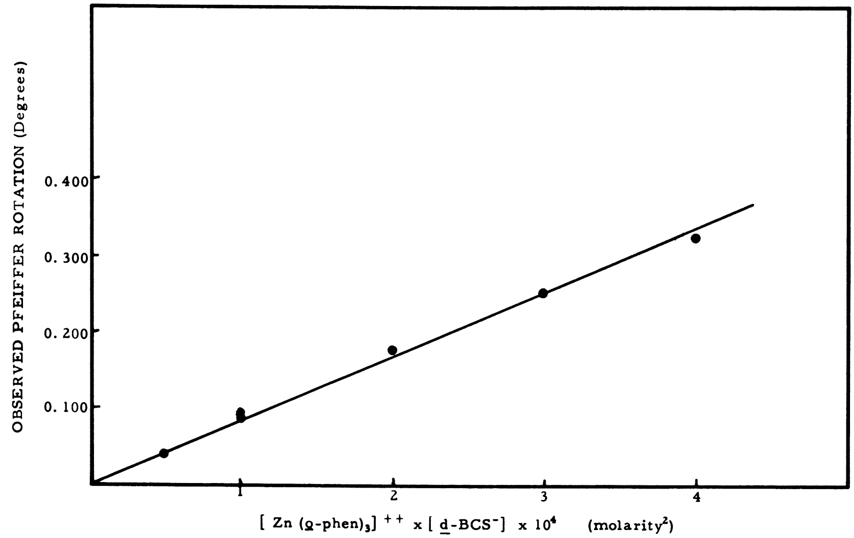

Figure 6. Variation of Pfeiffer effect with concentration

Source of the Pfeiffer Effect. No completely satisfactory explanation has yet been set forth which accounts for all of the observations associated with the Pfeiffer effect. Dwyer and co-workers (*7*) have proposed a "configurational activity" explanation which states that the *dextro* and *levo* enantiomers of optically active, labile complexes in solution are in equilibrium (with $K_{eq.} = 1$), but that in the presence of an optically active "environment" the equilibrium shifts in favor of one of the enantiomers, resulting in a change in optical rotation. However, this proposal does not account for the fact that the effect is observed for some labile complexes and not for others.

In an interesting thesis, Nordquist (*13*) notes some correlation between the occurrence of the effect and hydrophobic bonding, but this proposal does not account for the effect appearing in nonaqueous solvents.

It is of interest to note that the effect has so far been observed only on systems containing ligands which have unsaturated ring systems.

Summary of New Systems Exhibiting the Pfeiffer Effect. In the course of this work several systems were studied to determine whether they exhibited the Pfeiffer effect. Some new systems were found which do exhibit the effect, and these are listed in Table V.

Table V. New Systems Exhibiting the Pfeiffer Effect

Complex[a]	*Optically Active Environment*	*Solvent*
$[Zn(o\text{-phen})_3]^{++}$	*d*-α-bromocamphor-π-sulfonate	DMF
$[Zn(o\text{-phen})_3]^{++}$	*d*-α-bromocamphor-sulfonate	Acetic Acid
$[Zn(dipy)_3]^{++}$	*d*-α-bromocamphor-π-sulfonate	Acetic Acid
$[Zn(o\text{-phen})_3]^{++}$	*d*-cinchonine	Acetic Acid
$[Hg(o\text{-phen})_3]^{++}$	*d*-α-bromocamphor-π-sulfonate	Water
$[Zn(o\text{-phen})_3]^{++}$	(−)-dibenzoyl-*d*-tartrate	Water
1 $Zn^{++}\cdot 4$ pyim	*d*-α-bromocamphor-π-sulfonate	Water
1 $Zn^{++}\cdot 3$ pybim	*d*-α-bromocamphor-π-sulfonate	Acetic Acid

[a] Abbreviations: pyim = 2-(2-pyridyl)-imidazoline; pybim = 2-(2-pyridyl)-benzimidazoline; *o*-phen = *ortho*-phenanthroline; dipy = 2,2′-dipyridyl; and DMF = *N*,*N*-dimethylformamide.

Summary of New System Found Not to Exhibit the Pfeiffer Effect. During the course of this work several systems did not exhibit the Pfeiffer effect, and these are listed in Table II.

Acknowledgment

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25

The Interaction of Metal Ions with Polynucleotides and Related Compounds

VIII. The Selectivity of Metal Ions for Coordination Sites on Biological Macromolecules

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The nucleic acids offer a diversity of electron donor sites among which a coordinating metal ion may choose. There is opportunity for coordination to phosphate groups as well as to oxygen and nitrogen atoms on the heterocyclic components of the nucleotides. Some metals (e.g., zinc (II), nickel (II), lanthanum (III)) select phosphate. Others, such as copper (II), silver (I), and mercury (II), prefer the heterocyclic electron donors. The phosphate binders stabilize the hydrogen-bonded conformation of the nucleic acids at low temperatures; at high temperatures they cleave the phosphodiester bonds. The metals binding to heterocyclic donors bring about the destruction of the hydrogen bonds because they react with hydrogen-bonded sites. Thus, metal binding to nucleic acids aids in understanding selective coordination and many facets of coordinated ligand reactions.

Among the applications of Werner's coordination theory that have gained momentum in recent years has been the study of coordination compounds of biological importance. The participation of metal ions in enzymatic reactions is so widely understood that the activation of enzymes by metal ions is one of the properties of enzymes that is almost universally studied when new enzymes are isolated. Such activation involves the formation of a metal complex of the enzyme protein. Many studies have been carried out recently on the nature of this metal-protein interaction. We have been particularly interested in the reaction of metal ions with another group of biological macromolecules—the nucleic acids. Interest in such reactions was initiated in the hope of attaining two objectives of biochemical importance: (1) the determination of nucleotide sequence (the genetic code) by selective reactions of metal ions with the various nucleotide bases and (2) the elucidation of the biological role of metal ions in the transmission of hereditary information.

Although our primary interest has been the use of coordination chemistry to solve biological problems, I believe that these studies have aided in elucidating some problems of coordination chemistry. The coordination chemist has long been interested in the selectivity of the various metal ions for different electron donors. The attention of inorganic chemists interested in this phenomenon has been generally directed to a comparison of stability constants of metal complexes that are mostly similar but differ in some one structural feature. The study of biological macromolecules has led to an understanding of the behavior of metal ions with long polymers that provide a large variety of electron donors among which a metal ion can choose. It is interesting that different metal ions make different choices and that the nature of the metal's choice can have a profound effect upon the structure of the macromolecule.

In the present paper we shall be concerned mainly with the results of previously published experiments on the reaction of metal ions with nucleic acids. This symposium presents a good opportunity to bring together the results scattered in the literature and to make appropriate generalizations. The experiments themselves can only be alluded to, but the references cited should provide the reader with ample opportunity to verify the conclusions.

Structure of Nucleic Acids

In order to understand the nature of the interaction of metal ions with macromolecular ligands, it is necessary to understand the structure of the ligands themselves. There are two types of naturally occurring nucleic acids—RNA and DNA. Each of these consists of a sugar ribose backbone to which the four bases shown in Figure 1 are attached (in RNA). (Ribose attached to 3 or 9 positions produces a nucleoside, and ribose phosphate a nucleotide. When the ribose has no 2′-OH group, deoxynucleoside and deoxynucleotide are produced.) The relationship of these bases to the sugar phosphate is indicated in Figure 2. As shown, the bases are attached in various sequences. The top ribose shows the numbering used. (Adenine and guanine are bound by loss of the 9-proton; cytosine and uracil by that of the 3-proton.) The biological function of one type of RNA

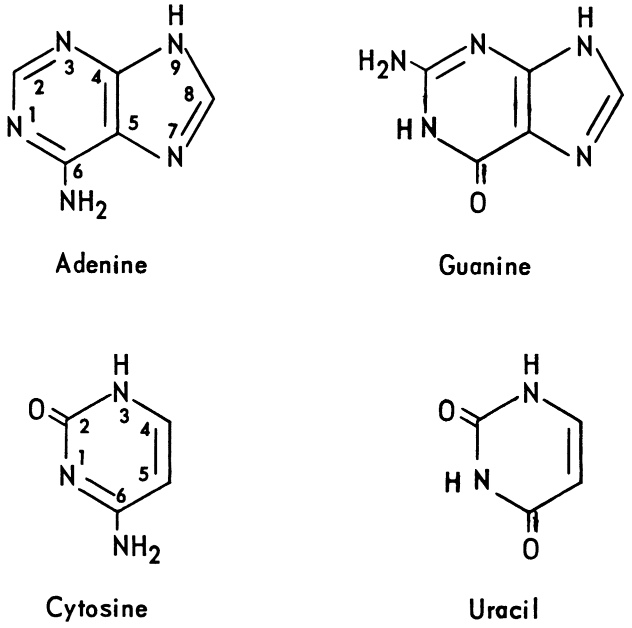


Figure 1. Structures of nucleotide bases

molecule is to transmit the genetic message from DNA in the nucleus to the cytoplasm where protein synthesis occurs.

DNA resembles RNA in that it contains adenine, cytosine, and guanine, but instead of uracil it has a 5-methyl derivative called thymine. The sugar in DNA is deoxyribose—i.e., the 2′-hydroxy group of the ribose present in RNA has been removed. The native DNA structure consists of two strands of "polydeoxyribonucleotide," each containing the four bases, intertwined as shown in Figure 3, with hydrogen bonding between the guanines on either chain and the cytosines on the other, and the adenines on either chain and the thymines on the other.

It is immediately apparent that there are two very different kinds of sites for metal coordination available on an RNA and DNA molecule—i.e., (1) the phosphate groups on the sugar phosphate backbone and (2) the oxygen and nitrogen donor atoms on the "bases." We shall first discuss the consequences of binding to phosphate.

Metal Ions Binding to Phosphate

The first such consequence is to stabilize the ordered form of the nucleic acid molecule. In DNA this means that phosphate-binding metals will stabilize the double helix. It was discovered quite some time ago that, if DNA is dissolved in distilled water, the double helical structure is "denatured"—i.e., it is dissociated into two randomly coiled, single strands, as determined primarily from absorbance measurements (*25*, *27*). The reason for this dissociation lies in the fact that the surface of the DNA molecule is laden with negative charges on the phosphates that repel each other, thus rendering the ordered structure unstable (*5*, *18*, *27*, *29*). The neutralization of this charge by metal ions therefore stabilizes the molecule. High concentrations of alkali or alkaline earth metal salts will serve in this stabilization process as will much lower concentrations of divalent transition metals such as Mn (II), Co (II), Ni (II), and Zn (II).

Thus, metal ions are required to preserve the structural integrity of the DNA molecule. Peculiarly these same metal ions that stabilize the ordered structure of the DNA molecule can be used for the depolymerization of

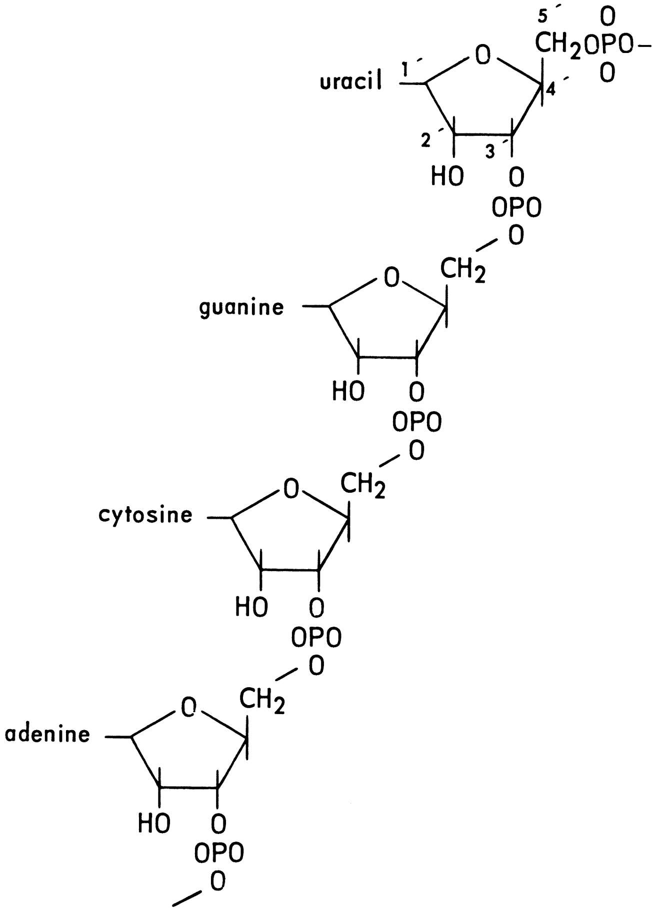


Figure 2. Portion of RNA structure

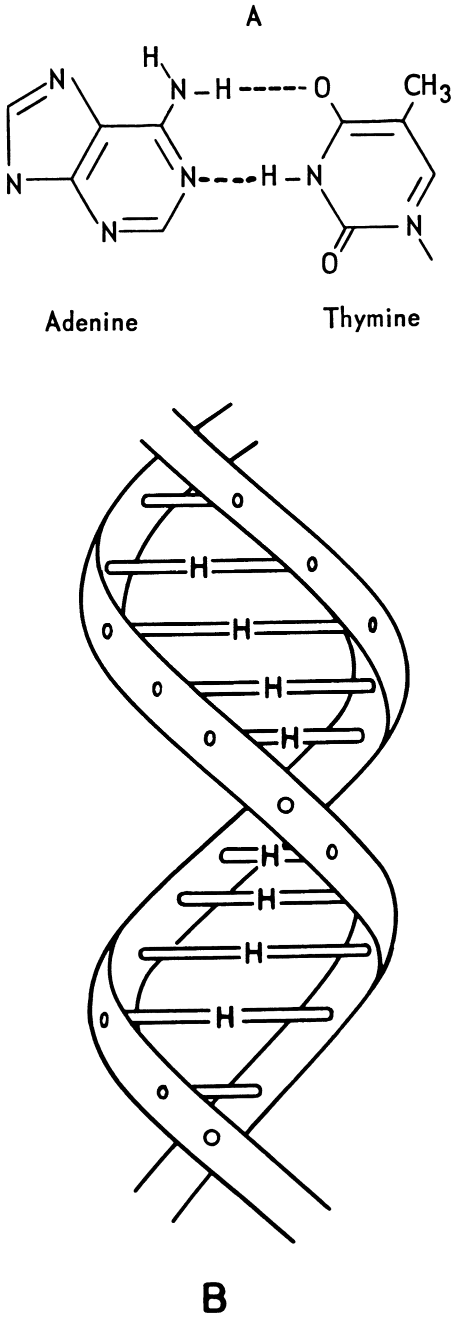
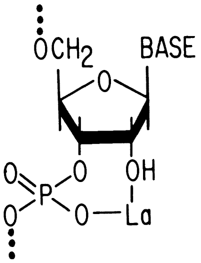


Figure 3. Structure of DNA: A. Hydrogen-bonded base pairing of adenine and thymidine; B. Portion of double helix structure (30)

RNA and synthetic polyribonucleotides that, like RNA, contain ribose as the sugar component but, unlike RNA, contain only one of the four bases in a polymeric chain (e.g., polyadenylic acid, or poly A).

This depolymerization was discovered by Dimroth *et al.* (*6, 7, 8, 9*) and Bamann, Trapmann, and Fischler (*1*) and has been investigated extensively recently in various laboratories (*21, 23*), including our own (*2, 12*). It consists of the scission of the phosphodiester linkages between the ribose and phosphate in the backbone of the molecules. The reaction does not occur with DNA (*1, 12*), thus implicating the participation of the 2′-OH group of ribose and leading to a structural intermediate involving complex formation as follows:



The mechanism of this reaction resembles that of many coordinated ligand reactions in that the positive charge on the metal draws electrons (*11, 16*) from the phosphate and further labilizes the weakest link in the chain, which happens in this instance to be the 5′-linkage.

Among the divalent ions of the first transition series, rates of depolymerization were studied with Mn (II), Co (II), Ni (II), Cu (II), and Zn (II). This is illustrated in Figure 4, where the ordinate is a measure of the extent of depolymerization (*2*). It is of interest to note that the reaction with zinc is approximately 10 times as rapid as with any of the other metals. Rates were also determined with trivalent rare earths [La (III), Ce (III), Lu (III)], and these were similar to the rate with zinc (II).

It should be pointed out that these depolymerization reactions are carried out at elevated temperatures. At low temperatures RNA, like DNA, is stabilized by metal ions through the charge neutralization effect (*18, 29*). We have thus seen that coordination of metal ions with the phosphate group produces two strikingly different results with nucleic acid. At low temperatures the conformation of the macromolecules is stabilized by a charge neutralization mechanism, and at high temperatures RNA and the polyribonucleotides are depolymerized.

Metal Ions Binding to "Bases"

Some of the most interesting reactions of the nucleic acids with metals are those in which the electron donors are the heterocyclic "bases." Intensive studies have been carried out with copper (II), especially the reaction of Cu (II) with DNA. These studies have shown that Cu (II) binds weakly to three of the four DNA bases (adenine, cytosine, and guanine), but apparently not thymine (*15*, *17*). NMR studies to this effect are shown in Figure 5, where the compounds are all 0.1*M* solutions in D_2O. For each set of spectra in this figure the top curve is the metal-free solution and the copper concentration is indicated for the others. The consequence of this type of binding on the structure of DNA has led to some very interesting findings.

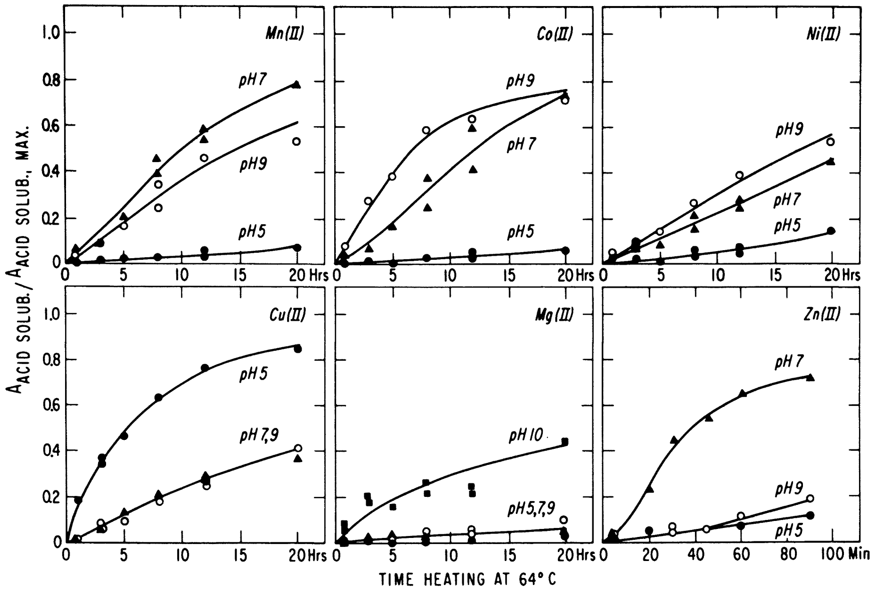


Figure 4. Depolymerization of polyadenylic acid by divalent ions

When native double-stranded DNA molecules are heated with copper (II) at low ionic strength, some of the copper ions displace the hydrogen bonds that hold the two strands together (*10*, *14*, *20*, *28*); the resulting structure is one in which single strands of DNA are weakly held together at some points by copper ions binding the bases. When the electrolyte concentration of such a solution is then increased, the copper ions are displaced from their coordination sites, and the hydrogen bonds of the double-helical structure are reformed. (The evidence for the initial scission of the hydrogen bond by copper (II) is derived mainly from "melting" curves, which show that the double-helical structure of DNA "melts out" into single strands of DNA at a much reduced temperature in the presence of copper (II). The most essential evidence that copper ions take the place of hydrogen bonds is provided by the fact that the DNA regenerated

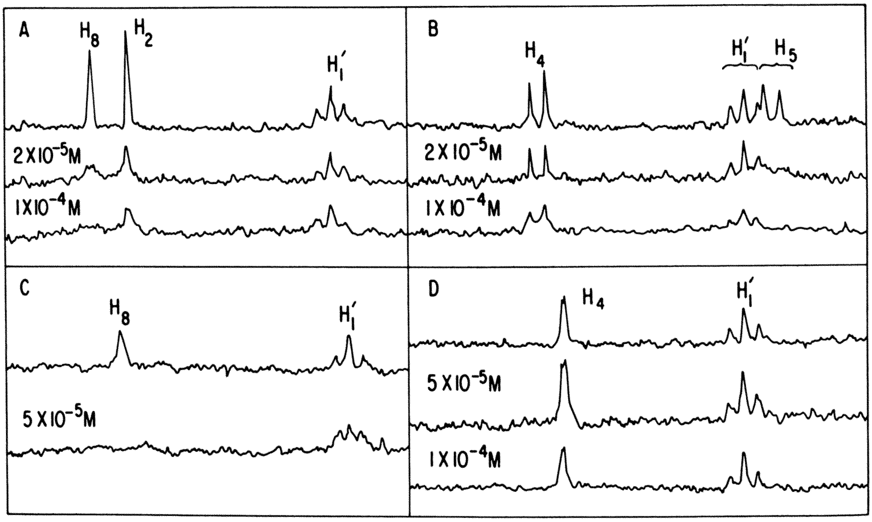


Figure 5. Proton NMR spectra of the copper complexes of deoxynucleosides of (A) adenine, (B) cytosine, (C) guanine, and (D) thymine

by strong electrolyte is completely double-helical, as determined by several criteria—e.g., absorbance, sedimentation rate, optical rotation, and density gradient sedimentation. The reformation of the double helix after its destruction by copper ions can be explained only if the copper (II) holds the complimentary base pairs of the single strands in register while the DNA is in the denatured state.) The reaction of DNA with copper (II) therefore takes place in a delicate equilibrium, low ionic strength favoring displacement of hydrogen bonds by copper (II), and high ionic strength favoring displacement of copper (II) by hydrogen bonds. A few other metal ions [e.g., Cd (II)] behave in a similar fashion, but copper (II) is virtually unique among metal ions in its pronounced tendency to function in this reversible reaction. The reason for the ability of copper (II) to demonstrate such behavior must lie, at least in part, in the relative stability of the complexes of copper (II) with the "bases" and of the double-stranded structure of native DNA. If the copper complexes were weaker, they would probably not form at all. If they were stronger, it would be impossible to replace copper (II) by hydrogen bonds through the addition of electrolyte. The fact that the "reversible" reaction with copper occurs must be explained by the circumstance that the copper complexes of the "bases" exhibit just the right stability range for the process to occur.

It is in this manner, in fact, that it is possible to explain why some other metal ions that might be expected on the basis of their ordinary coordination behavior to react in a manner similar to copper (II) do not do so. For example, Mn (II), Co (II), Ni (II), and Zn (II) do not displace the hydrogen bonds from double-stranded DNA (*10*). One could invoke complicated steric or electronic explanations for the difference between Cu (II) and the other first transition elements, but the simplest explanation appears to be that the copper complex, though weak, is just strong enough to compete with the hydrogen-bonded double helical structure of DNA. The nickel (II) complex simply doesn't make the grade.

Another type of interaction between metal ions and the bases of DNA is represented by the mercury (II) and silver (I) complexes. These substances, first discovered by Katz (*22*), and having received considerable attention recently by a number of investigators (*3, 13, 26*), especially Davidson and co-workers (*4, 19, 24, 31, 32*), resemble the copper (II) complexes in that silver and mercury ions also displace the hydrogen bonds of the double helix of DNA. They differ from the copper complex in that the reactions of these metals with DNA are not reversed by addition of electrolyte; in fact, the complexing reactions are carried out in the presence of strong electrolyte. The mercury (II) and silver (I) can be displaced from DNA binding by strong complexing agents such as EDTA.

Conclusions

The effects of different metal ions in the nucleic acids can be summarized by considering the action of nickel (II), copper (II), and mercury (II).

Nickel (II) reacts only with the phosphate groups; it stabilizes the ordered structure of DNA or RNA at low temperature by neutralizing the mutually repulsive negative charges on phosphate. At higher temperature it depolymerizes RNA and RNA-like structures by the scission of the ribose-phosphate bonds.

Copper (II) ions react with the phosphate in a similar manner, and will also cleave the phosphodiester linkage of RNA. In addition, copper (II) ions react weakly with the heterocyclic "bases" and, for this reason, will bring about the splitting of the double helix in weak electrolyte and its reformation in strong electrolyte. Copper ions can therefore split an RNA molecule perpendicular to its axis and a DNA molecule along its axis.

Mercury (II) does not react with the phosphates on the nucleic acids. It does react very strongly with the "bases" and therefore replaces the hydrogen bonds of DNA in a manner not reversible by strong electrolyte.

To illustrate the versatility of the metal complexes of polynucleotides, it has recently been shown that zinc (II) can bind to the phosphate groups of the macromolecules to which "bases" silver (I) has already been attached. Evidence for this simultaneous binding is provided by the fact that the characteristic effect of silver (I) on the spectrum of the polynucleotides is observed at the same time that depolymerization by zinc (II) takes place.

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26

Aspects of Nuclear Magnetic Resonance and the Coordinate Covalent Bond

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Chemical shielding and spin-spin coupling have been examined in a variety of trialkylphosphine-platinum(II) compounds and the results interpreted in terms of current bonding theory. Covalent bond energies have been calculated from coupling constants and correlated with trans-effect phenomena. The data agree with chemical information and show that trans-labilizing activity increases in the series: Cl^-, Br^-, I^-, PR_3, CN^-. Chemical shielding is considered in terms of the interdependent effects of ionic contributions generated at phosphorus due to substituent atoms and temperature independent paramagnetism. Cis- trans-isomers are easily differentiated. Changes in the Y substituent of Y_3P ligands are shown to be systematic in their influence on bond parameters.

Coordinate covalent bond formation as we view it today is a result of information assembled over many years. Its general features were first outlined by Alfred Werner in 1893 (*34*). The electronic basis was established in 1916 (*14, 16*). From structural data made available by systematic chemistry, methods such as x-ray diffraction, and electronic information resulting from magnetic susceptibilities and dipole moments, our knowledge of this bonding process was greatly increased (*22*). In recent years nuclear magnetic resonance has been particularly useful in expanding information on the bonding process.

Much work in high resolution, nuclear magnetic resonance has been devoted to establishing parameters which correlate chemical shielding and spin-spin coupling with particular bond structures. Shielding has been associated with diamagnetic and paramagnetic terms acting at the nucleus, with paramagnetic terms predominating (*11, 15, 19, 27, 29, 35*). Coupling of spins has been related primarily to the degree of *s*-hybridization and to ionic character contributions to the total wavefunction (*12, 13, 20, 21, 25*). In addition, useful relations between spin coupling and bond parameters, such as overlap integral and covalent bond energy, have been developed (*33*). Extension to the coordination process has been particularly useful.

Early P^{31} magnetic resonance studies of square planar $[Ni(R_3P)_2X_2]$ complexes have shown that ligand field stabilization energies appear to be moderate and strongly influenced by secondary ligands (*18, 32*). Paramagnetic-diamagnetic equilibria have been observed in some instances (*23*). Generally, paramagnetic terms are an inverse function of singlet-triplet transition energy and related to the degree of electron delocalization in the molecule. A temperature and solvent dependence is not uncommon.

Magnetic resonance spectra of platinum(II) compounds of the type $[Pt(R_3P)_2X_2]$ have been of particular interest (*4, 24, 26, 31*). Though phosphorus-31 has a natural abundance of 100% with a spin of one-half, platinum is composed of several isotopes, of which only Pt^{195} has a nuclear spin ($I = \frac{1}{2}$, natural abundance is 33.7%). This gives rise to a doublet spectrum with a net relative area of 0.337 symmetrically superimposed upon a central absorption having a relative area of 0.643. Typical spectra are given in Figures 1 and 2. Phosphorus-31 magnetic resonance data for the $[Pt(R_3P)_2X_2]$ system are in general agreement with coordinate bond theory. Strong ligand field splitting and $d\pi$-$d\pi$ back bonding predominate (*1, 3, 6, 7, 24, 31*). These compounds exhibit strong bonding and trans-activating behavior (*2, 28*). Upon coordination, trialkylphosphines assume a nearly tetrahedral geometry (*30*).

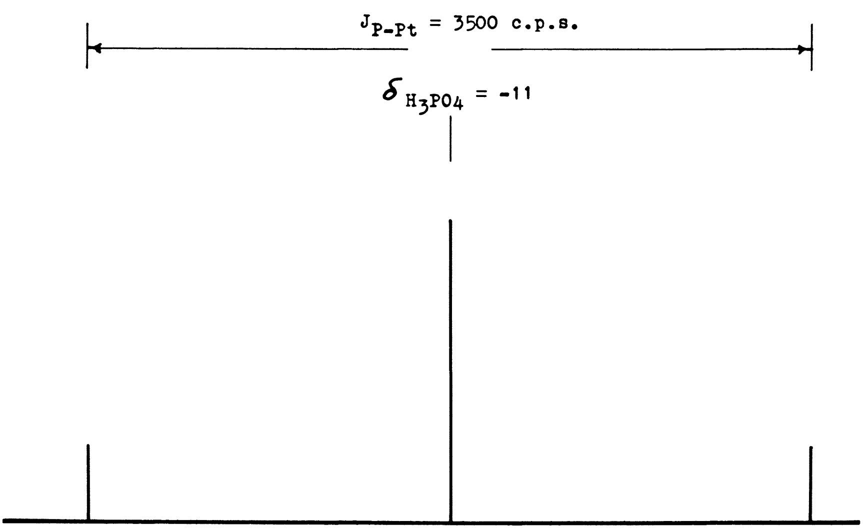

Figure 1. P^{31} *magnetic resonance in* $[Pt((C_2H_5)_3P)_2Cl_2]$

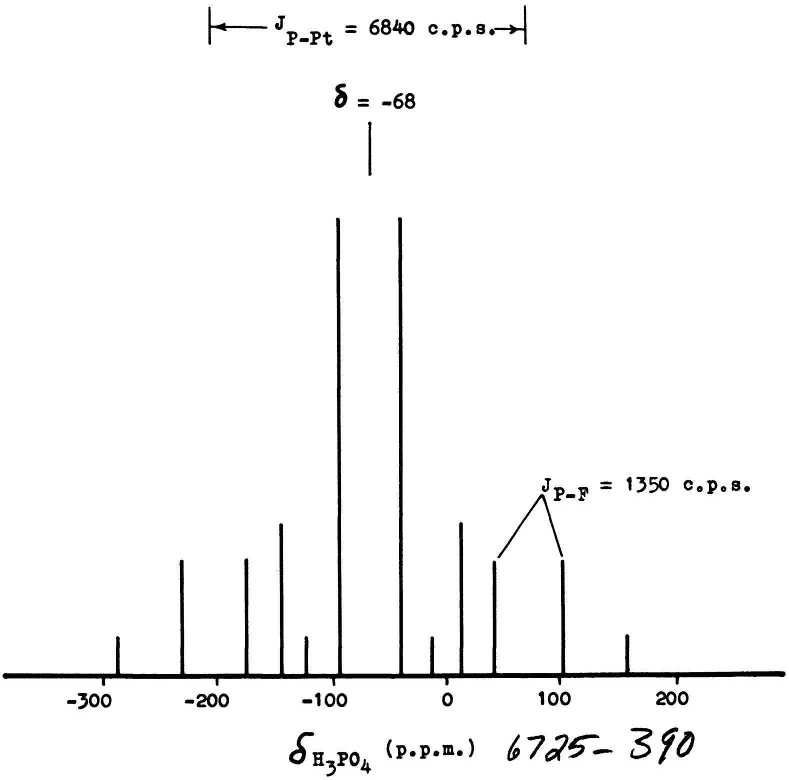

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Figure 2. P^{31} magnetic resonance in $[Pt(PF_3)_2Cl_2]$

Phosphorus-31 chemical shifts are not susceptible to simple interpretation. Many molecular and bond properties determine the distribution and propagation of spin density throughout the molecule. These include: 1) ionic terms generated at the phosphorus atom due to substituents, 2) temperature independent paramagnetism arising from the central metal (*9, 10, 17, 32*), and 3) electron delocalization giving rise to a charge balance. Generally, singlet-triplet excitation energies are large. In comparison with similar nickel complexes, which can have relatively large paramagnetic terms, the chemical shift in platinum compounds is small, ranging from −19.3 to 8 ppm (Table I). For a given isomer where electronegativity of the secondary ligand, X^-, increases, chemical shifts occur at a lower applied field. In addition, cis isomers have a smaller down-field shift than do trans isomers. The dependence of the chemical shift on alkyl substituents directly connected to phosphorus is somewhat variable. Coupling constants are usually large, ranging from 2100 to above 6800 cps. They are only slightly altered by changes in electronegativity of the secondary ligand (becoming smaller as the electronegativity decreases) and by changes in alkyl substituents. The difference between cis and trans isomers is striking. Where X^- is a halide, coupling constants of isomers are in the ranges 3515 ± 15 cps and 2395 ± 25 cps, respectively.

Table I. P^{31} NMR Data on the Trialkylphosphine-Platinum(II) System (*30*)

cis-$[Pt(R_3P)_2X_2]$		$\delta^a{}_{H_3PO_4}$	$J_{P^{31}-Pt^{195}}{}^b$	D^c
R	X^-			
C_2H_5	Cl	−11	3500	12.0
n-C_3H_7	Cl	− 1	3530	12.0
n-C_4H_9	Cl	− 2.4	3510	12.0
n-C_4H_9	I	8	3500	12.0
n-C_4H_9	CN	− 7	2100	10.1
trans-$[Pt(R_3P)_2X_2]$				
C_2H_5	Cl	−12.4	2400	10.6
n-C_3H_7	Cl	− 3.8	2420	10.6
n-C_4H_9	Cl	− 5.9	2410	10.6
C_2H_5	Br	− 7.8	2390	10.5
n-C_4H_9	Br	0	2380	10.5
n-C_4H_9	I	4	2370	10.5
$[Pt((C_2H_5)_3P)_4]Cl_2$		−19.3	2240	10.3

[a] Chemical shift given in ppm with reference to 85% H_3PO_4.
[b] Spin-coupling constant given in cps.
[c] Bond energy given in kcal./mole.

Employing the relation, $D = 0.79\ J_{P-Pt}^{1/3}$ (*33*), it is possible to determine approximate bond energies for P-Pt complexes (Table I). For cis- and trans-halide complexes bond energies are 10.5–10.6 and 12.0 kcal./mole, respectively. The difference in energy is somewhat smaller than the 2.5–5 kcal./mole suggested in earlier work (*5*). An examination of the data shows that as trans-labilizing activity of the secondary ligand increases in the series, Cl^-, Br^-, I^-, R_3P, CN^-, P^{31}-Pt^{195}, coupling decreases. This is in agreement with established literature (*1*, *2*, *28*). The role of π interactions in trans-labilizing activity of ligands is emphasized by the relatively small dependence of coupling constants on ligand size and electronegativity. For example, strong π-electron acceptor ligands, such as CN^- in the trans position, greatly decrease the coupling constant between alkylphosphine and platinum. A somewhat low value for the coupling constant of $[Pt((C_2H_5)_3P)_4]^{+2}$ may be attributed to additional terms generated in orbitals of B_{2g} symmetry and to an increase in net positive charge on the complex, thus reducing π back bonding.

An examination of *cis*-$[Pt(Y_3P)_2Cl_2]$ and *trans*-$[Pt(Y_3P)Cl_2]_2$ complexes (*8*), with respect to changes in the Y substituent, shows several trends: 1) As the electronegativity of the Y group decreases, the chemical shift (with reference to the parent phosphine) increases linearly until ionic terms at phosphorus approach zero, where a marked change in paramagnetic terms is observed (Figure 3). 2) A plot of P^{31}-Pt^{195} coupling data

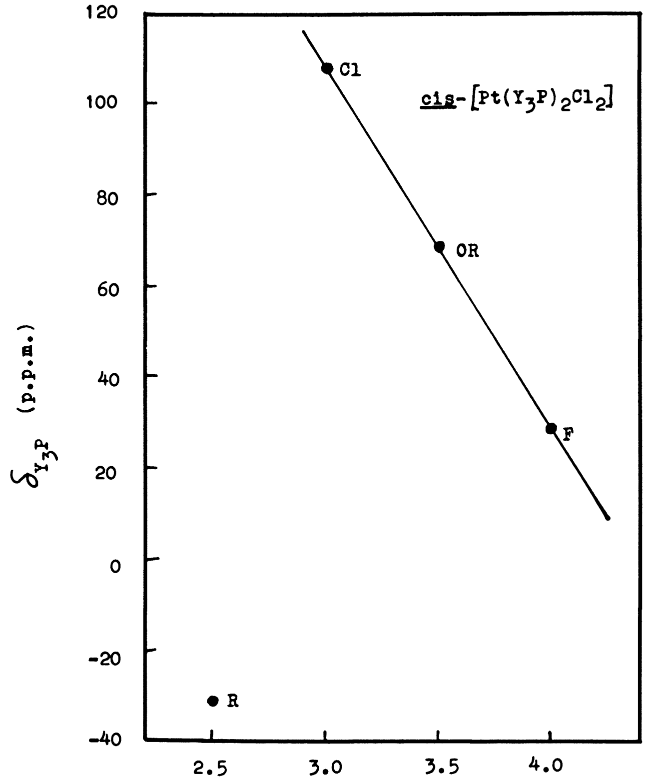

Figure 3. Changes in P^{31} chemical shift with electronegativity of substituent Y

against electronegativity of Y shows a simple linear relationship (Figure 4). Bond energies increase to 15 kcal./mole (Tables II and III).

Bond multiplicity may be estimated using the expression:

$$M = \frac{D}{D*} = \left(\frac{J}{J*}\right)^{1/3}$$

where M, D, D*, J, and J* are the multiplicity, bond energy, bond energy of the single bond, spin-coupling constant, and spin-coupling constant for the single bond, respectively. Assuming that the P-Pt bond in *cis*-

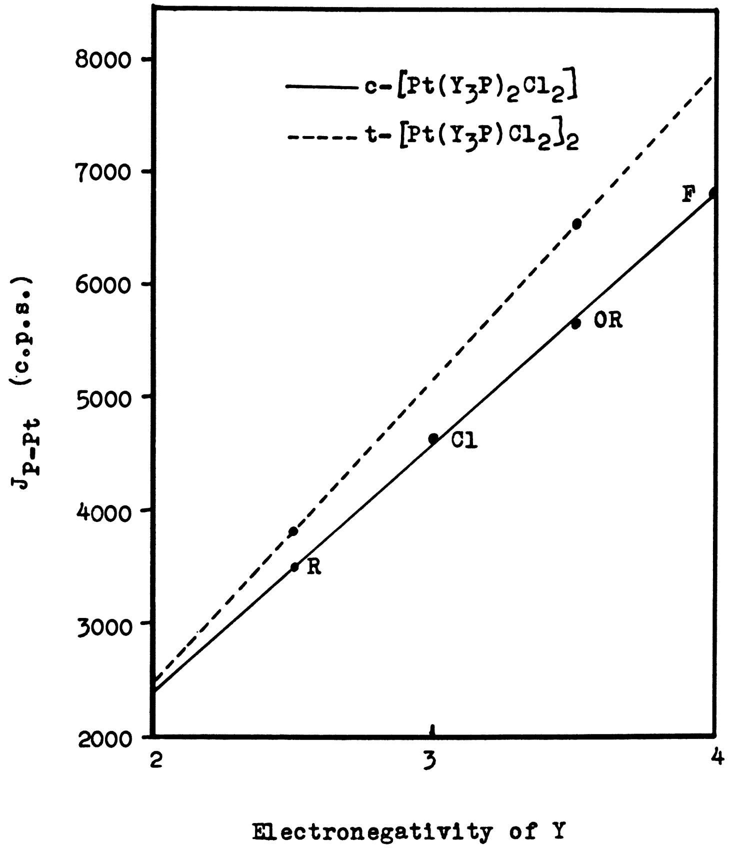

Figure 4. Relation of electronegativity of alkylphosphine substituent to coupling constant

Table II. P^{31} Chemical Shifts and P^{31}-Pt^{195} Coupling Constants in *cis*-$[Pt(Y_3P)_2Cl_2]$

Y	$\delta^a_{H_3PO_4}$	$J^b_{P^{31}\text{-}Pt^{195}}$	D^c
C_2H_5	−11	3500	12.0
n-C_2H_5O	−70	5675	14.0
n-C_4H_9O	−71	5650	14.0
Cl	−112	4650	13.2
F	−60	6840	15.0

[a] Chemical shift given in ppm with reference to 85% H_3PO_4.
[b] Spin-coupling constant given in cps.
[c] Bond energy given in kcal./mole.

$[Pt((n\text{-}C_4H_9)_3P)_2(CN)_2]$ is essentially a single bond, multiplicities can be estimated for remaining compounds. These range from 1 to 1.49.

Table III. P^{31} Chemical Shifts and P^{31}-Pt^{195} Coupling Constants in $[Pt(Y_3P)Cl_2]_2$

Y	$\delta^a_{H_3PO_4}$	$J^b_{P^{31}-Pt^{195}}$	D^c
C_2H_5O	−30	6562	14.7
n-C_4H_9O	−45	6537	14.7
n-C_4H_9	—	3810(23)	12.3

[a] Chemical shift given in ppm with reference to 85% H_3PO_4.
[b] Spin-coupling constant given in cps.
[c] Bond energy given in kcal./mole.

Platinum(II) *d*-orbital splitting for *cis*- and *trans*-$[Pt(Y_3P)_2X_2]$ complexes is given in Figure 5. Orbital splitting is generally largest where P-Pt bond multiplicity is greatest—i.e., in cis isomers. It is usually difficult to prepare trans isomers when Y_3P ligands participate in bonds of high multiplicity; cis, trans equilibria strongly favor the formation of cis compounds. Trans-labilizing ability of Y_3P ligands increases with electronegativity of the substituent, Y.

An examination of spin coupling and bond energy data for $[Pt((C_2H_5)_3P)_4]^{+2}$, *cis*-$[Pt((C_2H_5)_3P)_2X_2]$, and *trans*-$[Pt((n\text{-}C_4H_9)_3P)Cl_2]_2$ complexes indicates that, similar to trans-labilizing effects of alkylphosphines, a small cis labilization also occurs. As the number of adjacent alkylphosphines decreases, the bond energy of the P-Pt bond increases. This is in agreement with the increase in chemical stability one observes as the number of cis-alkylphosphines decreases.

In summary, variations in δ and J reflect in considerable detail the chemical properties of the coordinate covalent bond. In strong ligand field Y_3P-Pt adducts, paramagnetic terms are small. Spin-spin coupling, however, is large and variable, depending to a large degree on π-acceptor activity of the trans ligand.

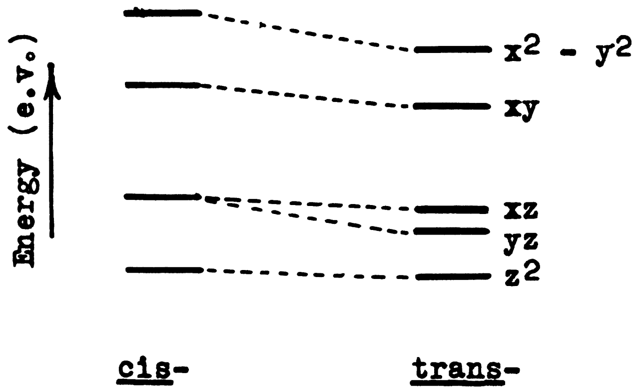

Figure 5. d-Orbital splitting in $[Pt(Y_3P)_2X_2]$ complexes

Acknowledgment

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Recent Infrared Studies on Werner Complexes

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Werner proposed the structure of a number of metal complexes on the basis of his coordination theory. Infrared spectroscopy has proved to be a powerful means of distinguishing various types of isomers proposed by Werner. Furthermore, recent infrared studies on Werner complexes provide detailed information about their structure and bonding.

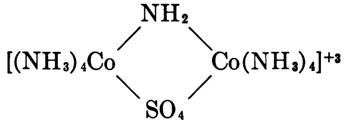
It is well-known that Werner determined the structure of a number of metal complexes by skillfully combining his famous coordination theory with chemical methods (*30*). Modern physico-chemical methods such as x-ray diffraction and infrared spectroscopy, used in the study of Werner complexes, have paralleled the development of these techniques. The results of these investigations have not only confirmed the validity of Werner's coordination theory but have also provided more detailed structural and bonding information. In early 1932, Damaschun (*13*) measured the Raman spectra of seven complex ions, such as $[Cu(NH_3)_4]^{+2}$ and $[Zn(CN)_4]^{-2}$, and these may be the first vibrational spectra ever obtained for Werner complexes. In these early days, vibrational spectra were mainly observed as Raman spectra because they were technically much easier to obtain than infrared spectra. In 1939, Wilson (*35, 36*) developed a new theory, the "GF method," which enabled him to analyze the normal vibrations of complex molecules. This theoretical revolution, coupled with rapid developments of commercial infrared and Raman instruments after World War II, ushered in the most fruitful period in the history of vibrational studies of inorganic and coordination compounds.

One of the most important and interesting results obtained from Werner's coordination theory is the prediction and verification of various types of isomerism. It is, therefore, appropriate to review recent infrared studies in this area and to show how infrared spectroscopy can be used to distinguish various types of isomers.

Ionization Isomerism

One of the most fundamental ideas in Werner's coordination theory is the distinction of molecules or ions in the "inner sphere" and the "outer sphere." For example, there are two isomeric forms for $Co(NH_3)_5Br \cdot SO_4$; in solution, one isomer does not react with the bromide ion but does with the sulfate ion, whereas the other does not react with the sulfate ion but does with the bromide ion. From such chemical observations, Werner (*30*) concluded that the former solution contains the $[Co(NH_3)_5Br]^{+2}$ ion, whereas the latter solution contains the $[Co(NH_3)_5SO_4]^+$ ion. He called them "ionization isomers." Nowadays, it is a rather routine procedure to differentiate these isomers from infrared spectra because the vibrations of the free and coordinated (covalently bonded) ligands are markedly different. The SO_4^{-2} ion in the outer sphere is essentially regarded as a free SO_4^{-2} ion of T_d symmetry, whereas that in the inner sphere is regarded as being of C_{3v} symmetry in unidentate coordination because one of the four oxygens bonded to the Co atom is different from the others. This lowering of symmetry results in changes in the infrared selection rules. Thus, the triply degenerate SO stretching vibration (F_2 species, IR active) of the free ion splits into two peaks (A_1 and E species, both IR active), and the totally symmetric SO stretching vibration (A_1 species, Raman active) becomes infrared active as a result of unidentate coordination (*22*). This is clearly demonstrated in Figure 1, which compares the infrared spectra of $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

This method is further extended to distinguish unidentate and bidentate coordination. If the SO_4^{-2} ion acts as a bidentate ligand, two of its four oxygens are different from the remaining two. As a result, the symmetry of the SO_4^{-2} ion is further lowered to C_{2v}. Thus, the triply degenerate vibration (F_2 species) splits into three components (A_1, B_1, and B_2 species), and the totally symmetric vibration (A_1 species) becomes infrared active. Therefore, it is expected that a complex ion such as $[Co(en)_2SO_4]^+$ exhibits four SO stretching bands. In fact, $[Co(en)_2SO_4]Br$ recently prepared by Barraclough and Tobe (*5*) exhibits four bands at 1211, 1176, 1075, and 993 cm.$^{-1}$ It is rather difficult, however, to distinguish from the selection rules alone bidentate SO_4 groups from bridging SO_4 groups, such as those in



because both SO_4 groups belong to the same C_{2v} point groups. The variation of the spectra in the OSO bending region (650-550 cm.$^{-1}$) is also similar to that in the SO stretching region described above. It should be added

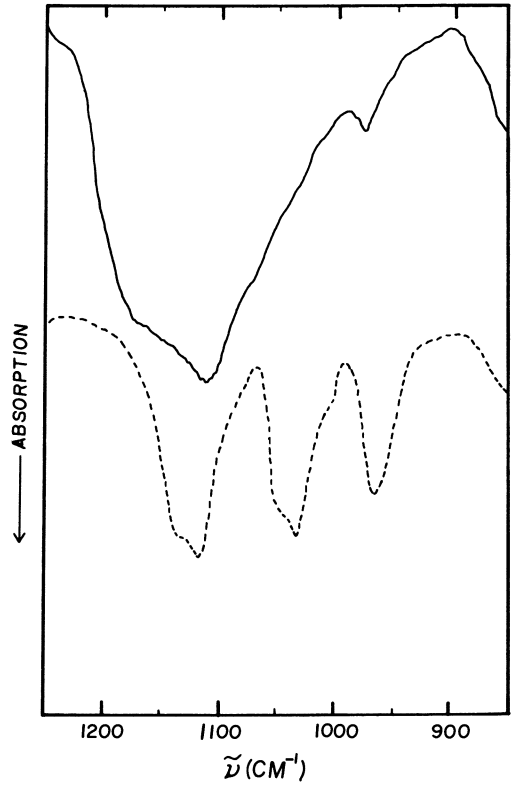


Figure 1. Infrared spectra of $[Co(NH_3)_5Br]SO_4$ (——) *and* $[Co(NH_3)_5SO_4]Br$ (------) *in the SO stretching region*

that this technique has been used successfully for other acid ions such as ClO_4^-, PO_4^{-3}, CO_3^{-2}, NO_3^-, and SO_3^{-2} in determining their sites of coordination (*22*).

If the symmetry of the ligand is already low in the free state, the number of infrared bands will not change upon coordination. However, differences in frequency may be used to distinguish free and coordinated ligands. For example, the free NO_2^- ion (C_{2v} symmetry) absorbs at 1335, 1250, and 830 cm.$^{-1}$, whereas the coordinated NO_2 group (N-bonded) absorbs at 1450–1335, 1350–1325, and 840–830 cm.$^{-1}$ If the ligand is a monoatomic ion such as Cl^- or Br^-, it is necessary to investigate the far-infrared region where the metal-halogen stretching bands appear. For example, ionization isomers such as $[Pt(NH_3)_4Cl_2]Br_2$ and $[Pt(NH_3)_4Br_2]Cl_2$ can be distinguished easily because the Pt-Cl stretching bands appear near 340 cm.$^{-1}$, whereas the Pt-Br stretching bands appear near 240 cm.$^{-1}$ (*3*). It should be mentioned that the metal-halogen stretching frequencies such as these have been established recently for various metals by a number of investigators (*1, 2, 11, 12*).

Hydrate Isomerism, Coordination Isomerism, and Polymerization Isomerism

Werner called ionization isomerism involving solvent molecules, such as H_2O, hydrate isomerism. A typical example of hydrate isomerism given by Werner is $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (light green), $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (dark green), and $[Cr(H_2O)_6]Cl_3$ (violet). Although the first and the second complexes are difficult to distinguish, the third can be distinguished from the others by examining the spectra in the Cr-Cl stretching region (350–300 cm.$^{-1}$). Furthermore, the coordinated water can be distinguished easily from the crystal water because the former exhibits, in addition to the metal-oxygen stretching vibration, the rocking and wagging vibrations which correspond to rotation of the whole water molecule in free state. For example, Nakagawa and Shimanouchi (*19*) have located the rocking, wagging, and Cr-O stretching vibrations of the $[Cr(H_2O)_6]^{+3}$ ion at 800, 541, and 490 cm.$^{-1}$, respectively.

As stated above, coordinated ligands exhibit infrared absorptions which are different from those of free ligands. Furthermore, the frequencies of the coordinated ligand vibrations are metal-sensitive, differing with the nature of the metal. As an example, infrared frequencies of the $[Co(NH_3)_6]^{+3}$ and $[Cr(NH_3)_6]^{+3}$ ion are compared in Table I (*10, 20, 26*). It is seen that both ions can be distinguished easily by comparing the NH_3 rocking or the metal-nitrogen stretching frequencies. Table I also compares the infrared frequencies of the $[Co(CN)_6]^{-3}$ and $[Cr(CN)_6]^{-3}$ ions.

Table I. Infrared Frequencies of Ammine (*26*) and Cyano (*10, 20*) Complexes of Co(III) and Cr(III)

(cm.$^{-1}$)

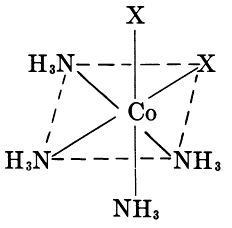
$[Co(NH_3)_6]^{+3}$	$[Cr(NH_3)_6]^{+3}$	*Assignment*[a]
3240	3260	$\nu_a(NH_3)$
3170	3205	$\nu_s(NH_3)$
1600	1600	$\delta_d(NH_3)$
1325	1310	$\delta_s(NH_3)$
820	745	$\rho_r(NH_3)$
503	470	$\nu(M—N)$
325	—	$\delta(N—M—N)$
$[Co(CN)_6]^{-3}$	$[Cr(CN)_6]^{-3}$	
2118	2127	$\nu(C \equiv N)$
565	457	$\nu(M—C)$
414		$\delta(M—C \equiv N)$

[a] Abbreviations listed below are as follows: ν_a, antisymmetric stretching; ν_s, symmetric stretching; δ_d, degenerate deformation; δ_s, symmetric deformation; ρ_r, rocking.

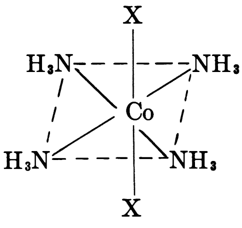
Again, the metal-carbon stretching frequencies are markedly different in these two hexacyano complex ions. It is, therefore, relatively easy to differentiate coordination isomers such as $[Co(NH_3)_6]\ [Cr(CN)_6]$ and $[Cr(NH_3)_6]\ [Co(CN)_6]$. Coordination isomers involving the same central metal may be more difficult to identify from their infrared spectra. Thus, $[Pt(NH_3)_4]\ [PtCl_4]$ and $[Pt(NH_3)_3Cl]\ [Pt(NH_3)Cl_3]$ may exhibit very similar spectra. This is also expected for polymerization isomers such as $[Co(NH_3)_3(NO_2)_3]$ and $[Co(NH_3)_6]\ [Co(NO_2)_6]$ because the central metal is the same in both compounds. However, minor differences may possibly be seen in the far-infrared region where the skeletal vibrations of these complexes appear.

Stereoisomerism

One of the most fundamental results of Werner's coordination theory is the recognition of the fact that the complexes of the types $[Co(NH_3)_4X_2]^+$ and $[Co(NH_3)_4XY]^+$, where X, Y = NO_2^-, NCS^-, Cl^-, Br^-, etc., must exist in two forms: cis and trans.



cis isomer



trans isomer

Werner himself (*32*) isolated the two isomers of $[Co(NH_3)_4Cl_2]Cl$: violeo salt (cis) and praseo salt (trans). He then determined their structures by chemical methods. A number of investigations have been made to distinguish these and other stereo isomers by infrared spectra (*22*).

It has been found that (1) the frequencies of some ligand vibrations are different in the cis and trans isomers, and (2) the cis isomer generally exhibits more bands than the trans isomer because the symmetry of the former is lower than that of the latter. It should be pointed out, however, that these previous investigations are largely limited to the NaCl region where the vibrations caused by the ligands appear. Infrared studies in the high frequency region sometimes fail to give a clear-cut diagnosis in distinguishing stereoisomers because the bands characteristic of the X group (*see* structure) overlap strongly with those of the NH_3 group. Because the essential difference between cis and trans structures is in the spatial arrangement of the coordinate bonds, more marked differences are expected in the far-infrared region where the coordinate bond stretching and bending modes appear. In order to illustrate this point, the infrared spectra of *cis*- and *trans*- $[Co(NH_3)_4(NO_2)_2]ClO_4$ are compared in Figure 2.

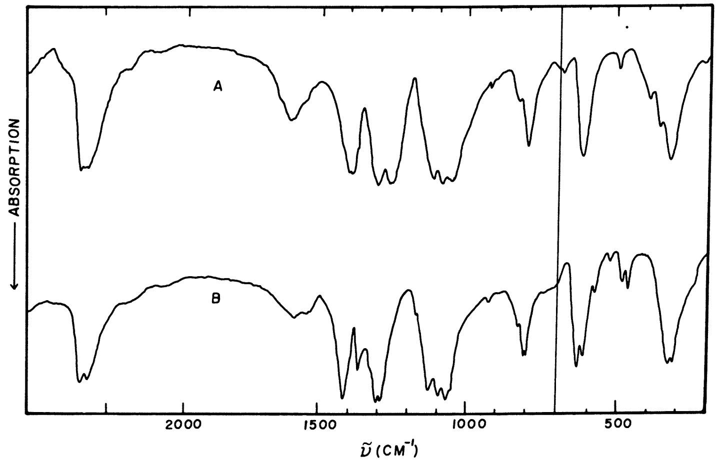


Figure 2. Infrared spectra of cis and trans $[Co(NH_3)_4(NO_2)_2]ClO_4$ *(curve A, trans; curve B, cis)*

Other well-known stereoisomers established by Werner (*33*) are the square planar complexes of the type, $[Pt(NH_3)_2X_2]$, where X is a halogen. Werner again assigned the cis and trans structures using chemical methods. Figure 3 illustrates the infrared spectra of *cis*- and *trans*- $[Pt(NH_3)_2X_2]$, where X = Cl, Br, and I (*23*). As is seen above, it is easy to differentiate two isomers by means of the splitting patterns of (1) the NH_3 deformation bands at *ca.* 1600 and 1300 cm.$^{-1}$, (2) the Pt-N stretching bands near 500 cm.$^{-1}$, and (3) the NH_3 rocking bands between 800 and 600 cm.$^{-1}$

Salt Isomerism

A complex of the composition $[Co(NH_3)_5NO_2]Cl_2$ exists in two forms, an unstable, red form and a stable, yellow form (*16*). Werner (*30*) found that the NO_2 group in the former is O-bonded (nitrito), whereas that in the latter is N-bonded (nitro). These he called salt isomers. Using infrared spectroscopy, they can be readily distinguished because the NO_2 group absorptions in each isomer are notably different, as is shown in Table II. The nitrito complex is gradually converted into the corresponding nitro complex in the KBr pellet. It is, therefore, possible to follow the kinetics of this conversion by observing the disappearance of the 1065 cm.$^{-1}$ band as a function of time. Basolo and Hammaker (*6*, *7*) have done this for pentammine nitrito complexes of Rh(III), Ir(III), and Pt(IV).

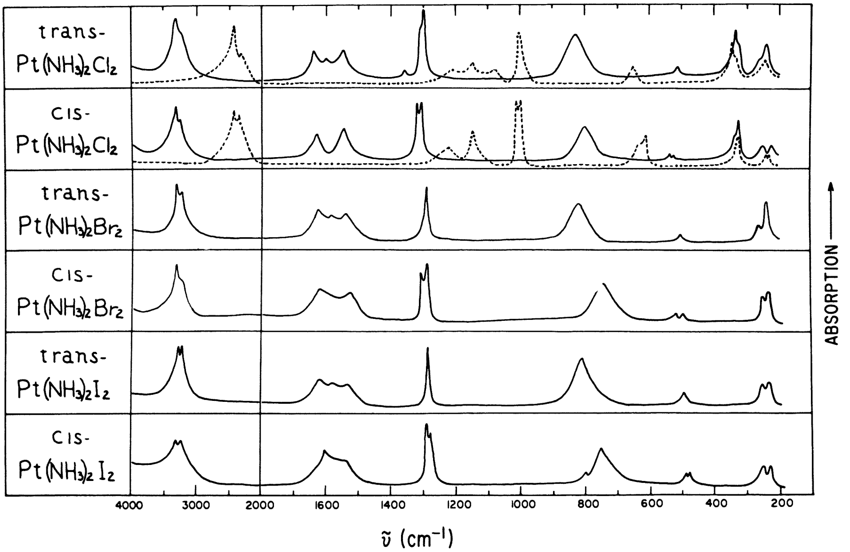
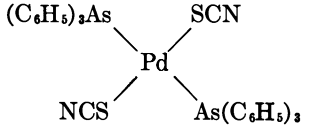
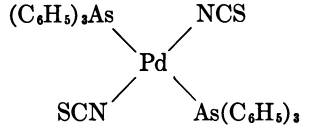


Figure 3. Infrared spectra of cis and trans $[Pt(NH_3)_2X_2]$ where $X = Cl$, Br, and I. Dotted lines are for the corresponding deuterated compounds

Werner (*34*) has discussed an example of what he believes to be salt isomerism, namely $[Co(en)_2(NCS)_2]Cl$, in which the NCS group can be N-bonded or S-bonded. It seems, however, that true salt isomers involving the NCS groups are not yet known for Co(III) complexes. Recently, Basolo *et al.* (*8*, *9*) have prepared them for the first time for Pd(II).



S-bonded isomer



N-bonded isomer

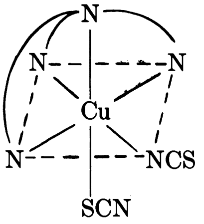
Table II. Nitrito and Nitro Group Frequencies in Pentammine Co(III) Complexes

(cm.$^{-1}$)

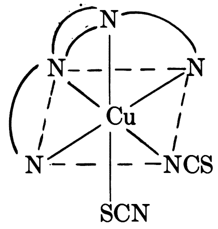
$[Co(NH_3)_5(ONO)]Cl_2$	$[Co(NH_3)_5(NO_2)]Cl_2$	*Assignment*[a]
1468	1428	$\nu_a(NO_2)$
1065	1310	$\nu_s(NO_2)$
825	824	$\delta(ONO)$
—	594	$\rho_w(NO_2)$
—	500	$\nu(Co—N)$

[a] Abbreviations listed below are as follows: ν_a, antisymmetric stretching; ν_s, symmetric stretching; ρ_w, wagging.

A number of other infrared works (*22*) have led to the conclusions that: (1) the C≡N stretching frequency is higher in the S-bonded than in the N-bonded isomer, and (2) the C–S stretching frequency is higher in the N-bonded than in the S-bonded isomer. In fact, the N-bonded isomer mentioned above exhibits the C≡N and C–S stretching bands at 2089 and 854 cm.$^{-1}$, respectively, whereas the S-bonded isomer exhibits them at 2119 and 720–690 cm.$^{-1}$, respectively. Recently, Raymond and Basolo (*25*) prepared a complex, [Cu(tren)(NCS)(SCN)] (tren = triaminotriethylamine, $N(CH_2CH_2NH_2)_3$), in which M–NCS and M–SCN bonds are mixed in one complex. Its structure may be depicted as

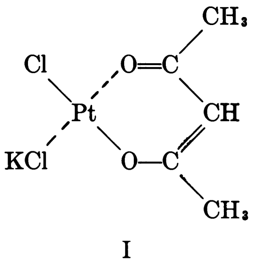


or

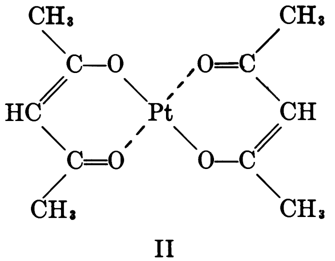


In fact, this complex exhibits two C≡N stretching bands at 2094 and 2060, and two C–S stretching bands at 745 and 818 cm.$^{-1}$ The former frequency in each pair may correspond to the S-bonded group.

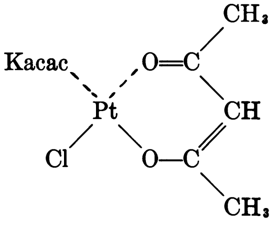
Acetylacetone was the first compound employed by Werner (*31*) as a chelating agent. He prepared four complexes of the composition, $K[Pt(acac)Cl_2]$ (acac = acetylacetonate anion, $CH_3COCHCOCH_3^-$), $Pt(acac)_2$, $K[Pt(acac)_2Cl]$, and $Na_2[Pt(acac)_2Cl_2]$, and formulated their structures as follows:



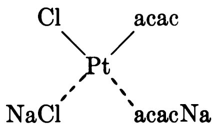
I



II

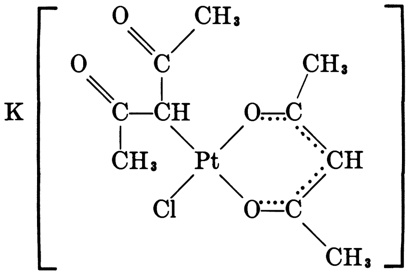


III



IV

Although he did not state clearly how the acetylacetonato group denoted by acac in the above diagrams is bonded to the Pt atom, it was found recently by x-ray analysis (*14*) that the acac group in III is C-bonded as is shown below:



V

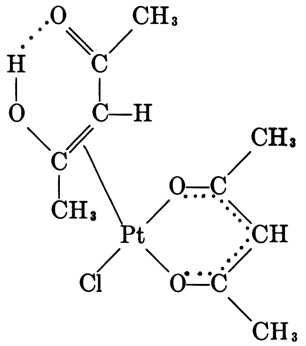
Recently, Lewis *et al.* (*18*) measured the infrared spectra of a number of acetylacetonato complexes of Pt(II) and have shown that the O-bonded (chelated) and C-bonded structures can be distinguished easily from their infrared and NMR spectra. We (*24*) have carried out normal coordinate analyses on both types of structures and have obtained the results shown in Table III. As is seen in this table, these two types of coordination exhibit very different spectra.

Table III. Infrared Spectra of $K[Pt(acac)Cl_2]$ and $Na_2[Pt(acac)_2]\cdot 2H_2O$ (cm.$^{-1}$)

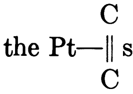
$K[Pt(acac)Cl_2]$ (O-bonded)	*$Na_2[Pt(acac)_2Cl_2]\cdot 2H_2O$ (C-bonded)*	*Assignment*
—	1652 1626	$\nu(C{=}O)$
1563 1380	—	$\nu(C\overset{\cdots}{-}O)$
1538 1288	—	$\nu(C\overset{\cdots}{-}C)$
—	1352 1193	$\nu(C{-}C)$
1212($\parallel$) 817($\perp$) [a]	1193 852	$\delta(C{-}H)$
650 478	—	$\nu(Pt{-}O)$
—	567	$\nu(Pt{-}C)$

[a] $\parallel$, in-plane; $\perp$, out-of-plane.

Recently, Allen *et al.* (*4*) reported a third type of complex in which the Pt atom is bonded to the C=C bond of acetylacetone:



VI

This complex was prepared by acidifying the solution of Compound III (Structure V). This type of coordination is characterized by the presence of the OH stretching (2950-2860 cm.$^{-1}$), C=O stretching (1627 cm.$^{-1}$), and the  $\mathrm{Pt}{-}\overset{\mathrm{C}}{\underset{\mathrm{C}}{\|}}$ stretching bands (360 cm.$^{-1}$).

Other Work on Werner Complexes

It is clear from the above that infrared spectroscopy is useful in distinguishing the various types of isomers proposed by Werner. Several recent works may also be cited, which provide more detailed structural and bonding information on Werner complexes.

Rotation of NH_3 Group. The question as to whether the ammonia molecule in metal complexes rotates freely about its threefold axis has not yet been settled completely. Leech *et al.* (*17*) have shown, for example, that the NH_3 groups in *trans*- $[Pd(NH_3)_2Cl_2]$ are probably not rotating appreciably at or below room temperature because rotational wings are not seen in the infrared spectrum. Nakamoto *et al.* (*23*) have also postulated that the NH_3 groups in *trans*- $[Pt(NH_3)_2Cl_2]$ and other Pt(II) ammine complexes do not rotate freely because the filled *d*-orbitals of the Pt atom interact with one of the hydrogens of the NH_3 group.

Conformation of Ethylenediamine. Whether the ethylenediamine chelate ring is completely planar or puckered has also been a subject of controversy. The conformation of ethylenediamine may be cis if planar and gauche if puckered. Infrared studies have proved to be very useful in distinguishing cis, trans, and gauche conformation of 1,2-substituted ethanes like ethylenediamine (*22*). Thus far, the conformation of chelated (not bridging) ethylenediamine has proved to be gauche without exception.

Normal Coordinate Analysis. In order to obtain quantitative information about the strength of the coordinate bond, it is necessary to carry out normal coordinate analysis using Wilson's GF method (*35*, *36*). Such attempts have been made recently on ammine (*27*, *28*), halogenoammine (*27*, *28*), halogeno (*15*), nitro (*21*), and cyano (*20*) complexes of Co(III) and have given the following Urey-Bradley force constants for the coordinate bond stretching vibration:

$$\begin{array}{ccccccccccc} CN^- & > & NO_2^- & > & NH_3 & > & Cl^- & \sim & Br^- & > & I^- \\ 2.31 & & 1.16 & & 1.05 & & 0.96 & \sim & 1.06 & & 0.62 \end{array}$$

(millidynes/A.)

It is interesting that the order of stretching force constants obtained above is similar to the spectrochemical series obtained from the UV spectra of various Co(III) complexes (*29*).

Acknowledgment

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28

Stereochemistry and Mechanisms of Reactions of Werner Complexes

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Any detailed description of the mechanism of an octahedral substitution must also account for the stereochemical changes that accompany reaction. Werner recognized this and made use of it in his discussions of the stereochemistry of reactions of cobalt(III) complexes. The available experimental results can be explained on the basis of possible molecular rearrangements, and some cautious predictions can even be made. The base hydrolysis of cobalt(III)ammines appears to be unique in that it often occurs with rearrangement; it also affords the few known examples of optical inversion. These results can be explained by formation of a 5-coordinated species with a trigonal bipyramidal structure. Optically active metal complexes racemize by either an intramolecular or an intermolecular process. Substitution reactions of platinum metal complexes often occur with retention of configuration.

Stereochemistry has played a major role in the development of chemistry, and it continues to be most significant. Werner made extensive use of the information available to him on the stereochemistry of metal complexes in developing his coordination theory. He made the first meaningful attempt to understand the mechanisms of substitution reactions of these systems on the basis of the stereochemical changes accompanying such reactions. The paper (*49*) he wrote in 1912 is a real milestone and should be read by anyone interested in octahedral substitution reactions. It is valuable because of the large amount of experimental data it contains on reactions of *cis* and *trans*-cobalt(III) complexes, but it is also of interest because it shows how closely Werner's ideas on the mechanisms of these reactions anticipate our current views on the subject.

Werner called attention to the fact that cobalt(III) complexes frequently react with rearrangement and suggested that a satisfactory explanation for this is necessary. In his own words, "two main questions must be answered, namely: (1) which causes require a rearrangement; and (2) how does the rearrangement take place?" It is only fair to say that after 54 years we are still not able to answer these questions unequivocally.

The answers offered by Werner are very similar to those given today. He suggested that rearrangement was not caused by the formation of the more stable product because examples were known in which the less stable geometrical isomer was preferentially formed. It was further suggested that a dissociation process is not involved for, if the vacated coordination position were merely occupied by the entering ligand, then there would be no rearrangement. Alternatively, the active intermediate may have time to rearrange to its more stable configuration, whereupon the ligand enters to give the more stable isomer. Since rearrangements do occur, and since the more stable isomer is not always formed, Werner concluded that such a dissociation mechanism is not involved.

Werner favored what we now call a ligand interchange mechanism. In his own words, "—then when such a molecule (in the second sphere) gets included in the first sphere an acid group becomes transferred from the first sphere into the second." (The terms first and second spheres used by Werner correspond to what is now called the inner and outer coordination spheres (or shells), respectively.) A modern representation of this statement is shown by Figure 1. It was suggested that a metal complex has a residual attraction for groups in a second sphere, and it was assumed this attractive effect is greater toward certain directions than toward others. Thus, the direction favored by this interaction determines the position occupied by the entering ligand and may be the cause of rearrangement during substitution.

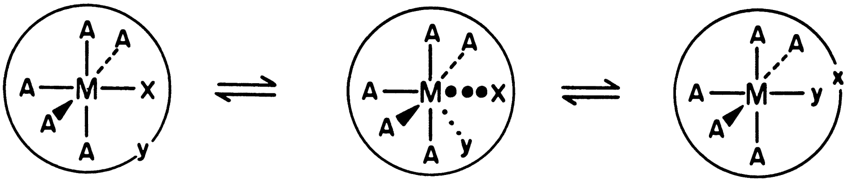


Figure 1. Ligand interchange mechanism as modified from Reference 48. The circles represent the outer ligand spheres and Y may be either solvent or other reagent. Heavy dots, M···X, are to represent the greater importance of bond-breaking relative to bond-making, M···Y

Having answered the question of the cause of rearrangement, Werner then addressed himself to the second question—how the rearrangement takes place. His conclusions on this can best be described with reference to Figure 2 which he proposed for the reaction of *trans*-$[Co(en)_2Cl_2]^+$ to yield *cis*-$[Co(en)_2NH_3Cl]^{2+}$. He assumed that the molecule of NH_3 (or H_2O) follows the attraction effects of the complex which are in the direction of a chloro group, and thus NH_3 transfers from the second sphere to the first sphere in a position cis to one of the chloro groups. Experiments show that the cis isomer is formed, and this was explained by the trans-chloro group transferring from the first to the second sphere while one end of the chelate ring moves to fill this position and vacates a spot for NH_3.

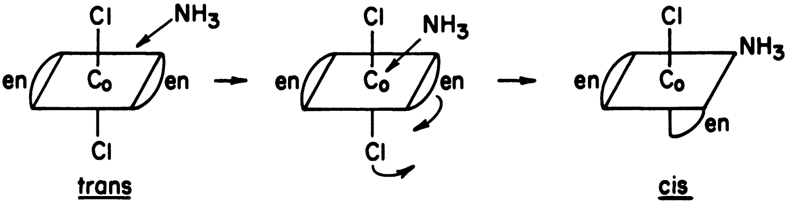


Figure 2. Mechanism of reaction proposed in 1912 by Werner (49)

Although Werner's interpretation of the cause of stereochemical changes during substitution and how they take place adequately explains the experimental facts, it has almost no predictive value. This is not intended as a criticism for we will see in the discussion which follows that we are still largely unable to predict the steric course of a substitution reaction of an octahedral metal complex. This is true despite the availability of much more experimental data and more sophisticated theories of bonding. Excellent reviews (*27*) have been written on the stereochemistry of octahedral substitution reactions. The discussion that follows deals almost exclusively with cobalt(III) complexes, but the principles involved are generally applicable to other octahedral systems.

Steric Changes

Before presenting some experimental observations on stereochemical changes accompanying octahedral substitutions, it is desirable to consider some of the changes that appear to be theoretically possible. In order to do this, it is convenient to consider what may happen for two types of mechanisms: (1) dissociation (S_N1(lim) or S_N1) with a decrease in coordination number; and (2) displacement (S_N2(lim) or S_N2) with an increase in coordination number.

What would appear to be the more plausible reaction paths for a dissociation mechanism are illustrated in Figure 3 for the reactions of *trans*-MA_4BX. Obviously, if X leaves and there is no extensive atomic motion, then Y may readily take the place vacated by X, and there is no rearrangement. If instead, as X leaves, two of the adjacent groups move

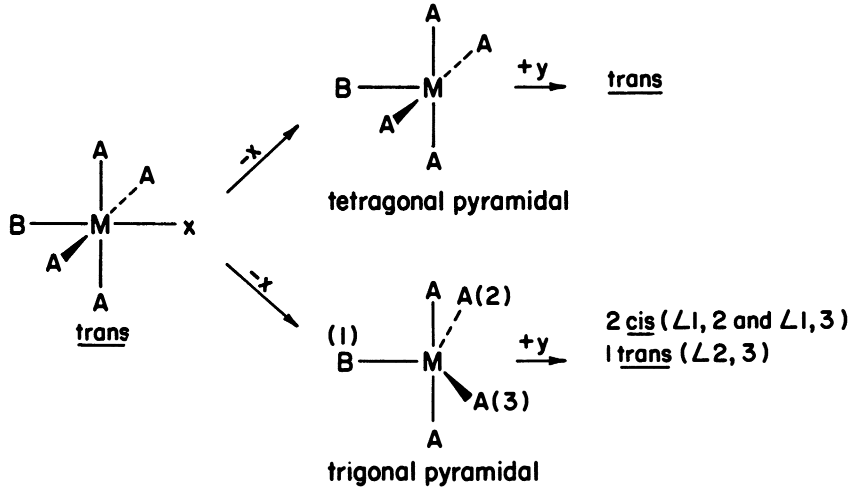


Figure 3. Possible stereochemical changes for a dissociation reaction of trans-MA_4BX

in to fill the gap, then the entry of Y in this trigonal plane may lead to rearrangement. Therefore, the conclusion is that substitution involving a tetragonal pyramidal structure takes place with retention of configuration, whereas a trigonal bipyramidal structure can lead to rearrangement. Both of these structures are known (*26*) to exist for stable 5-coordinated complexes.

Two different reaction processes also appear to be available for a displacement mechanism, and these are shown in Figure 4 for the reaction of

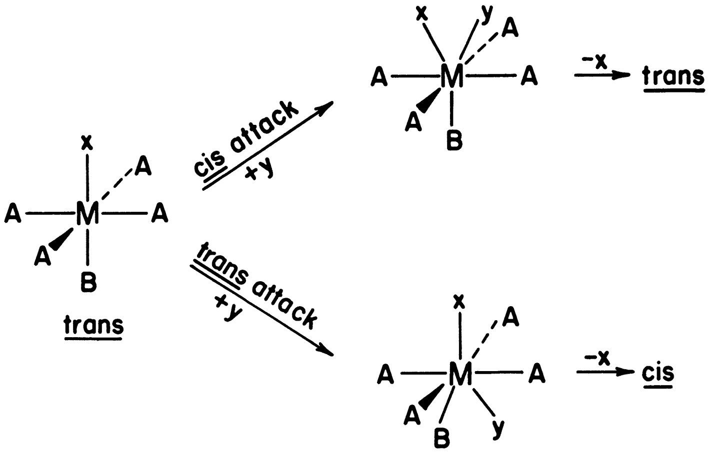


Figure 4. Possible stereochemical changes for a displacement reaction of trans MA_4BX

trans-MA_4BX. Attack by the entering nucleophile at an octahedral face adjacent to the leaving X group (cis-attack) takes place with retention of configuration. Nucleophilic attack at an octahedral face opposite the leaving group X (trans-attack) takes place with rearrangement. A trans-attack displacement on *cis*-MA_4BX (not shown) may take place with retention and/or rearrangement of configuration. Since a cis-attack requires much less ligand motion around the central metal than does a trans-attack, it would appear that a cis-attack may be energetically favored. Ingold (*14*) has used the terms edge and nonedge displacements which are equivalent to trans- and cis-attacks, respectively.

Aquation

Although aquation (or acid hydrolysis) reactions of cobalt(III) complexes have been studied more extensively than any other octahedral substitutions, it still is impossible to assign detailed mechanistic paths for them. An aquation reaction takes place at a pH less than 4 and is one in which a ligand is replaced by a molecule of water, such as that shown by Equation 1.

$$[Co(NH_3)_5Cl]^{2+} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{3+} + Cl^- \qquad (1)$$

Some of the recent discussion has been mostly concerned with the proper terminology and symbolism to describe what appears to be happening (*34*, *48*). It is generally agreed that the separation of charge between the metal and the departing ligand is more important than the neutralization of charge between the entering water and the metal, but the latter is a necessary part of the overall act of substitution (*8a*). Other ways of saying much the same thing are that in the transition state for reaction, bond-breaking is more important than bond-making, or that the reactions are primarily dissociative in type. In addition to other evidence there are also some stereochemical observations which suggest that dissociative processes of the S_N1(lim) type are not operative.

Tobe (*48*) and his students have carefully studied the stereochemistry of some substitution reactions of cobalt(III) complexes. In particular they have investigated the effect of L on the steric course of the aquation of *cis*- and *trans*-$[Co(en)_2LX]^{n+}$. Some of their results are summarized in Table I. The most striking feature of these results is that, regardless of L, cis substrates yield exclusively cis products, whereas trans substrates often form a mixture of geometrical isomers. Assuming that these reactions take place primarily by a dissociative process, these results can be explained with reference to the reaction paths shown in Figure 2. Thus, the cis substrates appear to react via a tetragonal pyramidal structure leading to the formation of cis products. In contrast, except for L =

Table I. Steric Course of the Acid Hydrolysis of Some Cobalt (III) Complexes

$$Co(en)_2LX^{n+} + H_2O \rightarrow Co(en)_2LH_2O^{(1+n)+} + X^-$$

cis-L	*S*	*% cis in Prod.*[a]	*Reference*	*trans-L*	*X*	*% cis in Prod.*[a]	*Reference*
OH^-	Cl^-	100	*5*	OH	Cl^-	75	*5*
OH^-	Br^-	100	*17*	OH^-	Br^-	73	*17*
Br^-	Cl^-	100	*17*	Br^-	Cl^-	50	*17*
Cl^-	Cl^-	100	*5*	Br^-	Br^-	30	*17*
Cl^-	Br^-	100	*17*	Cl^-	Cl^-	35	*5*
N_3	Cl^-	100	*45*	Cl^-	Br^-	20	*17*
NCS^-	Cl^-	100	*4*	NCS^-	Cl^-	50–70	*4*
NCS^-	Br^-	100	*4*	NH_3	Cl^-	0	*47*
NO_2^-	Cl^-	100	*2*	NO_2^-	Cl^-	0	*2*

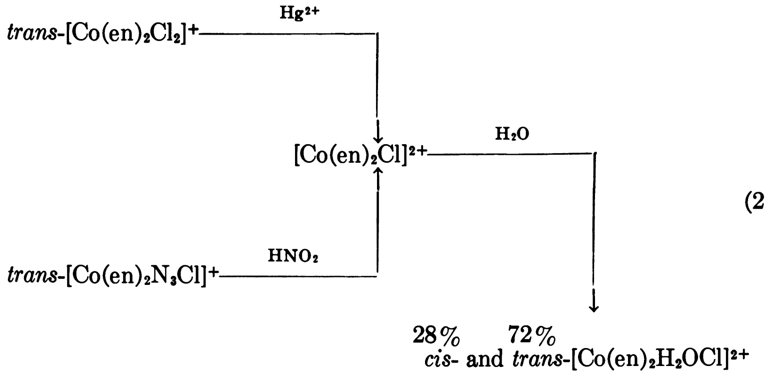
[a] The reaction products are a mixture of cis and trans isomers, therefore, % trans = 100% cis.

NH_3 or NO_2^-, the trans complexes seem to react by way of a trigonal bipyramidal structure which permits the formation of cis and trans products. It has been suggested (*39*) that π bonding of the type $M \overset{\leftarrow}{=} L$ may be important in these 5-coordinated systems. In such a case, the orbitals involved in π bonding are of the correct symmetry for the species produced by the cis isomers without the need of rearrangement. However, such π bonding can become effective in the species generated by the trans complexes only if rearrangement to a trigonal bipyramidal structure takes place. The fact that no rearrangement takes place for the trans isomers, where L = NH_3 or NO_2^-, may be caused by these ligands being unable to form ligand-to-metal π bonds. These results and this explanation lead to the prediction that the aquation of *cis*-$[Co(en)_2LX]^{n+}$ will yield *cis*-$[Co(en)_2LH_2O]^{(1+n)+}$, whereas the trans complex may form a mixture of cis and trans aquo products, providing L is a ligand such as OH^- capable of ligand-to-metal π bonding.

A closer examination of some of the data given in Table I reveals that the above discussion is a simplified version of what possibly happens. Consider the entries in the top six rows for the aquation of *trans*-$[Co(en)_2LX]^+$. Taken in three separate pairs, it is seen that for the same L there are two different leaving groups (X = Cl^- or Br^-). If the reaction process were that described above, then a given pair would form the same 5-coordinated species ($[Co(en)_2L]^{2+}$ (Figure 3) and must give the same distribution of products. Chan and Tobe (*17*) have called attention to the fact that this does not happen; they suggest that the leaving group (X) has not completely departed and exerts an influence on the position of attack of the entering water molecule. This requires a modification of the reaction paths given in Figure 3 to include the presence of X.

However, the gross features of the reaction mechanisms remain the same, and it appears that with the added modification owing to the influence of X the above discussion remains satisfactory.

Recent stereochemical studies by Loeliger and Taube (*35*) support the view that the departing X may have an effect on the steric course of aquation reactions in these systems. For example, the spontaneous aquation of *trans*-$[Co(en)_2Cl_2]^+$ yields 35% *cis*- and 65% *trans*-$[Co(en)_2(H_2O)Cl]^{2+}$, whereas the induced aquation with the addition of Hg^{2+} yields 28% *cis*- and 72% *trans*-$[Co(en)_2(H_2O)Cl]^{2+}$. Also, the rapid reaction of *trans*-$[Co(en)_2N_3Cl]^+$ with HNO_2 to liberate N_2 and N_2O in aqueous solution yields $[Co(en)_2(H_2O)Cl]^{2+}$ in the same isomeric quantities as for the induced aquation with added Hg^{2+}. Since these two different rapid reactions give the same products, it is assumed that the products are formed from the same 5-coordinated intermediate, as represented by Equation 2.



(2)

It then would appear that the spontaneous aquation of *trans*-$[Co(en)_2Cl_2]^+$, which gives a different product ratio, must not involve the same 5-coordinated species. A plausible interpretation is that in the normal aquation process the leaving Cl^- is still near enough to the pseudo 5-coordinated species to affect the position of attack by the entering H_2O. In relation to Equation 2, spontaneous aquation can be illustrated by Equation 3.

$$\textit{trans}\text{-}[Co(en)_2Cl_2]^+ \rightarrow [Co(en)_2Cl\cdots Cl]^+ \xrightarrow{H_2O} \overset{35\%}{\textit{cis}\text{-}} \text{ and } \overset{65\%}{\textit{trans}\text{-}}[Co(en)_2H_2OCl]^{2+} \qquad (3)$$

Earlier isotopic studies (*42*) on the aquation of $[Co(NH_3)_5X]^{2+}$ in the presence of Hg^{2+} also agree with the formation of a 5-coordinated intermediate in the induced aquation reactions.

Recent investigations show that isotopic fractionation studies of the type reported in Reference *42* do not establish whether a 5-coordinated intermediate is involved in aquation reactions of Co(III) complexes (Dolbar, G. E., Taube, E., *Inorg. Chem.*, in press.).

Base Hydrolysis

The hydrolysis of Co(III) ammines in alkaline solution (Equation 4) is often several orders of magnitude faster than the corresponding hydrolysis in acid solutions (Equation 1).

$$[Co(NH_3)_5Cl]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + Cl^- \qquad (4)$$

This contrasts markedly to the fact that no other reagent in water solution has more than just a secondary effect on the rate the leaving group is released. There has been much discussion as to the mechanism of base hydrolysis. Various types of evidence have been obtained which agree with a mechanism that involves first a rapid acid-base reaction (Equation 5), followed by the rate determining dissociation of the amido complex (Equation 6), and finally the rapid addition of water (Equation 7).

$$[Co(NH_3)_5Cl]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4NH_2Cl]^+ + H_2O \qquad (5)$$

$$[Co(NH_3)_4NH_2Cl]^+ \xrightarrow{\text{slow}} [Co(NH_3)_4NH_2]^{2+} + Cl^- \qquad (6)$$

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+} \qquad (7)$$

The best stereochemical data in support of this mechanism are those described by Jordan and Sargeson (*29*), some of which are shown in Table

Table II. The Lack of Influence of X on Stereochemistry of the Base Hydrolysis Reaction[a]

$$Co(en)_2LX^{n+} + OH^- \rightarrow Co(en)_2LOH^{n+} + X^-$$

trans-L	*X*	*% cis*	*cis-L*	*X*	*% cis*
Cl	Cl	5	Cl	Cl	30
Cl	Br	5	Cl	Br	37
NCS	Cl	76	NH_3	Cl	84
NCS	Br	81	NH_3	Br	85
NCS	N_3	70	NH_3	NO_3	86
N_3	Cl	27	NCS	Cl	80
N_3	N_3	30	NCS	N_3	70
OH	Cl	94	N_3	Cl	59
OH	Br	90	N_3	N_3	55
NO_2	Cl	6	OH	Cl	97
NO_2	NCS	10	OH	Br	96

[a] From Reference *29*.

II. These results show that for a particular isomer of a complex of the type $[Co(en)_2LX]^{n+}$, where L is the same but X differs, the concentrations of isomeric products from different parents are almost the same. This suggests that products come from a common intermediate, presumably a 5-coordinated amido species as is shown by Equation 8.

$$\left.\begin{array}{l} cis\text{-}[Co(en)_2NH_3Cl]^{2+} \\ cis\text{-}[Co(en)_2NH_3Br]^{2+} \\ cis\text{-}[Co(en)_2NH_3NO_3]^{2+} \end{array}\right] \xrightarrow{OH^-} [Co(en)_2NH_2]^{2+} \xrightarrow{H_2O} \underset{cis\text{- and } trans\text{-}[Co(en)_2NH_3H_2O]^{3+}}{85\% \qquad 15\%} \qquad (8)$$

If the leaving groups were present, as in a bimolecular displacement process, then the product ratios may differ for different substrates.

That the amido Co(III) complexes are much more reactive than the corresponding ammine complexes has been attributed (*39*) to the basicity of the amido group and to its π bonding in the fashion $Co \leftrightharpoons NH_2$. If the amido group formed is cis to the leaving group, then π bonding can take place without rearrangement, but π bonding is more efficient if the 5-coordinated species rearranges to a trigonal bipyramidal structure. In order for this to happen the amido nitrogen must be in the same trigonal plane as the vacant $d_{x^2-y^2}$ orbital on Co(III). Assuming a minimum of atomic motion, it follows that *trans*-$[Co(en)_2LX]^{n+}$ can readily form only structure A shown in Figure 5 (*40*). This same structure and also struc-

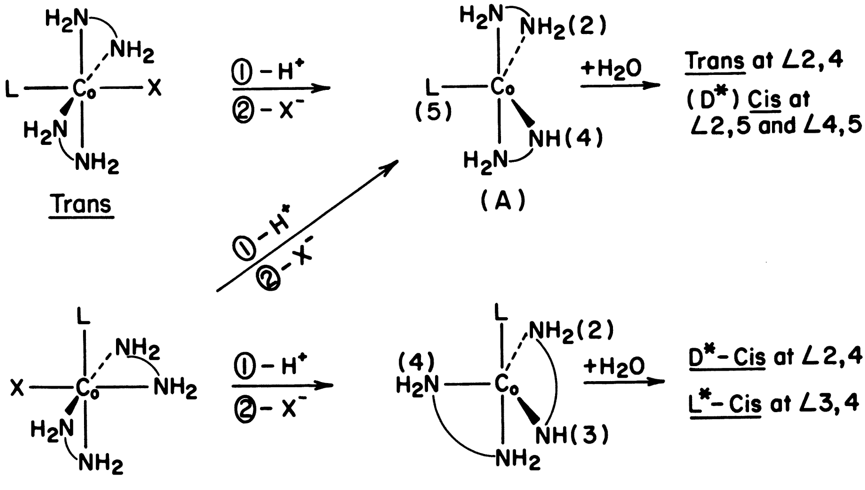


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Figure 5. Mechanism proposed (40) for the base hydrolysis of $[Co(en)_2LX]^{n+}$

ture B can be formed by the cis isomer. Furthermore, if the addition of water is fast compared to proton transfer, then B is asymmetrical and can permit a net retention or inversion of configuration. If proton transfer is faster than water addition, then racemic cis product must form from B. In any event, B can only form the cis isomer, whereas A can yield both cis and trans isomers.

Since the common intermediate A is the only one for the trans isomer, this allows the statement of a rule that *for base hydrolysis of complexes of the type* $[Co(en)_2LX]^{n+}$ *the cis isomer must never give less cis product than does the trans form.* The data in Table III show that this rule is obeyed.

Table III. Steric Course of Base Hydrolysis of Some Cobalt(III) Complexes[a]

$$Co(en)_2LX^{n+} + OH^- \rightarrow Co(en)_2LOH^{n+} + Cl^-$$

		% cis Product[b]				*% cis*
D*-*cis*-L	*X*	D*	L*	*trans*-L	*X*	*Product*[b]
OH^-	Cl^-	61	36	OH^-	Cl^-	94
OH^-	Br^-	96[b]		OH^-	Cl^-	90
Cl^-	Cl^-	21	16	Cl^-	Cl^-	5
Cl^-	Br^-	30[c]		Cl^-	Br^-	5
Br^-	Cl^-	40[c]		Br^-	Cl^-	0
N_3^-	Cl^-	51[c]		N_3^-	Cl^-	13
NCS^-	Cl^-	56	24	NCS^-	Cl^-	76
NH_3	Br^-	59	26	NCS^-	Br^-	81
NH_3	Cl^-	60	24	NH_3	Cl^-	76
NO_2^-	Cl^-	46	20	NO_2^-	Cl^-	6

[a] From Reference *40*.

[b] The total % cis product is the sum of D* and L* obtained from the D*-cis starting material. The optically inactive trans isomer will of course yield racemic-*cis*.

[c] The starting material was racemic and the cis product must also be racemic.

Based on this mechanism (Figure 5), it is possible to estimate what fractions of A and B are formed in the base hydrolysis of *cis*-$[Co(en)_2LX]^{n+}$. For example, *trans*-$[Co(en)_2Cl_2]^+$ gives 95% *trans*- and 5% *cis*-$[Co(en)_2ClOH]^+$, which establishes the behavior of the common intermediate A. Thus, the 37% of *cis*-$[Co(en)_2ClOH]^+$ formed by *cis*-$[Co(en)_2Cl_2]^+$ must come from the formation of 33.6% of B, which gives all cis product, and 66.4% of A, which gives 0.05 × 0.664 or 3.3% additional cis product. Other examples in Table III are used in this same way to estimate the fractions of A and B formed, and these are given in Table IV. This table also includes the modes of reaction of B when optically active cis isomers are used. For example, the data in Table III show that the base hydrolysis of D*-*cis*-$[Co(en)_2NH_3Cl]^{2+}$ gives 60% D*-*cis* and 24% L*-*cis*-$[Co(en)_2NH_3OH]^{2+}$. This is explained in Table IV which shows that 67%

Table IV. Calculated Stereochemical Results in Base Hydrolysis of *cis*-Co(en)$_2$LX Assuming S$_N$1CB Mechanism

L	*X*	*% Intermediate B*[a]	*% Retention*[a] *for B*
Cl^-	Cl^-	34	53
OH^-	Cl^-	50	26
OH^-	Br^-	60	—
Br^-	Cl^-	40	—
Cl^-	Br^-	26	—
N_3^-	Cl^-	44	—
NH_3	Cl^-	33	27
NO_2^-	Cl^-	64	69

[a] For a discussion of estimates of % of B and % retention for B, *see* text. For the structures of intermediates A and B, *see* Figure 5. Note also that % of A = 100 + % B, and that B need not be symmetrical, as discussed in text.

A and 33% B are formed, and in Table III which shows that A forms 76% cis and 24% trans products. The cis product via A must have the same absolute configuration as that of the substrate, D*-cis, which then gives 0.67 × 0.76 or 51% D*-cis product by this route. The remaining 9% of this product must come from B, which must then add water, with retention of configuration 27% of the time, 0.27 × 0.33, giving 9%. This method is used to obtain the data shown in Table IV for the per cent retention by B.

On the basis of such a mechanism, a second rule must be obeyed by the base hydrolysis reactions of $[Co(en)_2LX]^{n+}$ complexes, which is that *the per cent retention of configuration by a cis substrate must be greater than or equal to the per cent of intermediate A times the fraction of cis product from A.* This rule is followed by the data given in Table IV. In anticipation of the discussion in the next section, it should be noted that since B may not be symmetrical, it can provide a path for the reaction of an optically active complex to give an optically active product of inverted configuration.

Optical Inversion

Substitution reactions of optically active metal complexes to yield reaction mixtures with some remaining optical activity usually owe this to the occurrence of optical retention reactions. Only five examples of optical inversion reactions have been reported, and all but one of these were discovered by Bailar (*3*) and his students. This is a somewhat surprising result because the types of rearrangements described above must also be involved in optical inversion reactions. In some of these cases the authors prefer to explain the mechanism of inversion on the basis of a trans-attack displacement (*19, 33*). One reason for this may be due to the erroneous assumption that a dissociation process could not provide a path for optical inversion (*8b*). Having been responsible for the original error, I should like now to correct it.

All of the optical inversion reactions reported for aqueous solutions are base hydrolysis reactions of Co(III) complexes containing some N—H hydrogens. This suggests there may be something unusual about these reactions, and the unique behavior of OH^-, as a reagent, was described in the previous section. Since there is considerable support for such base hydrolyses taking place by a conjugate base-dissociation mechanism, it is gratifying that this mechanism can also be used to account for the observed optical inversion reactions.

The base hydrolysis of D*-*cis*-$[Co(en)_2Cl_2]^+$ gives $[Co(en)_2OHCl]^+$ as an isomeric mixture but with some remaining optical activity. At low concentrations of OH^- the optical activity is due to optical retention (*16*), but in the presence of Ag^+ (*19*), or at high OH^- concentrations (*12*), optical inversion takes place (*9*). Referring again to Figure 5, it is seen that

$$\text{D*-}cis\text{-}[Co(en)_2Cl_2]^+ + OH^- \rightarrow \text{L*-}cis\text{-}[Co(en)_2OHCl]^+ + Cl^- \qquad (9)$$

optical inversion can take place through intermediate (B), providing proton transfer is slower than adding water. This is illustrated in Figure 6 by the attack of water at ∠1,3 of intermediate (B). It is not clear why attack of this position appears to be enhanced by Ag^+ or high concentrations of OH^-, but an explanation has been offered in terms of ion-pair formation (*12*).

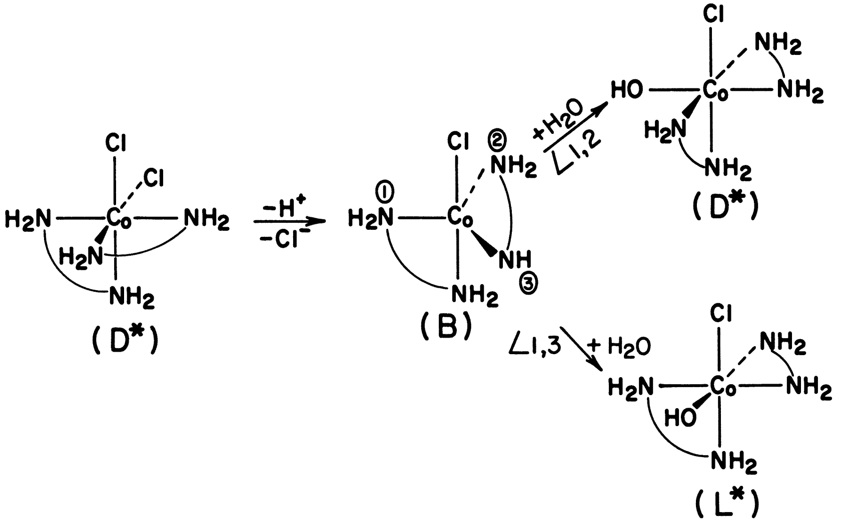


Figure 6. Conjugate base mechanism for the optical inversion of D**-cis-*$[Co(en)_2Cl_2]^+$ *into* L**-cis-*$[Co(en)_2ClOH]^+$ *via water attack of (B) at ∠1,3*

Recent studies (*32*) show that the base hydrolysis of D*-α-[Co(trien)OHCl]$^+$ also results in a net optical inversion reaction (Equation 10). On the basis of a conjugate base-dissociation mechanism this re-

$$\text{D*-}\alpha\text{-[Co(trien)OHCl]}^+ + \text{OH}^- \rightarrow \text{L*-}\beta\text{-[Co(trien)(OH)}_2]^+ + \text{Cl}^- \qquad (10)$$

arrangement can take place as is shown in Figure 7 by the attack of water at ∠1,3 of intermediate (B). Attack at ∠1,3 over ∠1,2 is preferred due to the greater stability of the β form compared with the α form. In support of this is the observation (*33*) that L*-β-[Co(trien)Cl$_2$]$^+$ reacts with OH$^-$ with almost complete optical retention to give L*-β-[Co(trien)(OH)$_2$]$^+$. The optical inversion reactions observed in liquid ammonia (*3*, *33*) solutions can also be explained by this same type of mechanism.

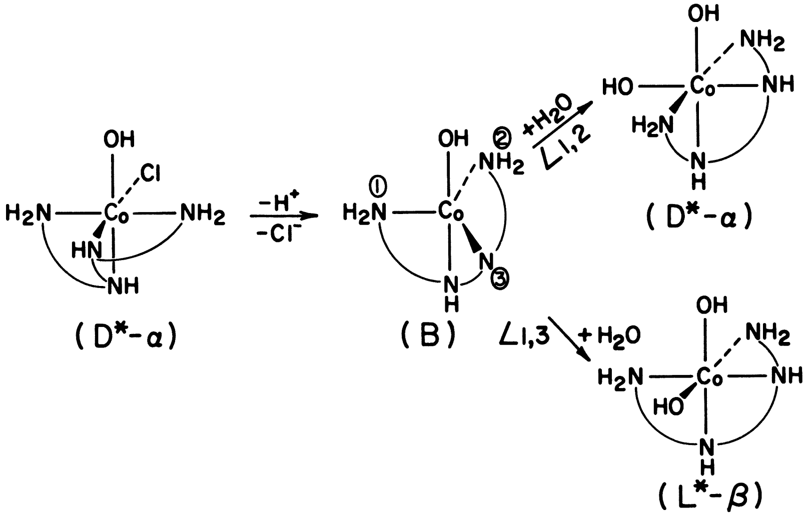


Figure 7. Conjugate base mechanism for the optical inversion of D*-α-*[Co(trien(OCHl]$^+$ into* L*-β-*[Co(trien)(OH)$_2$]$^+$ by water attack of (B) at ∠1,3; trien = $NH_2C_2H_4NHC_2H_4NHC_2H_4NH_2$*

Cis-Trans Isomerization

In addition to the stereochemical changes that accompany chemical reaction, these systems can be rearranged without chemical change. Several such examples of geometrical and of optical rearrangements are known for metal complexes. A brief account is given of some examples of geometrical (or cis-trans) isomerization in this section, and the next section contains a few examples of optical isomerization (or racemization).

Most of the investigations on the kinetics and mechanisms of cis-trans isomerizations of metal complexes deal with systems of the type $M(AA)_2X_2$, where AA and X are bidentate and unidentate ligands, respectively. The immediate question that must be answered in such a study is whether isomerization takes place by an intramolecular or an intermolecular process. Fortunately, this is readily amenable to experimental testing by the use of labeled isotopes of the most labile ligand in the complex. If ligand exchange takes place at a rate which is slower than the rate of isomerization, then this requires an intramolecular mechanism (Figure 9), whereas if exchange is as fast or faster than isomerization then this permits an intermolecular process for rearrangement. The results obtained often support an intermolecular mechanism, and a possible rearrangement by this process is that shown in Figure 8.

That geometrical isomerization of metal complexes can occur was reported as early as 1889 by Jørgensen (*30*) for the system represented by Equation 11.

$$\underset{\text{violet}}{cis\text{-}[Co(en)_2Cl_2]^+} \rightleftharpoons \underset{\text{green}}{trans\text{-}[Co(en)_2Cl_2]^+} \tag{11}$$

The violet and green solid chlorides are readily interconverted. Thus, if *cis*-$[Co(en)_2Cl_2]Cl$ is dissolved in a small amount of water containing hydrochloric acid and the solution is concentrated on a steam bath, green crystals of *trans*-$[Co(en)_2Cl_2]Cl \cdot H_5O_2Cl$ (*24*) separate. Removing H_2O and HCl from the green solid at elevated temperatures and dissolving it in water followed by evaporation on a steam bath restores the violet crystals of *cis*-$[Co(en)_2Cl_2]Cl$. This interconversion occurs because the cis isomer is less soluble than the trans and separates from water solution, whereas the *trans*-H_5O_2Cl adduct is less soluble than the cis and separates from a hydrochloric acid solution.

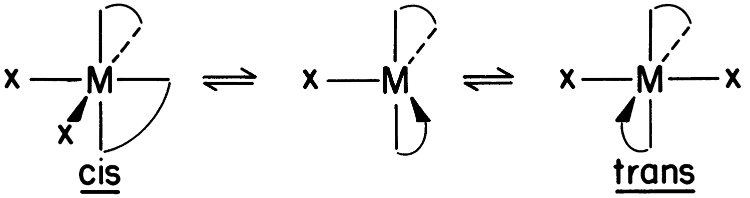


Figure 8. Possible intermolecular cis-trans isomerization of $[M(AA)_2X_2]$

One of the earliest experiments on the application of radioactive isotopes to the study of mechanisms of reactions of metal complexes was that of Ettle and Johnson (*22*). They added radiochloride ion to solutions of $[Co(en)_2Cl_2]^+$ and found that cis-trans isomerization in this system is accompanied by a complete random distribution of radiochloride ion in the complex. This suggests that isomerization takes place by an intermolecular mechanism. Considering what is now known about the water solution chemistry of these complexes, it appears that rearrangements may take place by the equilibria shown in Equation 12.

$$\begin{array}{ll} \mathit{cis}\text{-}[Co(en)_2Cl_2]^+ + H_2O \rightleftharpoons \mathit{cis}\text{-}[Co(en)_2H_2OCl]^{2+} + Cl^- & (12) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \nwarrow\!\searrow & \\ \mathit{trans}\text{-}[Co(en)_2Cl_2]^+ + H_2O \rightleftharpoons \mathit{cis}\text{- and } \mathit{trans}\text{-}[Co(en)_2H_2OCl]^{2+} + Cl^- & \end{array}$$

In addition to the data on the aquation reactions (Table I), it is also known (*5*) that isomerization of the chloro-aquo products can take place. Equation 12 is sufficient to permit isomerization by an intermolecular process, but it is an over-simplification of what happens in the experiments described above. Equilibria for the replacement of the second chloro group, as well as acid-base equilibria between aquo and hydroxo species, must also be involved. Less complicated is the isomerization of *cis*-$[Co(en)_2Cl_2]^+$ in methanol solution where the rate of rearrangement equals the rate of chloride ion exchange (*48*).

Because an intermolecular isomerization is nothing more than a substitution reaction, the problem of assigning a detailed mechanism is the same as that described above for stereochemical changes accompanying octahedral substitution. For a dissociation process, isomerization can readily take place by rearrangement to a common intermediate as is shown by Figure 8. This simple representation does not include any solvation steps, nor does it show the presence of the leaving group near the intermediate.

Oxygen-18 experiments show that geometrical isomerizations of the complexes $[Co(en)_2(H_2O)_2]^{3+}$ (*31*) and $[Co(en)_2NH_3H_2O]^{3+}$ (*37*) may take place by a water exchange path. However, the trans → cis rearrangement of $[Co(en)_2NH_3OH]^{2+}$ occurs without any exchange of the hydroxo group with the solvent water. This intramolecular isomerization is believed to involve a chelate ring opening-closing process (Figure 9). A similar process may be responsible for rearrangements in the system $[Cr(C_2O_4)_2(H_2O)_2]^-$ at pH less than 2, whereas above this pH water exchange may account for the isomerization (*25*). Fay and Piper (*23*) have used NMR techniques to investigate the change *cis* → *trans*-[M(tfacac)$_3$], where tfacac-trifluoroacetylacetone and M(III) = In, Ga, Al, Co, Rh. This ordering of M(III) is the same as that of the decrease in rates of isomerization which appear to take place by an intramolecular mechanism.

Racemization

Speculations as to the mechanisms of racemization of metal complexes began almost with the discovery of optical activity in these systems by

Werner (*50*) and his students. He was the first to recognize that racemization of complexes such as $M(AA)_3$, where AA is a bidentate, can take place by a chelate ring opening-closing process. Such a mechanism and two others are shown in Figure 9. These are called intramolecular processes, because racemization takes place without the complete departure of a ligand from the first coordination sphere.

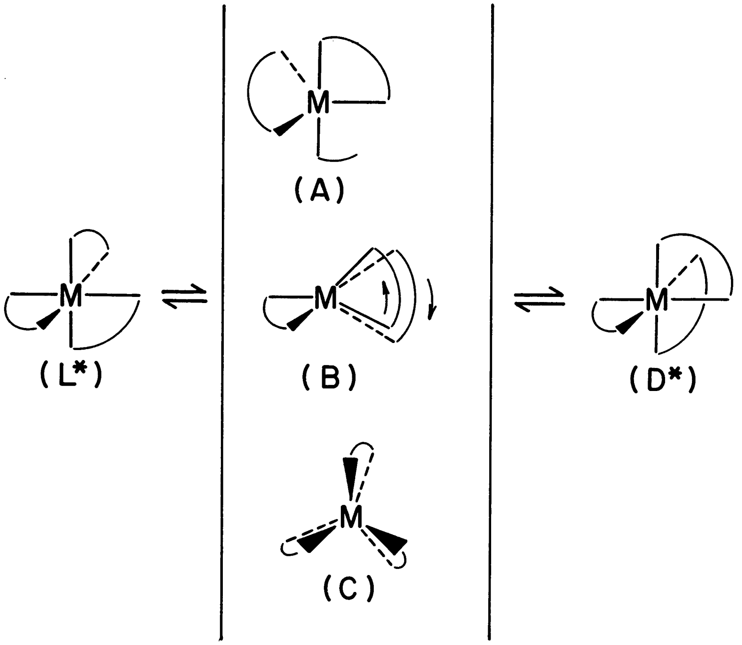
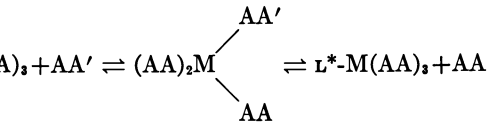


Figure 9. Intramolecular racemization of $[M(AA)_3]$ *by the following mechanisms: (A) chelate ring opening-closing; (B) rhombic twist; and (C) trigonal twist*

In contrast to this is the loss of optical activity by a ligand interchange process which permits accompanying rearrangements to occur, as was discussed earlier. Racemization by such a process is called an intermolecular mechanism. Such mechanisms would require equilibria permitting ligand interchange, as perhaps occur in Equation 13.



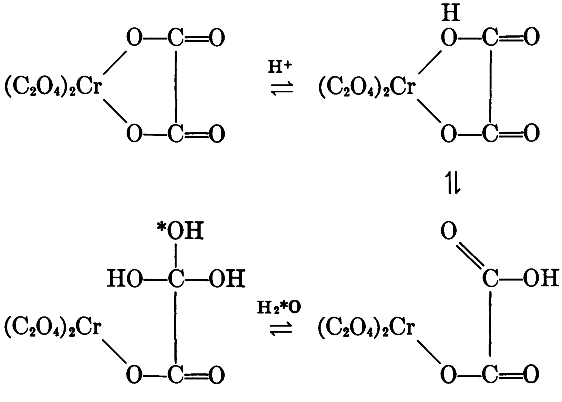
$$\text{D}^*\text{-M(AA)}_3 + \text{AA}' \rightleftharpoons (\text{AA})_2\text{M}\begin{matrix} \diagup \text{AA}' \\ \\ \diagdown \text{AA} \end{matrix} \rightleftharpoons \text{L}^*\text{-M(AA)}_3 + \text{AA} \qquad (13)$$

These reactions are surely an over-simplification of what happens and may involve additional steps with the intermediate formation of solvated species.

If one of the intermediates is symmetrical, or rapidly rearranges, this provides a ready means for racemization. Experimental evidence in support of such a mechanism is obtained if one finds that the rate of ligand interchange is the same or faster than the rate of racemization. This has been found to be true for the racemization of the optically active complexes $[Ni(ophen)_3]^{2+}$ (*7*), $[Ni(bipy)_3]^{2+}$ (*7*), *cis*-$[Co(en)_2Cl_2]^+$ (*48*), *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ (*31*), and *cis*-$[Co(en)_2NH_3H_2O]^{3+}$ (*37*).

Much more fascinating and challenging are the investigations of metal complexes that racemize by intramolecular mechanisms. These include the optically active complexes $[Co(C_2O_4)_3]^{3-}$ (*36*), $[Cr(C_2O_4)_3]^{3-}$ (*36*), $[Co(acac)_3]$ (*23*), $[Cr(acac)_3]$ (*23*), [Co(EDTA)] (*18*) and, in part, $[Fe(ophen)_3]^{2+}$ (*6*) and $[Fe(bipy)_3]^{2+}$ (*6*). It is easy to show that the loss of optical activity in these systems does not involve ligand interchange. Long (*36*) did this for the trioxalato complexes by using carbon-14 oxalate ion and observing that oxalate ion exchange with the complex was slower than its racemization. What is not easy is to design definitive experiments which permit a choice of the intramolecular rearrangement, three possibilities of which are shown in Figure 9.

For the trioxalato system, which has been the subject of extensive investigations, the experimental results support a chelate ring opening-closing mechanism (Figure 9A) for racemization. Thus, it was observed that the rate of acid-catalyzed oxygen exchange in the system $[Cr(C_2O_4)_3]^{3-}$—$H_2{}^*O$ is only slightly slower than the rate of racemization of the complex, but much faster than its exchange with $^*C_2O_4{}^{2-}$. Furthermore, all 12 of the oxygen atoms in the complex exchange at the same rate, requiring that the chelate ring open and close. The mechanism proposed for the oxygen-18 exchange is illustrated by Equation 14.

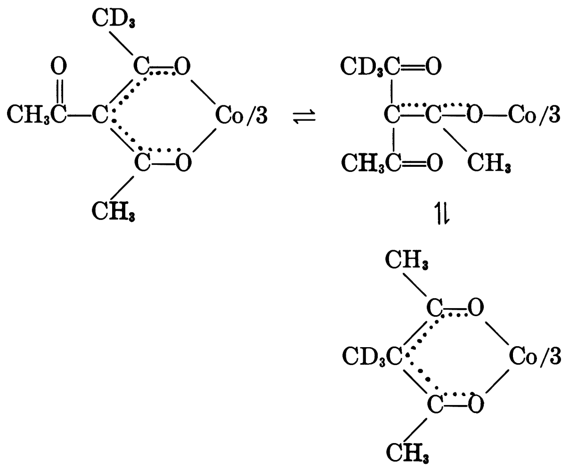


(14)

This implies that the oxalato chelate rings are opening and closing rapidly and that frequently this occurs with retention of configuration, but occasionally inversion takes place which then is responsible for the racemization of the complex.

It may *a priori* seem almost impossible to design an experiment to distinguish between the twisting paths (B) and (C) shown in Figure 9, but Fay and Piper (*23*) have cleverly done this. This was done using complexes of the type $M(AB)_3$, where AB is an unsymmetrical bidentate ligand, which exist in the form of optically active cis-trans isomers. An examination of molecular models shows that the trigonal twist (Figure 9C) mechanism permits racemization without cis-trans isomerization, whereas the rhombic twist (Figure 9B) leads to simultaneous racemization and isomerization. It was observed that the racemization of *tris*(benzoylacetonato)chromium(III) is accompanied by cis-trans isomerization, which then rules out a trigonal twist mechanism.

Unfortunately, the same racemization-isomerization result can also take place by a chelate ring opening-closing process. (It has recently been pointed out (Springer, C. S., Jr., Sievers, K. E., *Inorg. Chem.*, in press.) that two other twisting mechanisms are possible (Figure 10). For a complex of the type $M(AB)_3$, rhombic twist (D) permits racemization without isomerization, whereas trigonal twist (E) requires that both take place simultaneously.) Piper (*41*) designed an elegant experiment to distinguish between this and the rhombic twist. Making use of NMR he determined that isomerization of the type shown by Equation 15 takes place in solution.



(15)

This type of isomerization cannot take place by a twisting process and requires a metal-ligand bond rupture mechanism.

Although there is no direct proof that a simple twisting mechanism causes racemization, there is reason to believe that this should be possible.

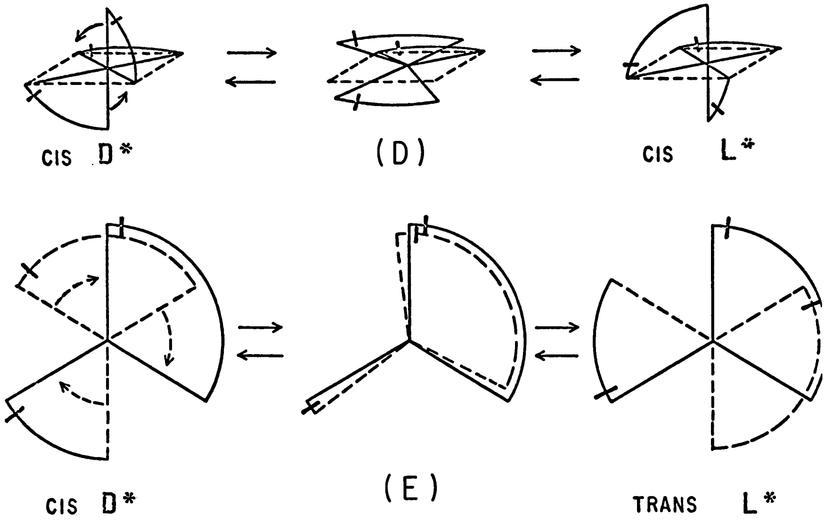


Figure 10. Additional twisting processes for the racemization and isomerization of $M(AB)_3$

This is particularly true now with the recent discovery of trigonal prismatic structures for some 6-coordinated metal complexes (*21*). Surely the proper metal-ligand combination should give a system in which the difference in energy between an octahedral and a trigonal prismatic structure is small. As a result, racemization may take place by a trigonal twist mechanism. Twisting processes of the square-planar-tetrahedral type are known to occur readily in certain nickel(II) complexes (*20*).

Perhaps the racemization of $[Fe(ophen)_3]^{2+}$ takes place by a twist mechanism (*6*). This is because the rate of loss of optical activity is not acid catalyzed, as is true of $[Fe(bipy)_3]^{2+}$, where it appears the flexible chelate ring opens and is protonated. The rigid structure of 1,10-phenanthroline would suggest that it does not behave as a unidentate ligand, and therefore the intramolecular racemization does not take place by chelate ring opening-closing. The same may also be true for that portion of the intramolecular racemization of $[Fe(bipy)_3]^{2+}$ that proceeds by an acid independent path. Busch (*18*) and his students have investigated the racemization of $[Co(EDTA)]^-$ and conclude that it proceeds by a special trigonal twist mechanism. This is one in which a molecule of water is added in the process to form a 7-coordinated species with a structure analogous to that found (*43*) for $[Mn(EDTA)H_2O]^{2-}$.

Miscellaneous

The steric course of substitution reactions of octahedral metal complexes other than cobalt(III) has been studied to a limited extent. Garner

(*38*) and his students have investigated some reactions of *cis*- and *trans*-$[Cr(en)_2X_2]^+$ and find that these complexes react with less rearrangement than do the corresponding cobalt(III) systems. Stereochemical studies made on platinum metal complexes show that these generally react with retention of configuration. For example, the base hydrolysis of D-*cis*-$[Rh(en)_2Cl_2]^+$ takes place without rearrangement (*28*), as does also the base hydrolysis of D-*cis*-$[Ru(en)_2Cl_2]^+$ (*13*). These results support the view (*1*) that systems of high crystal field strength are less apt to undergo stereochemical change because of the greater loss of CFSE required for molecular rearrangement.

Square-planar complexes react by a displacement process with retention of configuration (*10*). This involves an expansion of coordination number of the metal with the formation of a trigonal bipyramidal species. The entering group and the leaving group are believed to be in the trigonal plane, and the net result is that the entering group occupies the position vacated by the leaving group.

Extensive investigations have been made on redox reactions of metal complexes (*46*), but very little has been done with the role of stereochemistry in these reactions. Some investigations on the reduction of *cis*- and *trans*-$[Co(en)_2X_2]^{n+}$ with Fe(II) (*11*) and with Cr(II) (*15*) have been made, and these show that the geometrical isomers react at different rates. The same is true for the Pt(IV) systems in which it was observed (*9*) that *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$ reacts 10^3 times faster than does the cis isomer with $[Pt(NH_3)_4]^{2+}$. It would also be interesting to examine the rates of redox reactions in optically active systems. For example, one may like to know if the rate of reaction differs markedly for a system in which the oxidant and reductant have the same absolute configuration from that where they have opposite configurations. This question and others will have to await some stereochemical investigations of redox reactions.

Acknowledgment

I wish to thank M. L. Tobe for giving me a copy of his English translation of the paper by Werner (*49*). Our research on the stereochemistry of metal complexes has been supported in part by a National Institutes of Health grant RG-7488.

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29

The Crystal Field Splitting Parameter *Dq*: Calculation and Significance

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This paper reviews methods which have been used to elucidate the quantity Dq in cubic and non-cubic molecules. A novel graphical method allowing the rapid determination of Dq and B from spin-allowed absorption bands of high-spin d^2, d^3, d^7, and d^8 complexes is introduced. It is possible to calculate both in-plane and out-of-plane ligand field strengths in tetragonal complexes. Calculations with tetragonal nickel(II) complexes indicate that the axial field strengths in complexes involving bulky in-plane ligands can be remarkably weak. There are many difficulties in obtaining a meaningful value of Dq; different methods of analyzing the same spectrum may yield different Dq quantities. Despite such uncertainties, detailed studies of series of analogous complexes provide useful chemical information.

While Werner's classic paper (*49*) of 1891 can be regarded as the foundation of modern inorganic coordination chemistry, it has been only during the past 10 to 15 years that a rationalization of the many stereochemistries possible for a coordination complex has become possible—through the modern techniques of spectroscopy and magnetism. Even today, however, many problems remain to be solved, and it is the purpose of this review to outline some of these difficulties.

The major feature of a transition metal coordination complex is the presence of an incomplete *d* shell in which the energies of the *d* orbitals, which are no longer fivefold degenerate, are determined by the stereochemistry of the complex. The electronic absorption spectrum and, therefore, the color of the complex depends upon the arrangement and energies of the d electrons within the d shell. Conversely, a study of the spectrum can reveal the stereochemistry of, and the electronic levels within, a coordination complex. The basis for understanding electronic absorption spectra was laid down in 1929 by Bethe (*3*) in his development of crystal field theory, but modern inorganic electronic spectroscopy, as we know it, was not really underway until the early 1950's. Since then the development has been rapid (*2*, *5*, *12*, *23*, *35*, *43*). Crystal field theory has now been largely superseded by ligand field theory in which the interaction between the metal ion and ligand orbitals is taken into account.

Of major importance in either theory is the crystal field (or ligand field) parameter Dq, where $10Dq$ is the energy separation between the e_g and t_{2g} d orbitals in a cubic environment (*2*, *12*, *23*). The term cubic environment covers 4-coordinate tetrahedral, 6-coordinate octahedral, and 8-coordinate cubic complexes. The g subscripts are not necessary for a tetrahedral environment which lacks a center of symmetry. Henceforth, for simplicity, these subscripts will be dropped.

This paper reviews the measurement of this parameter, both in cubic and in non-cubic complexes, and discusses its significance. A novel method for the rapid calculation of Dq and B from the spectra of cubic molecules of high-spin d^2, d^3, d^7, and d^8 ions is introduced, and the spectra of some tetragonally distorted nickel(II) complexes are interpreted in terms of unusually low, crystal field strengths for the axial ligands.

It should be mentioned that although Dq is formally an ionic parameter and crystal field theory is not held in very high acclaim today, it is still important as an empirical ligand field parameter. There are, however, many difficulties involved in obtaining a meaningful value of Dq in a given system.

Ionic Model

On the basis of crystal field theory, the octahedral crystal field potential Dq is as follows:

$$Dq = \frac{ze^2 r_2^4}{6a_0^5} = \frac{1}{6}\alpha\, 4 \qquad (1)$$

(r_2^4 is the average quartic radial displacement of a d electron; a_0 is the metal ligand distance; and α_4 is called a radial integral (*3*, *6*, *10*, *19*).) It is well-known (*12*) that inserting appropriate values of the various parameters into this expression does not reproduce the experimentally observed value, primarily because the ionic model is an unreal approximation to the bonding in the complex. When covalency is taken into account, the calculated and observed values can be made to agree well (*42*).

Determination of Dq-Cubic Molecules

There are two principle methods for determining *Dq* spectroscopically —the method used depending upon the metal ion in question. With some ions the lowest energy, spin-allowed transition corresponds exactly with 10*Dq*, at least to a first order approximation. In these circumstances, 10*Dq* is simply the energy of this absorption band and is obtained without recourse to calculation. All other spin-allowed transitions in cubic molecules will be functions of 10*Dq* and also of the Racah interelectronic repulsion parameters *B* and/or *C* (*2*) (or alternatively the Slater-Condon F_k parameters (*40*)). Where 10*Dq* cannot be directly estimated from an absorption band energy, two or more observed transition energies must be used to solve the appropriate secular equations.

Tanabe and Sugano first calculated the required energy (*44*) matrices which have since been repeated by other authors (*17*, *34*). Simplified equations have been presented by Jørgensen (*24*). These latter equations are not always exact solutions to the Tanabe-Sugano secular determinants because the assumption is made that $C = 4B$ to aid simplification.

Tanabe-Sugano diagrams are graphical representations (*17*, *34*, *44*) of the energy matrices in which the ratio Dq/B is plotted against E/B. Plots of *Dq vs. E*, sometimes called Orgel diagrams, in which a value of *B* is assumed, have also been published (*37*). The Tanabe-Sugano equations were calculated on a strong field basis, while Orgel used a weak field basis. The terms "strong field" and "weak field" refer to the situations in which the crystal field is either large or small, compared with the interelectronic repulsion, respectively. In the weak field calculation, interelectronic repulsion is considered first, then the free ion spectroscopic terms of the central ion are derived. Subsequently, the crystal field potential is considered as a perturbation upon these terms, the degeneracies of which may now be partially or wholly lifted to give a number of levels described by group theoretical labels. In the strong field treatment, the effect of the crystal field upon the *d* orbitals is first considered. The possible electron configurations in the particular molecular environment are obtained, and then the interelectronic repulsion within each configuration is evaluated. Provided that configurational interaction is included, both approaches lead to the same conclusions (*2*, *12*).

The various ions may be conveniently divided into a number of categories.

High-spin Complexes in which the Central Ion-free Ion-ground Spectroscopic Term is ^nD; $d^1(^2D)$, $d^4(^5D)$, $d^6(^5D)$, $d^9(^2D)$—e.g., Ti(III), V(IV), Mn(III), Fe(II), Cu(II), etc. In all cases, in cubic symmetry, the degeneracy of the *D* term is lifted to give two levels, T_2 and *E*, the energy separation of which is 10*Dq* to a first approximation (Figure 1). In this

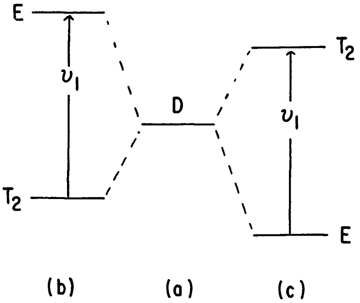

Figure 1. Energy level diagram for high-spin ions with a D-free ion ground term. a) Free ion in a spherical potential; b) splitting diagram for d^1 and d^6 ions in an octahedral field, and d^4 and d^9 ions in a tetrahedral field; c) splitting diagram for d^4 and d^9 ions in an octahedral field, and for d^1 and d^6 ions in a tetrahedral field.

situation then, the band energy of the only spin-allowed transition gives a direct measure of $10Dq$.

Those ions with T_2 ground states (e.g., octahedral Ti(III), V (IV), Co(III) high-spin, etc.) generally give rise to an asymmetric spectrum consisting of a peak with a shoulder on the low energy side. This phenomenon is believed to occur as a consequence of the lifting of the degeneracy of the excited E term by the Jahn-Teller effect (*12*). Although the sense of the splitting is not known, the energy of the peak is usually taken to represent $10Dq$. Complexes with E ground states (e.g., octahedral Cu(II) and Cr(II)) are usually so tetragonally distorted that they cannot be considered to have cubic symmetry; their spectra are generally extremely broad, and a precise value for $10Dq$ cannot be assigned without a detailed spectral analysis. (*See* tetragonal complexes below.)

High-spin Complexes in which the Central Ion-free Ion-ground Spectroscopic Term is ^nF; $d^2(^3F)$, $d^3(^4F)$, $d^7(^4F)$, $d^8(^3F)$—e.g., V(II), V(III), Mn(IV), Mo(III), Cr(III), Co(II), Ni(II), etc. The degeneracy of the F term is lifted in a cubic environment to yield the group theoretical terms A_2, T_2, and T_1 (Figure 2). In all cases, there is an ^nP term lying $15B$ above the ^nF term. The P term will transform as T_1 in a cubic environment. Two basic situations arise: a) the A_2 term lies lowest in energy; b) the $T_1(F)$ term lies lowest in energy (Figure 2).

A_2 TERM AS GROUND STATE, OCTAHEDRAL d^3 AND d^8, TETRAHEDRAL d^2 AND d^7 (ALL HIGH-SPIN). The lowest energy, spin-allowed transition, $T_2 \leftarrow A_2$, corresponds directly with $10Dq$. This is generally observed in the octahedral complexes but is rarely observed in tetrahedral complexes,

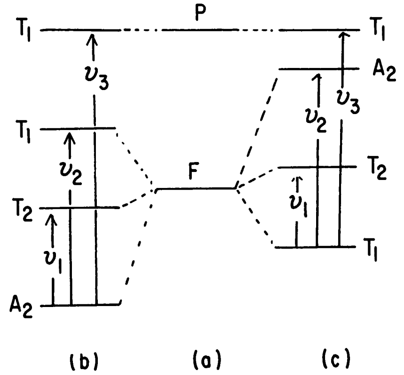

Figure 2. Energy level diagram for high-spin ions with an F-free ion ground term. a) Free ion in a spherical potential; b) splitting diagram for d^3 and d^8 in an octahedral field, and for d^2 and d^7 in a tetrahedral field; c) splitting diagram for d^2 and d^7 in an octahedral field, and for d^3 and d^8 in a tetrahedral field.

partly as a consequence of its being of very low energy (3000 to 5000 cm.$^{-1}$ for a divalent ion) and therefore in a somewhat inaccessible region of the spectrum, and partly because it is expected to be very weak (it is formally forbidden electronically) and will tend to be obscured by the vibrational spectrum of the ligands.

When this transition is not observed, $10Dq$ must be obtained from the energies of the second and third spin-allowed transitions, ν_2 and ν_3, respectively (Figure 2). The method employed is discussed below.

$T_1(F)$ TERM AS GROUND STATE, OCTAHEDRAL d^2 AND d^7, TETRAHEDRAL d^3 AND d^8 (ALL HIGH-SPIN). In the limit of a very weak crystalline field, the energy of the first spin-allowed transition is $8Dq$ (*2*, *23*). However, in the complexes commonly investigated the crystal field strength is such that this approximation is not valid. In the so-called intermediate or medium field region the T_1 terms derived from the F and P free ion terms will mix together so that the energy of the ground state, with reference to the free ion in a spherical field, will be not only a function of Dq, but also of the Racah parameter B. Values of $10Dq$, and also of B, may be found by solving the appropriate secular equations, utilizing two of the spin-allowed transition energies.

Direct solution of the rather complicated equations involved (*2*, *23*) is rather tedious, especially so when the ground state is T_1 and a graphical solution is to be preferred. The method commonly used involves the computation of the ratio of two of the spin-allowed transition energies, say ν_2 and ν_3, and the location on the appropriate Tanabe-Sugano diagram of a position where the ν_3/ν_2 ratio agrees with the experimental ratio. Dq/B, $E(\nu_3)/B$, and/or $E(\nu_2)/B$ can then be directly obtained from the diagram and values of Dq and B evaluated (*12*).

This method has the disadvantage that virtually all published Tanabe-Sugano diagrams are physically rather small so that the location of a position, where the ν_3/ν_2 ratios tally and the reading of the Dq/B and E/B ratios are inaccurate. Moreover, the actual process of locating the correct position on the diagram is slow.

These disadvantages are eliminated by diagrams in which the transition energy ratios themselves are directly plotted against Dq/B and against E/B. These are illustrated for all high-spin ions with F ground terms in Figures 3–5. Larger scale diagrams may be found elsewhere (*25*).

Consider the three following examples:

1) The octahedral complex ion Ni(dimethylsulfoxide)$^{+2}$ has absorption bands at 7728 (ν_1), 13000 (ν_2), and 24040 (ν_3) cm.$^{-1}$ The observation of ν_1 means that Dq is 773 cm.$^{-1}$ A value for B may be found from the ν_2/ν_1 ratio, which is 1.682. Reading from Figure 3, Dq/B = 0.82, hence B = 942 cm.$^{-1}$ Direct solution of the secular equation yields B = 948 cm.$^{-1}$ The energies of ν_2 and ν_3 may also be used to compute Dq and B. The ratio ν_3/ν_2 is 1.854, hence from Figure 3, Dq/B = 0.84, and from Figure 4, $E(\nu_3)/B$ = 26.05, hence Dq = 775 and B = 923 cm.$^{-1}$ Direct solution of the secular equation gives Dq = 773 and B = 921 cm.$^{-1}$

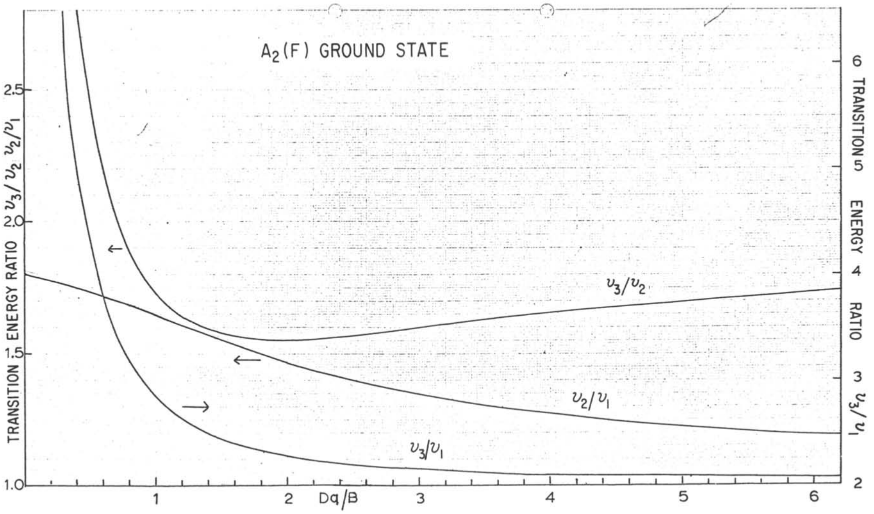

Figure 3. Transition energy ratios, ν_3/ν_2, ν_2/ν_1 (left-hand scale), and ν_3/ν_1 (right-hand scale) vs. Dq/B for $A_2(F)$ ground state ions

2) The tetrahedral complex ion $CoCl_4^{-2}$ has bands centered at 6200 (ν_2) and 16000 (ν_3) cm.$^{-1}$ The ratio ν_3/ν_2 is 2.581. Using Figure 3, $Dq/B = 0.465$ and from Figure 4, $E(\nu_3)/B = 20.8$, hence $Dq = 357$ and $B = 769$. Direct solution of the secular equation yields $Dq = 356$ and $B = 768$ cm.$^{-1}$

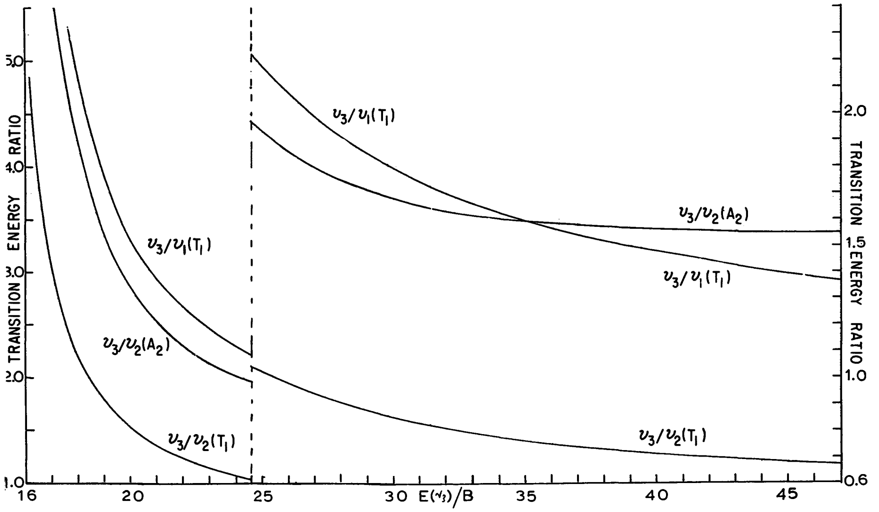

Figure 4. Transition energy ratios, ν_3/ν_2 (for A_2 ground state ions) and ν_3/ν_2 and ν_3/ν_1 (for $T_1(F)$ ground state ions) vs. $E(\nu_3)/B$. Left-hand scale for $E(\nu_3)/B$ less than 24.6; right-hand scale for $E(\nu_3)/B$ greater than 24.6

3) The octahedral complex ion $Co(H_2O)_6^{+2}$ has absorption bands at 8100 (ν_1), 16000 (ν_2), and 19400 (ν_3) cm.$^{-1}$ Because this ion has a T_1 ground term, the first band does not correspond with $10Dq$. Dq may be obtained from the energy ratios ν_3/ν_1 or ν_3/ν_2. The energy ratio ν_2/ν_1 is almost independent of Dq/B and should not be used. The ratio ν_3/ν_2 is 1.213, hence from Figure 5, $Dq/B = 0.99$ and from Figure 4, $E(\nu_3)/B = 22.3$, hence $Dq = 861$ and $B = 870$ cm.$^{-1}$ The energy ratio ν_3/ν_1 is 2.395, from which $Dq/B = 1.11$ and $E(\nu_3)/B = 23.4$; therefore, $Dq = 920$ and $B = 829$ cm.$^{-1}$

In this manner values of Dq and B may be rapidly and accurately obtained. Where the use of two different ratios gives rise to two different sets of Dq and B values, it is customary to accept the set which gives the best fit to the spectrum for all three bands.

Using the cobalt hexahydrate complex as an example, if $Dq/B = 0.99$ as determined from the ν_3/ν_2 ratio, the position of ν_1 can be rapidly calculated by reading off the ν_3/ν_1 ratio from Figure 3 at $Dq/B = 0.99$. In this way, ν_1 is predicted to lie at 7550 cm.$^{-1}$, in fair agreement with the experiment.

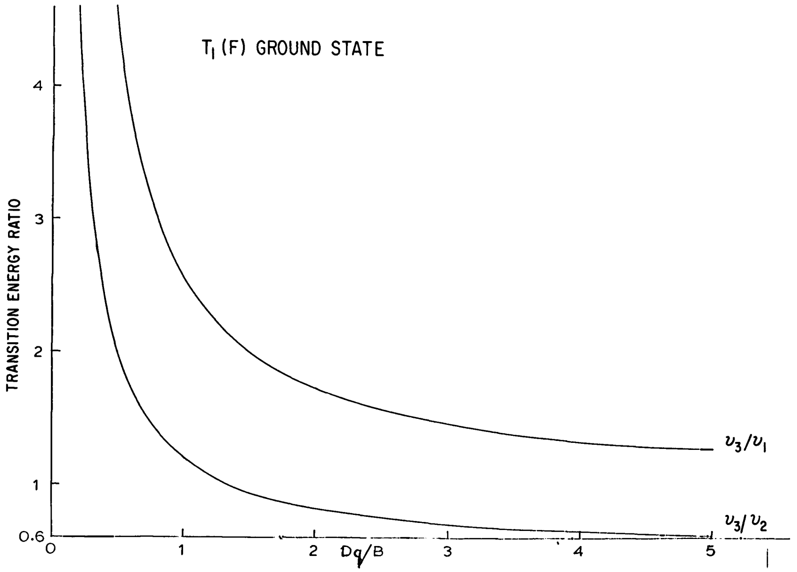

Figure 5. Transition energy ratios ν_3/ν_1 and ν_3/ν_2 vs. Dq/B for $T_1(F)$ ground state ions

From the second set of data, with $Dq/B = 1.11$, ν_3/ν_2 is seen to be 1.13, hence ν_2 lies at 17,170 cm.$^{-1}$, in rather poor agreement with experiment. Therefore, the first set of data fits better to the spectrum as a whole than the second set. The reasons different sets of *Dq* and *B* values might be obtained by using two different analyses are discussed later.

It should be emphasized that inaccurate values of *Dq* and *B* are likely to be derived if the transition energy ratio used is relatively insensitive to *Dq/B*. For example, considering Figure 3, use of the ratio ν_3/ν_2 would be inadvisable in systems where this ratio lies between 1.55 and 1.7. Similarly, the ν_3/ν_1 ratio will provide very inaccurate values if it is less than about 2.2. It is equally true that inaccurate data may be obtained if the energy ratio is highly sensitive to *Dq/B* because, in this case, a small experimental error will lead to a large change in *Dq/B*.

Of course if exact results are required, nongraphical methods should be employed. The computer provides the easiest way of processing a large amount of data. However, in view of the experimental uncertainty in the positions of the absorption bands observed, the graphical method described above will provide correct solutions to the secular equations to within experimental error.

Spin-orbit coupling has been neglected in this treatment because the spin-orbit coupling coefficient, λ, is relatively small in first row, transition metal ions. Large scale energy level diagrams for d^2, d^3, d^7, and d^8 ions, relating *Dq* and *E*, and taking spin-orbit coupling into account, have been published (*31*, *32*). As far as determining *Dq* is concerned, however, they suffer the same disadvantage as the graphs published by Orgel (*37*), in that they are constructed with a constant value of *B*.

Spin-orbit coupling may be of greater importance in tetrahedral complexes which frequently exhibit multi-component bands (*17*, *41*, *47*). Because such structure is not understood, at present it is best to use the center of such bands for *Dq* determinations (*7*).

Ions Not Falling into the Above Categories: d^5 Ions, Low-spin Complexes, etc. In low-spin complexes and in complexes of the d^5 ions, both low-spin and high-spin, the transition energies are generally functions not only of *Dq* and *B*, but also of *C*. *C* is generally taken to be equal to 4*B* and therefore eliminated from the equations. This is a rather dangerous, if not a common, procedure. There is evidence (*50*) that the *C*/*B* ratio can be considerably higher than 4. Moreover, *B* is not constant but varies from one spin state to another (*23*).

If three or more bands in the spectrum can be assigned, then an approximate value of *Dq* may be derived by fitting the spectrum to the appropriate Tanabe-Sugano diagram, or by solving the secular equations directly.

Derivation of *Dq* from Charge Transfer Spectra. In addition to crystal field bands, many ions exhibit absorption due to transfer of an electron from the metal to the ligand or from the ligand to the metal—the so-called "charge transfer" or "electron transfer" bands (*23*). In many cases, it is possible to assign bands due to the transfer of an electron from the ligand to the *e* orbital on the metal and from the same ligand orbital to the t_2 orbital on the metal. Clearly the energy separation between bands of this nature is related to 10*Dq* (*23*). Unfortunately, the energy separation is also a function of the difference in interelectronic repulsion of the various states concerned and, unlike the simple crystal field transitions, will involve coulomb and exchange integrals between electrons on different atoms. These are difficult to evaluate.

Such a method of derivation offers no advantages as far as d^n ions are concerned but has a very clear advantage for d^o ions where crystal field transitions cannot occur. Gray (*16*, *46*), for example, has interpreted the charge transfer spectra of a series of tetroxo anions and concludes that the crystal field splitting energies in the tetrahedral d^o manganate(VII) and chromate(VI) ions are 26000 and 24000 cm.$^{-1}$, respectively. (*See* Reference *36* for an alternative interpretation.)

Thermodynamic Methods. Since many thermodynamic properties depend upon the crystal field stabilization energy (e.g., lattice energy, solvation energy, electrode potentials, etc.), *Dq* may in principle be estimated by thermodynamic rather than spectroscopic means. The agreement between the thermodynamic and spectroscopic values of *Dq* is moderately good for ionic complexes of the lower oxidation state ions (e.g., M(II)·hexahydrates) but becomes very poor when the higher oxidation state, more covalent compounds are considered (*12, 13*).

Determination of Dq in Non-Cubic Molecules

Dq is proportional to the average quartic radial displacement of the *d* electrons. In cubic molecules, as we have seen, the energy separations are functions, at least as far as the crystal field potential is concerned, only of this fourth power radius. In non-cubic molecules, however, the energy separations may also be functions of the average *quadratic* radial displacement of the *d* electrons (*3, 6, 10, 19, 35*), and under such circumstances *Dq* is not so readily evaluated.

Nevertheless, the spectra of a number of tetragonal complexes have been interpreted to reveal both in-plane and out-of-plane ligand field strengths.

It is important to realize first that many formally non-cubic complexes, such as 6-coordinate derivatives of the type MX_aY_{6-a}, give spectra which are almost indistinguishable in type from those of regular octahedral complexes. This is principally due to the fact that spin-allowed transitions are fairly broad with half-widths of some 500–1000 or more wavenumbers (*2, 12*). Distortion from octahedral symmetry must be quite large before it manifests itself experimentally. In other words, although the degeneracy of the orbital doublet and triplet levels described above will be partially or wholly lifted by the lower symmetry component to the ligand field, the splitting must be quite large before it will be observed experimentally. This is particularly true of the ν_2 and ν_3 transitions of *F* term ions. Similar arguments apply to the 4-coordinate quasi tetrahedral complexes of the classes MX_3Y and MX_2Y_2, which often have spectra almost indistinguishable in type from their regular tetrahedral, MX_4 analogues.

Under such circumstances it is legitimate to obtain solutions of the secular equations as though the complex were cubic. The value of *Dq*, so obtained, is referred to as the mean crystal field strength *Dq′* of the various ligands involved. This mean crystal field strength may be related to the crystal field strengths of the ligands concerned by means of the "average environment rule" (*4, 45*), which states that in mixed ligand complexes the central ion will experience a crystal field which is the average of the crystal fields of each of the ligands.

In the case of 6-coordinate complexes MX_aY_{6-a}

$$Dq' = \frac{1}{6}\left[a\,Dq_X + (6\text{-}a)\,Dq_Y\right] \qquad (2)$$

Such an equation implies that the field strength of a ligand is constant for a given metal ion in a given stereochemistry for all such complexes of that ion. While this is approximately true for σ-bonding ligands, there is evidence (*28*) that it is invalid for ligands capable of forming π bonds with the metal ion. It will also be invalid for sterically bulky ligands, where steric hindrance may tend to lengthen the metal ligand bond and hence reduce Dq (*8*, *28*).

Computation of the mean crystal field strength is also legitimate when the ν_1 transition of an F term ion is split by a low symmetry component to the ligand field, but the ν_2 and ν_3 transitions are not. It is likely, however, that the Dq parameter obtained in this case appertains to the excited state of the molecule and is not necessarily related to the ground state, crystal field, splitting energy. (*See* below.)

Tetragonal Centric (D_{4h}) and Tetragonal Acentric (C_{4v}) Complexes. The effect upon the d orbital energies of a charge of -2 placed at a distance of, say, $+1$ *a.u.* along the z axis, is *exactly* the same as the effect of two individual charges, each of -1, one placed at $+1$ *a.u.*, and the other at -1 *a.u.* along the z axis. In other words, for a given metal-ligand distance, only the *total* charge along each of the cartesian axes is relevant. Hence, square planar MX_4, 5-coordinate square pyramidal MX_4Y, and 6-coordinate MX_5Y and MX_4Y_2 complexes may all be treated in a similar manner.

We consider the compounds *trans* MX_4Y_2 and define the Y-M-Y axis as the z axis, then with α_n^{xy} and α_n^{z} being the equatorial (xy) and axial (z) radial integrals (*3*, *6*, *10*, *19*, *35*), the single electron energies of the d orbitals are (neglecting the zeroth order integrals, α_o, which raise the energies of all the d orbitals by the same amount):

$$\begin{aligned}
E\, d_{x^2-y^2}\ (b_{1g}) &= +\frac{4}{7}\alpha_2^{xy} - \frac{4}{7}\alpha_2^{z} + \frac{19}{21}\alpha_4^{xy} + \frac{2}{21}\alpha_4^{z} \\
E\, d_{z^2}\ (a_{1g}) &= -\frac{4}{7}\alpha_2^{xy} + \frac{4}{7}\alpha_2^{z} + \frac{3}{7}\alpha_4^{xy} + \frac{4}{7}\alpha_4^{z} \\
E\, d_{xy}\ (b_{2g}) &= +\frac{4}{7}\alpha_2^{xy} - \frac{4}{7}\alpha_2^{z} - \frac{16}{21}\alpha_4^{xy} + \frac{2}{21}\alpha_4^{z} \\
E\, d_{xz}, d_{yz}\ (e_g) &= -\frac{2}{7}\alpha_2^{xy} + \frac{2}{7}\alpha_2^{z} - \frac{2}{7}\alpha_4^{xy} - \frac{8}{21}\alpha_4^{z}
\end{aligned} \tag{3}$$

The corresponding energies for square planar MX_4 complexes are obtained by equating all the α_n^{z} integrals to zero and, for 5-coordinate MX_4Y complexes, by halving the coefficients of all the α_n^{z} integrals. The energies for the 6-coordinate MX_5Y complexes may be obtained by assuming that the field of the X ligand along the z axis is the same as the in-plane (equatorial) field due to the X ligands (perhaps a somewhat uncertain assumption if X and Y differ much in their bonding capability). The coefficients of the α_n^z integrals are halved, and one-half of the coefficient of each of the α_n^z integrals is added to the corresponding α_n^{xy} integral. Thus, for example, the energy of the d_z2 orbital becomes:

$$-\frac{2}{7}\alpha_2^{xy} + \frac{2}{7}\alpha_2^{z} + \frac{5}{7}\alpha_4^{xy} + \frac{2}{7}\alpha_4^{z}$$

These equations may be simplified by introducing two new parameters, *Ds* and *Dt* (*30, 35, 48*), in terms of the radial integrals above (*48*), as follows:

$$Ds = \frac{2}{7}\left(\alpha_2^{xy} - \alpha_2^{z}\right) \tag{4}$$

$$Dt = \frac{2}{21}\left(\alpha_4^{xy} - \alpha_4^{z}\right) \tag{5}$$

for tetragonal centric molecules belonging to the group D_{4h} and:

$$Ds = \frac{1}{7}\left(2\alpha_2^{xy} - \alpha_2^{z+} - \alpha_2^{z-}\right) \tag{6}$$

$$Dt = \frac{1}{21}\left(2\alpha_4^{xy} - \alpha_4^{z+} - \alpha_4^{z-}\right) \tag{7}$$

(α_n^{z+} and α_n^{z-} refer to the Y and X ligands along the *z* axis, respectively) for tetragonal acentric molecules belonging to the group C_{4v}. If it is assumed that $\alpha_n^{xy} \cong \alpha_n^{z-}$, these last equations may be rewritten:

$$Ds = \frac{1}{7}\left(\alpha_2^{xy} - \alpha_2^{z+}\right) \tag{8}$$

$$Dt = \frac{1}{21}\left(\alpha_4^{xy} - \alpha_4^{z+}\right) \tag{9}$$

Substituting Equation 1 into Equation 5 and defining Dq^{xy} and Dq^z as the equatorial (in-plane) and axial (out-of-plane) ligand field strengths, respectively, then (*48*):

$$Dt\ (D_{4h}) = \frac{4}{7}\left(Dq^{xy} - Dq^{z}\right) \tag{10}$$

The single *d* electron orbital energies become:

$$\begin{aligned} E\ b_{1g} &= 6Dq^{xy} + 2Ds - Dt \\ E\ a_{1g} &= 6Dq^{xy} - 2Ds - 6Dt \\ E\ b_{2g} &= -4Dq^{xy} + 2Ds - Dt \\ E\ e_{g} &= -4Dq^{xy} - Ds + 4Dt \end{aligned} \tag{11}$$

These equations are valid for both the centric and the acentric cases. For molecules belonging to the group C_4 we can define:

$$Dt\ (\mathrm{MX_5Y},\ C_{4v}).\ = \frac{2}{7}\ (Dq^{xy} - Dq^{z+}) \tag{12}$$

$$Dt\ (\mathrm{MX_4Y},\ C_{4v})\ = \frac{2}{7}\ (2Dq^{xy} - Dq^{z+}) \tag{13}$$

In those circumstances where it is possible to determine a value of Dt from analysis of the spectrum of a complex, a value for the difference in the equatorial and axial Dq parameters may be estimated. If the assumption is made that Dq^{xy} corresponds exactly with Dq in the $\mathrm{MX_6}$ compounds, or if Dq^{xy} can be observed directly, then the axial crystal field strength can be evaluated.

The calculation of such axial field strengths should be useful in probing into the nature of the chemical bond in compounds of this type.

Wentworth and Piper (*48*) used this approach to analyze the spectra of tetragonal chromium(III) and cobalt(III) complexes.

The lowest energy, spin-allowed transition in a low-spin cobalt(III) complex is ${}^1T_1 \leftarrow {}^1A_1$. In C_{4v} or D_{4h} symmetry, the ${}^1T_1$ orbital degeneracy is partially lifted to give ${}^1E$ and ${}^1A_2$ levels. The second band in an octahedral complex is the ${}^1T_2 \leftarrow {}^1A_1$ transition, but this does not seem to be so susceptible to lower symmetry fields. Transitions are expected to take place with the following energies (*24*, *48*):

$$\begin{array}{rll}
O_h & E\,[{}^1T_1 \leftarrow {}^1A_1] & = 10Dq^{xy} - C \\
O_h & E\,[{}^1T_2 \leftarrow {}^1A_1] & = 10Dq^{xy} + 16B - C \\
C_{4v}\text{ or }D_{4h} & E\,[{}^1E \leftarrow {}^1A_1] & = 10Dq^{xy} - C - \frac{35}{4}Dt \\
C_{4v}\text{ or }D_{4h} & E\,[{}^1A_2 \leftarrow {}^1A_1] & = 10Dq^{xy} - C
\end{array} \tag{14}$$

Many cobalt complexes of the type $\mathrm{CoX_5Y}$ or *trans* $\mathrm{CoX_4Y_2}$ have electronic spectra in which the first absorption band has two components attributed to transitions to the ${}^1E$ and ${}^1A_2$ levels, with energy separations of 2000–5000 cm.$^{-1}$ A value for Dt may be obtained by observing that the energy separation between these components should be 35/4 Dt. The energy of the A_2 component of the first band is predicted, by Equation 14, to lie at the same energy as the transition to the ${}^1T_1$ level in the parent octahedral complex, $\mathrm{MX_6}$. This is observed to be experimentally true to within 1000 cm.$^{-1}$ or so. Given a value for C, which was assumed by Wentworth and Piper to be the same as in the parent complex, it is possible to calculate a value for the crystal field strength of the axial ligand (Y). In their analysis, Wentworth and Piper chose to evaluate Dt as 4/35ths of the difference between the ^1E transition energy in the tetragonal complex and the $^1T_1$ transition energy in the parent octahedral complex, rather than utilize the energy separation of the components of the $^1T_1$ level. There is little doubt that this procedure does generate an apparently consistent set of axial field strengths (Table I), while making the assumption that the crystal field strength of the in-plane ligands is a constant.

Table I. Spectral Analysis of Tetragonal Cobalt(III) and Chromium(III) Derivatives

(All Data in Wavenumbers.)

Complex	Dt^e	$^a\,Dq^{xy}$	$^n Dq^z$	*Reference*
^{c} $Co(NH_3)_5F^{+2}$	231	2455(NH_3)	1647(F)	*48*; this work
	183	^{b} 2490(NH_3)	1849(F)	*48*
^{c} $Co(NH_3)_3Cl^{+2}$	301	2413(NH_3)	1361(Cl)	*48*; this work
	266	^{b} 2490(NH_3)	1461(Cl)	*48*
^{c} $Co(NH_3)_4Cl_2^+$	583	2278(NH_3)	1258(Cl)	*48*; this work
	583	^{b} 2490(NH_3)	1461(Cl)	*48*
^{d} $Coen_2F_2^+$	619	2500(en)	1416(F)	*48*; this work
	488	^{b} 2530(en)	1676(F)	*48*
^{d} $Coen_2Cl_2^+$	728	2412(en)	1138(Cl)	*48*; this work
	612	^{b} 2530(en)	1439(Cl)	*48*
$Cren_2Cl_2^+$	538	2200(en)	1258(Cl)	*48*; this work
	496	^{b} 2188(en)	1320(Cl)	*1*; this work
	525	^{b} 2188(en)	1272(Cl)	*48*
$Cren_2Br_2^+$	573	2179(en)	1177(Br)	*1*; this work
$Cren_2I_2^+$	531	2100(en)	1171(I)	*1*; this work
$Cren_2(OH)_2^+$	191	1992(en)	1638(OH)	*1*; this work
$Cren_2(H_2O)_2^+$	331	2260(en)	1681(H_2O)	*48*; this work
	319	2247(en)	1689(H_2O)	*1*; this work
	227	^{b} 2188(en)	1790(H_2O)	*48*
$Cr(bipy)_2Cl_2^+$	509	2247(Bipy)	1357(Cl)	*1*; this work

[a] Compare $CrCl_6^{-3}$ $Dq = 1318$ (Cl), $Cr(H_2O)_6^{+3}$ $Dq = 1750(H_2O)$.
[b] Assumed value based on octahedral parent.
[c] Assuming $C/B = 7.24$.
[d] Assuming $C/B = 7.64$.
[e] Reference *1*.

An alternative method of analyzing the spectra is to evaluate Dt as 4/35ths of the distance between the two components of the $^1T_1$ level, and to evaluate B as 1/16th of the separation of the $^1A_2$ transition from the unsplit $^1T_2$ transition. If the ratio C/B is assumed to be the same in these lower symmetry complexes as in the parent octahedral complex (or if the transition to the $^3T_1$ level can be observed (*24*)), then both Dq^{xy} and Dq^z may be evaluated (Equations 10, 12, 14), thus removing the uncertain assumption that the in-plane ligand field strength is a constant. Table I compares the values of Dt, Dq^{xy}, and Dq^z obtained using the Wentworth and Piper analysis and using the above analysis.

Data for some chromium(III) complexes are also included in Table I. The first spin-allowed transition of octahedral chromium(III), ${}^4T_2 \leftarrow {}^4A_2$, lies at exactly $10Dq$. In the lower symmetry, the degeneracy of the T_2 level is partially lifted to give ${}^4E + {}^4B_2$ with transition energies:

$$\begin{aligned} E\,[{}^4B_2 \leftarrow {}^4B_1] &= 10Dq^{xy} \\ E\,[{}^4E \leftarrow {}^4B_1] &= 10Dq^{xy} - \frac{35}{4}Dt \end{aligned} \qquad (15)$$

Wentworth and Piper evaluated $10Dq^{xy}$ using the first band of the parent octahedral molecule.

The Wentworth and Piper analysis seems more satisfying in that the axial field strengths (Y), so derived, agree more closely to the field strengths in the corresponding MY_6 compounds than those of this analysis. At present, however, it would be dangerous to assume that the field strength of ligand Y in MX_aY_b must necessarily be the same as its field strength in MY_6. There is already much evidence to show that the X ligand must influence the M-Y bond and *vice versa*.

The same theory may be applied to tetragonally distorted nickel(II) complexes which commonly show a splitting of the first spin-allowed transition, ${}^3T_2 \leftarrow {}^3A_2$. The energies and orbital representations of the two components generally observed are exactly the same as for chromium(III) above (Equation 15) (*18*).

(It should be noted that the energies given in Table III of Reference *18* are incorrect. All the coefficients of the tetragonal *Ds* and *Dt* parameters should be multiplied by -1. Assignments of the spectra of the compounds reported in Reference *17* should be changed where appropriate to take into account this change in sign. Correct assignments are given in Table II of this paper.

(Transition energies (Equation 15) were calculated from Table III of Reference *18* after noting that the ground state energy of nickel in a tetragonal field, relative to the spherically perturbed free ion, is:

$$E\,({}^3B_1) = -12Dq + 7Dt)$$

The results of a calculation of the in-plane and out-of-plane field strengths for a series of tetragonally distorted nickel(II) complexes are summarized in Table II. *Dt* was determined as 4/35ths of the splitting of the first band. The sign of *Dt* was determined, using Equation 10, by considering the relative sizes of the in-plane and out-of-plane ligand field strengths. This then leads, via Equation 15, to the assignment of the ${}^3B_2 \leftarrow {}^3B_1$ and ${}^3E \leftarrow {}^3B_1$ transitions. The assignments were authenticated by noting that the reverse assignments would lead in all cases to unreasonable values of the in-plane and/or out-of-plane field strengths.

Table II. Spectral Analysis of Tetragonal Nickel(II) Derivatives[a]

Complex[c]	${}^3B_2 \leftarrow {}^3B_1$	${}^3E \leftarrow {}^3B_1$	*Dt*	Dq^{xy}[l]	Dq^z
1	10450	7520	+335	1045(Dieen)[d]	459(H_2O)
2	10350	7870	+283	1035(Dieen)	539(NO_2^-)
3	[b] 11350	8910	+279	1135(Dieen)	647(NCS^-)
4	10100	7750	+269	1010(Dieen)	540(Cl_2A^-)[f]
5	9890	7550	+267	989(Dieen)	521(Cl_3A^-)
6	10150	7550	+297	1015(Dieen)	495(CF_3A^-)[h]
7	10150	7870	+261	1015(Dieen)	559(Ph_2A^-)[k]
8	[b] 11850	7840	+458	1185(Dimen)[e]	383(NO_3^-)
9	11000	8600	+274	1100(Dimen)	620(Cl_3A^-)[g]
10	10950	8740	+253	1095(Dimen)	653(NO_2^-)
11	6600	8250	−330	660(Cl^-)	990(CH_3CN)
12	5800	8000	−251	580(Br^-)	1020(Pyridine)
13	6000	7550	−177	600(Cl^-)	910(Quinoline)
14	6000	8400	−274	600(Cl^-)	1080(Pyridine)
15	6040	7580	−176	604(Cl^-)	912(Quinoxaline)
16	11200	12000	− 91	1120(NH_3)	1280(NO_2^-)
17	8200	7100	+126	820(Tu)[i]	600(Cl^-)
18	7460	8550	+125	746(Etu)[j]	528(Br^-)
19	7800	[k]8550	+ 86	780(Etu)	630(Cl^-)

[a] All data in wavenumbers.

[b] These band positions may not reflect the true ${}^3B_2$ transition energy due to possible mixing with a spin-forbidden transition.

The complexes were: 1 $Ni(dieen)_2Cl_2 \cdot 2H_2O$, 2 $Ni(dieen)_2(NO_2)_2$, 3 $Ni(dieen)_2(NCS)_2$, 4 $Ni(dieen)_2(CHCl_2 \cdot CO_2)_2$, 5 $Ni(dieen)_2(CCl_3 \cdot CO_2)_2$, 6 $Ni(dieen)_2(CF_3 \cdot CO_2)_2$, 7 $(Ni(dieen)_2(CHPh_2 \cdot CO_2)_2$, 8 $Ni(dimen)_2(NO_3)_2$, 9 $Ni(dimen)_2(CCl_3 \cdot CO_2)_2$, 10 $Ni(dimen)_2(NO_2)_2$, 11 $Ni(CH_3CN)_2Cl_2$, 12 $Ni(pyridine)_2Br_2$, 13 $Ni(quinoline)_2Cl_2$, 14 $Ni(pyridine)_2Cl_2$, 15 $Ni(quinoxaline)Cl_2$, 16 $Ni(NH_3)_4(NO_2)_2$, 17 $Ni(thiourea)_4Cl_2$, 18 $Ni(ethylenethiourea)_4Br_2$, 19 $Ni(ethylenethiourea)_4Cl_2$.

[c] Complexes 1–10, Reference *15*; Complex 11, Reference *20*; Complexes 12–14, Reference *14*; Complex 15, Reference *26*; Complexes 16–17, Reference *18*; Complexes 18–19, Reference *21* (Figure 2).

[d] Dieen = diethylethylenediamine.

[e] Dimen = dimethylethylenediamine.

[f] Cl_2A^- = dichloroacetate ion.

[g] Cl_3A^- = trichloroacetate ion.

[h] CF_3A^- = trifluoroacetate ion.

[i] Tu = thiourea.

[j] Etu = ethylenethiourea.

[k] Ph_2A^- = diphenylacetate ion.

For comparison purposes note that—Dq($NiCl_2$) = 720; Dq($Me_4N^+NiCl_3^-$) = 660; Dq($NiBr_2$) = 700; Dq($Ni(H_2O)_6^{+2}$) = 850; Dq($Nien_3^{+2}$) = 1150; and Dq($NiEtu_6^{+2}$) = 800; *Dq*($Ni(NO_2)_6^{4-}$) = 1340. *See* also Table III.

In discussing Table II, the following general statements may be made.

In Complexes 1–7 the in-plane field strength of the diethylethylenediamine ligand is almost independent of the axial ligand. In Complexes 8–10 the in-plane field strength of the dimethylethylenediamine ligand is fairly constant. Comparison of the field strengths of dieen and dimen shows that the former has the lower field strength in agreement with its being the more bulky (*4*, *48*). The axial ligands in Compounds 1–10 have field strengths considerably weaker than those observed in the corresponding MY_6 compounds. This observation is readily rationalized in terms of a steric interaction between the bulky ethylenediamine ligand and the axial ligand, causing an increase in the length of the axial metal-ligand bond. As the bulkiness of the in-plane ligands decreases (dieen to dimen), the axial field strengths increase (e.g., NO_2 from 5390 to 6530 $cm.^{-1}$), in agreement with the expectation that the axial metal-ligand bond length will shorten.

In Compounds 11–17 the in-plane field strengths are, for the most part, similar to those of the corresponding MX_6 parent octahedral complexes, though there is a tendency in some cases for the field to be somewhat weaker than anticipated. The axial field strengths, on the other hand, in Compounds 11–16, where the in-plane ligand is not bulky, are very closely similar to those of the parent octahedral MY_6 compounds. The remarkably good agreement in these cases makes the unusually low axial field strengths in Compounds 1–10 more credible.

In Complex 17 both the in-plane and the out-of-plane fields are weaker than those of the parent complexes. This is in perfect accord with the crystal structure of this complex (*33*), which shows that the nickel atom does not lie exactly in the molecular plane of the sulfur atoms but is slightly above it, and that one of the nickel chlorine bonds is exceptionally long.

With the more bulky ethylenethiourea (Etu) complexes, the tetragonal distortion (in the complexes $Ni(Etu)_4X_2$) increases as the size of the halogen increases, the iodo complex being diamagnetic. This is reflected in the relative values of the *Dt* parameter in Compounds 18 and 19, and by the fact that while the axial chlorine ligand has a field strength not greatly dissimilar from that in Complex 17 the bromide field strength is noticeably weak.

Thus, the data in Table II appear to correlate very well. They certainly suggest that future investigations into this area might prove very beneficial. X-ray studies would be particularly useful in substantiating the correlations discussed above.

Earlier it was pointed out that square planar complexes should also fall into this treatment. In practice, of the ions discussed above, only nickel forms square planar derivatives. Because these are diamagnetic, the transition energies will be functions not only of Dq^{xy}, *Ds*, and *Dt*, but also of the interelectronic repulsion parameters. In principle, values of Dq^{xy} may be derived, but they are much greater than those observed in octahedral nickel complexes because the nickel-ligand bond length in a square diamagnetic complex is very much smaller than in an octahedral paramagnetic complex.

The Accuracy of Dq

Having considered methods for the determination of *Dq*, it is relevant to examine the authenticity of the results obtained. If we consider, for example, a d^8 ion, then 10*Dq* is effectively the energy separation between the $t_2{}^6e^2(^3A_2)$ and $t_2{}^5e^3(^3T_2)$ configuration in an octahedral field *at the equilibrium, metal-ligand, internuclear distance of the ground state.* This condition is necessary in that the equilibrium metal-ligand distance of the excited configuration will be longer (*9*) than that of the ground state.

According to the Franck-Condon principle (*9*), transitions from the ground state must occur without change in internuclear distance ("vertical" transitions) so that the transition noted above might be expected to occur with the energy 10*Dq* as defined. However, in addition to transitions from the lowest vibrational level of the electronic ground state, the thermal population of higher vibrational levels of the ground state at room temperature will ensure that transitions from these levels also occur. Moreover, transitions can take place to various vibrational levels of the excited state. Another factor is the variation of *Dq* as the metal-ligand bond vibrates so that the absorption band will comprise transitions over a range of *Dq* values.

Hence, the absorption band of any spin-allowed transition is expected to be broad and, at least at room temperature, the absorption maximum, for example, of the transition quoted above may not correspond exactly with 10*Dq* as defined. The actual error is hard to assess because it must vary greatly from one situation to another, but it may be of the order of several hundred wavenumbers.

Other effects such as intermediate coupling (the mixing of the high-spin excited state with a low-spin excited state by spin-orbit coupling) (*22*) and the differential expansion of the t_2 and e orbitals (the energy separation between the configurations quoted above will not be exactly 10*Dq* unless both t_2 and e orbitals suffer the same radial displacement) (*38*) may serve to modify transition energies in individual cases.

In addition, lower symmetry components to the ligand field often have a considerable effect upon the lowest energy spin-allowed transition broadening and perhaps shifting the absorption maximum.

Direct measurement of 10*Dq* in fact has many difficulties. Nevertheless, the reader should not be discouraged from quoting ν_1 energies, in appropriate cases, as 10*Dq*, provided the uncertainty in the value is realized. Absolute values of *Dq* should not be taken as too significant unless very sophisticated experiments, especially at low temperatures, have been carried out.

The reliability of the data obtained in discussion of tetragonal complexes above must also be considered. In calculating the out-of-plane field strengths, *Dt*, as determined from the splitting of the first spin-allowed absorption band, has been used. For reasons similar to those already discussed for *Dq*, the absolute value of *Dt* has little meaning. However, the spin-allowed transitions concerned split into two components as a direct consequence of the tetragonal component to the ligand field, the degree of splitting being proportional to this tetragonal component and to *Dt*. Therefore, it is probable that, used in a relative sense, both *Dt* and Dq^z derived therefrom have chemical significance. Where the splitting of a term is a function of both *Ds* and *Dt*, such splitting is no longer directly proportional to the tetragonal component of the ligand field, and values of *Dt* (and *Ds*) computed from such a system are almost certainly meaningless. Can the energies of ν_2 and ν_3 transitions (cubic complexes) in *F* term ions provide an accurate value of 10*Dq*? These transitions are also subject to vibrational broadening, but because of their higher energy the error this introduces will generally be much smaller than in the case of ν_1.

In using this method for calculating *Dq*, one must assume that the energies of the ground state and the two excited states may be described by the same identical values of 10*Dq* and *B*—i.e., that these parameters are strictly constant. There seems no reason why this should necessarily be the case. In a series of presumably regular octahedral nickel complexes, the agreement between the values of *Dq* and *B* calculated from ν_1 and ν_2 and from ν_2 and ν_3 is often very good, but sometimes very poor (Table III) (*29*). Although this may be due, in part, to ν_1 not adequately representing 10*Dq*, the fact that 10*Dq* calculated from ν_2 and ν_3 is sometimes larger

Table III. 10*Dq* and *B* Values for Octahedral NiL_6^{+2} Complexes (*29*)

Ligand L	[a] *10Dq*(ν_1)	[b] *B*(ν_1, ν_2)	[a] *10Dq*(ν_2, ν_3)	[b] *B*(ν_2, ν_3)
Caprolactam	8320	715	8030	936
Tetramethylsulfone	7750	913	7750	917
N-Dimethylformamide	8500	680	8120	949
N-Methylacetamide	7520	931	7530	918
Pyridine *N*-Oxide	8400	1021	8440	976
Ammonia	10750	904	10950	818
Ethanol	8180	779	7990	949
n-Propylamine	9920	1043	10180	872
N-Dimethylbutamide	7490	605	7080	973
N-Methylformamide	8380	770	8160	945
N-Diethylformamide	8400	770	8180	952
Acetonitrile	10600	1062	11040	832
Valerolactam	8330	676	7970	937
Butyrolactam	8100	806	7960	939

[a] In view of the lack of x-ray evidence, it is not possible to exclude the possibility that, in some cases at least, the poor agreement between the two 10*Dq* values is due to distortion of the octahedron.

[b] Notice that the variation in *B* is very much more marked than that in 10*Dq*. The first *B* value, from ν_1 and ν_2, is the least reliable. *B* may also be calculated from ν_1 and ν_3.

and sometimes smaller than ν_1 reflects an unsystematic variation in these parameters in the excited states. With cobalt(II), the agreement between the parameters obtained using different transition ratios is very poor. However, in the absence of a sufficient number of compounds for study it is not known whether this is a basic property of a $T_1(F)$ ground-term ion or whether, less likely, it is due to missassigning the absorption bands. It was noticed some time ago (*39*) that the third transition, ν_3, of octahedral chromium(III) derivatives lies at appreciably lower energies than expected on the basis of the ν_1 and ν_2 transition energies.

At least as far as the room temperature spectra of first row transition metal ions are concerned, the introduction of λ into the theory is of little value (*11*). More data are required before it can be judged whether, with $A_2(F)$ ground-state ions, the correction to ν_1 for the differential expansion of the t_2 and e orbitals (*38*) is a useful procedure. This modifies the two parameter theory by permitting the B parameter to vary. It should be remembered that, in discussing crystal field transitions, we are dealing with relatively small energy separations between levels, with absolute energies relative to the free ion being extremely high. It is fortunate that such a simple theory, requiring only two parameters to predict three spin-allowed transitions (in high-spin cubic *F*-term ions), is as successful as it is. The variation in 10*Dq*, from ν_1 and from ν_2 and ν_3 in Table III, is less than 10%. This might well be regarded as remarkably good agreement.

Nevertheless, the possibility that 10*Dq* (γ_1) and 10*Dq* (γ_2, γ_3) can provide meaningful chemical information about the crystal field splitting energies in the ground state and in the excited states must be explored (*29*).

This paper has outlined the methods for determining *Dq* but, at the same time, casts doubt on the significance of individual results. In closing, it is worthwhile to emphasize the usefulness of *Dq* as an empirical parameter despite these doubts. Provided that series of complexes are studied rather than individual compounds, and provided that, where possible, the same mode of analysis of the spectrum is employed, useful chemical information may be derived.

The variation of *Dq* as a function of the ligand, as represented by the well-known spectrochemical series (*23*), illustrates this point quite clearly. It is evident from the series that *Dq* varies as a function of the π capacity of the ligand (*Dq*, π donor < *Dq*, no π orbitals, < *Dq*, π acceptor), rather than its σ propensity. In a similar way, the variation of *Dq* with a metal ion for a given ligand reflects the importance of the polarizing power of the central ion (*23*).

Variations in *Dq* have also indicated more subtle phenomena whereby the extent of π bonding from metal to ligand, Y, in a series of complexes of octahedral microsymmetry, MX_4Y_2, is a function of the nature of X (*28*). Here *Dq* reflects the synergic effect well-known in metal carbonyl chemistry.

It is now well-established that in a series of analogous ligands, such as substituted amides (*8*) or substituted pyrazines (*27*), *Dq* decreases and *B* increases with increasing steric interaction. These compounds were essentially of cubic stereochemistry; earlier in this article it was suggested that *Dq* also reflects steric phenomena in non-cubic complexes.

Despite the fall of crystal field theory, it is evident that *Dq*, used essentially as a ligand field parameter, and with caution, can be extremely useful in elucidating molecular and electronic structure.

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30

Intermediate Octahedral Ligand Fields and Substitution Reaction Stereomobility

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Alfred Werner discovered the concept of octahedral coordination and coordination sphere rigidity in substitution reactions. On the other hand, he also noted reactions involving stereomobility. A generalized scheme for determining potential reaction products in octahedral substitution reactions is given and used to discuss species known to exhibit stereomobility. The availability of a thermally accessible, spin-free, excited state is shown for complexes which undergo interesting stereochemical changes. A correlation of this ligand field strength concept with π-donor, steric, solvent, and charge effects allows a rather comprehensive understanding of d^6 octahedral substitution reactions. Extension to other configurations is possible.

Alfred Werner and his students studied the stereochemistry of numerous substitution reactions with octahedral complexes. Often the products of a substitution reaction appeared capable of existing in more than one isomeric form, but no evidence of their configurations could be obtained by the methods available at that time. Werner would assume that the product has the same configuration as the reactant—and he was correct more often than not. Crystal field calculations (Table I) also imply that the d^3 and spin-paired d^6 species studied by Werner should give retained configurations. The dissociative tetragonal pyramid and the associative 1:4:2 intermediates, which yield all of the product with retained configuration, have lower activation energies than the other intermediates which can give changes in configuration. Hence, the concept of coordination sphere rigidity has become a useful concept in octahedral coordination chemistry.

Table I. Octahedral Crystal Field Activation Energies[a]

	$(t_{2g})^3$	$(t_{2g})^6$	$(t_{2g})^4(e_g)^2$
Dissociative			
Tetragonal pyramid (C_{4v})[b]	0.20	0.40	0
Trigonal bipyramid (D_{3h})[c]	0.57	1.14	0
Associative			
1:4:2 Intermediate of C_{2v} symmetry[d]	0.18	0.36	0
Pentagonal bipyramid (D_{5h})[b]	0.43	0.85	0

[a] In units of Δ.
[b] (*20*).
[c] Calculated from the *d*-orbital energy levels (*19*).
[d] Based on the calculations by Hush (*45*).

On the other hand, Werner was aware of and did investigate substitution reactions of octahedral complexes which yield isomer mixtures (*97–102*). Furthermore, he knew that isomerization sometimes occurred without apparent reaction. In fact, his contemporary, S. M. Jørgensen, observed the isomerization of $[CoCl_2(en)_2]^+$ before the turn of the century (*52*). Therefore, the stereomobility of substitution reactions of inert, octahedral species has long been of interest to coordination chemists.

General Substitution Reaction Stereomobility

Before considering the results of previously studied complexes, it would seem wise to consider a general scheme for classifying the products of octahedral substitution reactions in general.

The products of the substitution of a ligand G for ligand A of the species $[M\ ABCDEF]^n$ (in which M is a metal ion and A, B, C, D, E, and F are monodentate ligands or donor atoms of chelating ligands of an octahedral complex) are shown in Figure 1. Letters under the arrows indicate positions made adjacent by the loss of A, or the insertion position of G. The products are based on the principle that minimal atomic motion accompanies the attainment of the transition state, the reaction intermediates (if any), and the products. The results of a large number of studies support this principle, which was assumed by Werner, and which recently has been used by Pearson and Basolo (*81*) and by Kyuno, Boucher, and Bailar (*67*).

Although the product isomers are shown as resulting via a dissociation process, the products are equally valid for associative mechanistic considerations, as indicated by Figure 2. Attachment of G anywhere on the top half of $[M\ ABCDEF]^n$ prior to the release of A will result in isomer G. (The designation "isomer G" is based on the ligand atom which is trans to atom F in the octahedron and is the atom at the top of the octahedron as drawn. The other isomers can be similarly differentiated.) Isomer G

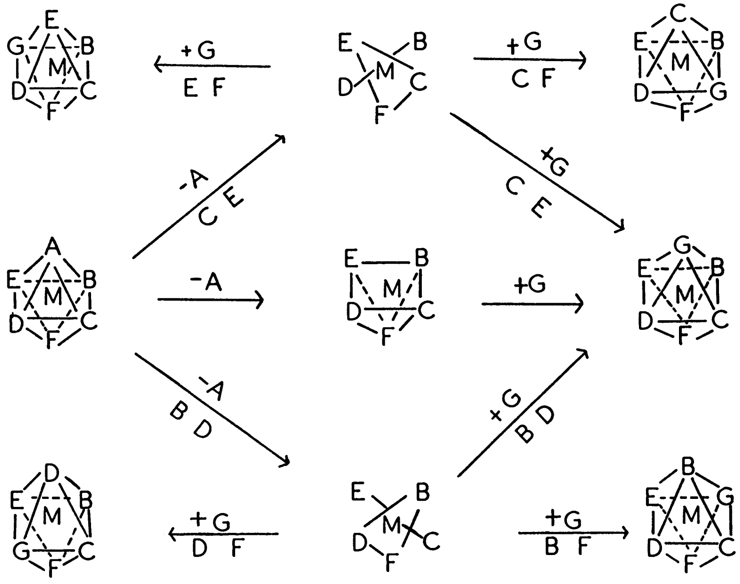

Figure 1. A general scheme for octahedral substitution reaction products assuming a dissociative mechanism

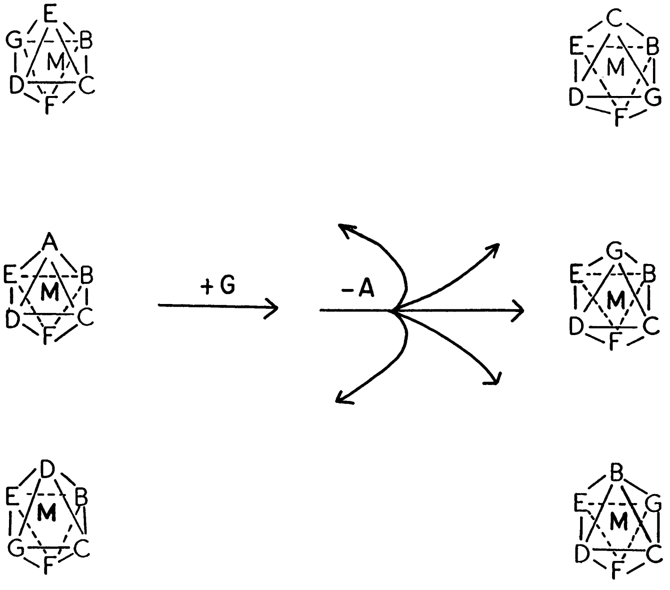

Figure 2. A general scheme assuming an associative mechanism

will result irrespective of whether a 1:4:2 intermediate (*45*), an approximation of a pentagonal bipyramid (*16*), or related interchange process (*68*) occurs, provided the principle of minimal atomic motion for the atoms not directly involved in the reaction is valid. On the other hand, attachment of G on the bottom side of the complex prior to release of A will result in isomers E, C, D, and B being formed. This is true either by a consideration of face attack, edge displacement (*28*), or edge shift (*21*, *46*).

Application of this general product prediction to real situations is straightforward. Figures 3 and 4 show the application to cis and trans complexes with two bidentate groups and two monodentate groups. The D* and L* cis isomer designations represent right- and lefthandedness with respect to the C_2 axis of complexes with symmetrical bidentate ligands (*7*, *67*) and are based on the absolute configuration of $(+)\text{-}[\mathrm{Co(en)_3}]^{+3}$ (*86*). However, the diagrams are applicable to unsymmetrical ligands as well. Note that the chelate ring structure eliminates one potential product for the cis reactant because normal size chelate rings (five or six atoms) cannot span the trans positions. Therefore, G cannot end up between D and F either by a dissociative or by an associative mechanism. Another point of interest, to which we will return later, is the nature of the postulated trigonal bipyramids necessary for dissociative stereomobility *sans* scrambling.

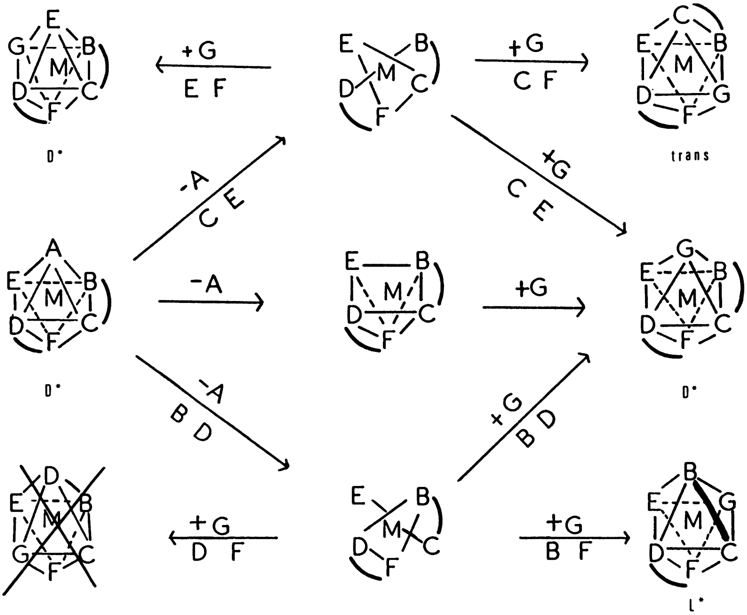

Figure 3. Product expectations for an octahedral reactant with two bidentate and two cis monodentate ligands

Considering the related D*-cis ion in which BC = DF = unsymmetrical chelating ligands, we note that *only three* of the six geometrically possible isomers would be produced. The expected products are the symmetrical trans isomer, the retained D*-α cis isomer, and a L*-β cis isomer in which the identical ends B and D are cis to each rather than trans.

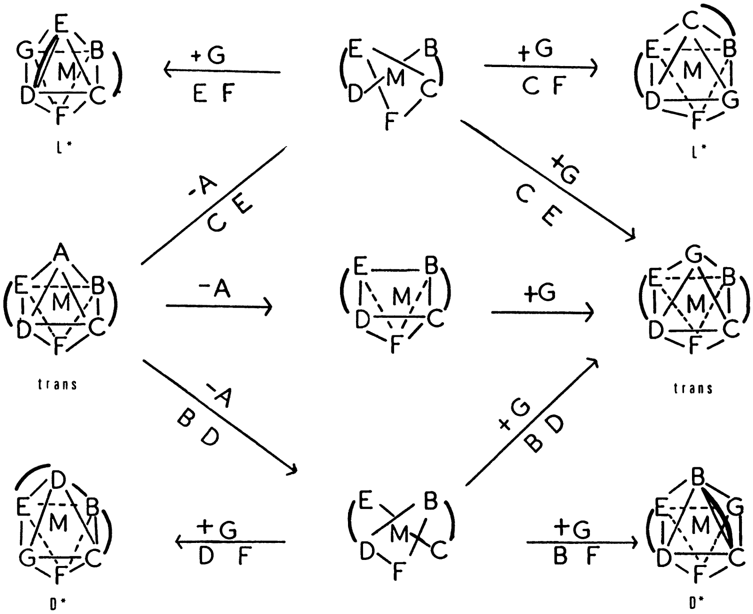

Figure 4. Product expectations for an octahedral reactant with two bidentate and two transmonodentate ligands

Extension to the triethylenetetramine complexes shows that the cis isomer labeled D*-α (Figure 5) should give only D*-α and L*-β cis isomers, as previously suggested by Kyuno, Boucher, and Bailar (*67*). All D* designations are D*-α-cis and the L* is L*-β-cis. The corresponding D*-β diagram (not shown) would show the possibility of obtaining products with D*-β, L*-α, and trans configurations. Similarly, a trans isomer might give trans, D*-β, and L*-β products.

One last example, the racemization of a tris(bidentate) ion by an intramolecular mechanism in which one end is temporarily uncoordinated is shown in Figure 6, where A = G. The bond rupture mechanism is considered the probable mechanism for racemization of unsymmetrical β-diketone complexes based on the nuclear magnetic resonance studies by Fay and Piper (*39*). Extension of the scheme shown in Figures 1 and 2 to other systems is almost limitless.

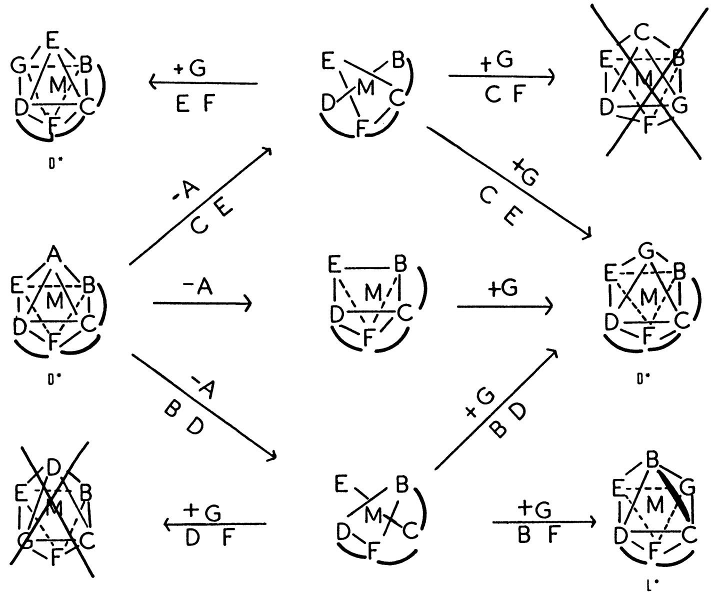

Figure 5. Product expectations for a complex similar to a D***-α-*triethylenetetramine complex with two cis monodentate ligands*

Cobalt(III) Stereomobility

The semiquantitative stereochemical observations of Alfred Werner and his students, as well as later contributions by J. C. Bailar, Jr., J. P. Mathieu, P. Pfeiffer, M. Delephine, and others, have been ably reviewed by Fred Basolo (*16*, *17*, *21*, *22*). Reviews emphasizing more recent investigations have also appeared (*18*, *68*, *103*), as have short reviews emphasizing aquation (acid hydrolysis) (*47*) and base hydrolysis (*48*, *90*), both in terms of stereochemistry and kinetics.

Since the reviews have stressed the numerous stereochemical studies which have been conducted on the octahedral bis(ethylenediamine) complexes of cobalt(III), those results will be reiterated only briefly.

Aquation (acid hydrolysis) of *cis*-$[CoXY(en)_2]^n$ complexes

$$[CoXY(en)_2]^n + H_2O \rightleftharpoons [CoY(H_2O)(en)_2]^{n+1} + X^- \qquad (1)$$

takes place with apparently 100% retention of configuration, where en = ethylenediamine, $X^- = Br^-, Cl^-$, or NO_3^-, and $Y = N_3^-, Cl^-, OH^-, H_2O, NCS^-, NH_3$, or NO_2^-, and n = the charge on the cobalt(III) complex. Although not all combinations of the above have been studied, enough have been investigated to suggest a generality. The corresponding trans ions aquate with complete retention of configuration, if $Y = NH_3$ or NO_2^-,

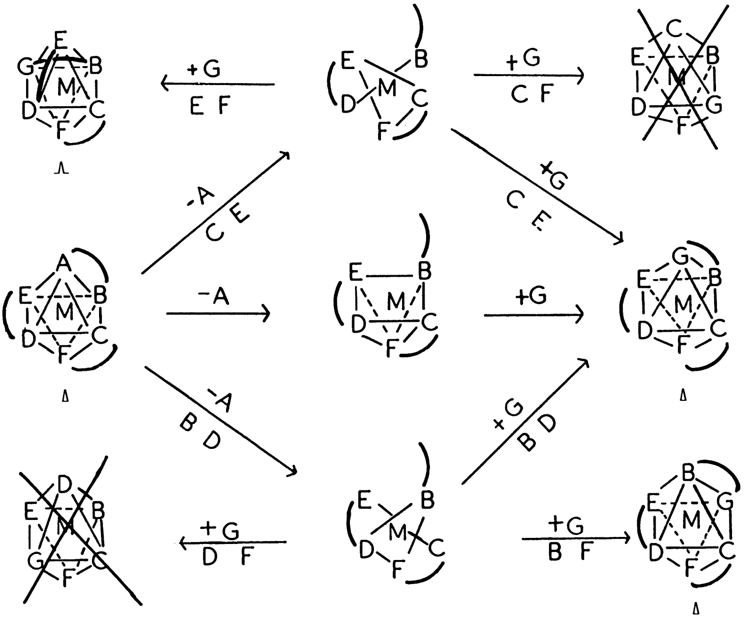

Figure 6. An intramolecular bond rupture racemization mechanism; A = G

but not if Y = N_3^-, Cl^-, OH^-, or NCS^-. This definite ligand field correlation is considered to be due to π donation by the low field ligands into an empty orbital in a dissociative intermediate. Overlap for this π interaction is obtained only if a trigonal bipyramidal type intermediate is generated (*80*). Stronger field ligands lack this π-donating ability. A duality of mechanisms is indicated even in these relatively simple aquations since water exchange and racemization of *cis*- and *trans*-$[Co(H_2O)(NH_3)(en)_2]^{+3}$ occur at different rates (*73*).

Table II. One-step Base Hydrolysis

Reactant		*% cis reactant*	*% trans reactant*
E	*A*	*→ cis product*[b]	*→ cis product*[b]
Cl^-	Cl^-	37	5
NO_2^-	Cl^-	66	6
NCS^-	Cl^-	80	76
NH_3	Cl^-	84	76
OH^-	Cl^-	97	95

[a] Figure 3 shows the general reaction sequence for the cis complexes where G = OH^-
[b] The first three percentage columns are based on experimental observations.

Base hydrolysis of $[CoXY(en)_2]^n$ complexes normally involves considerable stereomobility during the substitution process. Illustrative studies for which both the optical and geometrical isomer composition of the products are known are given in Table II. A tabulation of the cis and trans product ratios for a large number of such reactions has been made by Ingold, Nyholm, and Tobe (*48*) and by Jordan and Sargeson (*50*). The latter have noted a similarity in product ratios for the same E ligand in a cis reactant or F ligand in a trans reactant (Figures 3 and 4, respectively), even though A may vary somewhat (N_3^-, Cl^-, Br^-, NCS^-). An almost general agreement has been reached that the reacting species in these hydrolyses is the conjugate base $[CoXY(en\text{-}H)(en)]^{n-1}$ (*68, 82*). However, Green and Taube (*43*) have noted that the molecularity of the conjugate base reaction appears to vary. Competition from an interchange process between the first and second coordination spheres with a unimolecular conjugate base mechanism (*30–33, 68, 89*) merits consideration.

A comparison of these base hydrolysis results with the trigonal bipyramidal intermediates postulated for dissociative stereomobility is interesting. The two trigonal bipyramidal intermediates for the trans reactant (Figure 4) are mirror image optical isomers of the same geometrical isomer. One of the trigonal bipyramids of the cis reactant (Figure 3) is identical to one of the optical isomers of the trans reactant, but the other bipyramidal intermediate is different and only yields cis products of D* and L* chirality. If the DF chelating group is asymmetric, Pearson and Basolo (*81*) suggest that any isomer ratio can be explained in terms of a dissociative type mechanism, provided (1) the cis reactant yields more cis product than the trans reactant, and (2) provided the per cent retention of configuration by the cis reactant is greater than or at least equal to the per cent of the top intermediate (Figure 3) necessary to obtain a product balance times the fraction of cis product obtained from the trans reactant, all of which must go through that intermediate and its mirror image. However, in order to make a postulated unimolecular conjugate

Products of $[CoEA(en)_2]^n$ Complexes[a]

% cis reactant → inverted cis product[b]	*% cis reactant thru lower intermediate*[c]	*DB:BF attack*[c,d]	
16	34	18:16	9:8
20	64	44:20	11:5
24	16	−8:24	1:∞
24	33	9:24	3:8
36	50	14:36	7:18

[c] These columns are based on the same treatment as above but with Figure 3 nomenclature.

[d] This ratio should be related to the relative acidity of the two types of amine nitrogens in the complexes.

base (S_N1CB) mechanism include the five cobalt(III) bis(ethylenediamine) complexes for which isomer data are available, the acidity of the NH_2 groups at the opposite ends of the ethylenediamine molecules must vary from a factor of about 2:1 in one direction to 1:∞ in the other. (*See* Table II.) Furthermore, the temperature and concentration dependence of the isomer ratios observed for reactions of the D*-*cis*-$[CoCl_2(en)_2]^+$ ion (*7, 9, 12–14, 26, 34*) suggests that the S_N1CB treatment is an oversimplification for these complexes. The Bailar inversions (*7, 12–14, 26, 38*) (octahedral D* → L* inversions similar to the tetrahedral Walden inversions) have been noted for $[CoCl_2(en)_2]^+$ and the corresponding chlorobromo (*14*) and dibromo (*14*) species. Dwyer, Sargeson, and Reid (*38*) found that hydroxide rather than carbonate is responsible for the aqueous inversion. Subsequently, Boucher, Kyuno, and Bailar (*26*) have shown that Ag^+ is not necessary for the reaction. The cis to trans ratios of the products in the inversion compared to the same ratios for dilute solution would be enlightening. Stronger field ligands, such as fluoro (*74*), hydroxo (*26, 38*), ammine (*78*), or nitro (*38*), show no such inversion. Again, this ligand field correlation may be due to low π donation by the higher field ligands.

The closely related triethylenetetramine complexes show a D*-α to L*-β inversion (*66, 67*) similar to that expected (Figure 5). Although the investigators suggested complete inversion in the second step (*67*)—the opposite of the ethylenediamine complexes—their data on direct hydrolysis suggest considerably more inversion for the two-step reaction than for the second step alone. No configurational change was noted for the β isomer reaction (*65*).

None of the substitution reactions of the bis(dimethylglyoximato) complexes of cobalt(III) have been found to exhibit configurational changes (*1*). All reactants and products possess the strongly hydrogen-bonded trans configuration.

Cobalt(III) stereomobility has been noted in complexes other than those with four nitrogen donors. For example, the base hydrolysis of *trans*-$[Co(acac)_2(NO_2)(H_2O)]$ (acac = acetylacetonato ligand) appears to give some *cis*-dihydroxo products (*37*), even though the first step gives retention (*10, 25*). Another ligand field correlation is that although $[Co(C_2O_4)_2(H_2O)_2]^-$ decomposes easily, even in water at 0°C. (*5*), $[Co(C_2O_4)_2(NO_2)_2]^{-3}$ is quite stable when isolated (*69*). Both *cis*- and *trans*-$[Co(CO_3)_2(NH_3)_2]^-$ react with two moles of acetylacetone to give only *cis*-$[Co(acac)_2(NH_3)_2]^+$ (*8*). Ring strain appears to determine the intermediate for this reaction. A series of synthetic and stereochemical studies by Kyuno (*55–64*) also has indicated stereomobility for several cobalt(III) complexes, including the dicarbonatodiamminecobaltate(III) isomers, both of which yield *trans*-$[Co(NO_2)(_4(NH_3)_2]^-$ upon reaction with nitrite (*58, 85*). Kyuno assumed stereorigidity in some of the aquations, which might be questionable for species such as the two [$Co(NO_2)_2(C_2O_4)(en)$] isomers (*61*). In fact, anation of the corresponding nitroaquo species was found to involve isomerization. Isomerization had previously been noted for the dicarbonato complexes of cobalt(III) (*75–77*), some of which appear sterically impossible (e.g., *trans*-[$Co(CO_3)_2(en)]^-$) (*76*).

The bimolecular racemization of ethylenedinitrilotetraacetatocobaltate(III) (*29,36*) should be noted. This racemization suggests that bimolecularity should not be excluded in mechanistic considerations of octahedral complexes. Base hydrolysis studies of other complexes without ionizable protons would be of considerable value, provided they are of intermediate field strength.

Other d^6 Complexes

Rhodium(III) acid and base hydrolyses appear to go with almost complete retention of configuration (*49*). Furthermore, base hydrolysis rates are not much greater than the corresponding acid hydrolysis rates. This lack of stereomobility can be correlated with the larger Δ (or *Dq*) values for rhodium(III) (*15*, *51*).

Nucleophilic reactions of the spin-paired tris(*o*-phenanthroline) iron(II) ion are bimolecular (*70–72*). The tris complex is close to the spin-free complex in energy since dithiocyanatobis(*o*-phenanthroline) iron(II) exists in a spin-free $\rightleftharpoons$ spin-paired equilibrium (*53*). The corresponding tris(*o*-phenanthroline)nickel(II) ion is unaffected by the same nucleophile, which probably rules out S_N2 attack on the organic ring as the predominant factor.

Studies with platinum(IV) complexes are complicated by platinum(II) catalysis (*18*). Some of the recent Russian work has considered this aspect (*44*), but correlations are still being made without consideration of the catalytic problem (*104*). The recent isolation of several optically active platinum(IV) complexes with all inorganic, monodentate ligands (*35*) should allow substantiation for older work which has always suggested retention, in agreement with the high Δ values for platinum(IV).

Spin-free Intermediate

Although a large number of electronic and steric factors appears to be important in determining the rates and stereomobility for reactions of the inert, octahedral complexes which have been studied (*19–22*, *68*, *87*), the simple ligand field parameters are quite useful in ascertaining both rates and stereochemistry. This correlation is related to the ligand field activation parameter (Table I) and to the π-donating ability of the lower field ligands. Several factors suggest another possibility — a spin-free intermediate — advanced previously (*19*, *85*) to explain the bimolecular base hydrolysis of tris(*o*-phenanthroline) iron(II).

Whereas the ligand field activation energy of the spin-paired paths allowing configurational change have very high activation energies (Table I), spin-free d^6 complexes can undergo dissociative or associative rearrangements without any ligand field activation energy. Therefore, the spin-free state might function as a precursor to a stereomobile substitution reaction provided the energy of the spin-free state is not greater than the ligand field activation energy of an alternate spin-paired path. This concept allows competition by the spin-free state to about 0.4 Δ in d^6 systems.

The results of calculated Δ values and spin-free activation energies for the extremely stereomobile conjugate base of $[CoCl_2(en)_2]^+$ and some related ions are given in Table III. The average Δ values for spin-paired cobalt(III) species and some related rhodium(III) complexes necessary for the calculations in Table III are tabulated in Table IV. The energy values in both tables have been calculated from spectra of known species using the average environment approximation and values of B and C, based on the method of Wentworth and Piper (*94*, *96*).

The calculations of Δ for the cobalt(III) conjugate base are based on related rhodium(III) species. The spectrochemical position of the nitrogen conjugate base ligand can be estimated from Δ, B, and C values for known rhodium(III) complexes (*51*) and the recent observations that $[Rh(en\text{-}H)_3]$ is diamagnetic (*91*), whereas $[Rh(en\text{-}H)_2(en\text{-}2H)]^-$ is paramagnetic (*92*). Since the magnetic crossover occurs at $2\Delta = 5\text{ B} + 8\text{ C}$ for d^6 species, and B and C values for known rhodium(III) complexes are about 310 and 3000 cm.$^{-1}$, respectively, the conjugate base ends of the ethylenediamine ligands must have a Δ of only about 1200 cm.$^{-1}$ to account

Table III. Estimated Spin-free Activation Energies for Selected Cobalt(III) Species

	$\Delta(kK)$[a]	*Spin-free* E_a *(kcal./mole)*[b]	*Spin-paired*$_a$ *(kcal./mole)*[c]
$[CoCl_2(en)_2]^+$	21.7	31	25
$[Co(H_2O)_6]^{+3}$ (observed)[d]	20.4	23	23
$[CoCl_2(en\text{-}H)(en)]$[e]	19.2	16	22
$[Co(H_2O)_6]^{+3}$ (calculated)[a]	18.8	14	22
$[CoCl_2(en\text{-}H)(en)]$[f]	17.7	7	20
Spin-paired $[CoF_6]^{-3}$ [a]	16.8		
Estimated crossover[g]	16.5		
Spin-free $[CoF_6]^{-3}$ (observed)	13.0		

[a] The Δ values are based on Dq' values of Wentworth and Piper, $kK = 1000$ cm.$^{-1}$ (*95*).

[b] Spin-free $E_a = E(^5T_{2g}) - E(^1A_{1g}) = 2\Delta - 5\text{ B} - 8\text{ C}$; 1 kcal./mole = 350 cm.$^{-1}$

[c] Spin-paired $E_a = 0.4\Delta$.

[d] Reference (*51*).

[e] The Δ for the conjugate base donor estimated as 10 *kK*.

[f] The Δ for the conjugate base donor estimated as 1.2 *kK*.

[g] Crossover based on B = 0.5 *kK*; C = 3.8 *kK* (*95*).

Table IV. Average Δ Values for Cobalt(III) and Rhodium(III) Complexes[a]

	I^-	N_3^-	Br^-	Cl^-	F^-	OH^-	CO_3^{-2}	H_2O	$C_2O_4^{-2}$
Co(III)	10	11	13	15	17-18	18	19	19-20	20
Rh(III)			21	22		27		28	28

	edta	NH_3	*en*	NO_2^-	CN^-
Co(III)	22	25	25	31	36
Rh(III)	31	36	36		

[a] For the complexes which have been measured, the corresponding iridium(III) and platinum(IV) complexes have Δ values approximately double the cobalt(III) values, whereas the iron(II) species have slightly lower Δ values than the cobalt(III species. Δ Values are in *kK* units of 1000 cm.$^{-1}$, edta = ethylenedinitrilotetraacetate anion.

for the diamagnetic to paramagnetic transition in the rhodium conjugate base series. A higher value would require that both complexes be diamagnetic. Considering the dearth of B and C data for rhodium(III) complexes, this estimate could be somewhat low. Even so, the Δ value for NH_2^- is undoubtedly considerably less than the iodide ion value given in Table IV. Both extreme values (1200 and 10,000 cm.$^{-1}$) have been used to calculate the maximum range of Δ values for the cobalt(III) conjugate base species (Table III).

Cobalt(III) complexes appear to have B and C values of about 500 and 3800 cm.$^{-1}$, respectively. These typical values give a crossover point of 16,500 cm.$^{-1}$, which has been used in Table III to estimate the spin-free activation energies of the other species, the spin-free activation energies being the amount by which 2Δ exceeds 5 B + 8 C. That the position of the spin-free crossover is not too low is indicated by the fact that the hypothetical spin-paired $[Co\ F_6]^{-3}$ ion has a Δ value (Table IV) about equal to the crossover point estimated from the Racah parameters, B and C. The spin-paired activation energies, estimated at 0.4Δ, are also given in Table III for comparison purposes.

The Δ value of the hexaaquocobalt(III) ion is important since spin-free activation estimates of only 4 or 5 kcal./mole have been made to account for the rapid ligand exchange rate observed for this complex (*23*, *40*, *41*, *88*). Unfortunately, two Δ values must be given for the hexaaquo ion since the spectrum reported for the metastable complex (*51*) gives a result which differs somewhat from the calculated value (*95*). All of the values in the spin-free column could be lowered by 9 to 18 kcal./mole, depending on the proper hexaaquo Δ value, if the 5 kcal./mole spin-free activation assumption were correct.

In any case, the spin-free state of the conjugate base in question is low enough in energy to provide competition for the spin-paired paths.

Similarly, the dichlorotriethylenetetraminecobalt(III) isomers, which possess almost identical ligand field parameters, show marked stereomobility. All isomers yield primarily the β isomer during base hydrolysis. On the other hand, bis(ethylenediamine) complexes having higher field monodentate ligands show less stereomobility during base hydrolysis, in agreement with the spin-free concept.

Even though the activation energy of this process may be less than that for other paths, a low frequency factor would allow other paths to compete at higher temperatures. This postulate would also explain the temperature dependence of the Bailar inversions. An alternate, oriented ion-pair mechanism has been suggested previously (*9*, *26*, *69*), but the observations with $[CoCl_2(en)_2]^+$ in methanol (*24*) make this less probable because both the ion pair and the solvated ion appear to give trans and racemic cis isomers under the conditions studied. Some orientation effects would be expected for the ion-pair reaction if it were operative in the inversion reactions.

The availability of a spin-free state at the right energy does not mean that the species use that path. The frequency factor may be too low, either as a result of the $^1A_{1g} \rightarrow {}^5T_{2g}$ transition rate being too slow to compete with other paths, or because the lifetime in the $^5T_{2g}$ state is too short to allow the requisite atomic motion for substitution. A long lifetime would facilitate reduction of cobalt(III) to cobalt(II). In fact, cobalt(II) species are often found in cobalt(III) products when low ligand field ligands are involved in substitution reactions.

It appears possible that only the conjugate bases of the bis(ethylenediamine) and triethylenetetramine cobalt(III) ions have low enough energies for competition by this mechanism. A consideration of the acid hydrolysis of $[CoCl_2(en)_2]^+$ shows no competition by the spin-free path if Wentworth and Piper's B and C values are right. The observation of retention for this and the related triethylenetetramine aquation reactions is in agreement with a lack of competition. On the other hand, if the lower activation energy suggested by the hexaaquo species were correct, competition could exist. Martin and Tobe (*73*) found that the water exchange of the $[Co(H_2O)(NH_3)(en)_2]^{+3}$ isomers proceeds at less than a hundred times the rate of racemization — suggesting similar activation parameters. Since these ions have Δ values of about 24 kK, the spin-free state could not compete unless the lowest hexaaquo value were correct. Hence, no definite conclusions can be drawn for the acid hydrolyses at this time.

Extension of the spin-free idea to other species is also possible. Of the rhodium(III) amine species, only a multiple conjugate base species would be suitable, since Δ values are larger and the B and C parameters are lower (*15*). Spin-paired iron(II) species and certain cobalt(III) complexes with several ligands lower than the amines might also use the spin-free path. Bis(oxalato) complexes of rhodium(III) isomerize (*54*), also in agreement with their relatively lower ligand field, whereas configurational changes are difficult with higher field rhodium complexes. Bimolecular processes are apparently more important in rhodium(III) reactions (*49*, *83*). The racemization of tris(ethylenediamine) ions may also need a bimolecular path (*42*, *84*).

Caution should be suggested against using this or any other effect as a cure-all for octahedral kinetics and mechanisms. For example, steric hindrance can change a planar d^8 system, which normally reacts by a bimolecular path (*18*) to unimolecular reactivity (*11*, *93*). (On the other hand, even the concept of molecularity in complex ion reactions has been questioned by Adamson (*3*) who initiated and made good use of the S_N2FS path (*2*, *4*). Some of the manifestations of this problem have been discussed by others as well (*68*, *90*).)

Other Electronic Configurations

The correlation of rates with ligand field strength can also be made for other electronic configurations. For example, whereas $CrCl_6^{-3}$ hydrolyzes almost instantaneously, $MoCl_6^{-3}$ has a specific rate constant of less than 10^{-3} at 0°C. (*6*), in keeping with the 50% greater Δ values of the second transition series (*51*). In fact, the rate is about the same as for chromium(III) species about that much higher in the series. The lack of a strong conjugate base effect (*17*, *68*) in d^3 systems can also be related to the unavailability of a state with lower ligand field activation. On the other hand, d^3 species racemize more readily than the corresponding d^6 complexes, in agreement with the ligand field parameters. (*See* Table I.)

The d^5 ruthenium(III) species exhibit intermediate behavior (*27*). The interelectronic repulsions for a d^5 system ($15B + 10C$ *vs.* 2Δ) are greater than those of a d^6 system ($5B + 8C$ *vs.* 2Δ), suggesting a greater ligand field effect for ruthenium(III) than for rhodium(III). But the greater Δ values and lower B and C values relative to those of cobalt(III) are insufficient to compensate fully for the 10B and 2C differences.

Other relationships could also be mentioned, but the preceding should give an indication of general relationships which exist among ligand field strength, reaction rates, and stereomobility.

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Square Planar Complexes of the First Row Transition Metals

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Numerous complexing agents are available for preparing planar complexes of the first row transition metals. Porphins, phthalocyanines, quinolines, and pyridines form planar complexes with certain metal ions under controlled conditions. Appropriate sulfur-containing ligands can also be used, and the resulting complexes often can be further oxidized or reduced. Planar, octahedral, or tetrahedral complexes of the salicylaldimines, β-ketoimines, and related compounds can be prepared by choosing the appropriate ligand substitution. In β-ketoaminate and tertiary phosphine complexes an equilibrium between planar and tetrahedral forms can be observed. Complexing agents without extensive π systems are capable of holding the metal ion in a planar configuration if certain steric requirements are fulfilled. Carbon substituted ethylenediamines and several cyclic ring systems have been used successfully.

The origin of inorganic complexes possessing the planar configuration is generally placed at the preparation of the α- and β- forms of dichlorodiammineplatinum(II) by Peyrone (*76*) and Reiset (*78*). However, it was not until 50 years later that the structures of these compounds were adequately explained by Werner (*96*) as the cis- and trans- isomers of square planar platinum (Figure 1). Werner did not employ the expression "square planar," but his drawings are those of the spatial orientation which is now implied by that expression. "Square coordination," as a term, came into usage with Pauling's (*73, 74, 75*) development of the directed valence bond.

Historically, the study of the square planar configuration has developed primarily through the preparation and property studies of platinum

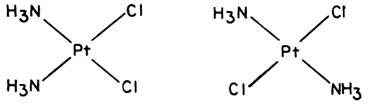
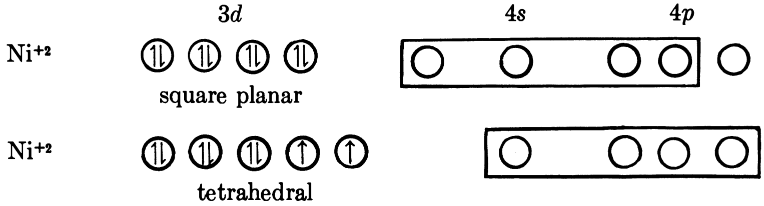


Figure 1. Planar platinum(II) complexes

and palladium compounds. Extensive reviews (*5, 7, 64, 77*) with this emphasis are available; it is the almost totally neglected area of first row transition elements having square planar geometry which will be summarized here.

Experimental evidence supporting the square planar structure of first row transition metal ions was presented in 1931: $[Ni(CN)_4]^{-2}$ complexes were found to be diamagnetic, and $K_2Ni(CN)_4 \cdot H_2O$ and $K_2Pd(CN)_4 \cdot H_2O$ were found to be isomorphous (*73, 74*). Pauling's prediction (*75*) that bivalent nickel complexes could be either square planar (dsp^2 hybridization) or tetrahedral (sp^3 hybridization) stimulated interest in the square configuration which, with the magnetic measurement indicating bond type, resulted in the discovery of many square planar complexes.



Pauling (*75*) also considered the problem of configuration from the standpoint of properties of the complexing agent which stabilize the square planar configuration. In general, ligands containing an atom with a strong tendency to form covalent bonds favor the square planar geometry. Pauling (*75*) thus enumerated a series of nickel compounds as follows:

Square Planar	*Tetrahedral or Octahedral*
cyano	aquo
glyoximate	ammine
dithiooxalate	hydrazine
diacetyldioxime	ethylenediamine
ethylxanthogenate	acetylacetonate
ethyldithiocarbamate	
stilbenediamine (yellow form)	stilbenediamine (blue form)
phenylethylenediamine (yellow form)	phenylethylenediamine (blue form)
$Ni(P(C_6H_5)_3)_2X_2$ X = Cl, Br, I (red)	$Ni(P(C_6H_5)_3)_2(NO_3)_2$ (green)
disalicylaldimine (orange form)	disalicylaldimine (green form)

In this discussion, the square planar geometry of first row transition metal complexes will be treated, emphasizing the use of structural modifications of the ligand in order to influence the geometry of the complex. Detailed descriptions of the properties of these complexes are found in the accompanying references.

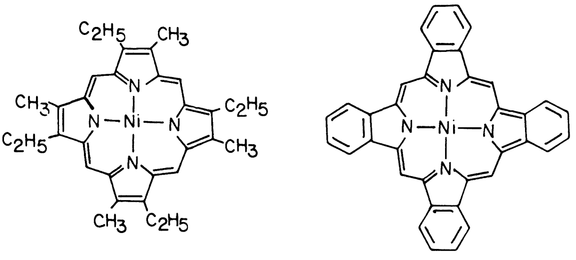
Porphyrins, Phthalocyanines, and Other Polycyclic Chelating Agents

In principle, square planar configuration about a metal can be assured by appropriate choice of a single ligand. The ligand, in the most rigorous case, must contain four atoms in the same plane capable of coordinating to the metal, have sufficient space between them to accommodate the metal in the plane, and be sufficiently stable to be practical. The porphyrin (*33*) and phthalocyanine (*57*) (Figure 2) systems meet these requirements.

Of the first row transition metals, the nickel(II), cobalt(II), and copper(II) porphyrins are the most thermodynamically stable (*33*). A crystal structure determination of nickel(II) etioporphyrin confirmed (*24*) (Figure 2(a)) the planarity of the true porphyrin nucleus. Moreover, most of the first row transition metal ions form planar porphyrin complexes, but certain of these must be regarded as square pyramidal or octahedral complexes inasmuch as one or two additional ligands occupy positions perpendicular to the ring system. The stability of these compounds as well as of the strictly square planar complexes is generally attributed to the high degree of conjugation which is transmitted through the entire system (*33*). The effect of substitution of the porphyrin thus is readily felt in all parts of the ring system and in the extra planar substituents, when present. All positions of the pyrrole rings can be substituted with alkyl groups, etc., and replacement of the =CH linkage by an aza linkage is common. Specific biological activity is frequently a function of the particular protein coordinated to one of the axial positions, the other axial position accommodating the same protein, a water molecule, oxygen, carbon monoxide, etc. (*33*).

Recent reviews of the phthalocyanines by Lever (*57*) and by Moser and Thomas (*66*) are available. Complexes of phthalocyanine with all of the first row transition elements, excepting scandium, have been prepared. However, titanium and vanadium phthalocyanines are known only as the oxy- or chloro-compounds and are not then strictly square planar. That phthalocyanine has considerable ability to promote the square planar configuration is further demonstrated by the existence of the chromium(III) and manganese(II) complexes (*57*).

Although oxidation states of the central atom may vary between 0 and +6, the +2 oxidation states are usual. Most complexes are thermally stable and sublime unchanged at 400°C. Phthalocyanines often exist in two or more polymeric modifications which, in certain cases, have different



(a) (b)

Figure 2. Square planar geometry of (a) nickel(II)-etioporphyrin and (b) phthalocyaninenickel(II)

structures. The α-form of phthalocyaninechromium(II) is polymerized through the crystal lattice (*29*), whereas the β-form, prepared by Ercolani (*56*), is square planar. These complexes are generally intensely colored and insoluble in common solvents.

Phthalocyanine complexes exhibit magnetic moments corresponding to low-spin, electron-paired species (*57*). One exception is lithium phthalocyanine manganate(0), a spin-free case which may occur for metals in their lowest oxidation state (*57*). On the basis of the low spin observed for phthalocyaninechromium(II) and phthalocyaninechloroiron(III), a metal-metal interaction which extends throughout the lattice has been postulated (*55*).

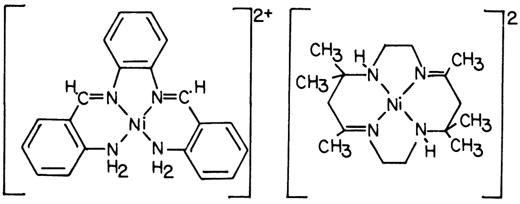
In order to increase the solubility of porphyrin and phthalocyanine complexes, several structural modifications have been made. α, β, γ, δ-Tetra-(4-pyridyl)-porphin complexes of copper(II), nickel(II), and zinc(II) have been synthesized (*35*) and their ultraviolet spectra determined in chloroform and in acid solution. By utilizing sulfonic acid groups to increase solubility, complexes of 4,4′,4″,4‴-tetrasulfophthalocyanine complexes of many metals were prepared (*94*, *95*). This chelating agent was found to have a ligand field strength comparable to cyanide (*94*, *95*).

The great stability of these ring systems was known, and possible biological implications of compounds having similar structures were postulated. As a result extensive research in macrocyclic chelating agents developed (*13*).

Quadridentate ligands can be obtained by condensing suitably substituted aldehydes and ketones with bidentate primary amines, and the resulting Schiff bases closely resemble the porphin ring system. Generally, one of the structural units $-\mathrm{N}{=}\overset{|}{\mathrm{C}}-\overset{|}{\mathrm{C}}{=}\mathrm{N}-$, $-\mathrm{N}{=}\overset{|}{\mathrm{C}}-\mathrm{NH}\overset{|}{\mathrm{C}}{=}\mathrm{N}-$, $-\mathrm{N}{=}\overset{|}{\mathrm{C}}-\mathrm{NH}-\mathrm{N}{=}\overset{|}{\mathrm{C}}-$, $-\overset{|}{\mathrm{C}}{=}\mathrm{N}-\mathrm{CH}{=}\mathrm{CH}-\mathrm{N}{=}\overset{|}{\mathrm{C}}-$, or $-\overset{|}{\mathrm{C}}{=}\mathrm{N}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{N}{=}\overset{|}{\mathrm{C}}-$ is incorporated into the structure for maximum stability. For example, if *ortho*-aminobenzaldehyde is condensed with *ortho*-

phenylenediamine the following chelate can be obtained with nickel(II) (Figure 3(a)). Many quadridentate and tridentate chelating agents have been reviewed by Goodwin (*40*).

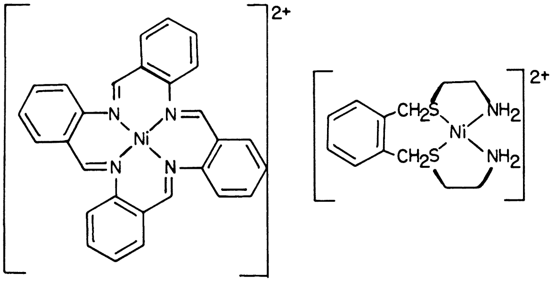
Metal ions have recently been used to direct the course of these condensation reactions. These "template syntheses" are the topic of a recent review by Busch (*13*). The compound shown in Figure 3(b), having square planar geometry, is one of the products formed by dissolving bis-(ethylenediamine)-nickel(II) perchlorate in acetone.



(a) (b)

Figure 3. Macrocyclic chelates

If *o*-aminobenzaldehyde is treated with metal salts in absolute ethanol, the following structure (Figure 4(a)) can be obtained (*13*). Ligands containing sulfur atoms have been alkylated to achieve planar coordination. If bis(mercaptoethylamine)nickel(II) is treated with *α,α′*-dibromo-*o*-xylene, the complex in Figure 4(b) is obtained (*13*).



(a) (b)

Figure 4. Chelates resulting from "template" syntheses

Quinoline and Pyridine Heterocycles

Although square planar structures are generally assured by the use of cyclic tetradentate ligands, the use of simpler heterocyclic ring systems often yields the square configuration with some first row transition metal ions.

Square planar complexes can be prepared which contain quinoline, pyridine, and substituted pyridines as ligands, and solvents are known to influence the geometry of the complexes. It has been shown in particular (*79*) that the solvent used for dissolving tetrapyridinenickel(II) perchlorate (and tetrafluoroborate) can affect the geometry of the complex. The solid complexes are 6-coordinate, spin-free, tetragonal complexes having mono-coordinated anions. However, when the complexes are suspended in chloroform, they do not dissolve but change in color from pale blue to yellow. These yellow chloroform solvates have a reduced magnetic moment and react with moist air to regenerate a blue complex. The yellow species have the properties of diamagnetic, square planar nickel.

Using substituted pyridines, a number of square planar complexes has been prepared with the empirical formula, ML_4X_2, for which structures in the solid and in noncoordinating solvents can be generalized in the following way (*91*).

Complex		*Solid*	*Solution CH_2Cl_2*
Ni(3,5-lutidine)$_4X_2$	$X = ClO_4^-, BF_4^-$	oct.	sq. pl.
Ni(4-picoline)$_4X_2$	" "	sq. pl.	oct.
Ni(3-picoline)$_4X_2$	" "	sq. pl.	oct.
		oct.	
Ni(3,4-lutidine)$_4X_2$	$X = I^-$	sq. pl.	oct.
	$X = ClO_4^-, BF_4^-$	sq. pl.	sq. pl.

The solid chlorides are octahedral when *pKa* of the ligand < 9.0; the iodides are octahedral when *pKa* < 6.5; the bromides, however, change from octahedral to square planar at an intermediate *pKa* value. In solution all halide complexes are octahedral. Similarly, the perchlorates and tetrafluoroborates are octahedral when the ligand *pKa* < 5.5 and are square planar when the *pKa* > 6.2 (*93*).

Quinoline and substituted pyridines also form complexes with nickel(II), with an empirical formula, ML_2X_2. Octahedral, tetrahedral, or planar species containing quinoline have been studied in this case as a function of the nature of X (*38, 39*).

Ni(quinoline)$_2$Cl$_2$	yellow form	polymeric octahedral
Ni(quinoline)$_2$Cl$_2$	blue "	tetrahedral
Ni(quinoline)$_2$Br$_2$	blue "	
Ni(quinoline)$_2$I$_2$	green	trans planar

The iodide complex is diamagnetic and gives a red solution in organic solvents with accompanying decomposition. A study (*20*) of the far infrared spectra of these complexes confirmed the suggested structures. For Ni(quinoline)$_2$I$_2$, the Ni-I vibration occurs at 218 cm.$^{-1}$ (similar to the tetrahedral vibration), but the Ni-quinoline vibration occurs at 299 cm.$^{-1}$, about 80 cm.$^{-1}$ higher than tetrahedrally-coordinated quinoline. This observation suggests that ν(M-L) vibrations occur with higher frequencies in planar situations than in other configurations. A tabulation of x-ray structures of M(py)$_2$X$_2$ complexes, where X = Cl and Br and M = Co, Ni, Cu, and Zn, is presented by Clark and Williams (*20*). These complexes are mainly distorted octahedral or tetrahedral with no square planar structures reported for unsubstituted pyridines (*37*). Chromium(II) complexes (*37*, *47*) of stoichiometry Cr(py)$_2$X$_2$ have distorted octahedral structures with powder patterns similar to the corresponding copper(II) complexes.

Here again, using substituted pyridines, trans planar structures can be obtained. Ni(2,5-lutidine)$_2$X$_2$ is reported to have a planar structure in the solid but, in solution in noncoordinating solvents, these compounds are distorted tetrahedral (*12*).

Complexes of the general formula, NiLX$_2$, where X = Br or I and L = 2,5- or 2,6-dimethylpyrazine, have planar geometry (*59*). The planarity of these structures was confirmed by an x-ray study (*3*) of Ni(2,5-dimethylpyrazine)Br$_2$. The intense purple color of this complex was attributed (*3*) to conjugation throughout the aromatic system in the solid state shifting the normal blue absorption into the green and therefore changing the observed color of the complex from yellow to purple. A spectroscopic study of numerous pyrazine nickel(II) complexes has been reported by Lever, Lewis, and Nyholm (*59*).

2,2′2″-Terpyridine was reported (*65*) to give square complexes with zinc(II), however, the complex has been found to be a trigonal bipyramid with the anions occupying two positions (*21*). Neither 2,2′-dipyridine nor *o*-phenanthroline complexes has been shown to form square planar structures with any of the first row transition metals (*2*, *10*), although in the presence of weakly coordinating solvents and anions this geometry may be achieved.

Phosphorus-Containing Ligands. A class of compounds analogous to the nitrogen donors and having a similar formula are the phosphine complexes, M(PR$_3$)$_2$X$_2$, where R may be alkyl or aryl and X is Cl, Br, or I. These complexes have been studied recently by Venanzi and Sutton (*11*, *23*) and by Hayter (*44*, *45*). Phosphine complexes are especially interesting in that tetrahedral or planar isomers can be isolated in the pure state, depending on the nature of R and X. When R is diphenylalkylphosphine, both isomers can be isolated. In fact, both isomers exist in the same unit cell in a similar complex, Ni(P(CH$_2$C$_6$H$_5$)(C$_6$H$_5$)$_2$)$_2$Br$_2$ (*52*). Differentiation between the planar and tetrahedral isomers was accomplished by considering their spectral and magnetic properties (*45*). Diamagnetic dark red or brown compounds which show no absorption in the 800-1000 mμ region and the powder patterns of which resemble palladium complexes are planar. Paramagnetic compounds (chlorides are blue-purple, bromides are green, and the iodides are brown) with an absorption in the 800-1000 $m\mu^{-1}$ region and with powder patterns resembling zinc or cobalt compounds are distorted tetrahedral (*45*).

For the complexes, $Ni(PR_3)_2X_2$, the tetrahedral form is favored over the square planar form as the substitution on phosphorus varies in the series (*23*, *45*) $Et_3P < Et_2PC_6H_5 < EtP(C_6H_5)_2 < P(C_6H_5)_3$, and as X varies in the series $SCN^- < Cl^- < Br^- < I^-$. The tetrahedral form is favored over the square planar form as the ligand field is decreased. A steric factor also favors the tetrahedral configuration because steric interactions between ligands are reduced in this conformation (*23*). It also appears that in the alkyldiphenylphosphines, as the size of the alkyl group increases from methyl to *n*-amyl, the tetrahedral form is favored. The diphenylphosphine complex, $Ni(PH\Phi_2)_2I_2$, was prepared and found to be planar, but the corresponding chloro- and bromo-complexes could not be isolated (*44*). In all of these planar compounds the trans-isomer is formed. It should be noted that the cobalt(II) complex, $Co(PEt_3)_2(SCN)_2$, is square planar in the solid state (*92*).

Chatt and Shaw (*17*) alkylated the tetrahedral molecule, $Ni(PR_3)_2Br_2$, with sodium acetylide in liquid ammonia and obtained planar $Ni(PR_3)_2(C{\equiv}CC_6H_5)_2$. Arylation of other bis(triarylphosphino)dihalonickel(II), cobalt(II), and iron(II) complexes with *ortho*-substituted aryl Grignard reagents has also been accomplished (*18*). Simple alkyl and aryl Grignard reagents, however, gave impure products. The first planar complex of iron(II) containing only monodentate ligands was $Fe(Et_2PC_6H_5)_2(C_6Cl_5)_2$ (*18*). An aryl substituted cobalt(II) complex, $Co(Et_2PC_6H_5)_2$(mesityl)$_2$, was proved to be planar by an x-ray study of its crystal structure (*72*).

Ditertiary phosphines also form planar complexes with nickel(II). $Ni((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)Br_2$ (*8*) and $Ni(Et_2P\text{-}CH_2\text{-}CH_2\text{-}PEt_2)Br_2$ (*99*) have been prepared and are diamagnetic and apparently planar.

Some planar complexes containing arsenic can be prepared. *o*-Phenylenebisdimethylarsine (diarsine) reacts with nickel carbonyl to form $Ni(CO)_2$(diarsine) (*70*). Oxidation of this complex with iodine gives a red, diamagnetic, planar complex, Ni(diarsine)I_2. The corresponding bromides and chlorides could not be purified and appear to be much less stable (*70*).

Ketones and Derivatives. Probably the most extensive series of ligands which form planar complexes studied to date are the derivatives of carbonyl compounds, primarily the Schiff bases. To include here all of the available data on these compounds would be a review in itself. Therefore, only a general outline will be presented.

In brief, the recent studies have sought to prepare various Schiff bases to distinguish between the square planar and tetrahedral configuration (*15*) and to determine how the ligand might be modified to favor one stereoisomer over the other. It was hoped that the correct ligand would produce an observable equilibrium in noncoordinating solvents between the planar and pseudo-tetrahedral forms.

The following general type of complexes has been studied extensively (Figure 5). These bidentate ligands, which form bis-complexes of nickel(II), copper(II), and cobalt(II), are nonelectrolytes and therefore have moderate solubility in nonpolar, noncoordinating solvents. Furthermore, using these solvents reduces additional coordination. The equilibrium between the planar and pseudo-tetrahedral conformations may be altered by changes in solvent, temperature, and substituents.

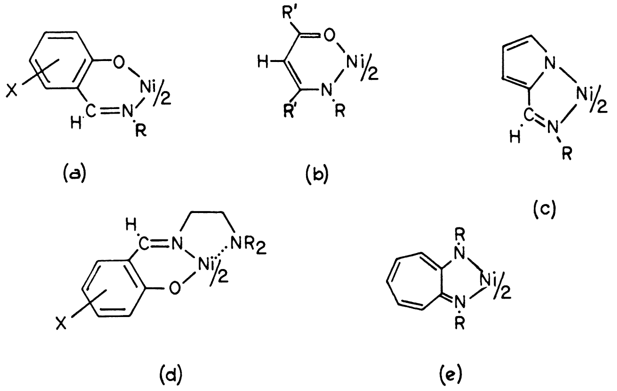


Figure 5. β-Ketoaminates and related complexes

By altering the structure of R in type **a** compounds of nickel(II), three classes of compounds in the aromatic series can be formed (*49*): (1) When R is an *ortho*-substituted aryl group, the compounds are either diamagnetic or weakly paramagnetic. (2) When R is phenyl or *p*-substituted phenyl, either diamagnetic (phenyl, *p*-fluorophenyl) or strongly paramagnetic solids (*p*-tolyl, *p*-chlorophenyl) are obtained, but these solids are always paramagnetic in solution. (3) When R is a meta-substituted phenyl, the compound is always paramagnetic. Species in Class 1 are planar, and those in Class 2 are considered to be an equilibrium mixture of diamagnetic and paramagnetic dimers. Species in Class 3 are tetrahedral. In the aliphatic series, as R varies from methyl to *sec*- and *tert*-alkyl groups, a change from essentially planar diamagnetic behavior to paramagnetic, pseudo-tetrahedral behavior was realized (*50, 71, 80, 85*). When R is *sec*-alkyl, a conformational equilibrium between planar and tetrahedral forms was proposed to exist in solution (*50, 80*). Copper(II) complexes of some of these ligands have also been prepared (*81, 100*).

The red diamagnetic nickel complex of acetylacetoneimine (type **b**) was interpreted (*1*) to have the trans-planar configuration as a result of analyzing the ligand field absorption bands. The presence of cis-isomer cannot be ruled out entirely but, since two isomers could not be detected by chromatographic methods, its existence is doubtful. By a comparison of the crystal structures of the acetylacetoneimines of nickel(II) and copper(II) with palladium(II), the square planar nature of these chelates was ascertained (*43*). The trans-arrangement of ligands and the planarity of the metal atom and its four nearest neighbors were also confirmed (*43*).

An extensive series of β-ketoimine complexes of type **b** with nickel(II) (*31*) and cobalt(II) (*32*) have recently been studied. Nickel(II) complexes, where R = H, have been found to be 100% planar up to 80°C. in chloroform solution. Similar nickel(II) complexes, where R = CH_3, are $<5\%$ tetrahedral at room temperature, whereas the corresponding cobalt(II) complexes are totally tetrahedral (*32*). Holm (*32*) proposed that the most important conclusion from these results is that ligands which stabilize a measurable amount of tetrahedral nickel(II) induce $\sim$100% tetrahedral cobalt(II), and ligands which stabilize a measurable amount of planar cobalt(II) induce $\sim$100% planar nickel(II). In the nickel(II) complexes, when R is *sec*-alkyl, the complexes are 100% tetrahedral, whereas with *n*-alkyl groups the planar form dominates. This behavior is similar to the salicylaldimines. In all these complexes there is little doubt that there is much π bonding between the metal ion and the ligand system.

Acetylacetonates with bulky substitution on the 1 and 5 positions may form square planar complexes (*22*). Bis(2,2,6,6-tetramethyl-3,5-heptanedione)nickel(II) is square planar, whereas bis(2,6-dimethyl-3,5-heptanedione)nickel(II) exhibits an equilibrium between the square planar and tetrahedral configuration (*22*).

Compounds of type **c** have been studied for cobalt(II), nickel(II), and copper(II) (*48*). Copper(II) complexes, with R smaller than *t*-butyl, are planar. Nickel(II) complexes, where R is *sec*-butyl, are involved in a planar pseudo-tetrahedral equilibrium. When R is smaller than *sec*-butyl, planar complexes are obtained. No planar complexes of cobalt(II) with this ligand were reported (*48*).

Nickel complexes of type **d** have been studied by Sacconi (*82–84,91*) and similar compounds by Holm (*16*). If NR_2 is an *ortho*-substituted anilino group, the complexes are planar and diamagnetic. If NR_2 is anilino or *para*-substituted anilino, the substances are octahedral or planar, depending on X. In inert solvents, compounds with a substituted anilino group exist as an equilibrium mixture of octahedral and planar forms, with the planar form predominating at higher temperatures (*83*). If the NR_2

group is a piperidino group, the complexes are square planar, whereas, if NR_2 is a dimethylamino group or pyrrolidino group, a distorted octahedral structure results. When NR_2 is a diethylamino group, the compound may be planar or octahedral depending on the substituent X (*84*). Tetracoordinated cobalt(II) complexes with similar ligands are tetrahedral rather than planar (*82*).

In summary it can be stated that, in general, as the size of the group R increases, the steric interference between ligands causes the planar configuration to be destabilized with respect to the tetrahedral or pseudotetrahedral configuration.

Numerous aminotroponeimineate complexes of type **e**, with nickel(II), have been prepared and are found to undergo square planar-tetrahedral interconversion (*27*). Extensive nuclear magnetic resonance data have been accumulated on this system along with magnetic moment and electronic spectral measurements (*27*).

Certainly a discussion of ketone derivatives would not be complete without mentioning the planarity of bis(dimethylglyoxime)nickel(II) in noncoordinating solvents. Other dimethylglyoxal derivatives such as the pyridylhydrazide form planar complexes with nickel(II) and copper(II) (*19*).

Sulfur-Containing Chelating Agents. Perhaps the greatest interest in square planar complexes has arisen in the area of sulfur donors and the resulting discussions concerning multiple oxidation states of nickel (*25, 63, 86, 87, 88*).

It was reasoned that the way to stabilize planar geometry was to involve the nickel atom in an extensive π system containing sulfur atoms; therefore numerous complexing agents were synthesized. The resulting complexes are very stable, and the crystal structures of several species have been determined (*28, 30, 36, 42*). A listing of some of the sulfur-containing ligands is given in Figure 6 (*41, 54*). Although Ni(II) has been the metal ion generally used in these complexes, $[Co(mnt)_2]^{-2}$ and $[Cu(mnt)_2]^{-2}$ have been prepared and are essentially planar (*36*).

By analogy to the spectrochemical series which Chatt suggested for the ligand field splitting of platinum(II) complexes, an approximate spectrochemical series for planar Ni(II) complexes was suggested by Gray (*41*): $mnt^{-2} = I^- < Br^- < Cl^- < R_2Te < dpt^- < R_2Se < dto^{-2} < R_2S < R_3As <$ piperidine $< R_3P < (RO)_3P$. Using polarography and comparing the half-wave potentials, the stability of the first row metal ions was determined with respect to different ligands (*41*). In the mnt^{-2} series Cu > Ni > Co ≫ Fe, and in the tdt^{-2} series Ni > Cu ≫ Co > Fe. Comparing the first, second, and third row transition metals with the same anion, Ni < Pd > Pt.

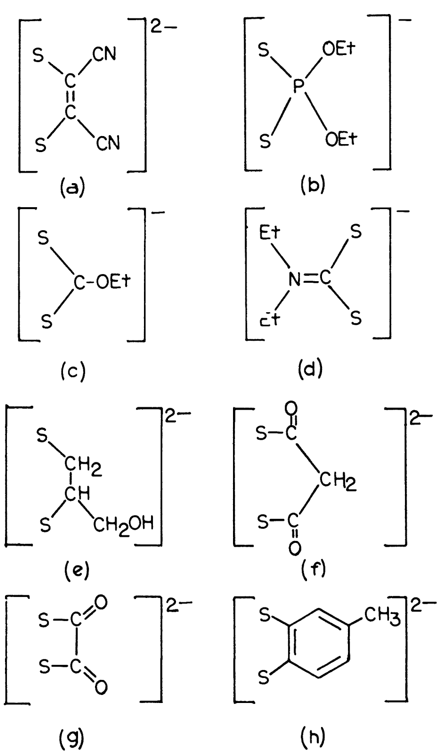


Figure 6. Sulfur-containing chelating agents which promote square planar geometry

If the cyano groups in *mnt*$^{-2}$ are replaced by phenyl groups, a nonelectrolyte, diamagnetic complex is obtained (Figure 7) (*86*, *87*). This complex can be reduced to give $[Ni(S_2C_2\Phi_2)_2]^-$ and $[Ni(S_2C_2\Phi_2)_2]^{-2}$.

The oxidation of $[Ni(mnt)_2]^{-2}$ to $[Ni(mnt)_2]^-$ to give Ni(III) complexes has been described (*25*, *63*). However, alternative formulations of these complexes as species containing nickel(II) and radicals have also been proposed (*86*, *87*, *88*, *90*). The best description of complexes of nickel, where the metal atom has a formal oxidation state different from Ni(II), is still being discussed. The extensive review of these sulfur donors and a

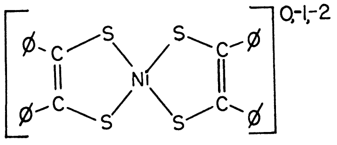


Figure 7. Planar complex having multiple oxidation states for nickel

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discussion of the electronic properties of square planar complexes should be consulted for additional data (*41*).

Complexes containing sulfur donors but which lack the extensive π system have been prepared. A cobalt complex of 2,5-dithiahexane, $[Co(CH_3S\text{-}CH_2CH_2\text{-}S\text{-}CH_3)_2](ClO_4)_2$, having a low magnetic moment, 2.46 B.M., indicates that this complex has square planar geometry (*14*). In addition, a series of complexes which are related to both the imines and sulfur donors are the *N*-alkylthiopicolinamides (*53*). The copper(II) and nickel(II) complexes have square planar geometry. Other complexes having nitrogen and sulfur donors are also reported (*34*, *90*, *98*).

Saturated Nitrogen Ligands. Square planar complexes of the first row transition metals, where there are no *p* or π electrons on the donor atom (sp^3 nitrogen), are extremely interesting. The *meso*-stilbenediamine (*meso*-stien) (Figure 8(a)) complexes of nickel(II) (Lifschitz complexes) (*60–62*) exist in two forms, a blue paramagnetic form and a yellow diamagnetic or sometimes weakly paramagnetic form. Both blue and yellow forms can be obtained containing the same anion, and in certain cases they are interconvertible.

Explanations of this behavior have been the subject of much speculation (*4*, *46*, *51*, *75*). Pauling (*75*) and Katzin (*51*) considered them to be tetrahedral (blue) and square planar (yellow) configurations. However, it appears from an examination of the electronic spectra that the blue form has octahedral coordination rather than tetrahedral. The yellow complex has but a single absorption maximum near 450 mμ. Complexes of the type Ni(*meso*-stien)$_2$(RCOO)$_2$ can be interconverted easily by gentle heating and cooling, by removing solvent or crystallization, or by dissolving in suitable organic reagents (*46*). In Ni(*meso*-stien)$_2$(Cl$_2$CHCOO)$_2$, both blue and yellow crystals can be obtained simultaneously from 95% ethanol (*46*). An x-ray study of these crystals showed that the blue crystals were indeed octahedral, and the yellow crystals contained both octahedral 6-coordinate nickel and planar 4-coordinate nickel (*69*). The absorption spectrum of this complex in aqueous acetone indicated the presence of both forms.

$$\mathrm{Ni}(\textit{meso}\text{-stien})_2(\mathrm{Cl_2CHCOO})_2 + \mathrm{H_2O} \rightleftharpoons \mathrm{Ni}(\textit{meso}\text{-stien})_2^{+2} + 2\mathrm{Cl_2CHCOO}^-$$

It was suggested that the geometric structure of the *meso*-stien complex caused the axial positions to become blocked and octahedral coordination was prevented. This was conditioned by the fact that in *d,l*-stien (Figure 8(b)), where the phenyl groups do not block the axis, square planar complexes cannot be isolated (*46*).

Utilizing the concept that appropriate carbon-substitution of ethylenediamine gives square planar complexes, Basolo (*6*) prepared a yellow dia-

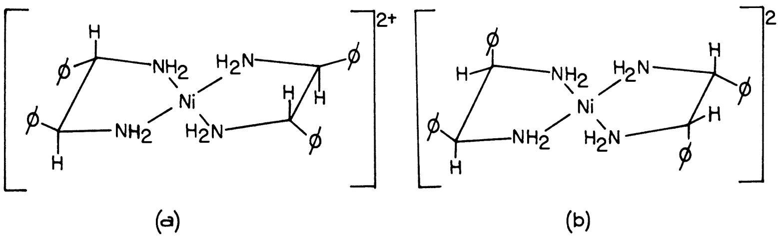

Figure 8. Lifschitz complexes

magnetic nickel(II) complex of 2,3-dimethyl-2,3-diaminobutane (C,C′-tetraMeen). This yellow color and diamagnetism persists in aqueous solution indicating that aquation of the planar species does not occur. Wilkins (*97*) determined that the rate of dissociation in aqueous acid of nickel(II) and copper(II) decreased as substitution on carbon increased. Going from methyl to ethyl substitution decreased the rate further.

Under certain conditions, ethylenediamine itself may form square planar complexes with nickel(II). Sone and Kato (*89*) reported that yellow $Ni(en)_2^{+2}$ is formed when $[Ni(en)_2(H_2O)_2]^{+2}$ is heated in alcohol. The bis-ethylenediaminenickel(II) complex, $Ni(en)_2(AgIBr)_2$, and the corresponding platinum(II) and palladium(II) derivatives are isomorphous, indicating square planar nickel in this complex (*58*). The anions may be changed to CuI_2^-, I_3^-, PbI_3^-, and HgI_4^- without destroying the planarity of nickel. Cobalt(II) and copper(II) also form square planar complexes of this type. These square planar species appear to be stable only in the solid state for they decompose when dissolved in water (*58*).

A tridentate ligand, 1,1,7,7-tetraethyldiethylenetriamine (Et_4dien), forms square planar complexes with nickel(II) (*26*). The $Ni(Et_4dien)Cl_2$ complex is diamagnetic in the solid state and in ethanol solution but exhibits some paramagnetism in acetonitrile, DMF, and acetone. In these latter solvents a pentacoordinate species is postulated (*26*).

The tetradentate ligand, 1,4,8,11-tetraazacyclotetradecane (cyclam), forms solid diamagnetic orange to brown Ni(II) complexes with iodide and perchlorate anions (*9*). When the anions are changed to chloride and bromide, the solid complexes are paramagnetic (*9*). However, all the complexes are soluble in water, methanol, and benzene, giving yellow solutions. The yellow color remains on treatment with 12*N* HCl and excess chloride ion (*9*). It is interesting to note that this amine is a derivative of a reduction product of the "template syntheses" between bis(ethylenediamine)-nickel(II) and acetone reported earlier.

Using the knowledge that sterically blocking the axial positions in square planar systems effectively prevents an octahedral configuration from forming, nickel(II) and copper(II) complexes of a secondary medium-ring diamine, 1,5-diazacyclooctane (daco), were synthesized (Figure 9) (*67*).

In the most stable configuration the axial positions are blocked by

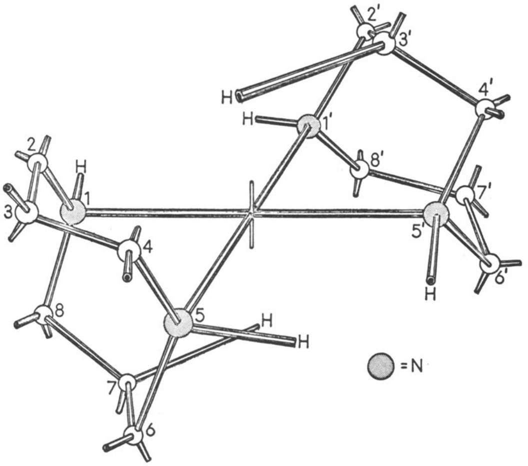

Figure 9. Idealized conformation for bis-1,5-diazacyclooctane complexes

the hydrocarbon system. The diamagnetic nickel(II) complex is yellow in the solid state and also in water, acetonitrile, and other solvents. No 1:1 nickel(II) amine complex can be detected spectrophotometrically. This behavior is similar to the [Ni(C,C′-tetraMeen)]$^{+2}$ reported by Basolo (*6*). The bis-daco complex can be heated with concentrated HCl or treated with excess EDTA with very slow decomposition. The bis-daco copper(II) complex is maroon in color, and its aqueous solution exhibits a single visible absorption maximum much higher in energy than other bis-diamine copper(II) complexes. The stability constant of the nickel(II) complex is higher than other bis-diamine complexes. We feel that this ligand may be a prototype for another series of square planar complexes with the first row transition metal ions.

This discussion has only presented an outline of the chelating agents which produce planar complexes. Extensive additional data on each topic can be obtained from the key references in the bibliography. Unfortunately, a number of chelating agents have been omitted from this presentation, but most of these are similar to those reported. Hopefully, this compilation has united the variety of ligands which have been used to form planar complexes of the first row transition metals.

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32

The History and Development of Organotransition Metal Chemistry

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Organotransition metal compounds have been known for over a century, but it has been only during the past 15 years that most of the major advances in this area have been made. Organotransition metal compounds consist of organic molecules or ligands coordinated to transition metals by one or more carbon atoms. In the present survey, the formation, properties, structure, and reactions of various classes of these substances are discussed. Emphasis has been placed on important discoveries and theories that have stimulated the rapid progress of organotransition metal chemistry. Pertinent reviews on various aspects of this subject have also been cited.

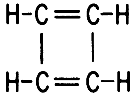
Organometallic compounds containing neutral, unsaturated organic molecules coordinated to certain transition metals were known long before the advent of Werner's theories on coordination compounds. Until about 1950, however, this aspect of coordination chemistry remained fallow, and the structure and bonding of the compounds known at that time were quite perplexing. The discovery of ferrocene and the development of a rational theory of bonding in olefin-transition metal complexes in the early 1950's prompted a vigorous research effort around the world that has attracted the attention of organic chemists, inorganic chemists, crystallographers, and scientists of many allied disciplines. Research in organotransition metal chemistry presently is proceeding at a very rapid rate, and the synthesis and properties of seemingly unlimited new types of "organometallic, π complexes" represent an important frontier in coordination chemistry.

The purpose of the present survey is twofold. Firstly, because the Werner Symposium is partly historical, some of the more important discoveries and theories that have led to the present high level of interest in organotransition metal chemistry are discussed. Some illustrative examples of synthetic methods and reactions of various types of organotransition metal compounds are also included. Secondly, reference is made to recent comprehensive reviews where the reader can learn more about various aspects of organotransition metal chemistry if he desires. This survey has therefore been prepared primarily for those persons who have little knowledge of this rather new branch of chemistry and who might like to learn more about it.

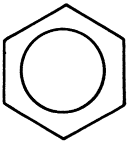
It is difficult to systematize organotransition metal compounds because almost every week another "nonclassical" compound of this type seems to be reported. Nevertheless, one approach based on the coordination chemistry of these substances is to consider each organic molecule or radical as a ligand which is bonded to the transition metal via *n* carbon atoms. In other words, a singly occupied orbital from each carbon atom of the organic molecule or radical is involved in bonding with the metal, and the resulting organic ligand may be considered to be an *n* electron donor. Except in a few instances, such as certain organometallic carbonium ions discussed below, each organic ligand should be considered as electrically neutral. Some examples of this generalization are as follows:

$CH_3CH=CHCH_3$

BUTENE (A MONO-OLEFIN; n=2)



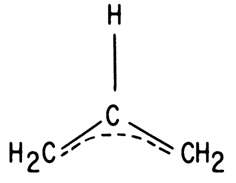
CYCLOBUTADIENE (A DIENE; n=4)



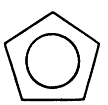
BENZENE (AN ARENE; n=6)

There is no reason, however, why an organic ligand must have an even number of carbon atoms involved in coordination with a transition metal. Organotransition metal compounds in which an orbital of a single carbon atom overlaps with an appropriate metal orbital are closely related to the well-known localized covalent or σ-bonded compounds in organic chemistry and represent a case where $n = 1$. Various other organotransition metal compounds are now known in which the organic ligand consists of three, five, or seven carbon atoms bonded to the transition metal. Compounds of this sort in which odd numbers of electrons can be considered to be formally donated to a metal are often referred to as "en-yl" derivatives. Typical organic ligands of this type are shown on the next page. Such ligands are best prefixed by the Greek letter "π" to clearly differentiate them from σ-bonded ($n = 1$) ligands.

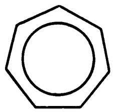
Carbon monoxide is an organic molecule that deserves special mention in any discussion of organotransition metal chemistry, because many organic derivatives of the transition metals are derived from metal carbonyls



π-ALLYL (n = 3)



π-CYCLOPENTADIENYL (n = 5)



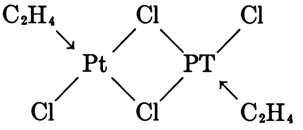
π-CYCLOHEPTATRIENYL (n = 7)

and frequently contain carbon monoxide as a ligand. It was Werner who first suggested that carbonyl groups in metal carbonyls are attached directly to the metal atom rather than in chains. In the 1920's, Sidgwick (*223*) formulated the very useful Effective Atomic Number (EAN) Rule. As applied to transition metals, this generalization simply postulates that these metals undergo chemical transformations by transferring or sharing electrons with ligands so that they can achieve a closed-shell configuration of the next higher inert gas in the periodic system. Using this scheme, carbon monoxide in metal carbonyls is best considered to be a two-electron donor.

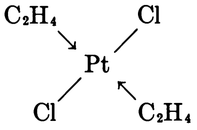
By means of the previously mentioned system of "electron-bookkeeping" for organic ligands, together with the Sidgwick EAN Rule, a large portion of experimental data on organotransition metal chemistry and metal carbonyl chemistry can be systematized. It must always be remembered, of course, that any methods of systematization are only useful formalisms and may not account for each and every new compound discovered. The factors that relate to bonding and structure in organotransition metal compounds are considerably involved, as is evidenced by recent theoretical treatments on the subject. In the present survey, a classification of organotransition metal chemistry on the basis of organic ligands will be followed.

Mono-olefin Complexes (*n* = *2*)

Organotransition metal chemistry had its beginning in 1827 when a Danish pharmacist named Zeise found that when platinum(IV) chloride was boiled in ethyl alcohol and potassium chloride subsequently added, a new compound having the composition $KCl \cdot PtCl_2 \cdot C_2H_4 \cdot H_2O$ could be isolated (*259*, *260*). The analysis of this compound, which is now formulated as $K[(C_2H_4)PtCl_3] \cdot H_2O$ (Zeise's salt), was soon challenged by Liebig, and the analytical composition of this substance became the center of considerable controversy (*158*, *159*, *258*, *261*). In 1869 Birnbaum (*14*) confirmed that ethylene exists in Zeise's salt when he synthesized this compound by treating platinum(II) chloride in hydrochloric acid solution with ethylene, followed by the addition of potassium chloride. Since these early findings, a variety of other nonionic ethylene-platinum complexes such as I and II have been prepared (*6*, *29*).



I



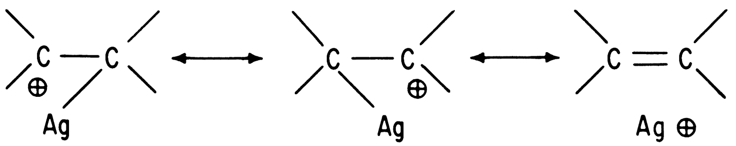
II

In 1938 Kharasch and co-workers described a method generally applicable for preparing mono-olefin palladium complexes (*147*). Palladium(II) chloride reacted with warm benzonitrile to form the complex bis(benzonitrile)-palladium chloride, and the latter reacted directly with olefins such as ethylene, styrene, cyclohexene, etc., as follows:

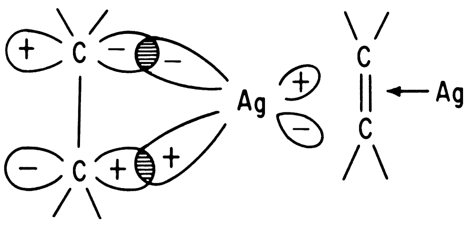
$$2\ (C_6H_5CN)_2PdCl_2 + 2\ \text{Olefin} \rightarrow [(\text{Olefin})PdCl_2]_2 + 2\ C_6H_5CN$$

This method was later extended to dienes and represents an early example of an important synthetic route in organotransition metal chemistry wherein one neutral ligand displaces another from the coordination sphere of a transition metal.

A major advance in theoretical aspects of organotransition metal chemistry came in 1951–1953 and has since become known as the Dewar-Chatt concept of bonding in olefin-metal compounds. Winstein and Lucas (*254*) had attempted earlier to explain the nature of the bonding in olefin-silver complexes on the basis of resonance stabilization:

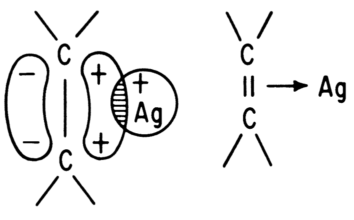


On the basis of molecular orbital theory, Dewar (*64*) divided the metal-olefin bond into a σ portion and a π portion. The former type of bond can result from a filled bonding olefin π orbital overlapped with a vacant *5s* orbital of silver (III), while the latter type of bond can result from a filled



π - TYPE BOND

III

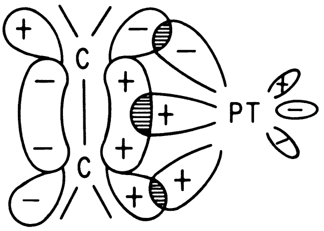


σ - TYPE BOND

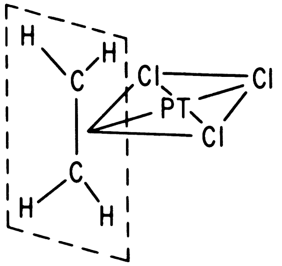
IV

silver *4d* orbital overlapped with the vacant π^* orbital (antibonding) of the olefin (IV).

Chatt and Duncanson extended this concept to platinum-olefin complexes such as Zeise's salt (*29*). In platinum-olefin complexes, the σ-type bond results from a filled π orbital of the olefin overlapped with a vacant $5d6s6p^2$ orbital of platinum, while the π-type bond results from a filled $5d6p$ orbital of platinum overlapped with the antibonding olefin π^* orbital (V).



V

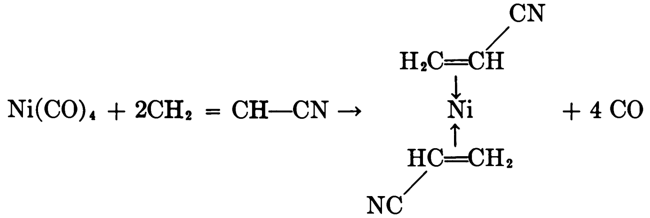


VI

This multiple, covalent bonding has often been referred to as "synergic," because π bonding tends to remove excess negative charge placed upon the metal by σ bonding, and *vice-versa.* Thus, one type of bonding can be regarded as reinforcing the other type, and such a process accounts for the unusual stabilities of these substances.

Chatt and Duncanson (*29*) proposed further a spatial arrangement of the atoms in the anion $[(C_2H_4)PtCl_3]^-$, as shown in Structure VI. The carbon atoms forming the double bond in the olefin are regarded as being perpendicular to the plane formed by the metal atom and the other ligands. Subsequent x-ray crystallographic studies on Zeise's salt and related olefin-metal complexes have confirmed these earlier postulations (*4, 63, 132, 256, 257*).

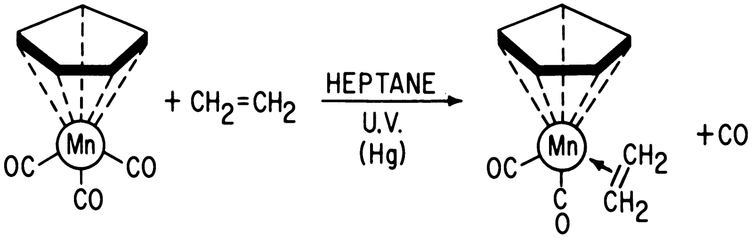
Until about 1957, only metals toward the end of the transition series, such as Pd, Pt, Cu, Ag, and Hg, were known to form mono-olefin complexes. In 1959 Schrauzer (*219, 220*) prepared the first olefin complex of nickel, starting with nickel carbonyl and acrylonitrile:



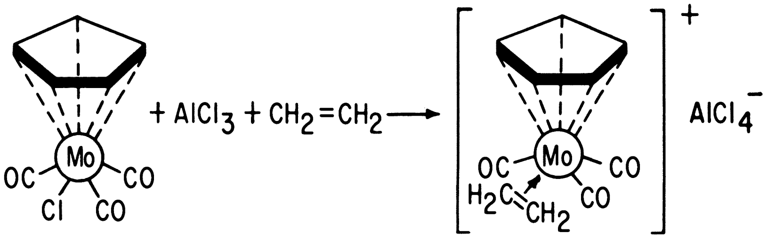
$$Ni(CO)_4 + 2CH_2 = CH\text{—}CN \rightarrow \begin{array}{c} CN \\ / \\ H_2C{=}CH \\ \downarrow \\ Ni \\ \uparrow \\ HC{=}CH_2 \\ / \\ NC \end{array} + 4\,CO$$

Spectral data indicate that ligand-metal bonding results primarily between the metal and the carbon-carbon double bond, and that the nitrile group interacts little if at all with the metal. Since 1959, many other complexes involving mono-olefins that contain electronegative groups have been described. Presumably, such a group being present significantly lowers the energy level of the olefin π^* orbital, and thus back donation from the metal is facilitated.

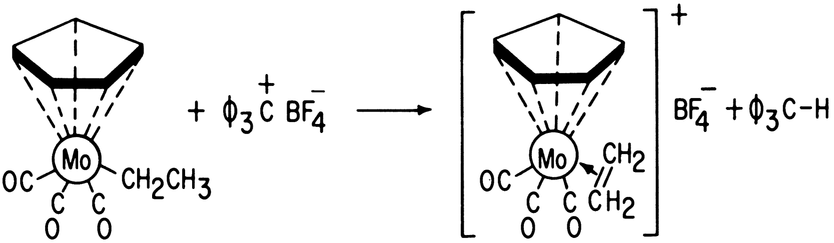
Ethylene complexes of transition metals near the beginning of the transition series are now known. A neutral complex was prepared in 1960 by the photochemical displacement of carbon monoxide by ethylene from cyclopentadienyl-manganese tricarbonyl (*156*):



Using a somewhat different approach, Fischer and Fichtel (*85*) have obtained a variety of ethylene-containing cationic complexes by reaction of π-cyclopentadienyl carbonyl halides of Mo, W, and Fe with ethylene under pressure in the presence of aluminum chloride. The cations were isolated in the form of their salts with heavy anions such as PF_6^-, $B(C_6H_5)_4^-$, etc. Presumably the aluminum chloride serves as a halogen acceptor and "activates" a coordination site on the metal, facilitating coordination of ethylene.



In related studies, Green and co-workers (*55*, *108*) prepared similar π-ethylene-containing cationic complexes directly from σ-ethyl derivatives by hydride abstraction techniques:



The latter complex can be converted to the former by adding hydride ion from sodium borohydride.

For the reader desiring more information on mono-olefin complexes of the transition metals, a number of excellent reviews are available. Early studies on olefin-metal complexes (primarily of Pt, Pd, Ag, and Hg) have been reviewed by Keller (*146*), Chatt (*27*), and Douglas (*70*). Two more recent reviews which comprehensively cover the literature up to 1961 have been prepared by Guy and Shaw (*113*) and by Bennett (*11*).

Carbonyl Complexes (*n* = *2*)

As mentioned earlier, the rapid development of organotransition metal chemistry has been paralleled by and intimately connected with the development of metal carbonyl chemistry. The discoveries of new metal carbonyls and the advances in understanding of the structures and bonding of these substances have been so profuse that they would require a special survey.

Historically, however, it should be mentioned that Mond and coworkers (*175*) found as early as 1890 that nickel valves were corroded by hot gases containing carbon monoxide. Subsequent investigations showed that a stream of this gas passed over finely divided nickel yielded a colorless (and highly poisonous!) liquid having the formula $Ni(CO)_4$.

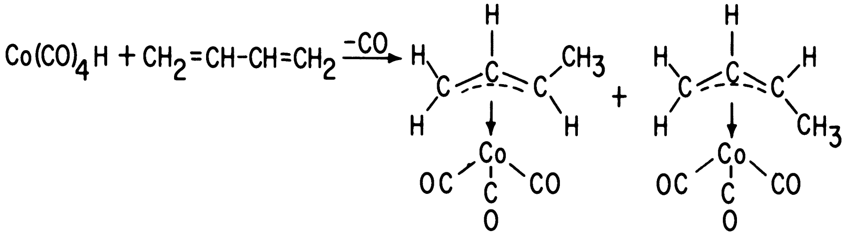
$$Ni + 4\,CO \rightarrow Ni(CO)_4$$

This discovery was soon followed by isolation of a series of iron carbonyls with compositions $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$.

Since these important findings near the end of the last century, metal carbonyls of a majority of the transition metals have been isolated and characterized. Many of these compounds are "pure" metal carbonyls, containing only the metal and CO. Many other types are also known, including metal carbonyl-halides, -hydrides, -anions, -π-cyclopentadienyls, etc. A number of earlier reviews dealing primarily with metal carbonyls has been published (*169*, *197*). Fortunately, there are also two recent reviews on the subject by Abel (*1*) and Hileman (*130*). A useful, recent review by King concerns the formation and reactions of metal carbonyl anions (*148*).

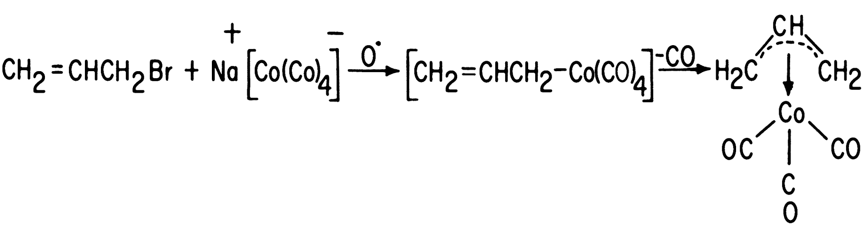
π-*Allyl* (*n* = *3*) *and Related Complexes*

Allyl derivatives of the transition metals can be classified as σ-allyl or π-allyl. In the former, the allyl ligand contributes one electron ($n = 1$) to the allyl-metal bond, while in the latter the allyl ligand may be regarded as contributing three electrons ($n = 3$) to the allyl-metal bond. Probably the first transition metal complex containing a π-allyl ligand was described by Pritchard (*198*) in 1952, although the composition and structure of the product were not known precisely. The substance was reformulated as



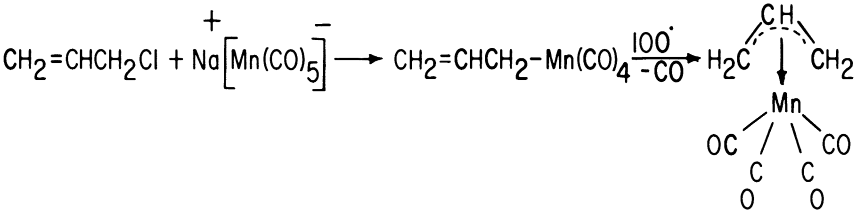
$C_4H_7Co(CO)_3$ in 1958 by Jonassen and co-workers (*142*). Subsequent detailed investigations (*5, 174, 176*) have shown that two isomers are in fact formed, and the formulation of each as π-allyl-cobalt complexes followed from considering their proton NMR spectra shown above.

In 1960 several groups of workers developed a route to the parent complex, π-allylcobalt tricarbonyl (VII) (*122, 123, 170*) and also to π-allylmanganese tetracarbonyl (VIII) (*143, 170*). These syntheses were based on reactions of appropriate metal carbonyl anions with allyl halides as shown below.



VII

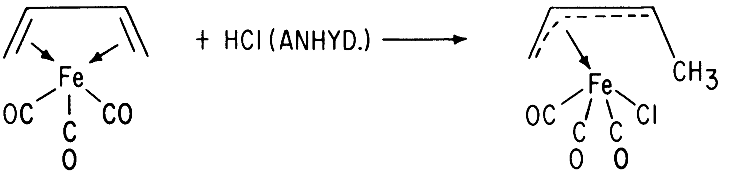
In the latter reaction, the initially-formed σ-allylmanganese pentacarbonyl can actually be isolated and identified. σ-Allylcobalt tetracarbonyl, on the



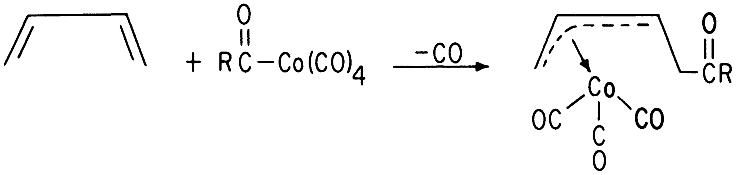
VIII

other hand, is thermally unstable even at room temperature and readily loses carbon monoxide to form the π-allyl complex (VII).

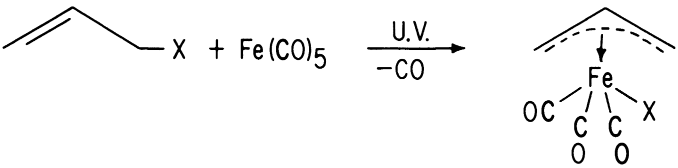
A wide variety of other routes has been developed for preparing π-allyl-transition metal compounds, and some representative examples are given below:



(*78, 139*)



(*117, 118*)

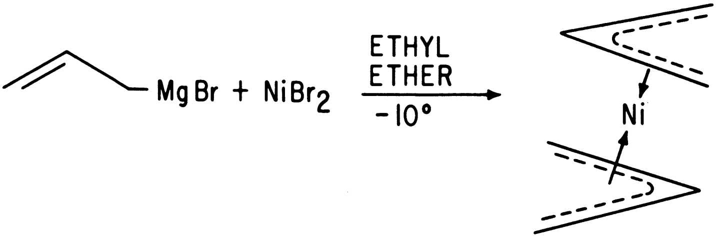


(*119, 181*)

$$CH_2{=}CHCH_2Br + Ni \longrightarrow [(\pi\text{-}C_3H_5)NiBr]_2$$ (*83, 84*)

$$CH_2{=}CHCH_2X + PdCl_2 \xrightarrow{50\%\ HOAc} [(\pi\text{-}C_3H_5)PdCl]_2$$ (*137, 138*)

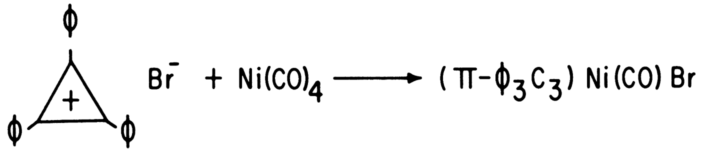
X = Br, Cl, OH



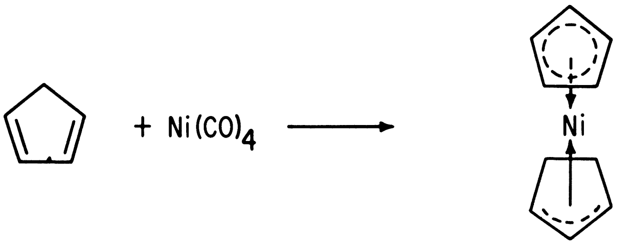
(248)

The proton NMR spectra of many of these π-allyl-metal complexes are similar and exhibit three resonances with intensities in a 2:2:1 ratio. The two methylene peaks are equivalent, but the two hydrogen atoms on each methylene group are magnetically nonequivalent—two being nearer to the metal atom and two away from it. Several x-ray studies on dimeric π-allylpalladium chloride confirm the structures proposed on the basis of NMR and infrared spectra (*157*, *188*, *189*, *218*, *218*, *227*).

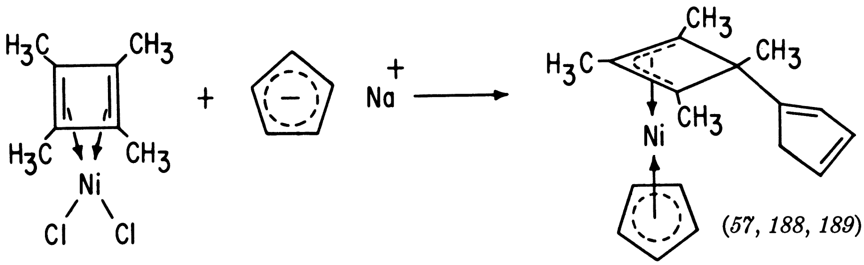
The topic of π-allyl-transition metal chemistry is considerably broader than complexes involving the π-C_3H_5 ligand itself. A variety of complexes is now known in which the π-allyl radical is part of a carbocyclic ring system. Some examples of π-cyclopropenyl-, π-cyclobutenyl-, and π-cyclopentenyl- transition metal complexes are presented below.



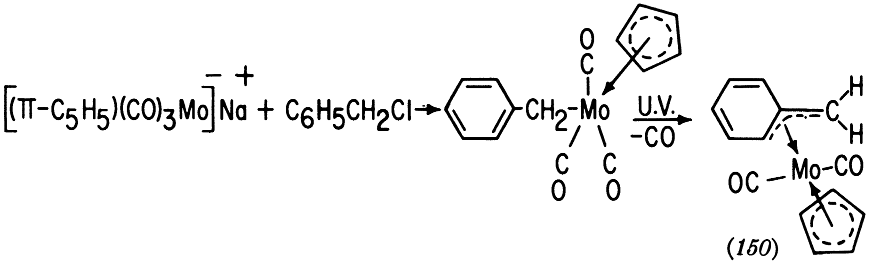
(106)



(101)



(*57*, *188*, *189*)

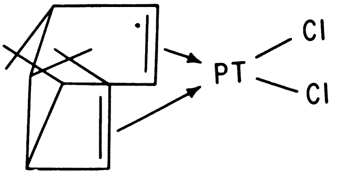


(*150*)

Although the area of π-allyl-transition metal chemistry is only eight years old, a number of recent reviews is available on the subject. The two most recent reviews have been prepared by Green and Nagy (*107*) and by Fischer and Werner (*100*). Earlier reviews by Guy and Shaw (*113*) and by Bennett (*11*) are also available. Most of the research on "pure" allyl-transition metal complexes—e.g., those with no ligands other than allyl groups bonded to the metal, have been conducted in the laboratory of Wilke and co-workers. A recent, excellent review of their work has been published (*249*).

Diene (n = 4) and Related Complexes

Organometallic, π complexes containing dienes as ligands coordinated to transition metals have been known since early in this century, although it has only been within the past 10 years that most of these complexes have been obtained and the nature of their bonding understood. As early as 1908, Hofmann and von Narbutt (*131*) studied the reaction between potassium platinum chloride and dicyclopentadiene in propyl alcohol solution and isolated a crystalline product having the composition $C_{10}H_{12}PtCl_2$. It was only in 1956, however, that Doyle and Jonassen (*71*) recognized this compound to be a diene-platinum complex. The structure they proposed (IX) was subsequently confirmed by x-ray crystallographic investigations (*7*).

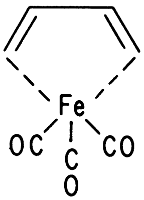


IX

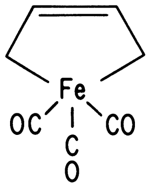
Another early discovery relating to diene-metal complexes was described by Reihlen and co-workers in 1930 (*210*). These workers treated iron pentacarbonyl with butadiene in a sealed tube and obtained an air-stable, yellow, diamagnetic liquid having the composition $C_4H_6Fe(CO)_3$. They presumed this product to have a heterocyclic structure, such as X or XI. In 1958 Hallam and Pauson (*115*) confirmed the earlier findings of Reihlen *et al.* but stated that the chemical and physical properties of the product were untenable with the structures originally proposed. Hallam and Pauson suggested Structure XII for $C_4H_6Fe(CO)_3$, in which extensive electron delocalization occurs in the butadiene ligand. The ligand is regarded as having a planar, *cissoid* configuration and being symmetrically located in a plane above the iron atom and the carbonyl groups.

An essentially equivalent way of representing $C_4H_6Fe(CO)_3$ is shown in Structure XIII (*192*), although such a formulation could be interpreted to infer more "double bond, single bond character" in preference to delocalization. While the four carbon atoms of butadiene largely retain their sp^2 state of hybridization in structures such as XII and XIII, another possible structure (XIV) has been considered (*109*), in which the terminal carbon atoms of the ligand are essentially sp^3 hybridized, and the finer olefinic carbon atoms are coordinated to the iron atom as in an olefin-metal complex. Although x-ray crystallographic studies (*171*, *172*) seem to support the formulation of Hallam and Pauson, a controversy regarding the precise nature of the bonding in diene-metal complexes nevertheless continues (*112*).

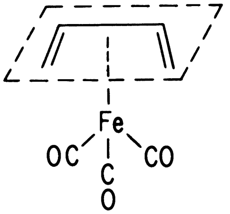
Another notable advance in diene-metal chemistry was made by Chatt and co-workers in 1957 (*36*, *37*, *38*), and somewhat later by Pettit (*190*) and by Wilkinson *et al.* (*23*, *110*). These groups of investigators established



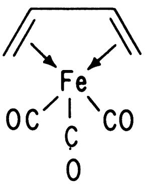
X



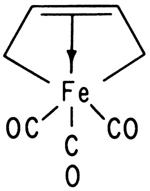
XI



XII

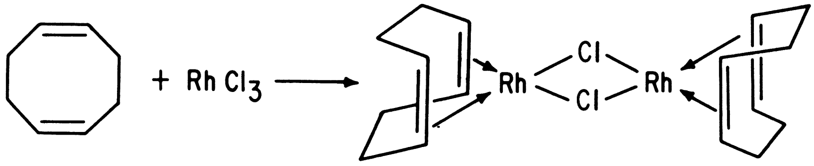


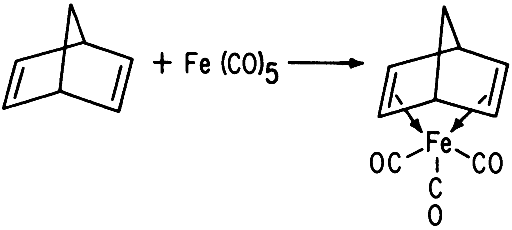
XIII

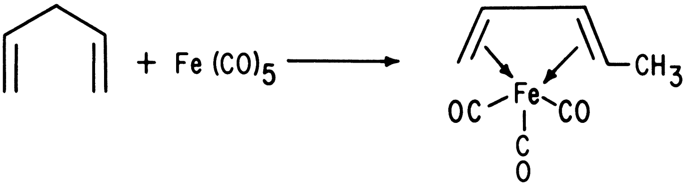


XIV

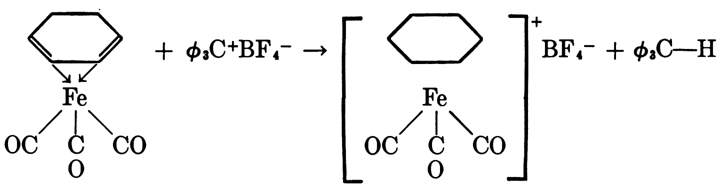
that nonconjugated dienes form π complexes with various transition metals, providing that the two double bonds are properly oriented in space so that they can bond with the metal. Nevertheless, nonconjugated dienes occasionally rearrange to form conjugated diene-metal complexes during the course of reaction (*77*, *151*). Some typical diene-metal syntheses reported by the above groups of investigators are outlined below:





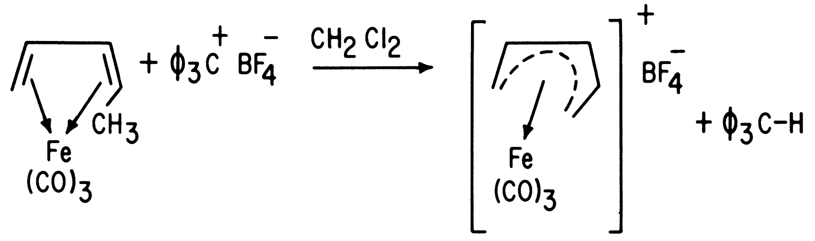


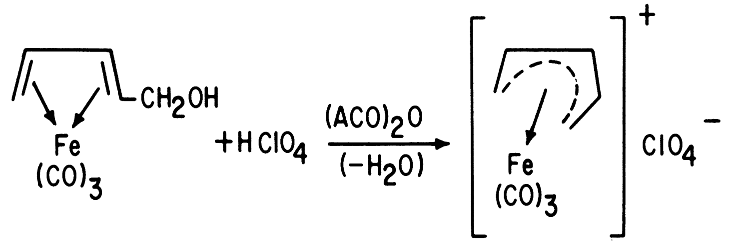
Dienes are generally much less reactive when coordinated to transition metals than when in an uncoordinated state. An important discovery was thus made by Fischer and Fischer (*86*) in 1960 when they found that cyclohexadiene-iron tricarbonyl (XV) (formed from 1,3-cyclohexadiene and iron pentacarbonyl) undergoes hydride ion abstraction by triphenylmethyl tetrafluoroborate to form π-cyclohexadienyl-iron tricarbonyl tetrafluoroborate (XVI):



XV XVI

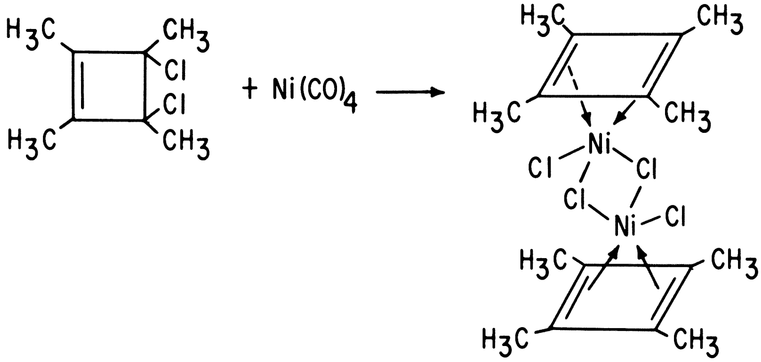
The resulting complex salt is so stable that it can be recrystallized from water. In this system, five sp^2 hybridized carbon atoms are necessarily held in a *cissoid* configuration. More recently, Pettit and co-workers (*192, 193, 194*) have studied acyclic systems of this type and have found that there is a strong driving force for a *cissoid* configuration of the resulting π-pentadienyl-iron tricarbonyl complexes.

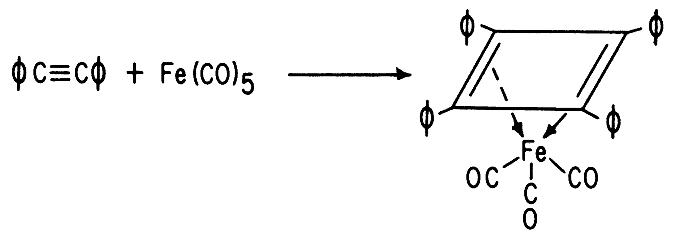




Using the "electron-bookkeeping" method described earlier, such products may be considered as complexes of π-cyclohexadienyl radicals, in which the ligand formally supplies five π-electrons to the iron, which has a formal positive charge. An alternative method is to consider such complexes as derivatives of the corresponding carbonium ions, which now are made exceedingly more stable by virtue of coordination with the metal. In such a scheme, the ligand can be considered to possess a positive charge and is formally a four π-electron donor, while the metal atom can be considered electrically neutral. Obviously, neither method entirely explains the properties of π-pentadienyl-metal complexes. The latter scheme is probably the preferred one at present, based on the reactions of these complexes. It is, however, clear that the metal can share the positive charge as well. Such conjecture points out that in these cases, as well as the uncertainties in the bonding in diene-metal complexes, experimental findings run considerably ahead of theory in organotransition metal chemistry!

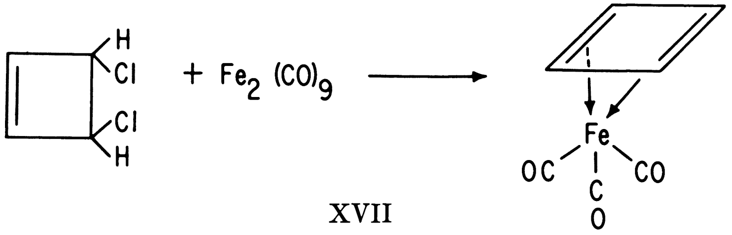
There is at least one important instance in organotransition metal chemistry, however, where a theoretical "prediction" preceded experimental discoveries. In 1956 Longuet-Higgins and Orgel (*161*) predicted from molecular orbital considerations that the long-sought and "unstable" molecule cyclobutadiene might well be isolable and stable in the form of an organometallic π-complex with transition metals such as Ni, Pd, etc. Almost concurrently in 1959, Criegee and Schröder (*56*, *58*), as well as Hübel and co-workers (*135*, *136*), reported the isolation of tetrasubstituted cyclobutadiene-metal complexes by two entirely different routes as shown below.





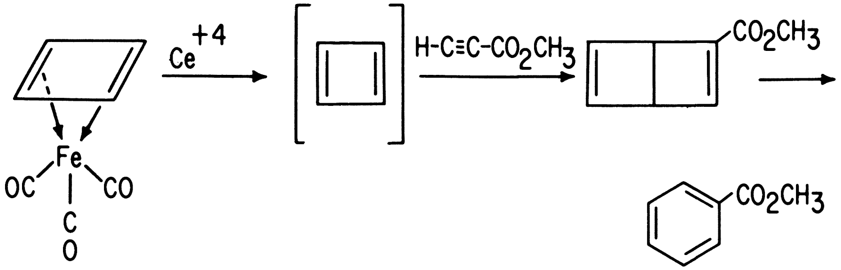
The structures of both complexes were subsequently confirmed by x-ray analyses (*68*, *69*, *72*, *73*) which showed that the cyclobutadiene ligand was square planar in each complex, with the metal atom located symmetrically below the ring.

The area of cyclobutadiene-transition metal chemistry has expanded rapidly since these initial findings, largely through the work of Maitlis (*163*), Nakamura (*183*), Freedman (*104*), and others, but details will not be presented here. Several recent important discoveries by Pettit and co-workers (*22*, *79*, *102*, *241*), however, relate to the formation and chemistry of cyclobutadiene-iron tricarbonyl (XVII). This product is formed from the reaction of *cis*-3,4-dichlorocyclobutene and diiron nonacarbonyl and can be isolated in the form of yellow crystals of excellent stability. Cyclobutadiene can be liberated by treating the complex with oxidizing agents such as ferric or ceric ion. The free ligand has been trapped and demonstrated to possess a finite lifetime. It has also been shown to

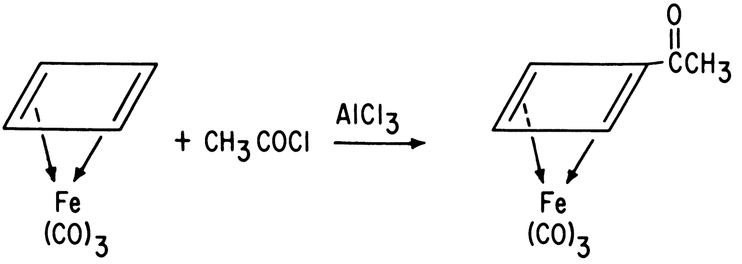


XVII

undergo a variety of novel reactions leading, for example, to Dewar benzene derivatives.

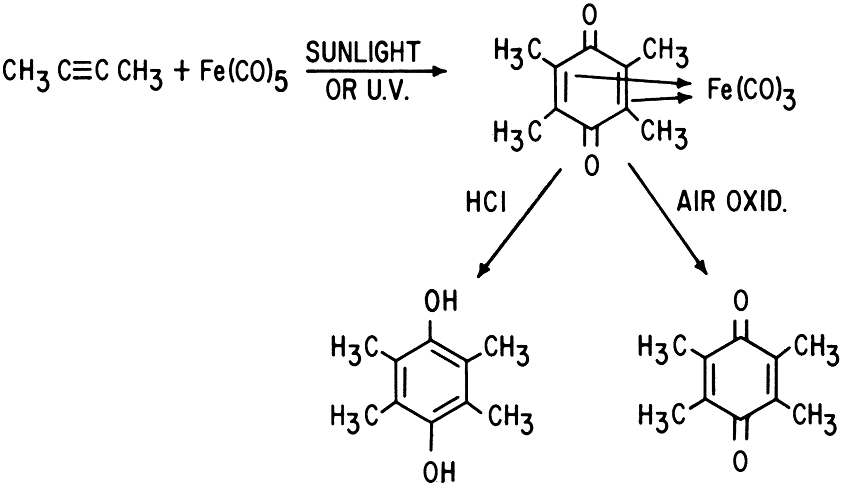


Cyclobutadiene-iron tricarbonyl itself is unique in that it undergoes many "aromatic-type" ring substitution reactions, such as Friedel-Crafts acylation.



The reactions of acetylenes with metal carbonyls can be briefly mentioned at this point. Although a number of acetylene-transition metal complexes is known, in the vast majority of reactions involving metal carbonyls and acetylenes, the latter are converted into other ligands (often dienes) which in turn undergo complex formation. Reactions of this sort also often lead to new uncoordinated organic compounds and have been of distinct importance in organic synthesis.

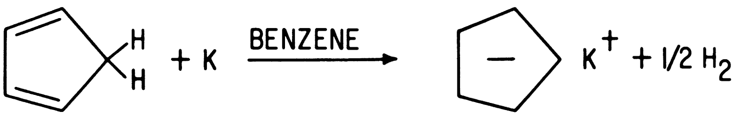
Historically, reactions of metal carbonyls and acetylenes were first studied extensively by Reppe and co-workers during the period of World War II. In the 1950's, several groups of investigators extended the earlier work (*212*) of Reppe, often with surprising results. For example, in the reaction between diphenylacetylene and iron carbonyls referred to previously, Hübel and co-workers (*135, 136*) isolated at least five other organometallic π-complexes, hexaphenylbenzene, and tetracyclone, in addition to tetraphenylcyclobutadiene-iron tricarbonyl. Another early observation of this nature was reported by Sternberg and Wender (*228*).



The recent excellent monograph by Fischer and Werner (*100*) contains a comprehensive coverage of diene-metal complexes up to 1965. Earlier reviews on this topic were published in 1962–1963 by Bennett (*11*), Guy and Shaw (*113*), Cais (*24*), and Fischer and Werner (*99*). Reviews dealing specifically with the chemistry of diene-iron carbonyl complexes have recently been prepared by Pettit *et al.* (*191, 192*).

π-Cyclopentadienyl (n = 5) and Related Complexes

The cyclopentadienyl group is probably the most versatile of all the ligands in organotransition metal chemistry. Cyclopentadienyl-metal chemistry has its origin in 1901 when Thiele (*232*) discovered that the unsaturated hydrocarbon cyclopentadiene, when treated with potassium metal in benzene, liberated hydrogen and was converted to a potassium salt (XVIII).



XVIII

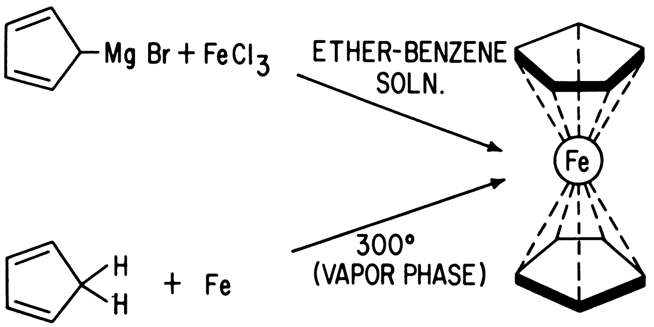
Several years later, Grignard and Courtot (*111*) found that cyclopentadiene reacted with ethylmagnesium bromide, liberated ethane, and formed a new Grignard reagent, cyclopentadienylmagnesium bromide.

$$C_5H_6 + C_2H_5MgBr \xrightarrow{\text{ether-benzene}} C_5H_5MgBr + C_2H_6$$

Reactions of this type were subsequently extended to indene and fluorene —another pair of "acidic" hydrocarbons.

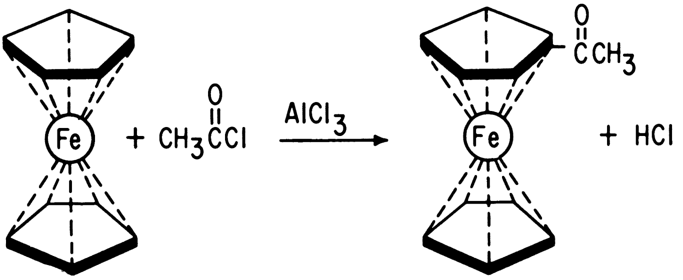
The literature seems well-documented with many attempts during the period 1900–1950 to prepare organotransition metal compounds from Grignard reagents (usually methyl, phenyl, etc. derivatives) reacting with transition metal halides. In retrospect, one can assume that cyclopentadienyl Grignard reagents or alkali metal derivatives were not included in these investigations, else the extensive developments that occurred in organotransition metal chemistry in the early 1950's might well have resulted many years before!

Clearly, two of the most important discoveries relating to organotransition metal chemistry were described in 1951–52. Kealy and Pauson (*144*) were attempting to "couple" cyclopentadienylmagnesium bromide by means of ferric chloride during the course of research directed toward isolating the hydrocarbon fulvalene. Work-up of the reaction instead produced a remarkably stable, orange, organo-iron compound of composition $C_{10}H_{10}Fe$. This same substance was almost simultaneously described by Miller, Tebboth, and Tremaine (*173*) who isolated it from a vapor phase reaction of cyclopentadiene and iron at elevated temperatures. Actually, the discovery was apparently known as early as 1948, but was not reported until 1952 since it was only incidental to other work.



XIX

The unique "sandwich" structure soon proposed for this new compound (XIX), bis(cyclopentadienyl)iron, was subsequently fully confirmed by x-ray analysis (*74*, *75*). The nature of the bonding between the cyclopentadienyl rings and the iron atom in this compound has been considerably disputed in recent years, and detailed arguments are contained in reviews referred to at the end of this section. A subsequent important discovery by Woodward, Rosenblum, and Whiting (*255*) in 1952 indicated that this compound would undergo Friedel-Crafts substitution reactions. This result, together with the remarkable stability and spectral properties of

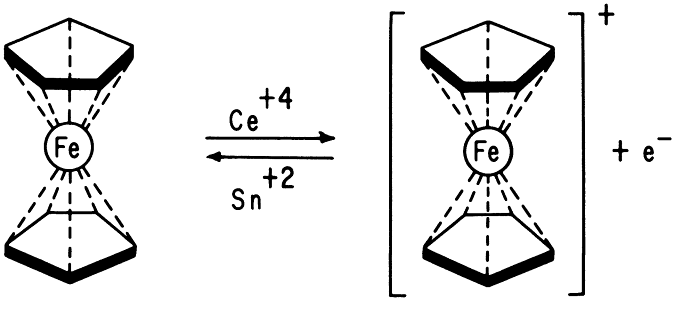


bis(cyclopentadienyl)iron, suggested that the compound represented a new type of aromatic system; hence, the name "ferrocene" was coined.

It was soon noted that iron was by no means unique in forming π-cyclopentadienyl derivatives, and research groups in several countries set out to determine the nature and scope of cyclopentadienyl-metal chemistry. At the present time, practically all the metals of the short transition series, as well as nearly all the metals and metalloids of the main group series, form one or more cyclopentadienyl compounds. In addition, cyclopentadienyl derivatives of over one-half the lanthanides have now been described, and even cyclopentadienyl derivatives of U, Th, and several *trans*-uranium elements are known. The present status of cyclopentadienyl-metal chemistry is illustrated in part in Figure 1. Elements designated by shaded areas are known to form one or more cyclopentadienyl derivatives.

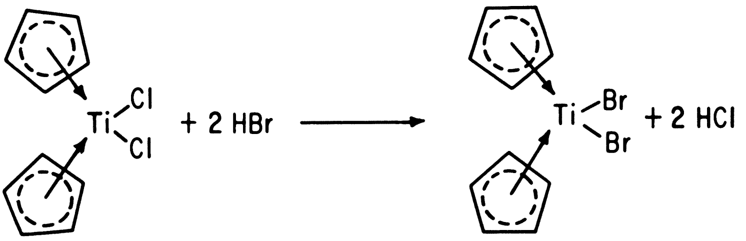
Metal-cyclopentadienyl compounds of the ferrocene-type (e.g., the metallocenes) undergo essentially four different types of chemical reactions, and a typical example of each of these is illustrated below:

Oxidation-Reduction



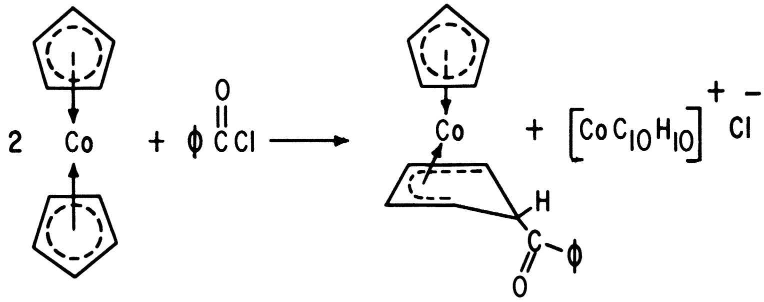
(*246*)

Ligand Replacement



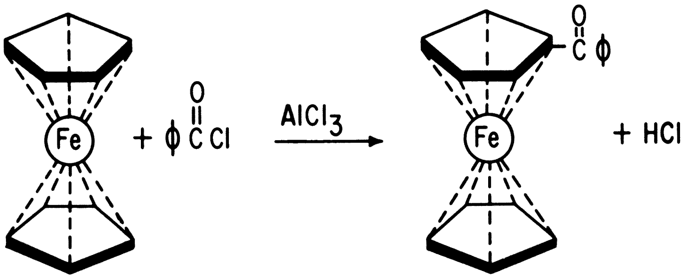
(*244*)

Ring Addition



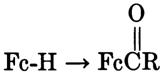
(*92*)

Ring Substitution



(*208*)

Reactions of the ring-substitution type have especially been studied in great detail. Ferrocene, for example, is known to undergo the following ring-substitution reactions (Fc = the ferrocenyl group):

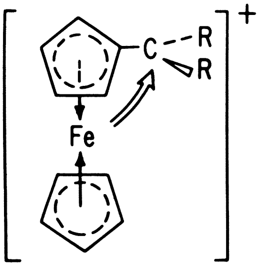
Friedel-Crafts acylation	 $\text{Fc-H} \rightarrow \text{Fc}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R}$
Friedel-Crafts alkylation	Fc-H → Fc-R
Mercuration	Fc-H → Fc-HgX
Vilsmeier formylation	Fc-H → Fc-CHO
Sulfonation	$\text{Fc-H} \rightarrow \text{Fc-SO}_3\text{H}$

Aminomethylation	Fc-H → Fc-$CH_2N(CH_3)_2$
Metalation	Fc-H → Fc-M
Arylation	Fc-H → Fc-Ar

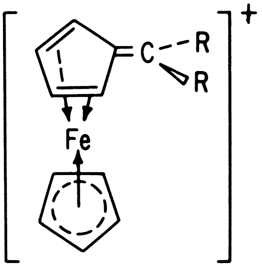
These reactions and their extensions have greatly broadened the scope of metallocene chemistry, especially since various other metallocenes also undergo certain of the above ring substitution reactions. A striking example concerns the relative ease of substitution reactions of the iron group metallocenes, namely, ferrocene, ruthenocene ($RuC_{10}H_{10}$), and osmocene ($OsC_{10}H_{10}$) (*205*, *206*).

One of the most fascinating areas of metal-cyclopentadienyl chemistry in recent years concerns the formation and relative stabilities of metallocenyl-carbonium ions. The ability of iron to stabilize cationic centers in certain ferrocene compounds was noted by Weliky and Gould (*243*) in 1957. In 1959 Richards and Hill (*213*, *214*, *215*) reported the results of some kinetic studies relating to the relative rates of solvolysis of metallocenylmethylcarbinyl acetates. They determined that these solvolyses proceeded via a carbonium ion mechanism and found that the ferrocenyl acetate, for example, solvolyzed nearly seven times faster than did triphenylmethyl acetate under the same conditions.

It is now well-documented that carbonium ions containing adjacent metallocenyl groups possess unusual stability (*20*, *21*, *213*, *214*, *215*, *237*). Richards and co-workers (*25*, *213*, *214*, *215*) propose that this stability stems from nonbonding electrons on the metal being directly coordinated with the carbonium ion center (XX).



XX



XXI

Others contend that the stability can be more conventionally related to a resonance effect via the cyclopentadienyl rings and the metal (XXI) (*103*, *240*). In either case, the positive charge which would develop on the exocyclic carbon atom would be delocalized considerably, which would aid the carbonium ion to form more easily. The differences between these interpretations are subtle but distinct, and the topic will no doubt be the subject of considerable future research.

–																															–	–
H 1.008																															–	He 4
Li 7.03																										Be 9.1	B 11	C 12	N 14.04	O 16.00	Fl 19	Ne 20
Na 23.05																										Mg 24 36	Al 27.1	Si 28.4	P 31.0	S 32.06	Cl 35.45	A 39.9
K 39.15	Ca 40.1																Sc 44.1	Ti 48.1	V 51.2	Cr 52.1	Mn 55.0	Fe 55 9	Co 59.0	Ni 58 7	Cu 63.6	Zn 65.4	Ga 70	Ge 72	As 75.0	Se 79.1	Br 79.96	Kr 81.12
Rb 85.4	Sr 87.6																Y 89.0	Zr 90.7	Nb 94	Mo 96.0	–	Ru 101.7	Rh 103.0	Pd 106	Ag 107 93	Cd 112.4	Jn 114	Sn 118.5	Sb 120	Te 127 6	J 126.95	X 128
Cs 133	Ba 137.4	La 138	Ce 140	Nd 143.6	Pr 140.5	–	–	Sa 150.3	Eu 151.79	Gd 156	Tb 160	Ho 162	Er 166	–	Tu 171	Yb 173.0	–	–	Ta 183	W 184.0	–	Os 191	Ir 193.0	Pt 194.8	Au 197.2	Hg 200.3	Tl 204.1	Pb 206.9	Bi 208.5	–	–	–
–	Ra 225	Laα ?	Th 232.5	–	–	–	–	–	U 239.5	–	–	–	–	–	Ac ?	–	–	–	–	–	–	–	–	–	–	–	–	Pbα ?	Biα ?	Teα ?	–	–

Figure 1. Periodic table of the elements

Fortunately, the area of organotransition metal chemistry dealing with π-cyclopentadienyl-metal compounds is well reviewed. Two comprehensive reviews covering the literature until 1959 have been written by Wilkinson and Cotton (*245*) and by Fischer and Fritz (*87*). Several more recent reviews have been written by Birmingham (*12*, *13*) and by Rausch (*200*, *202*). The topic of metallocenes has been extensively reviewed by Rausch (*199*, *200*, *202*, *204*), Plesske (*196*), and Little (*160*). The most recent review of metallocene chemistry is a two volume series by Rosenblum, the first volume of which has recently been published (*217*).

Arene (n = 6) and Related Complexes

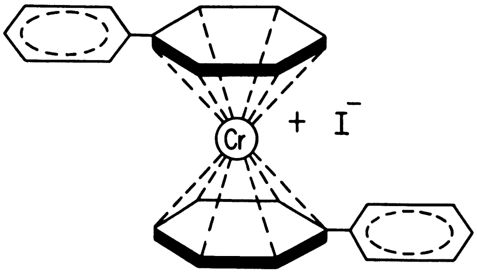
Organometallic π complexes in which a benzene ring serves as the ligand were first isolated by Hein (*124*) as early as 1919, although it has only been in recent years that the composition and structure of these substances have been known with certainty. Hein found that phenylmagnesium bromide reacted with a slurry of chromium trichloride in ethyl ether at ice bath temperature and produced, following hydrolysis and addition of potassium iodide, a series of "polyphenylchromium iodides." The latter could be reduced electrolytically in liquid ammonia to yield such compounds as "tetraphenylchromium" and "triphenylchromium."

$$C_6H_5MgBr + CrCl_3 \xrightarrow[0^\circ C]{\text{ethyl ether}} \xrightarrow[KI]{H_2O} \text{"polyphenylchromium iodides"}$$

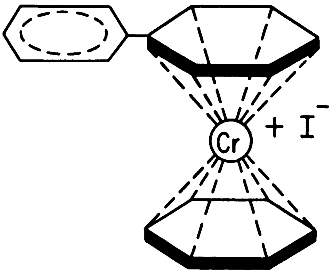
$$(C_6H_5)_4CrI \xrightarrow{\text{redn.}} (C_6H_5)_4Cr$$

$$(C_6H_5)_3CrI \xrightarrow{\text{''}} (C_6H_5)_3Cr$$

In 1953 Zeiss and Tsutsui (*262*, *266*, *267*) reinvestigated Hein's earlier studies. In 1954 together with Onsager they proposed π-bonded "sandwich" structures for compounds of the type isolated earlier by Hein and co-workers. Thus, "tetraphenylchromium iodide" was reformulated

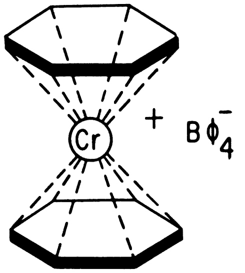


XXII

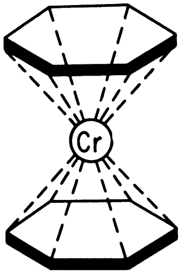


XXIII

as bis(biphenyl)chromium iodide (XXII); "triphenylchromium iodide" was reformulated as benzene-biphenyl-chromium iodide (XXIII), etc. Analogous structures were suggested for the neutral organochromium compounds obtained earlier. The formulation of Hein's compounds as organometallic, π complexes was shown by Zeiss and Tsutsui to be consistent with chemical and magnetic data obtained by them and by previous investigators. In 1956 Zeiss and Herwig isolated the parent bis(benzene)chromium cation as its tetraphenylboron salt (XXIV) and reduced the latter to the neutral complex bis(benzene)chromium (XXV) (*263*).



XXIV



XXV

Independent of these investigations, Fischer and co-workers reasoned that the compound bis(benzene)chromium (XXV), being isoelectronic with the "sandwich" compound ferrocene, should be capable of formation and study. In a research program initiated in 1954, Fischer and Hafner (*90, 91*) discovered that chromium trichloride, reduced by aluminum powder at 150°C. in the presence of benzene and aluminum chloride (Friedel-Crafts-type method), formed a bis(benzene)chromium salt. The latter was readily reduced to the parent substance bis(benzene)chromium (XXV) by alkaline sodium dithionite solution.

$$3CrCl_3 + 2Al + AlCl_3 + 6C_6H_6 \rightarrow 3[(C_6H_6)_2Cr]^+ [AlCl_4]^-$$

$$2[(C_6H_6)_2Cr]^+ + S_2O_4^{-2} + 4OH^- \rightarrow 2(C_6H_6)_2Cr + 2SO_3^{-2} + 2H_2O$$

The "sandwich" structure of bis(benzene)chromium (XXV) prepared by this new route was soon confirmed by Weiss and Fischer (*242*). Moreover, Fischer and Seus (*98*) prepared bis(phenyl)chromium iodide (XXII) by the Friedel-Crafts-type method, starting with biphenyl in place of benzene, and were able to show that the product obtained in this manner was identical to bis(biphenyl)chromium iodide (XXII) isolated via Hein's Grignard route. A longstanding and vexing problem in coordination chemistry was thus finally solved.

The Friedel-Crafts method is the most versatile route available for preparing arene-metal complexes, having been applied successfully to nearly a dozen transition metals. The method has definite limitations, however, with regard to the type of arene unit used, and only alkyl- and aryl-substituted benzenes in general can be successfully employed.

The discoveries by Zeiss and Tsutsui and by Fischer and Hafner were unquestionably of great importance for further expanding and developing organotransition metal chemistry. By 1956, it had become apparent to many investigators that the "sandwich" structure found in the compound ferrocene a few years earlier was not necessarily unique, and that other carbocyclic and even heterocyclic ring systems might be capable of serving as ligands in organometallic, π complexes.

Another important advance in organotransition metal chemistry was reported in 1957 by Zeiss and Herwig (*264*, *265*). These workers found that reaction of phenylmagnesium bromide with chromium trichloride in tetrahydrofuran (THF), rather than in ethyl ether, yielded a red, crystalline compound, triphenylchromium-tris-tetrahydrofuranate (XXVI).

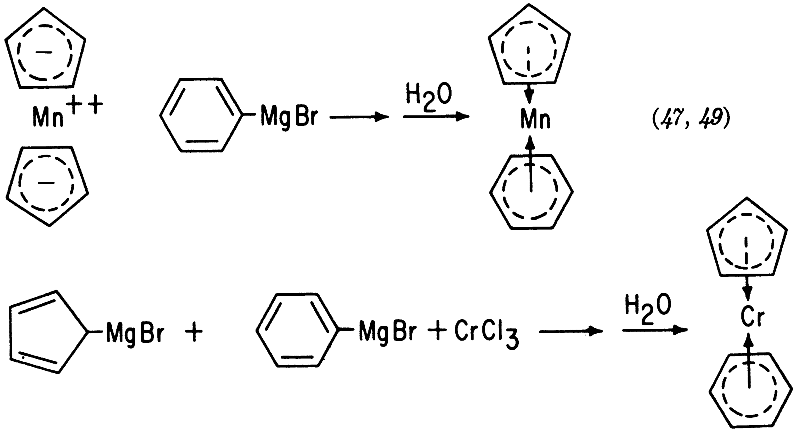
$$CrCl_3 + 3C_6H_5MgBr \xrightarrow{THF} (C_6H_5)_3Cr \cdot 3\ THF + 3MgBrCl$$

XXVI

This compound could be subsequently converted to arene-metal complexes by treating it with ethyl ether and hydrolysis. The substance probably contains three phenyl groups σ-bonded to the chromium atom, as well as three solvent molecules occupying the remaining coordination sites around the metal in an octahedral-type arrangement. Such a "σ-bonded," organochromium compound was, of course, the original goal of Hein and coworkers many years before. These earlier attempts failed partly because of choice of solvent. Tetrahydrofuran is known to be more basic than ethyl ether and evidently forms a stronger dative bond with the metal, thus stabilizing triphenylchromium as a hexacoordinate complex.

Zeiss and co-workers further found that acetylenes displace THF molecules in the coordination sphere of chromium and other metals in analogous complexes. The acetylenes subsequently condense in cyclic arrangements, and such cyclic condensation reactions have provided important new routes to both arene-metal complexes and uncomplexed arenes. Further details on these novel reactions are contained in the reviews at the end of this section.

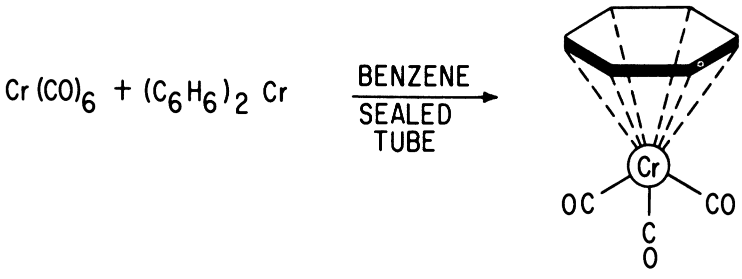
By 1957, a variety of both π-cyclopentadienyl and arene-metal complexes was known, and it was interesting to determine whether "mixed-sandwich" complexes containing both of these ligands around the same could be produced. Two early examples of such complexes are given below:



(*47*, *49*)

(*93*)

Yet another major advance in arene-metal chemistry was made in 1957 by Fischer and Öfele (*95*), who found that a sealed tube reaction involving chromium hexacarbonyl, bis(benzene)chromium, and benzene produced the "half-sandwich" compound benzene-chromium tricarbonyl (XXVII).



XXVII

The centrosymmetric structure proposed for benzene-chromium tricarbonyl was subsequently confirmed by x-ray analysis (*8*, *52*).

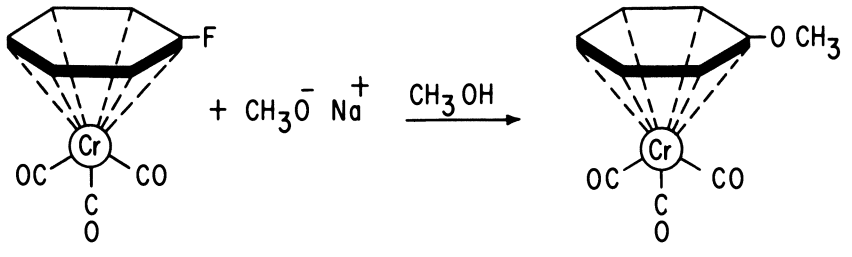
Following this initial discovery, several additional routes to benzene-chromium tricarbonyl and related complexes were developed, the most convenient of which involves the simple refluxing of the metal carbonyl and arene with concurrent loss of carbon monoxide (*96*, *97*, *184*, *186*, *187*).

$$\text{Arene} + M(CO)_6 \xrightarrow[\text{without solvent}]{\text{reflux, with or}} (\text{Arene})M(CO)_3 + 3CO$$

M = Cr, Mo, W

Arene = benzene, toluene, fluorobenzene, phenol, methyl benzoate, etc.

A wide variety of arene-metal tricarbonyl complexes are now known, and their chemistry largely waits to be developed. The effects of coordination on the reactivity of the arene ligand might be expected to be quite pronounced, and already a number of notable developments have been described in the literature. Thus, while benzene-chromium tricarbonyl undergoes Friedel-Crafts acylation readily (*17*, *81*, *216*), nucleophilic-type reactions such as the facile conversion of fluorobenzene-chromium tricarbonyl (XXVIII) to anisole-chromium tricarbonyl (XXIX) also occur in high yield (*17*, *186*, *187*).



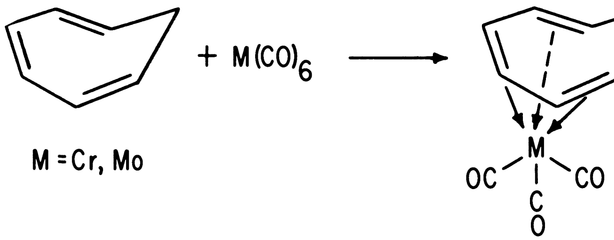
XVIII XXIX

Recently, Pettit and co-workers (*134*) have shown that the relative rate of solvolysis of benzyl chloride-chromium tricarbonyl is about a million times faster than for uncomplexed benzyl chloride under analogous S_N1 conditions. The area of carbonium ion formation and stabilization in arene-metal systems thus represents another fertile field for future investigation.

The topic of arene-metal chemistry has been the subject of several reviews. The most recent review by Fischer and Fritz (*88*) was published in 1961, while a still earlier review by these authors appeared in 1959 (*87*). Another review published in this same year was written by Wilkinson and Cotton (*245*), while an excellent source of information on the subject was prepared in 1960 by Zeiss (*262*).

π-Cycloheptatrienyl (n = 7) and Related Complexes

Following the successful isolation and characterization of many π-cyclopentadienyl- and arene-metal complexes as described above, it was only natural for investigators to attempt to form metal π-complexes containing C_7- and larger ring systems. It seemed entirely reasonable at this point that complexes containing the well-known cycloheptatrienyl (tropylium) ion might be capable of formation and isolation. In 1958 Abel, Bennett, and Wilkinson (*2*, *3*) found that cycloheptatriene, when refluxed with either molybdenum or chromium hexacarbonyl, yielded complexes of the type $(C_7H_8)M(CO)_3$(XXX). In these complexes, the cycloheptatriene ring system can be regarded as a six π-electron donor.



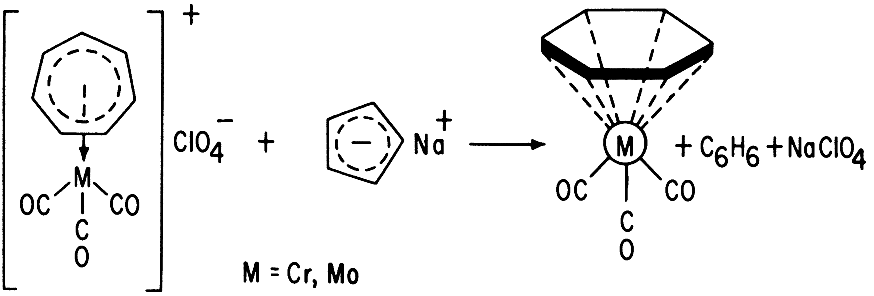
XXX

The structure of cycloheptatriene-molybdenum tricarbonyl (XXX, M = Mo) was subsequently confirmed by x-ray analysis (*76*). The six olefinic carbon atoms were found to be approximately planar and symmetrically bonded to the metal, with the methylene carbon bent away from the latter. Carbon-carbon ring distances indicated alternate double and single bonds in the planar portion of the molecule, rather than a delocalized π-electron system, as was originally suggested. The analogous complex $(C_7H_8)W(CO)_3$ was subsequently described in the literature (*62*, *164*).

Although Able *et al.* (*2*, *3*) had originally set out to prepare π-cycloheptatrienyl complexes of metals, the cycloheptatriene complexes they actually obtained served as key intermediates in forming the former complexes. In 1958 Dauben and Honnen (*61*) reported that cycloheptatriene-molybdenum tricarbonyl reacted with triphenylmethyl tetrafluoroborate in methylene chloride solution with abstraction of hydride ion from the molybdenum complex. The reaction products, obtained in nearly quantitative yields, were triphenylmethane and the π-cycloheptatrienyl complex $[(\pi\text{-}C_7H_7)Mo(CO)_3]^+BF_4^-$.

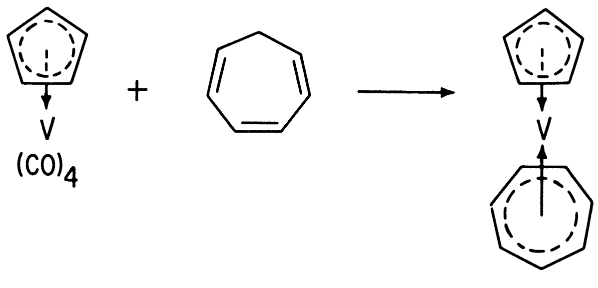
This significant finding was subsequently extended to the analogous chromium and tungsten derivatives (*61*, *62*, *179*, *180*) and has been useful in synthesizing still other types of "en-yl" metal π complexes. It should also be mentioned that organometallic, π complexes, reputed to be $[(\pi\text{-}C_7H_7)PtBr_2]_2$ and $(\pi\text{-}C_7H_7)PtBr_3$, were also described in 1958 (*89*). These complexes were obtained from reaction of platinum(IV) bromide with cycloheptatriene and with tropylium bromide, respectively. They were assigned π-cycloheptatrienyl structures primarily on the basis of comparisons of their infrared spectra with the spectrum of tropylium bromide.

In 1959 Munro and Pauson (*180*) announced some preliminary findings in what is the most detailed study thus far undertaken concerning the reactions of π-cycloheptatrienyl-metal derivatives. The reactions of the cations $[(\pi\text{-}C_7H_7)M(CO)_3]^+$ (M = Cr or Mo) with nucleophilic reagents proceeded by three different routes: (1) normal addition to the seven-membered ring (*177*); (2) reductive dimerization of the starting cation (*179*); (3) ring contraction to form benzene-metal tricarbonyls (*178*). The latter reaction results, for example, when the nucleophile is cyclopentadienide ion or diethyl malonate ion, and experiments have shown that the π-complexed ring is derived entirely from the π-cycloheptatrienyl ligand.



It has also been established that this novel type of rearrangement proceeds by initial attack of the nucleophile on the π-complexed ring to form substituted cycloheptatriene-metal tricarbonyl intermediates, although mechanistic details are still rather obscure.

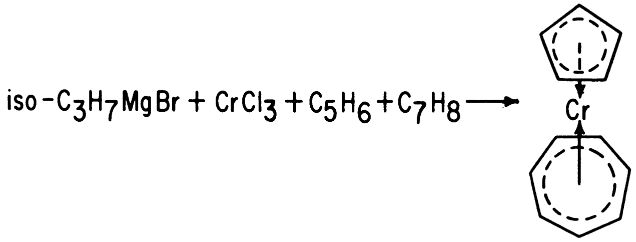
A variety of organometallic, π complexes are now known, in which both π-cyclopentadienyl and π-cycloheptatrienyl ligands are bonded simultaneously to the same transition metal, providing a series of unique "mixed sandwich" complexes. The first of these, π-cyclopentadienyl-π-cycloheptatrienyl-vanadium (XXXI), was described by King and Stone (*153*)



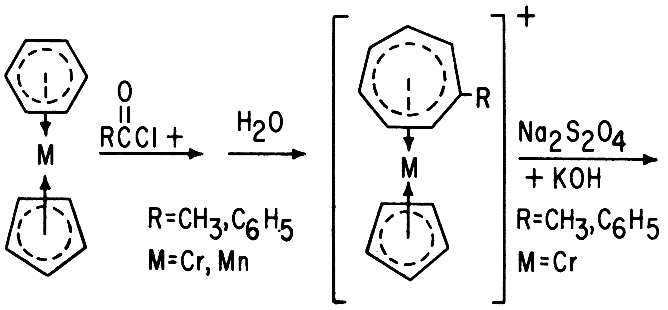
XXXI

in 1959, and its structure was subsequently confirmed by x-ray analysis (*80*).

Several novel routes to additional, mixed, ring complexes of this type are outlined below:

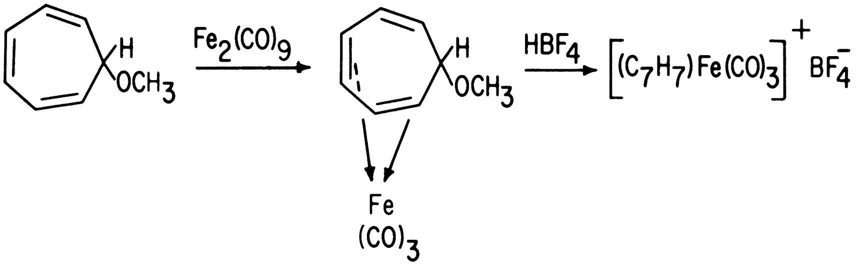


(*94, 149*)

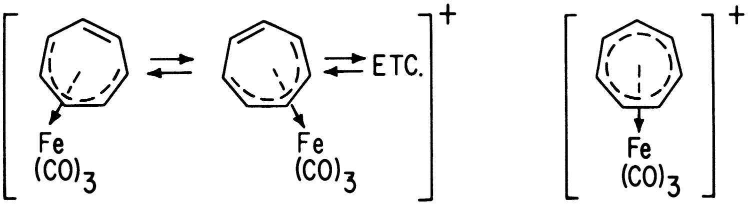


(*82*)

Initial attempts to prepare π-cycloheptatrienyl-iron tricarbonyl complexes were not successful—the products often being π-cycloheptadienyl-iron tricarbonyl derivatives (*60*). In 1964 Mahler, Jones, and Pettit (*162*) reported the synthesis of a complex $[(C_7H_7)Fe(CO)_3]^+BF_4^-$ by the following route:



It was postulated that three strong C-H stretching frequencies in the infrared spectrum of this complex reflect a lower symmetry of the C_7H_7-ligand than does the analogous series of complexes, $[(\pi\text{-}C_7H_7)M(CO)_3]^+BF_4^-$, mentioned above. The structure of the iron complex seems best represented by XXXII rather than by XXXIII, the iron atom being bonded to five carbons of the ring and leaving one double bond formally not coordinated to the metal. The fact that only a single sharp peak is observed in the NMR spectrum of the $[(C_7H_7)Fe(CO)_3]^+$ cation is believed to be due to a rapid valence tautomerism postulated previously by Dickens and Lipscomb (*65*, *66*, *67*) for cyclooctatetraene-iron tricarbonyl (*vide infra*).



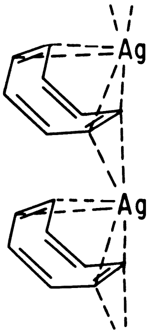
XXXII XXXIII

A variety of other π-cycloheptatrienyl and related metal complexes is known, as well as complexes in which 1,3-cycloheptadiene (C_7H_{10}) serves as a ligand. For details, refer to a recent comprehensive review by Fischer and Werner (*100*) and/or two earlier reviews by these authors (*99*) and by Bennett (*11*).

Cyclooctatetraene and Related Complexes

Cyclooctatetraene, C_8H_8, is a monocyclic organic ring system which contains four conjugated double bonds. A number of organometallic, π complexes containing cyclooctatetraene is now known in which the latter donates from two to seven π electrons to a transition metal. No complex is presently known in which cyclooctatetraene formally donates all eight π electrons to the same transition metal, although both chemical and physical evidence indicates that the remaining "uncoordinated" double bonds in many cyclooctatetraene-metal complexes are greatly effected by complexing of adjacent, conjugated double bonds.

Metal, π complexes of cyclooctatetraene were first described by Reppe *et al.* (*211*) in 1948. Silver and copper complexes were obtained during the synthesis of this hydrocarbon from acetylene. These complexes of cyclooctatetraene have since been investigated in considerable detail by several groups of investigators (*50*, *114*, *167*, *168*). An x-ray analysis of the complex $[(C_8H_8)Ag]^+NO_3^-$ (XXIV) indicates that the silver ion is coordinated to two nonadjacent bonds of cyclooctatetraene but is situated at differences from each. $[(C_8H_8)Ag]^+$ units are, furthermore, joined together by weak bonds.



XXXIV

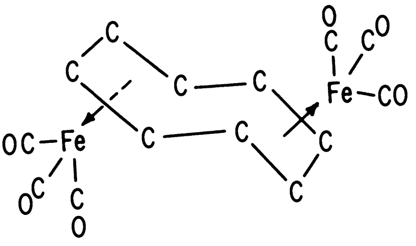
The two remaining double bonds of the ligand possibly interact to some extent with silver ions because the infrared spectrum of the complex shows no "free" double bonds, and solutions of the complex show only a single proton NMR signal (*105*).

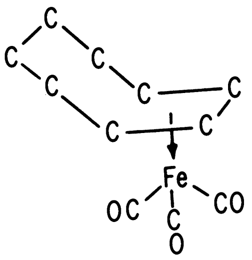
In 1953 Jensen (*141*) reported that the reaction between cyclooctatetraene and $K_2(PtCl_4)$ produced the complex $(C_8H_8)PtCl_2$. He likewise described the iodo derivative, $(C_8H_8)PtI_2$. A "tub" conformation was postulated for the cyclooctatetraene ligand in these structures. Subsequent, detailed, infrared and NMR studies of these and analogous palladium complexes indicate substantial π-electron delocalization (*105*).

In 1959 a remarkable class of compounds containing cyclooctatetraene coordinated to iron tricarbonyl units was discovered independently by three research groups (*165, 166, 182, 207*). Two principal products were obtained having the compositions $(C_8H_8)Fe(CO)_3$ and $(C_8H_8)Fe_2(CO)_6$, of

$$C_8H_8 + Fe(CO)_5 \xrightarrow[\text{u.v.}]{\text{heat or}} (C_8H_8)Fe(CO)_3 + C_8H_8Fe_2(CO)_6$$

which the latter complex could be prepared from the former by treating it with excess iron pentacarbonyl.





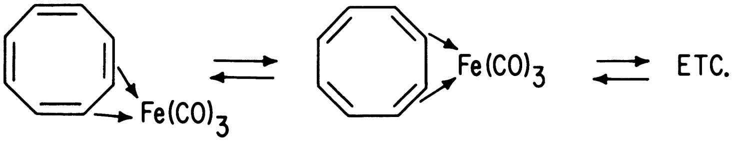
XXXV XXXVI

The binuclear iron complex $(C_8H_8)Fe_2(CO)_6$ had been expected from the reaction, but the "chair" conformation (XXXV), which was subsequently found for this substance, was entirely unexpected (*65, 66, 67*). In this complex, each end of the cyclooctatetraene ligand behaves as a butadiene-type ($n = 4$) ligand, and bond distance measurements indicate very little π-π interaction between the two halves of the ring. The proton NMR spectrum of the complex in solution exhibits two resonances of equal intensity, while the infrared spectrum is very similar to the spectrum of butadiene-iron tricarbonyl and similar diene complexes (*105*).

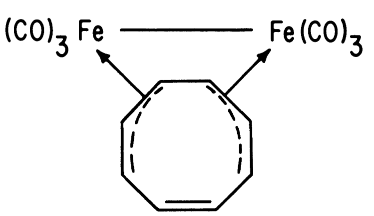
The properties and reactions of the complex $(C_8H_8)Fe(CO)_3$ proved to be even more unusual (*165, 166, 182, 207*). It might be assumed *a priori* that this complex possesses two uncoordinated double bonds. Treatment of the complex with bromine in carbon tetrachloride, however, did not cause a halogen to be added, and several attempts catalytically to hydrogenate the complex failed to result in hydrogen uptake. It should be mentioned that both cyclooctatetraene and cyclooctadienes undergo these reactions readily. Initial attempts to form Diels-Alder adducts by means of maleic anhydride under normal conditions were not successful, but recently use of the more reactive dienophile tetracyanoethylene has led to positive results (*59, 222*). Initial infrared studies indicated that no olefinic C=C stretching vibrations were present in the region expected for "free" olefinic, double bonds. Most striking of all was the observance of a single, sharp proton resonance signal in the NMR spectum of $(C_8H_8)Fe(CO)_3$ in a variety of solvents and at temperatures as low as $-60°C$.

Subsequently, Dickens and Lipscomb (*65, 66, 67*) conducted an x-ray analysis of this complex and found that the cyclooctatetraene ligand possessed a novel "dihedral" conformation (XXXVI). The $Fe(CO)_3$ group is bound to only one-half of the ring, and this portion of the complex is similar to the geometry in butadiene-iron tricarbonyl. Six of the eight carbon atoms are approximately planar, and this plane forms an angle of 41° with the butadiene-type fragment. Bond distances and angles as well as calculations of overlap integrals indicate appreciably more π-π interaction between the butadiene-type portions of the molecule than in the dinuclear-iron complex (XXXV).

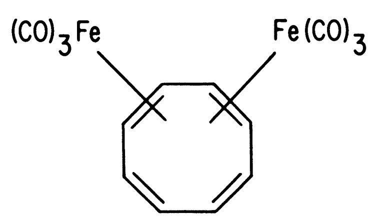
In view of the structure exhibited by $(C_8H_8)Fe(CO)_3$ in the crystal state, the apparent equivalence of the ligand protons of this complex in solution could be explained in several ways: (1) a negligible chemical shift of various protons; (2) a differing geometry in solid and solution states; and (3) a dynamic effect (*65, 66, 67*). Recent studies point to the latter effect as being operative in $(C_8H_8)Fe(CO)_3$ (*9*). In other words, the $Fe(CO)_3$ group is assumed to be rapidly rotating around the cyclooctatetraene ring in solution, and the rate of this rotation is great enough to cause proton equivalency on the NMR time scale of the various valence tautomeric structures:



In some additional studies concerning cyclooctatetraene-iron carbonyl chemistry, Keller, Emerson, and Pettit (*145*) have isolated two additional isomers having the composition $(C_8H_8)Fe_2(CO)_6$, for which Structures XXXVII and XXXVIII have been proposed on the basis of infrared, NMR, and Mössbauer measurements.

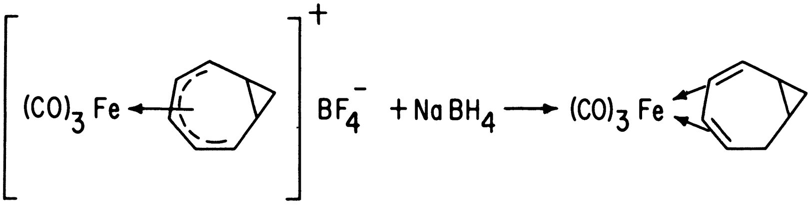


XXXVII



XXXVIII

Another important development in cyclooctatetraene-metal chemistry has concerned the protonation of C_8H_8-metal derivatives (*59, 221*). The complex $(C_8H_8)Fe(CO)_3$ is readily protonated in strong acids to yield salts of the type $[(C_8H_9)Fe(CO)_3]^+ X^-$, where X = Cl, ClO_4, or BF_4. The proton NMR spectrum indicates the complex contains the bicyclo-[5.1.0]-octadienyl-iron tricarbonyl cation (XXXIX), and this formulation is supported by the observation that when the tetrafluoroborate salt of



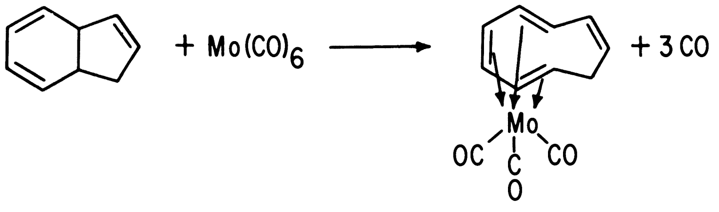
XXXIX XL

this cation is subsequently reduced by sodium borohydride, bicyclo-[5.1.0]-octa-2,4-diene-iron tricarbonyl (XL) is formed. In contrast, the protonation of the cyclooctatetraene complex $(C_8H_8)Mo(CO)_3$ (in which the C_8H_8 ligand serves as a six, π-electron donor) in concentrated sulfuric acid produces a complex which is best regarded as a homotropylium derivative (*253*).

Cyclooctatetraene also forms interesting complexes with cobalt, rhodium, nickel, and other transition metals, but these will not be elaborated on here. It should also be mentioned that other eight-membered ring systems, such as 1,5-cyclooctadiene, 1,3,5- and 1,3,6-cyclooctatrienes, etc., form a variety of metal, π complexes. The most recent survey of cyclooctatetraene and related metal, π complexes is the review by Fischer and Werner (*100*), as well as earlier reviews by these authors (*99*), and Bennett (*11*).

Complexes Containing Nine-, 10- and 12-Membered Ring Systems

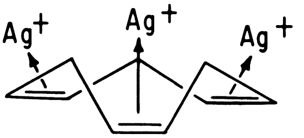
A number of organometallic, π complexes containing monocyclic ring systems larger than eight carbon atoms has been reported in which these rings formally donate two, four, or six π electrons to a transition metal. An early study along these lines was made by King and Stone (*152*, *154*), who investigated the reaction of bicyclo[4.3.0]-nona-2,4,8-triene (8,9-dihydroindene) (XLI) with molybdenum hexacarbonyl. The reaction product, $C_9H_{10}Mo(CO)_3$, seems best formulated as a cyclononatetraene complex (XLII), rather than as a derivative of the parent ring system (XLI) which, in fact, is a valence tautomer of cyclononatetraene. Formulation of $C_9H_{10}Mo(CO)_3$ as XLII allows one formally uncoordinated double bond in the organic ligand, and the complex was found to take up one molecule of hydrogen readily. An analogous tungsten complex was also prepared by these workers.



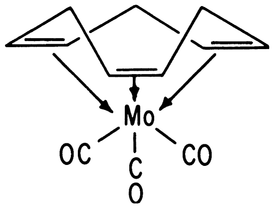
XLI XLII

Both silver nitrate and molybdenum hexacarbonyl react with the nine-membered ring system *cis,cis,cis*-cyclonona-1,4,7-triene to form complexes of the types $(C_9H_{12})\cdot 3\ AgNO_3$ and $C_9H_{12}Mo(CO)_3$, respectively (*238*). In the assigned structures, based on NMR and related data, the silver nitrate complex has the silver ions associated with the "outer" π-orbital lobes (XLIII), while the molybdenum tricarbonyl complex has the molybdenum bonded to the "inner" π-orbital lobes (XLIV). In both complexes, a "crown" conformation of the ligand is assumed.

Only a very limited amount of research has been published concerning 10-carbon, monocyclic olefins as ligands. In 1955 Cope and co-workers

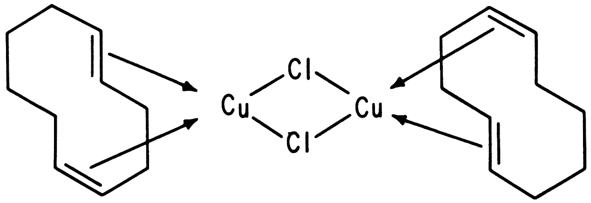


XLIII



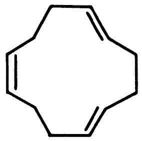
XLIV

(*51*) prepared silver complexes of both *cis*- and *trans*-cyclodecene. In 1965 Jonassen and co-workers (*233*) reported the synthesis of silver and copper complexes of the dienes *cis,trans*-cyclodeca-1,5-diene and *cis,cis*-cyclodeca-1,6-diene. Although a detailed structural investigation was not undertaken, these workers postulate that the cyclodeca-1,5-diene complex $(C_{10}H_{16})CuCl$ might have the dimeric structure (XLV), in analogy to the known structure of cycloocta-1,5-diene-copper chloride (*239*).

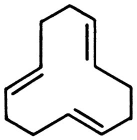


XLV

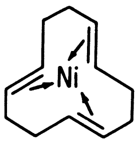
Two isomeric 1,5,9-cyclododecatrienes, namely, *trans,trans,cis*-$C_{12}H_{18}$ (XLVI) and *trans,trans,trans*-$C_{12}H_{18}$ (XLVII), are formed in good yield by the cyclic trimerization of butadiene using certain Ziegler-type catalysts (*247, 250, 251, 252*). The formation of these 12-membered ring hydrocarbons probably proceeds via metal π-complexed intermediates. When the cyclic triene (XLVII) is treated with nickel acetylacetonate and



XLVI



XLVII



XLVIII

aluminum alkyls, a very air-sensitive complex of composition $C_{12}H_{18}Ni$ is formed. The infrared spectrum of this complex indicates that all three double bonds participate in bonding with the metal. The complex decomposes thermally at about 140°C. with formation of a nickel mirror and cyclododecatriene, while reaction with hydrogen yields nickel and cyclododecane. Because the metal atom in $C_{12}H_{18}Ni$ is two electrons short of an inert gas configuration, it might be expected to react readily with electron donors. Such is the case, and both carbon monoxide and triethylphosphine adducts are known. On the basis of its properties and reactions, a structure such as XLVIII has been proposed for $C_{12}H_{18}Ni$.

Cyclododecatrienes likewise form π complexes with transition metals such as silver, copper, palladium, etc. Details of these studies, as well as the work on nickel complexes described above, are contained in the recent monograph by Fischer and Werner (*100*).

σ-Bonded Organotransition Metal Complexes ($n = 1$)

Early attempts to prepare stable, isolable, σ-bonded organic derivatives of the transition metals were almost uniformly unsuccessful, except for certain organometallic derivatives of platinum and gold. It has already been mentioned that the "σ-bonded" organochromium compounds of Hein and co-workers were in fact π-bonded arene-chromium derivatives. A detailed and critical account of these earlier studies was written in 1955 by Cotton (*53*).

Coincidentally with the discovery of ferrocene, σ-bonded organotitanium compounds were reported in 1952 by Herman and Nelson (*125, 126, 127*). Following an extensive study of the stabilities in solution of compounds of the type R_nTiX_{4-n}, these workers prepared phenyltitanium triisopropoxide (XLIX) from phenyllithium and titanium tetraisopropoxide. More recently, another convenient route to XLIX has been described (*133*).

$$C_6H_5Li + (\text{iso-}C_3H_7O)_3Ti\text{-}Cl \rightarrow (\text{iso-}C_3H_7O)_3Ti\text{-}C_6H_5 + LiCl$$

XLIX

In the years that followed, a number of investigators discovered that the presence of π-bonding ligands on a transition metal often facilitated the stabilization of a σ bond between an organic group and the same transition metal. An early example of this fact was indicated in 1955 by Summers, Uloth, and Holmes (*231*) when these workers isolated relatively stable, σ-bonded diaryltitanocenes from titanocene dichloride reacting with various aryllithium reagents.

$$(\pi\text{-}C_5H_5)_2TiCl_2 + 2ArLi \rightarrow (\pi\text{-}C_5H_5)_2Ti(\sigma\text{-}Ar)_2 + 2LiCl$$

Ar = aryl

Piper, Cotton, and Wilkinson in 1955 noted that stabilization effects also result from combining carbonyl and/or nitrosyl groups with a π-cyclopentadienyl ring (*195*). Compounds of this type were prepared as follows:

$$(\pi\text{-}C_5H_5)(NO)_2Cr\text{-}Br + CH_3MgBr \rightarrow (\pi\text{-}C_5H_5)(NO)_2Cr(\sigma\text{-}CH_3) + MgBr$$

$$(\pi\text{-}C_5H_5)(CO)_3Mo\text{-}H + CH_2N_2 \rightarrow (\pi\text{-}C_5H_5)(CO)_3Mo(\sigma\text{-}CH_3) + N_2$$

$$[(\pi\text{-}C_5H_5)(CO)_2Fe]^- Na^+ + CH_3I \rightarrow (\pi\text{-}C_5H_5)(CO)_2Fe(\sigma\text{-}CH_3) + NaI$$

Very effective stabilization of carbon-transition, metal, σ bonds has also been found with carbonyl groups as the sole π-bonding ligand; examples include R-Mn$(CO)_5$ (*44*, *129*) and R-Re$(CO)_5$ (*128*). As mentioned previously, in certain instances coordinative groups such as THF or dioxane stabilize carbon-transition, metal, σ bonds; examples include $(C_6H_5)_3Cr(THF)_3$ (*264*, *265*) and $CH_3TiCl_3(C_4H_8O_2)$ (*10*). Calvin and Coates (*26*), as well as Doyle and co-workers (*155*), have shown that π-bonding groups such as 1,5-cyclooctadiene, norbornadiene, etc., present on palladium or platinum are useful in stabilizing carbon-metal, σ bonds involving these metals.

A major advance in the chemistry of σ-bonded organotransition metal compounds occurred in 1959 when Chatt and Shaw (*31*, *32*, *33*, *34*, *35*) published the first of a series of papers dealing with the subject. Chatt and Shaw were able to demonstrate that stable alkyl and aryl complexes of the type $(R'_3P)_2M(X)R$ and $(R'_3P)_2MR_2$ (M = Pt, Pd, Ni) could readily be formed from organolithium reagents or Grignard reagents and the appropriate bis(phosphine)metal dihalide. These workers extended their studies to include similar derivatives of Co, Fe, and Rh. Calvin and Coates (*26*) likewise isolated organopalladium complexes containing carbon-palladium, σ bonds and phosphine ligands.

The theoretical conclusions of Chatt and Shaw (*28*, *31*, *32*, *33*, *34*, *35*) and of Coates (*45*, *46*) are of great significance in understanding the bonding in σ-bonded, organotransition metal compounds. The basic premise of these theories is that dissociation of carbon-transition, metal, σ bonds is likely to be a homolytic, irreversible process, and that this process would be facilitated by transfer of an electron from the highest filled non-bonding (metal) orbital and the lowest unfilled (carbon-metal, σ antibonding) orbital. Specific ligands such as tertiary phosphines tend to bond to transition metals by a combination of σ and π bonds. The presence of such groups in a σ-bonded, organotransition metal complex tends to stabilize the complex because π bonding or back donation from the metal to the phosphine lowers the energy of the highest occupied metal orbital which contains electrons by involving these electrons in bonding. In this manner, the energy difference required to promote an electron into the vacant orbital (and thus lead to decomposition) is consequently increased. These theories were originally intended to explain the remarkable stabilities of square-planar, σ-bonded complexes containing phosphine ligands, but it may well be that these general concepts can be used to account for the other types of "stable," σ-bonded organotransition metal derivatives described above.

Another approach to the stabilization and isolation of σ-bonded, organotransition metal compounds originated from early theoretical considerations of Jaffé and Doak (*140*) and has been largely developed by Stone and co-workers. Fluorocarbon groups, being "pseudo-halogens," should be capable of increasing the ionic nature of the carbon-transition, metal bond. Negative charge would be depleted compared with the same transition metal bonded to a common alkyl or aryl group, and the resulting increase in ionic resonance energy should stabilize the carbon-transition metal bond (*236*).

Another possible explanation for enhanced stabilities of perfluoroalkyltransition metal compounds concerns possible multiple bonding between the metal and the fluorocarbon group (*54*, *230*). Whatever the reason, a large number of fluorocarbon derivatives of the transition metals have now been described, and a study of their synthesis, properties, and reactions constitutes an important new branch of organotransition metal chemistry. Fluoroalkyltransition metal compounds were first described in 1959 (*48*), while perfluoroaryl-transition metal derivatives were discovered in 1963 (*201*, *234*). Some typical syntheses of fluorocarbon-transition, metal compounds are shown below:

$$CF_3C(O)Cl + Na^+[Mn(CO)_5]^- \rightarrow CF_3C(O)\text{-}Mn(CO)_5 \xrightarrow[(-CO)]{100°C.} CF_3\text{-}Mn(CO)_5 \quad (\mathit{48})$$

$$(\pi\text{-}C_5H_5)Mo(CO)_3H + CF_2{=}CF_2 \rightarrow (\pi\text{-}C_5H_5)(CO)_3M\text{-}CF_2CF_2H \quad (\mathit{235})$$

$$(CH_3)_3Sn\text{-}Mn(CO)_5 + CF_2{=}CF_2 \rightarrow (CH_3)_3Sn\text{-}CF_2CF_2\text{-}Mn(CO)_5 \quad (\mathit{42}, \mathit{43})$$

$$C_6F_5MgBr + Mn(CO)_5Br \rightarrow C_6F_5\text{-}Mn(CO)_5 + MgBr_2 \quad (\mathit{201}, \mathit{235})$$

A variety of reviews is available on the subject of σ-bonded, organotransition metal compounds. The most recent of these (1965) is a detailed review by Razuvaev and Latyaeva (*209*) which has recently been translated from the original Russian text. As mentioned earlier, the review by Cotton (*53*) comprehensively and critically covers the literature up to 1955. Several other reviews, by Coates and Glocking (*46*) and by Chatt (*28*, *30*), appeared in 1960. The specific area of fluorocarbon-transition metal chemistry has been covered in recent reviews by Clark (*41*) in 1963, Treichel and Stone (*236*) in 1964, and Rausch (*203*) in 1966.

Industrial Applications

The remarkable properties and reactions of organotransition metal compounds have stimulated a great deal of research in industrial laboratories in recent years, with the goal of finding practical applications for these substances. Although it is not the intent of this survey to discuss this aspect of organotransition metal chemistry in any detail, four important applications include:

(1) The use of methylcyclopentadienylmanganese tricarbonyl and related compounds as antiknock agents in gasoline (*18, 19, 39*).

(2) The catalytic polymerization of olefins using aluminum alkyls and titanium tetrachloride or organotitanium compounds (*15, 16, 40, 185, 229, 268*).

(3) The oxo or hydroformylation process, involving the intermediate formation of organocobalt compounds (*120, 121*).

(4) The oxidation of olefins to carbonyl compounds by means of palladium chloride catalysts (and involving intermediate organopalladium compounds) (*224, 225, 226*).

Many other applications of organotransition metal compounds have been cited. Continued industrial and governmental interest in this area will provide an important stimulus for further basic research and discoveries. Probably the best general reference concerning industrial applications of organotransition metal compounds is the recent book by Harwood (*116*).

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The Role of the Metal Atom in the Reactions of the Iron Group Metallocenes

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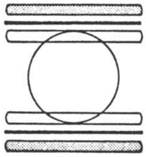
Oxidation of the iron group metallocenes apparently involves electron donation by the metal atom, and the dimerization of α-hydroxyalkylferrocenes similarly appears to take place by internal electron transfer from the metal atom to an α-ferrocenylcarbonium ion center. The high rates and stereoselectivity which characterize solvolysis reactions of α-acetoxyalkylmetallocenes have also been ascribed to metal atom participation. Alcohol groups in α- and β-hydroxyalkyl-metallocenes are capable of hydrogen bonding with the metal atom, and in strong acid solutions protonation of the metallocenes apparently takes place at this site. It has also been supposed that electrophilic ring substitution occurs preferentially through initial formation of an intermediate in which the electrophile is coordinated to the metal atom. Some recent experiments involving stereochemically directed electrophiles are shown to cast doubt on this hypothesis.

Since the discovery of ferrocene (*26*) and its aromatic character (*67*) considerable interest has been attached to the possible function of the metal atom in the reactions of this substance and of its congeners, ruthenocene and osmocene.

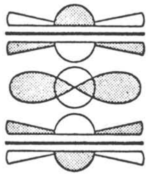
The purpose of this paper is to review the present state of our knowledge regarding participation of the metal atom in processes of electron transfer and as a neighboring group in solvolysis reactions and to consider lastly the question of the involvement of this center in the electrophilic substitution reactions of the metallocenes.

By way of preface to this general topic, it will be useful to consider the nature of the bonding interactions in these complexes. Figure 1 depicts in diagrammatic form the number and symmetry classification of ring and metal orbitals which combine by pairs and may therefore contribute to bonding of the metal atom with the cyclopentadienyl rings. Because only those ring and metal orbitals which belong to the same irreducible representation of the D_{5d} point group may combine to give bonding states, it is a simple matter to identify such combining pairs. Of course, this procedure merely tells us which orbitals are allowed by their symmetry properties to contribute to such bonding. It does not tell us to what degree each pair does, in fact, do so. To know this we must be able to evaluate the off-diagonal elements of the secular equations for each interaction which, in turn, requires determining the relative energies and overlap integrals for each of the orbital pairs.



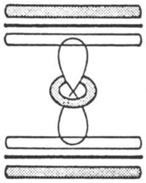
($cpA_{1g} - 4s$)

(A_{1g})



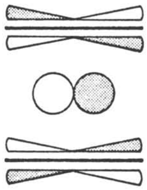
($cpE_{2g} - 3d_{xy,x^2-y^2}$)

(E_{2g})



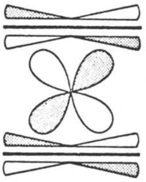
($cpA_{1g} - 3d_{z^2}$)

(A'_{1g})



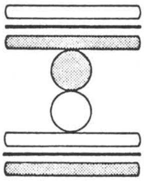
($cpE_{1u} - 4p_{x,y}$)

(E_{1u})



($cpE_{1g} - 3d_{xz,yz}$)

(E_{1g})



($cpA_{2u} - 4p_z$)

(A_{2u})

Figure 1. Number and symmetry of allowed ring-metal orbital combinations

Notwithstanding many of the approximations and uncertainties implicit in the calculation of energy levels for these rather complex systems, there is fairly general agreement (*12, 49, 51, 68*) that six molecular orbitals are principally responsible for metal-to-ring bonding. These are the A_{1g} and A_{2u} orbitals and the two doubly degenerate E_{1g} and E_{1u} orbitals.

In addition, there are three essentially nonbonding states, the A'_{1g}, and the doubly degenerate E_{2g} orbitals, which because of the small ring-metal overlap do not contribute greatly to bonding. When all six bonding orbitals are filled, as they are in the iron group metallocenes, six electrons remain to be disposed of. These must be placed in the A'_{1g} and E_{2g} orbitals which are largely metal orbitals in character.

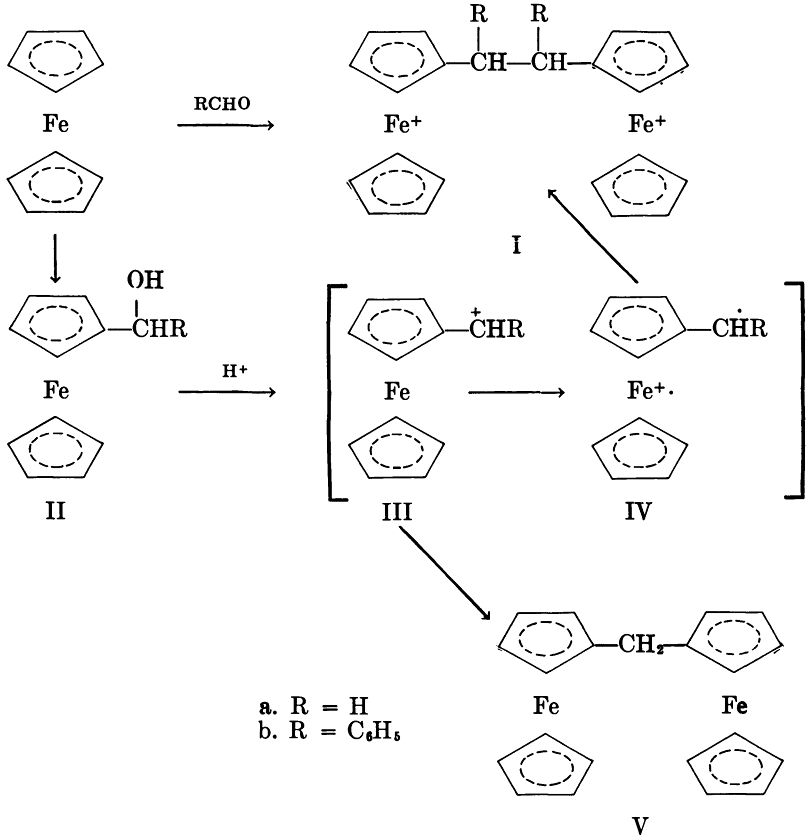
The electron distribution in these complexes is not then fundamentally different from that encountered in low-spin d^6 octahedral coordination complexes except that the degeneracy of the t_{2g} nonbonding levels in these latter compounds are lifted in the cyclopentadienyl complexes (*36*).

Although the exact relative placement of these orbitals may perhaps be considered unresolved, there is little doubt that their energies are rather close to one another and that they represent the highest filled levels in the metallocenes. The most recent ligand field treatment places the A'_{1g} orbital at 0.53 *e.v.* above the E_{2g} level (*50*).

The very characteristic oxidation reactions of these substances probably occur through removal of one or more of these nonbonding electrons. The magnetic susceptibility of the ferricenium ion (2.49 *BM*) (*52*) is in accord with the $^2E_{2g}$ state for this ion, as is a recent Mössbauer determination of the sign of the electric field gradient in ferrocene (*9*) and the observed decrease in quadrupole splitting in the Mössbauer spectrum of ferrocene on oxidation to the ferricenium ion (*69*).

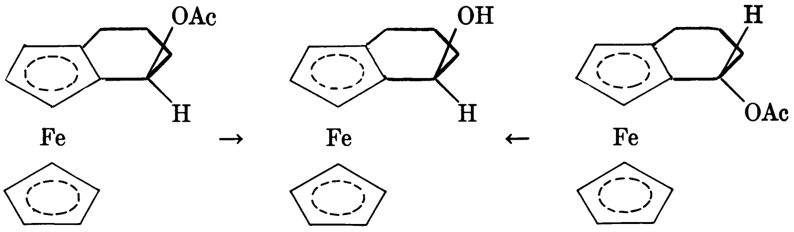
The oxidation potentials of substituted ferrocenes are, perhaps not unexpectedly, found to be a sensitive function of the number and type of ring substituents. The formal oxidation potentials of a considerable number of mono- and disubstituted ferrocene derivatives have been determined titrimetrically (*19, 20, 31, 35, 38*), as well as by chronopotentiometry (*5, 25, 27, 28, 29, 62, 63*) and polarography (*2, 39, 56, 57, 58*). The oxidation potentials of these substances appear to correlate rather well with σ_p or $\Sigma\sigma_p$ for disubstituted ferrocenes, although Nesmeyanov and his coworkers have more recently claimed (*35*) that a better correlation is obtained with the Taft σ°_p constants (*53, 54*).

Ferrocenylcarbinols undergo transformations in strong acid media which are believed to involve an internal oxidation-reduction step. These processes were first observed in the attempted hydroxyalkylation reactions of ferrocene with benzaldehyde or formaldehyde in the presence of sulfuric acid (*33, 34, 43, 66*). The product was not the anticipated carbinol but the dimeric substances (I a,b). Their origin has been accounted for by Rinehart, Michejda, and Kittle (*43*), who assumed that the carbonium ion (III), formed from the carbinol, is converted to the radical ferricenium ion (IV) by internal electron transfer. The radical then dimerizes to give the observed product which does, in fact, appear to be formed in the reaction as the diferricenium salt. In this form the substance is immune to



further electrophilic attack, and it is therefore not surprising that products derived from subsequent hydroxyalkylation of the dimer are not accumulated in the reaction.

Both hydroxymethylferrocene and phenylferrocenylcarbinol (II a and b) are, in fact, converted to the dimeric products on treatment with sulfuric acid (*33*, *34*, *43*). However, Pauson and Watts (*37*) have shown that when the reaction with ferrocenylcarbinol is carried out in the presence of excess ferrocene the product is diferrocenylmethane (V). Evidently, the internal electron transfer step, if it does in fact occur, is either reversible or can be made slower than the alkylation process in the presence of sufficient ferrocene. It is clear that a good deal more must be known of these reactions before the proposed mechanism can be said to be established. It



VI VIII VII

is possible that the radical ion (IV) is formed not by internal electron transfer but by external reduction of a ferricenium carbonium ion, or that the simple α-ferrocenyl radical derived by external reduction of Structure III is the actual intermediate whose dimerization eventually leads to Structure I.

The solvolytic reactions of α-metallocenylcarbinyl acetates, which presumably involve α-metallocenyl carbonium ions, provide further examples of reactions in which metal orbital electrons may be involved. Although the evidence for neighboring group participation by the metal atom is fairly compelling, the precise mode by which the metal atom may contribute to charge stabilization is still a matter of some dispute (*6*, *15*).

The solvolytic reactions of α-metallocenylcarbinyl acetates, which proceed by an S_N1 mechanism involving *O*-alkyl cleavage, are characterized by their extremely high rates and by their stereoselectivity. The former aspect is well-documented in Table I, in which the kinetic results of Richards and Hill (*23*, *24*, *40*) are summarized.

As a stabilizing group for carbonium ions, a single ferrocenyl nucleus is almost as effective as three phenyl substituents, and this stabilization increases progressively as the metal atom is changed to ruthenium and then osmium.

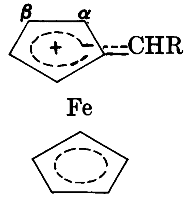
The stereoselectivity of these reactions, exemplified by the hydrolysis of the isomeric acetates (VI and VII), is no less striking. Both of these esters undergo hydrolysis by uncatalyzed ionization to give the exo alcohol (VIII), but the rate of hydrolysis of VI is some 2000 times that of its endo

Table I. Solvolysis Rates of α-Metallocenylcarbinyl Acetates in 80% Acetone-Water at 30° C.

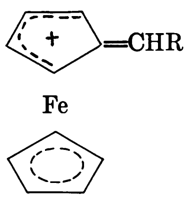
Acetate	*$kx10^5$ sec.$^{-1}$*	*ΔH^*(kcal./mole)*	*ΔS^*(e.u.)*	*Relative Rate*
Cp_2FeCH_2OAc	1.6	—	—	0.09
$Cp_2FeCHOAcCH_3$	17.02±0.15	19.0±0.06	−13.2	1.00
$Cp_2RuCHOAcCH_3$	23.22±1.10	19.34	−11.4	1.36
$Cp_2OsCHOAcCH_3$	91.5 ±1.16	18.54	−11.2	5.37
Ph_3COAc	2.58±0.033	21.1	−6.7	0.15

isomer, and the difference is due almost entirely to a lower enthalpy of activation for the exo isomer (*60*). These results have been interpreted as evidence for anchimeric assistance by the metal atom in these reactions.

In principle, two modes of electronic interactions are available by which charge stabilization in α-metallocenyl carbonium ions may be achieved. The first amounts to an enlargement in the metal-ring interactions by inclusion of the cationic center within the cyclopentadienyl framework, so that the bonding interactions between A_{2u}, A_{1g}, E_{1u}, and E_{1g} metal orbitals and extended ring orbitals of compatible symmetry are preserved. In addition, the hitherto unused E_{2g} metal orbital electrons may provide further stabilization by direct interaction with the electron-deficient center. It has been suggested (*6*) that the ring bearing the cationic center actually shifts slightly, as in IX, so as to facilitate these interactions by improving the overlap of the orbitals involved, and some evidence for this has recently been provided in a study of the chemical shifts of ring proton in α-ferrocenyl carbonium ions. While normally electron-withdrawing substituents in ferrocene derivatives tend to deshield protons α to the substituent to a greater degree than those further removed in the β position, precisely the reverse effect is observed in the carbonium ions. The difference in shielding, which is considerable and amounts to 118 cps in the unsubstituted cation (R = H), is accounted for on the basis of Structure IX, in which a shift of the upper ring results in a somewhat greater shielding of its α-hydrogens as a consequence of greater overlap of the metal atom with C-2 and C-5, together with anisotropy effects of the metal atom.

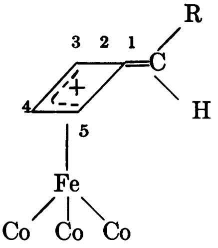


IX

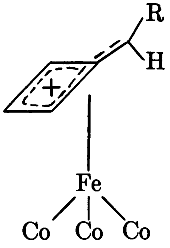


X

It would be premature to conclude that this structural deformation has been established beyond doubt, although it is certainly an attractive hypothesis. Fitzpatrick, Watts, and Pettit (*15*) have recently interpreted the NMR spectra of two cyclobutadienyliron tricarbonyl carbinyl cations, the stability of which is highly reminiscent of α-ferrocenyl carbonium ions as being more compatible with Structure XI, in which the metal has possibly moved in the direction away from the exocyclic center, than with Structure XII. The argument given here is that the chemical shifts of H_4 (τ 3.48) and $H_{3,5}$ (τ 4.56 and 4.16) in XIb (in which all the protons can be unambiguously assigned) are analogous to those in allyliron tricarbonyl systems (*14*), in which the proton atom likewise appears at lower field. Whether the same pattern for terminal and nonterminal protons would subsist in the butadiene cation complex (X), suggested by Fitzpatrick, Watts, and Pettit as an alternative formulation of the α-ferrocenyl carbonium ion, must remain for the present open to speculation. However, it must be noted that the neutral cyclopentadiene complexes, (XIII) (*13*) and (XIV) (*18*), do in fact show such an absorption pattern, and that the difference in chemical shifts between $H_{3,4}$ and $H_{2,5}$ in these substances is close to 3 ppm.

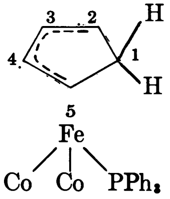


XI

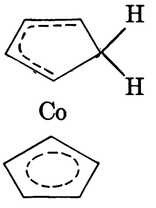


XII

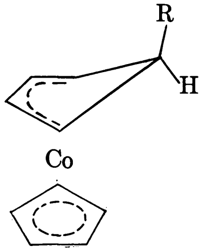
a. R = H
b. R = CH_3



XIII



XIV



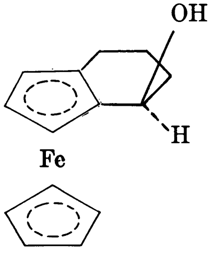
XV

a. R = C_6H_5
b. R = C_6H_5CO

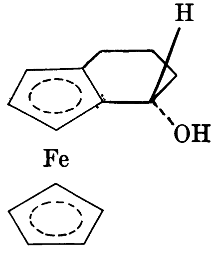
These large chemical shift differences may be due, in part, to a deformation of the five-membered ring similar to that which obtains in the closely related complexes XVa (*8*) and b (*7*). Such an additional structural feature must consequently also be considered as a possibility for the α-ferrocenyl carbonium ion. An x-ray structure determination of these cations would obviously be valuable in resolving these questions.

Ware and Traylor (*64*) have also suggested, on the basis of kinetic data, that no appreciable stabilization of the cation formed in the solvolyses of α-ferrocenylcarbinyl acetates need be attributed to direct participation by the metal ion in these processes. This conclusion rests in part on the assumption that the σ^+ value for the ρ-ferrocenyl group, used in the calculations and derived from the rate of solvolysis of ρ-ferrocenylphenethyl chloride, does not itself include a contribution from metal participation at the conjugate *para* position. The use of identical ρ values for the solvolysis reactions of α-ferrocenylethyl chloride and α-methoxyethyl chloride, although consistent with the conclusions derived therefrom, may also be questioned. Nevertheless, the results of Ware and Traylor do cast some doubt on the importance of the metal ion in providing anchimeric assistance in the ionization process, specifically by interaction of its nonbonding electrons with the developing cationic center. They suggest instead that the primary source of carbonium ion stabilization in these systems is the diffusion of charge through interactions with bonding orbitals within the ferrocene nucleus. (Whether one chooses to describe such stabilization as due to "metal" participation or ring conjugation is perhaps a matter of semantics. However, because the orbitals involved in stabilization of the cationic center are neither strictly ring nor metal orbitals, but combinations of both, each of these descriptions would appear to be inexact and tendentious. Metal participation as a descriptive term might best be confined to those interactions involving the nonbonding electrons localized on the metal atom.)

The infrared spectra of a number of hydroxyalkylmetallocenes have been interpreted in terms of hydrogen bonding involving the metal atom. The best example is provided by the epimeric alcohols (XVI and XVII), which exhibit absorption at 3610 and 3561 cm.$^{-1}$, respectively, in dilute carbon disulfide solution (*23*, *24*, *59*). The low frequency band which, with the absorption near 3600 cm.$^{-1}$ appears as well in the spectra of acyclic α- and β-hydroxyalkylferrocenes, has been assigned to the metal-bound hydrogen bond (*23*, *24*, *59*, *61*).

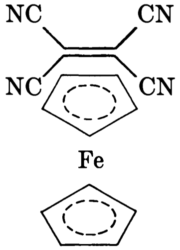


XVI

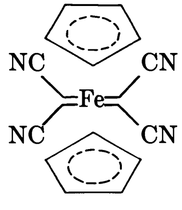


XVII

Ferrocene forms charge-transfer complexes with a number of acceptor molecules (*4, 16, 17, 21, 22, 46, 65*), of which that with tetracyanoethylene isolated as a green crystalline substance (*46, 65*) is perhaps the best characterized. In view of the electron-donor properties of the metal atom, it has been suggested that its structure might best be represented by XIX, rather than by the more classical formulation XVIII (*46*).



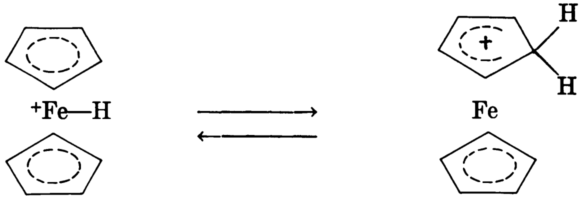
XVIII



XIX

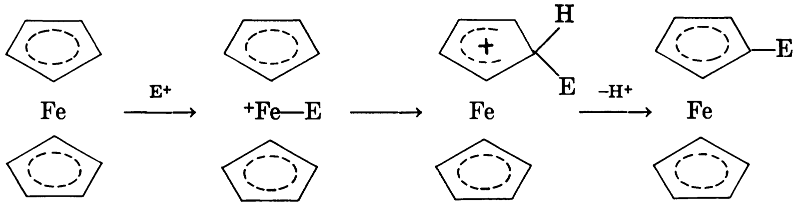
This question has now been resolved by an x-ray structure determination of the crystalline complex (*30*), from which it is clear that its structure, in this state at least, is best represented by XVIII.

The reactions of ferrocene and ruthenocene with strong acids provide perhaps the most direct evidence for the involvement of the metal atom. In solutions of sulfuric acid or boron trifluoride hydrate, or in the presence of Lewis acid combinations such as aluminium chloride-hydrogen chloride, ferrocene undergoes extensive protonation to give the cation ($C_{10}H_{11}Fe^+$) (*47*). The NMR spectrum (*11*) of this cation reveals a broad peak centered at τ 12.09—equivalent to one proton. This high field absorption, characteristic of protons bound to transition metals, is compatible with Structure XX for the cation, and it is reasonable to suppose that the electrons utilized in bond formation are the unshared electrons of the metal atom. (Ware and Traylor (*64*) have suggested that these data are compatible with a rapidly equilibrating σ complex (XXI) in which the endocyclic proton is rapidly exchanged between all 10 ring positions. However, it is difficult to reconcile the very high shielding of the acidic proton with such a structure because the endocyclic protons in the neutral complexes XIII and XIV are near τ 7.5, and the addition of a positive charge to the cyclopentadiene ring would be expected to decrease the shielding of this proton even further.) This does not mean that the σ complex (XXI) is not in equilibrium with XX and, in fact, the rapid deuteration of ferrocene in these acidic media requires that the latter complex or its equivalent be present in these solutions. Cyclopentadienyl proton resonance in these solutions gives rise to doublet absorption (τ 5.03, J = 1.3 cps), so that the external proton must spend an appreciable part of its time associated with a single ferrocene nucleus before it undergoes exchange either with the solvent or by the mechanism of ring substitution. Proton exchange, probably with the solvent primarily, must be somewhat more rapid with ruthenocene because both the high and low field absorptions (τ 17.2 and 4.67) of this substance in boron trifluoride hydrate are sharp singlets. Osmocene gives no direct evidence of protonation in these solutions, but a lower equilibrium concentration of the cation coupled with more rapid exchange of the acidic proton could readily account for this.



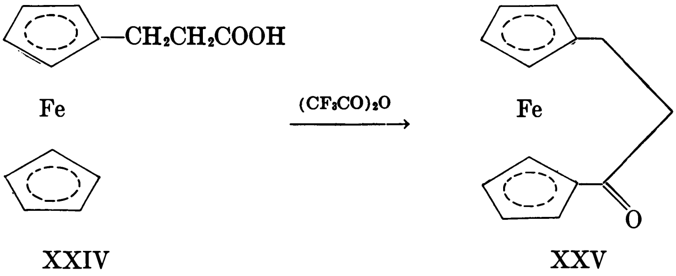
XX XXI

In part, these observations prompted the hypothesis that electrophilic substitutions of the iron group metallocenes might proceed through initial formation of a similar "μ-complex" (XXII), followed by rearrangement of this cation to the endocyclic σ complex (XXIII) and subsequent loss of a proton (*48*). (Certain other observations were not apparently in accord with this mechanism, but could not however exclude it. *See also* References *1*, *41*, and *44*.) Such a mechanism offered an attractive rationalization of the apparent anomaly that, although mono-substituted ferrocenes bearing an electron withdrawing substituent are strongly deactivated toward further electrophilic substitution (*47*, *48*), there does not appear to be any strong electronic conjugation between the rings (*48*). Thus, if as seems plausible the position of the equilibrium step leading to the formation of XXII were to be a sensitive function of the oxidation potential of metal, the apparent interannular effect of these substituents could then be accounted for simply in terms of their effect on the oxidation potential of the metal atom.



XXII XXIII

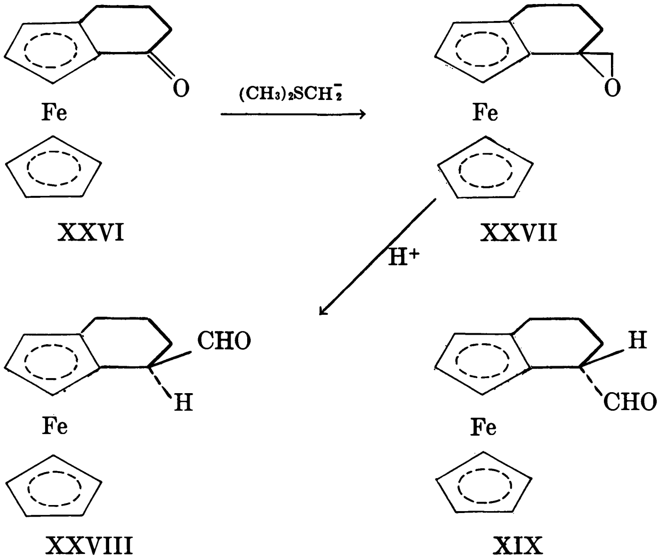
An essential aspect of this mechanism is the endocyclic mode by which ring substitution is presumed to take place by rearrangement of XXII to XXIII. The cyclization of β-ferrocenylpropionic acid (XXIV) to the



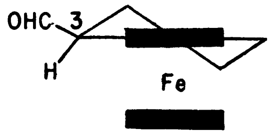
bridged derivative (XXV) (*42*) provides evidence that this mode of ring substitution is at least allowed because the internal acylonium ion derived from XXIV is sterically incapable of approaching the exocyclic face of the unsubstituted ring.

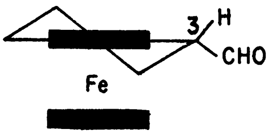
This latter aspect of the proposed mechanism provided the grounds upon which its validity could be tested by examining the relative rates at which an epimeric pair of ferrocene carboxylic acids, constrained by their stereochemistry to either exocyclic or endocyclic electrophilic attack, would undergo homoannular cyclization (*45*).

The synthesis of the required acids was effected as outlined below. Condensation of the cyclic ketone (XXVI) with· dimethylsulfonium methylide (*10*) afforded a mixture of exo and endo aldehydes (XXVIII and XIX) on acid work-up of the reaction. The very great ease with which the intermediate epoxide (XXVII) undergoes acid catalyzed isomerization is not surprising in view of the very great stability of α-ferrocenyl carbonium ions previously noted.

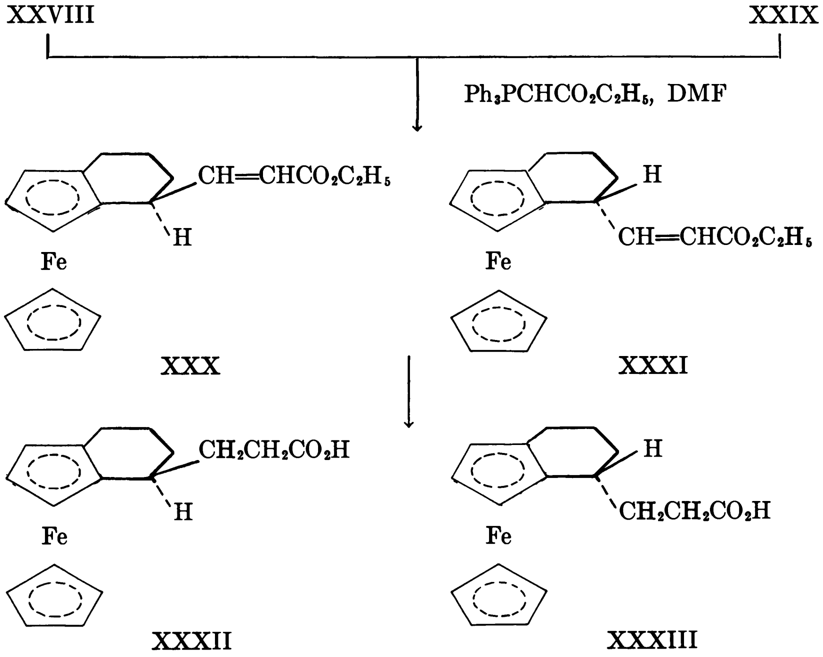


We had hoped to effect the requisite chain lengthening of each of the aldehydes separately and, accordingly, they were separated by fractional crystallization. In each of these epimers the aldehyde group is ψ-equatorial, as shown below in the projection structures. The average spatial dispositions of these groups are not widely disparate and, accordingly, the chemical shifts of the aldehyde protons in the two epimers differ by less than 5 cps (at 60 mc).





This is not true of the tertiary (H_3) protons which, because of their ψ-axial conformation, experience widely different, induced field effects. In the exo aldehyde this proton is held in the strongly deshielding region between the rings (*32*) and exhibits resonance at τ 6.43, whereas the signal for this proton in the epimeric aldehyde falls under the complex bond envelope of methylene protons—between τ 7.5–8.8. Both aldehydes, when condensed with carbomethoxymethylenetriphenylphosphorane, gave the same mixture of unsaturated esters (XXX and XXXI). (In a separate experiment, the aldehydes were shown to equilibrate under the conditions required to effect the Wittig condensation.) These were hydrogenated, saponified, and finally separated by fractional crystallization as shown below.

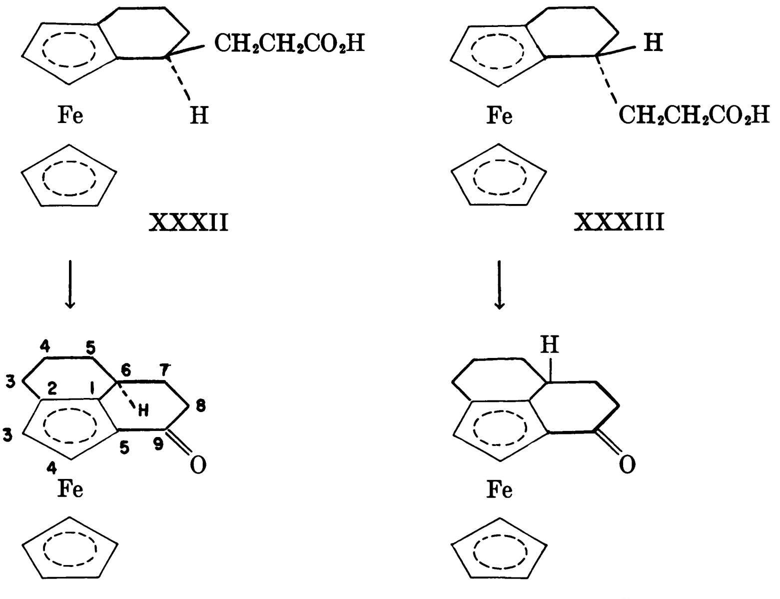


The structures of the acids (XXXII and XXXIII) were established by the following reactions.

The ketone (XXVI) was condensed with ethyl bromoacetate in a Reformatsky reaction, and the resulting unsaturated ester (XXXIV) was catalytically reduced and then saponified to give the endo acid (XXXV). Its configuration follows from its mode of formation and is confirmed by its cyclization in the presence of trifluoroacetic anhydride to the bridge ketone (XXXVI).

The acid was then converted to its acid chloride (XXXVII), thence to the diazoketone (XXXVIII), and finally to the acid (XXXIII) by Wolff rearrangement as shown below. Its endo configuration and the structures of the epimeric acids obtained in the Wittig reaction sequence are thereby established.

Both of the acids cyclized to the corresponding homocyclic ketones (XXXIX and XL) on treatment with trifluoroacetic anhydride. The relative rates of cyclization, summarized in Table II, were determined in a series of competitive reactions. Included is the comparative rate of cyclization of the open chain analog, γ-ferrocenylbutyric acid. The difference in reactivity between this acid and its ring-fused analogs may reflect the strain attending the formation of the 5,6,6 tricyclic system.



XXXII XXXIII

XXXIX XL

The relative rates of cyclization of the exo and endo acids are seen to vary somewhat in the presence and absence of trifluoroacetic acid. These results are as yet preliminary, and it is not known whether the

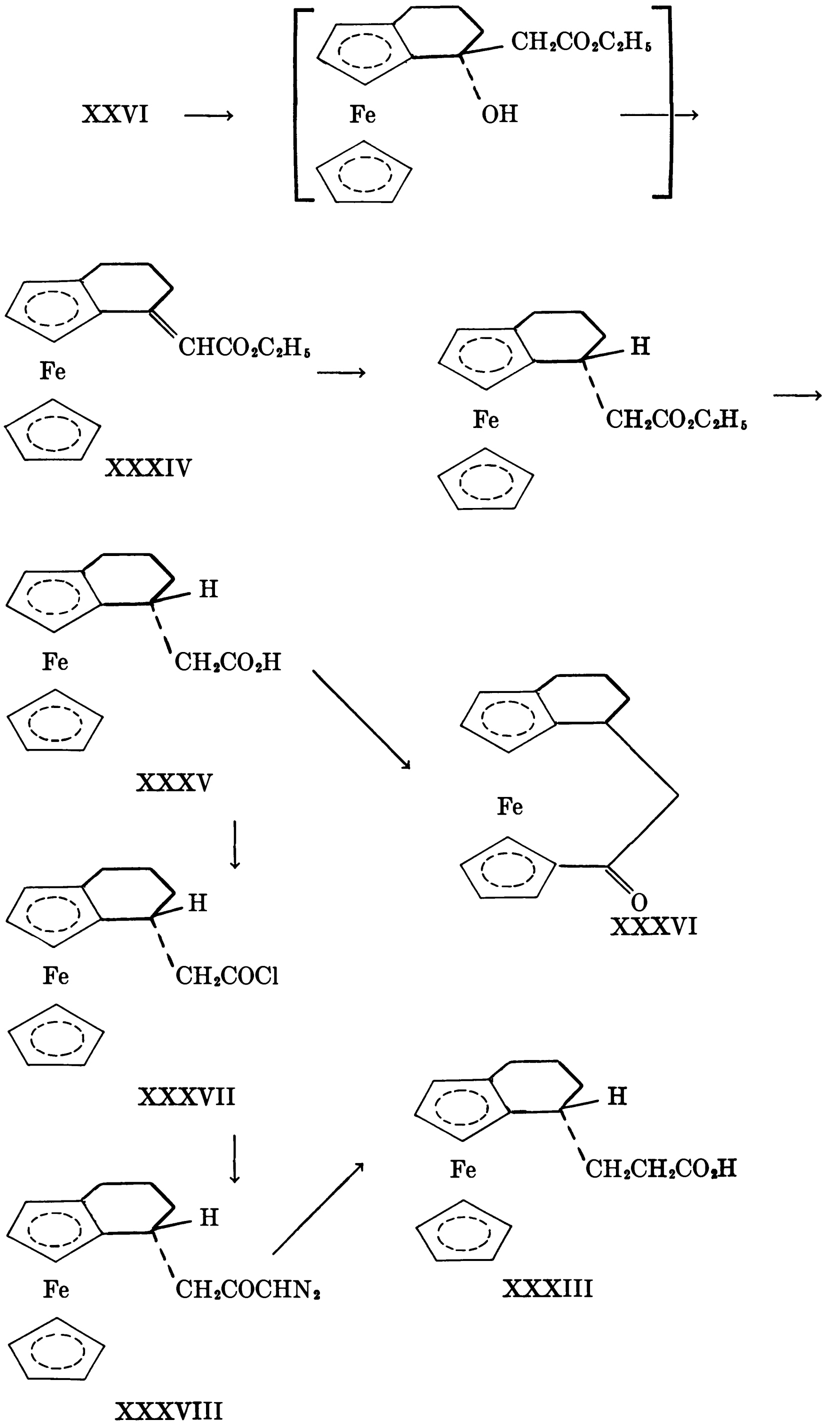

XXVI
CH₂CO₂C₂H₅
Fe
OH
CHCO₂C₂H₅
Fe
XXXIV
H
Fe
CH₂CO₂C₂H₅
H
Fe
CH₂CO₂H
XXXV
Fe
O
XXXVI
H
Fe
CH₂COCl
XXXVII
H
Fe
CH₂COCHN₂
XXXVIII
H
Fe
CH₂CH₂CO₂H
XXXIII

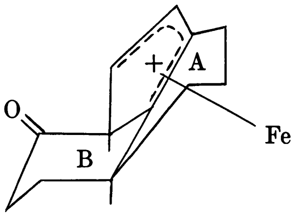
Table II. Relative Rates of Acylation with Trifluoroacetic Anhydride Methylene Chloride at 0°C.

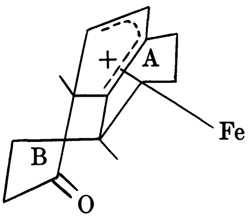
γ-Ferrocenyl-butyric acid	*Exo acid (32)*	*Endo acid (33)*
60	7	1
	4	1[a]

[a] A large molar excess of trifluoroacetic acid was added to the reaction initially.

observed variation is real. Furthermore, it must be noted that the difference between exo and endo acid rates of cyclization may in part reflect a difference in either the equilibrium concentrations of the epimeric mixed anhydride intermediates or in acid catalysis of the two reactions (*3*, *55*). Nevertheless, it seems unlikely that these differences are very large, and hence there would not appear to be strong energy factors favoring endocyclic substitution of the cyclopentadienyl rings.

Lastly, it does not seem likely that the exocyclic acid (XXXII) effects ring substitution through an endocyclic mode of attack for, although the spatial dispositions of the acid side chains in each of the epimeric acids do not differ widely with respect to the cyclopentadienyl ring plane, a "transoid" mode of cyclization for either of these acids involves a σ-complex intermediate of apparent strain.





It would appear that the metal atom plays no essential role in electrophilic ring substitution of ferrocene as we had previously supposed (*48*). It remains to be demonstrated whether endocyclic electrophilic ring substitution, which allows for prior formation of a μ-complex intermediate, provides any advantage to these processes. The present, preliminary results, however, provide little support for the view that it does.

It is clear that much remains to be learned before the function of the metal atom in the various reactions of the iron group metallocenes may be said to be well-defined.

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Chemistry of Cyclobutadiene-Iron Tricarbonyl

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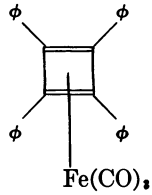
Cyclobutadiene-iron tricarbonyl is prepared through reaction of 3,4-dichlorocyclobutene and diiron enneacarbonyl. In an analogous manner, one can prepare 1,2-diphenyl-; 1,2,3,4-tetramethyl-; and benzocyclobutadiene-iron tricarbonyl complexes. Cyclobutadiene-iron tricarbonyl is "aromatic" in the sense that it undergoes facile attack by electrophilic reagents to produce monosubstituted cyclobutadiene-iron tricarbonyl complexes. Functional groups in the substituents display many of their normal chemical reactions which can be used to prepare further types of substituted cyclobutadiene-iron tricarbonyl complexes.

Following repeated failures during several decades to isolate cyclobutadiene, organic chemists came to recognize that this hydrocarbon, if it is thermodynamically stable at all, is at best an extremely reactive system (*1*). Hückel molecular orbital calculations supported these conclusions; such calculations predict that the system will possess no resonance stabilization energy and this, coupled with the fact that the double bonds are part of a highly strained ring system, allows one to predict a high degree of reactivity for the molecule.

It was, therefore, a most intriguing suggestion, proposed by Longuett-Higgins and Orgel in 1956 (*5*) that, despite its instability, cyclobutadiene nonetheless might be able to form stable complexes when coordinated to metal atoms of the transition series. The basis for this prediction was the fact that the molecular orbitals of cyclobutadiene are of the correct symmetry to interact with the atomic orbitals of the metal atom; these interactions allow bonding of the "forward coordination-back donation" type which is commonly necessary in metal complexes involving the metal atom in a low oxidation state.

Shortly thereafter, this prediction was essentially proved to be correct; Hubel and co-workers (*4*) in 1959 reported the isolation of tetraphenylcyclobutadiene-iron tricarbonyl(I) following reaction of diphenylacetylene and Fe(CO)$_5$ and, in the same year, Criegee and co-workers (*2*) prepared the dimer of tetramethylcyclobutadiene-nickel dichloride (II) through reaction of tetramethyldichlorocyclobutene and Ni(CO)$_4$. X-ray determinations have subsequently confirmed the presence of the tetra-substituted cyclobutadiene rings in these two complexes.



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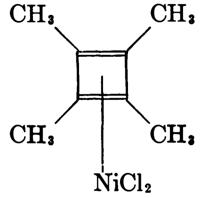
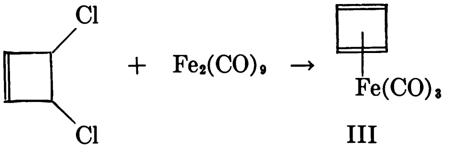


II

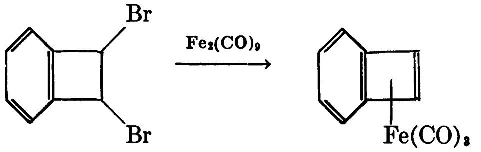
Since these two initial reports, several other complexes possessing tetra-substituted, cyclobutadiene ligands have been reported, notably by Maitlis and co-workers (*6*), who have demonstrated that one can transfer a cyclobutadiene ligand from one metal to another to produce new cyclobutadiene-metal complexes.

In 1964 we prepared cyclobutadiene-iron tricarbonyl (III), a complex possessing an unsubstituted cyclobutadiene ligand (*3*). The reaction employed in this preparation involves the interaction of *cis*-3,4-dichlorocyclobutene with Fe$_2$(CO)$_9$. It has subsequently been found that the dehalogenation of dihalocyclobutenes with diiron enneacarbonyl appears to be a general route for the preparation of cyclobutadiene-iron tricarbonyl complexes. Thus, in a similar manner, dibromobenzocyclobutene reacts with Fe$_2$(CO)$_9$ to produce benzcyclobutadiene-iron tricarbonyl (IV). Likewise, 3,4-dichlorotetramethylcyclobutene reacts to give tetramethylcyclobutadiene-iron tricarbonyl (V) (*7*) and 3,4-dibromo-1,2-diphenylcyclobutene affords 1,2-diphenylcyclobutadiene-iron tricarbonyl (VI) (*7*). However, perfluorocyclobutene does not react to give tetrafluorocyclobutadiene-iron tricarbonyl.

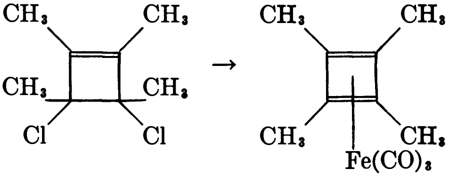


III

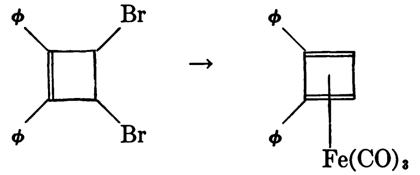
The mechanism of the formation of these cyclobutadiene complexes remains obscure; it is interesting to note that either the cis or trans isomer of 3,4-dichlorocyclobutene reacts with Fe$_2$(CO)$_9$ to give Complex III and that Complex IV can be produced from either the cis or trans isomer of diiodobenzocyclobutene (*7*).



IV



V



VI

Chemical Properties of Cyclobutadiene-Iron Tricarbonyl

Cyclobutadiene-iron tricarbonyl is a pale, yellow solid, m.p. 26°C., which exhibits a single, sharp NMR absorption at τ 6.09. In common with other diene-iron tricarbonyl complexes, the material displays appreciable thermal stability, as well as a pronounced resistance to further replacement of the CO ligands; several hours treatment with triphenylphosphine in refluxing toluene leaves the complex unaffected.

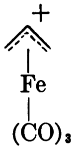
One of the most interesting properties of the complex concerns its reactions with electrophilic reagents. It is found that these reactions lead to substituted cyclobutadiene-iron tricarbonyl complexes and, in this sense, the complex is classified as aromatic just as ferrocene may be so classified. The substitution reactions which have been performed so far are summarized below.

Reaction of Complex III with acetyl chloride and aluminum chloride under typical Friedel-Crafts conditions affords acetylcyclobutadiene-iron tricarbonyl (VII) in high yields. The corresponding benzoyl derivative is similarly prepared with benzoyl chloride. Formylation with *N*-methylformanilide and $POCl_3$ produces cyclobutadienecarboxaldehyde-iron tricarbonyl (VIII), while chloromethylation with formaldehyde and HCl affords the chloromethyl derivative (IX).

It is possible to perform many of the usual reactions characteristic of the functional groups in these substituted complexes. Thus, reaction of Complex VII with $NaBH_4$ produces the secondary alcohol (X), which is also obtained when the aldehyde (VIII) is treated with methylmagnesium iodide. The aldehyde (VIII) can also be reduced with $NaBH_4$ to generate hydroxymethylcyclobutadiene-iron tricarbonyl (XI); the same complex is produced upon hydrolysis of the chloromethyl derivative (IX).

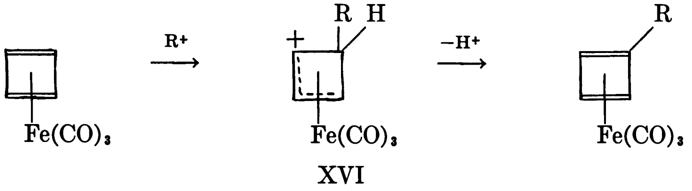
Reaction of cyclobutadiene-iron tricarbonyl with methylchlorothioformate followed by hydrolysis gives rise to cyclobutadienecarboxylic acid-iron tricarbonyl (XII). A Curtius rearrangement of the acid azide derived from Complex XII affords aminocyclobutadiene-iron tricarbonyl (XIII). The dimethylaminomethyl derivative (XIV) is readily available through the Mannich reaction with formaldehyde and dimethylamine. The chloromercury cyclobutadiene complex (XV) is produced upon reaction of Complex III with $Hg(OAc)_2$, followed by treatment with hydrochloric acid. In the simplest substitution reaction, treatment of cyclobutadiene-iron tricarbonyl with CF_3COOD produces a mixture of deuterated derivatives of Complex III.

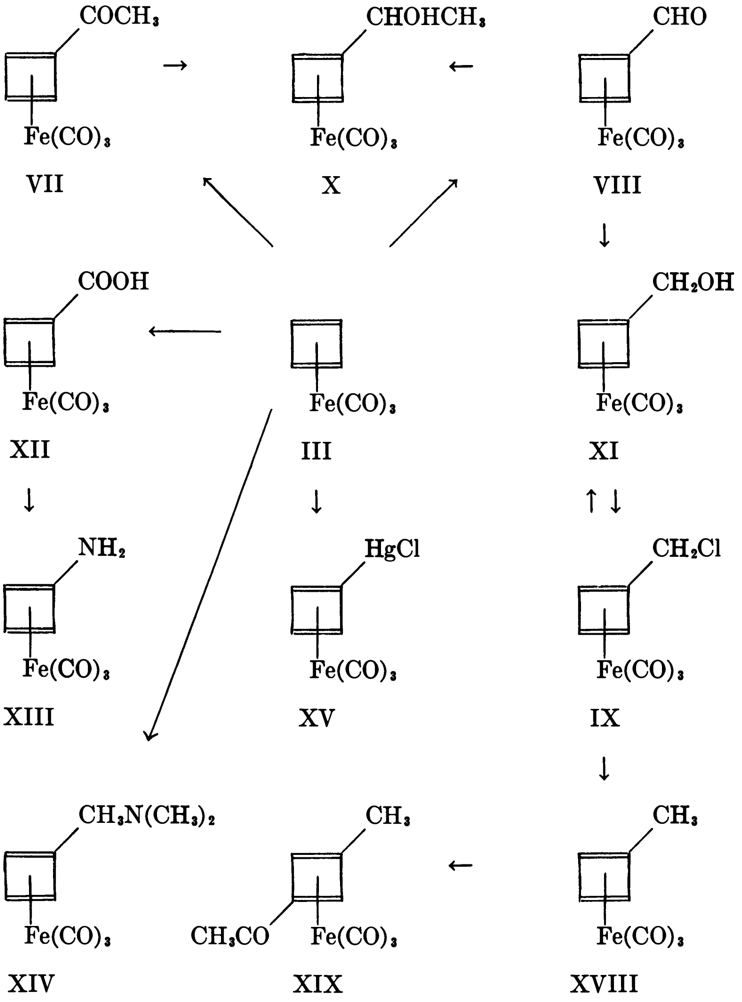
The mechanism of these substitution reactions can be readily rationalized in a manner which completely parallels the accepted electrophilic mechanism of benzene and other aromatic systems. The electrophile, R^+, adds to the cyclobutadiene ligand to produce the π-allyl-$Fe(CO)_3$ cationic intermediate (XVI); loss of a proton from this intermediate generates the substituted cyclobutadiene -$Fe(CO)_3$ complex. We have previously isolated salts of the π-allyl-iron tricarbonyl cation (XVII), as well as several of its simple alkyl derivatives; the fact that such cations can be isolated renders more plausible the intermediacy of the species (XVI) in the substitution process.



XVII

One final comment relating to the aromaticity of the cyclobutadiene ligand concerns the orientation effect of substituents towards introduction of a second substituent. To date, the only reaction bearing on this question which has been performed is the acetylation of methylcyclobutadiene -$Fe(CO)_3$ (XVIII), which was prepared by reducing the chloromethyl complex (IX). Acetylation of Complex XVIII produces a mixture of 2- and 3-acetyl-1-methylcyclobutadiene-iron tricarbonyl complexes with the latter isomer (XIX) predominating (~2:1). This is not the orientation





one would expect by analogy with the acetylation of toluene. Whether this is a result of electronic factors or is a consequence of enhanced steric hindrance to attack at the "ortho" position in Complex XVIII remains to be determined.

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Organometallic-Chelate Compounds: Organometallic Ions as Central Metal Ions

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This paper calls attention to the need for new ions in coordination chemistry—ions that would permit more detailed physico-chemical studies to be made, ions that would facilitate studies of less familiar metals and of less familiar coordination numbers, and ions that would help studies of chemical bonding and reaction mechanisms. Organometallic ions of the type R_mM^{+x} *are such ions, and these form metal-chelate compounds of the type* $R_mM(Ch)_x$*. Three aspects of the chemistry of organometallic-chelate compounds are described: (1) equilibria of compound formation; (2) kinetic and mechanistic studies of three types of reactions: (a) reactions of the coordinated ligand, (b) substitution at the 4-, 5-, or 6-coordinate metal atom, and (c) reactions of the organic moiety; and (3) studies of stereochemistry and chemical bonding.*

It has become apparent since the time of Alfred Werner, and particularly since the beginning of the period Nyholm (*31*) calls the renaissance of inorganic chemistry, that we need a new kind of metal ion in coordination chemistry. In effect, we need new central metal ions which can come only from well-known metals. This need arises because of the marked interest in physical-inorganic chemistry, an area which Werner pioneered and which has blossomed during the last two decades.

Because of current interest in solution equilibria, mechanisms of inorganic reactions, extension of Werner's work in stereochemistry to less familiar coordination numbers, and chemical bonding, it appears that typical metal atoms have certain limitations.

This novel metal ion, to be useful in the areas cited, should have the following features. It should be possible to vary the size while the charge remains constant. It should be possible to vary the coordination number of the ion markedly, say, from four to 10 or 12, though the oxidation state remains constant. It should be soluble in a variety of solvents besides highly polar ones. It should be asymmetric.

It appears that such metal ions are available as organometallic ions of the type R_nM^{+x} and, though some have been known for many years, the potential usefulness has only recently been realized. Nevertheless, many exciting possibilities become apparent from even a casual reading of reviews by Coates (*6*), Dessy (*11*), Kaesz (*17*), Pettit (*33*), Rausch (*36*), and Zeiss (*46*), among many others.

Organometallic-chelate compounds of the type R_nMCh_x (where Ch— is a chelating agent) are of interest for many reasons, including the fact that they are particularly useful in detailed studies of the behavior of the chelate group. For example, Dessy and co-workers (*42*), who formulated the pseudo-metal ion concept, used an incipient organometal cation as a pseudo-metal ion for which they were able to vary hybridization and charge properties without altering the size of the ion, and as an ion on which probes could be placed to permit a more detailed investigation of coordinate chelate groups.

Several workers have recognized that organometallic-chelate compounds form useful derivatives for the characterization and analysis of organometallic compounds. For example, as Coates and co-workers (*2*) noted, most compounds containing the dibutyltin and diphenyltin moieties are low-melting materials which are too soluble in most organic solvents for convenient purification, but the 8-quinolinol (HOx) derivatives are readily prepared and purified. Also materials of the type $R_2Sn(Ox)_2$ are colored, and the analytical applications have been noted (*37*). There are admittedly limitations to spectrophotometric determinations of organometallic ions, as revealed in a study (*12*) of the following compounds: $R_2Tl(Ox)$ ($R = Ch_3, C_2H_5, C_6H_5$), $(C_6H_5)_2Pb(Ox)_2$, $(C_6H_5)_3Pb(Ox)$, $CH_3Sn(Br)Ox_2$, and $C_6H_5SnCl(Ox)_2$. In addition, 8-quinolinol complexes of organogermanium compounds have been prepared (*15*).

Many organometallic compounds form organometallic-chelate compounds which are more stable to oxidation than the uncomplexed species. This is true of dimethylcadmium which forms 1:1 complexes with *N,N,N′,N′*-tetraethylethylenediamine, 2,2′-bipyridyl, and 1,10-phenanthroline (*40*). The stability of dialkylgold(III) derivatives can be increased by complexing with *N,N*-dialkyldithiocarbonate ion, and the products ($R_2AuSSCNR'_2$) do not decompose in dilute acids or bases and appear to be stable toward mild reducing agents (*3*). As would be expected, the enhancement of stability is a function of the nature of the organic group as well as the chelating group. For example, dimethyl(2,2′-bipyridine)zinc and dimethyl(1,10-phenanthroline)zinc are relatively stable toward air and moisture (*7*, *40*), but the higher alkyl- and diphenyl-derivatives, R_2ZnCh, are extremely sensitive to these reagents (*30*).

Moreover, some of the materials have therapeutic value, and some have useful bactericidal and fungicidal activity (*5*). In addition, the coordination chemistry of some of the metals involved has received little attention, though such knowledge would be valuable in understanding the chemistry of these metals.

As noted earlier, the substitution of organometallic ions or pseudometal ions for a central metal ion has applications which are of interest to the physical-inorganic chemist. These applications are best indicated by looking at examples from three representative areas: (1) the equilibria of complex formation; (2) studies of reaction mechanisms; and (3) problems of stereochemistry and chemical bonding.

Equilibria of Complex Formation

Studies of equilibria involved in the formation of coordination entities have been very helpful in understanding the behavior of these substances. However, much additional useful information could be obtained by using organometallic ions in these studies.

For example, consider a simple case—the interaction of a univalent-metal ion and a β-diketonate anion (Equation 1).

$$M^+ + \underset{(=\mathrm{Ch}^-)}{R'COCHCOR''} \rightleftharpoons M(R'COCHCOR'') \qquad (1)$$

The formation constant is $K_1 = (MCh)/(M^+)(Ch^-)$ where the activities of the species are indicated by parentheses. Even though this is a simple system, there are problems, the least of which is the limited number of univalent metal ions. On the other hand, compounds of the type $R_2Tl(R'COCHCOR'')$, R_2TlCh, are well-known examples of thallium(III) (*26*), and the remarkable stability of dialkyl- and diaryl-thallium(III) ions in water and in air, as well as the highly conducting nature of the aqueous solutions, is well known (*6*). These facts and the ready opportunity to vary the properties of the cation through changes in the organic moiety, R-, prompted studies of the solution stability of the complexes R_2TlCh. The chelating tendencies of several β-diketones with some dialkyl- and diaryl-thallium(III) were determined in 75 per cent (v/v) dioxane-water medium at 30°C. The following results, obtained for dibenzoylmethane, were typical (*9*).

(a) Only first complex formation constants (K_1) were obtained, and there was no indication that 5- or 6-coordinate species of the type $R_2Tl(R'COCHCOR'')_2^-$ were formed.

(b) The order of stability is (log K_1 values in parentheses) $(CH_3)_2Tl^+$ (6.90 ± 0.01) < $(CH_3CH_2)_2Tl^+$ (7.07 ± 0.03) < $(CH_3CH_2CH_2)_2Tl^+$

(7.51 ± 0.01) < $(C_6H_5)(p\text{-}CH_3C_6H_4)Tl^+$ (8.29 ± 0.01) < $(C_6H_5)_2Tl^+$ (6.88 ± 0.005).

(c) The dialkyl- and diaryl-thallium(III) derivatives are more stable (by factors of 10- to 100-fold) than the lithium derivative ($\log K_1 = 5.95$), which is the most stable of the alkali-metal derivatives (*43*).

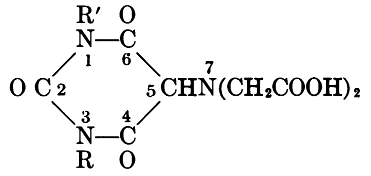
(d) For other β-diketones, a linear pK_D-log K_1 relationship is observed for each organometallic ion, which is typical of β-diketone-metal systems.

The significance of these and other results have been discussed in detail (*9*), but two significant points may be noted here.

First, simple inductive effects cannot be used to explain the order of stability of the dialkylthallium(III) derivatives. An increase in the chain length of the alkyl group should reduce the effective charge on the pseudo-metal ion, and the values of K_1 should decrease. Possibly increasing the chain length of R decreases the hydrophobic character of the pseudo-metal ion, and a solvation effect is really reflected by the stability order. A similar effect has been reported previously (*20*).

Secondly, any effects which might be ascribed to B-strain seem to be absent. It might be expected that B-strain would be significant because R_2Tl^+ is a linear ion, but R_2TlCh would be a tetrahedral molecule. It is possible that the critical pseudo-metal ion would be diisopropylthallium(III) ion.

The work of Irving and da Silva (*16*) shows how extensive a series of univalent pseudo-metal ions is available. These workers measured formation constants of complexes of ethylmercury(I), dimethylthallium(III), and uramil-7,7′-diacetic acid (R = R′ = H) and the 1-methyl- and 1,3-dimethylhomologs.



The formation constants of complexes of organometallic ions are likely to be complicated by competing hydrolysis. Nevertheless, Tobias and Yasuda (*41*) have analyzed the interaction of dimethyltin(IV) ion with bidentate ligands. This is a complicated system because of the hydrolysis of the pseudo-metal ion to $[(CH_3)_2Sn(OH)OH_2]^+$ which tends to condense to the dimer. Interestingly, of three ligands studied (picolinate, ortho-phenanthroline, and 2,4-pentanedionate), only picolinate was an effective chelating agent; the maximum fraction present as complex was only 15% and 20% for the 2,4-pentanedionate and phenanthroline systems, respectively. On the basis of this study, it might be anticipated that the formation constants of other pseudo-metal complexes will be studied. Logically, these studies would include the aquo dimethyllead(IV) ion, which has a linear skeleton (*13*).

Of course, the problems of hydrolysis can be obviated by using non-aqueous solvents, and pseudo-metal ions have the necessary solubilities. For example, spectrophotometric studies (*18*) of complex formation equilibria between 2,2′-bipyridine (bipy) and dialkyltin dichloride have been reported. The log K values for complexes $R_2SnCl_2 \cdot$bipy are 3.19 (R, n-C_4H_9), 3.36 (R, CH_3), and 6.7 (R, Cl) in acetonitrile. There is surprisingly little difference between the constants for dimethyl- and the dibutyltin dichloride complexes. The equilibrium constant for the dibutyltin dichloride complex increases with increasing dielectric constant of an alcohol solvent.

Probably more formation constants of organometallic-chelate compounds will be determined because of the importance of understanding mechanisms of reactions of these compounds.

Studies of Reaction Mechanisms

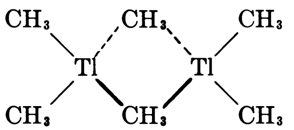
The use of organometallic ions as central metal ions not only increases the scope of inorganic reactions, but also increases the opportunity for detailed studies of these reactions because favorable properties (including solubility and volatility) are enhanced, and because it is now possible to place a probe on the metal. Possible reactions of organometallic-chelate compounds seem to be of three types.

Type I. Reactions of the Chelate Moiety. Examples of this type are surprisingly limited, probably because a systematic investigation has not been made. Perhaps one example is the interaction of a ferrocenebis (β-diketone) $Fe(C_5H_4COCH_2COR)_2$ with a nickel(II) template to give a trimeric Schiff base complex for which a cyclic structure was proposed (*32*). One may expect to find a number of useful and interesting reactions of the coordinated ligands, such as those outlined by Busch (*4*). The reaction of methyl iodide with 8-quinolinolato (Ox) derivatives in nitrobenzene can be followed by conductivity methods and is useful as a diagnostic test for the presence of a non-coordinated tertiary nitrogen (*35*). Other reactions of interest, which are suggested by the comprehensive studies by Collman and others (*8*), include: bromination (with NBS), transamination (with a coordinated imine), chloromethylation, and nitration. It would be of particular interest to study the effects of variations in the organic moieties.

Type II. Substitution at a 4-, 5-, or 6-Coordinate Metal Atom. A number of examples of substitution at 5-coordinate tin for compounds of the type $R_2Sn(Cl)(Ox)$ have been reported (*45*). These involve halide displacement with such reagents as iodide ion, chelate anions, and lithium butyl. In some instances, the products of the type $R_2Sn(X)(Ox)$ undergo disproportionation, and equi-molar mixtures of R_2SnX_2 and $R_2Sn(Ox)_2$ are isolated (*45*).

Type III. Reactions of the Organo Moiety. Few, if any, studies have been made of reactions of the organo moiety of pseudo-metal ions. Presumably the course of these reactions would be affected by the presence of coordinated ligands.

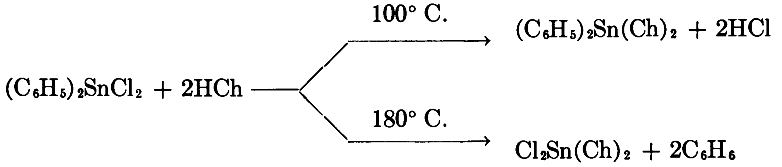
However, one difficulty of the proposed classification is the fact that reactions of Type III probably overlap with those of Type II. One good example of this is redistribution reactions, presumably a reaction of the organic group. However, Maher and Evans (*19*) find that intramolecular exchange of methyl groups of monomeric trimethylthallium follows second-order kinetics in deuterobenzene and suggest a dimeric transition state.



The exchange rates are slower in dimethyl ether and trimethylamine. This is attributed to the formation of a complex of low stability—e.g., $(CH_3)_3Tl \cdot N(CH_3)_3$. The fact that McCoy and Allred (*23*) do not observe a similar retarding effect in donor solvents for methyl exchange between dimethylzinc and dimethylcadmium was ascribed (*19*) to the lesser tendency of these alkyls to form complexes.

Another reaction of the organo moiety is metal-carbon cleavage, which has been a reaction useful in synthesis and in kinetic studies. Monoprotic chelating agents (HCh) cause tin-phenyl cleavage at 180–200°C., and compounds of the type $Cl_2Sn(Ch)_2$ are obtained using diphenyltin dichloride (*29*). Similarly, the interaction of chelating agents and $(C_6H_5)_2Sn(Ch)_2$ at 300°C. leads to 8-coordinate compounds of the type $Sn(Ch)_4$ (*35*). The reaction is not limited to tin. For example, dimethyl(2,4-pentanediono)-indium(III) results from trimethylindium and 2,4-pentanedione (*6*); Dessy and co-workers (*42*) have listed other examples.

Tin-phenyl cleavage of diphenyltin dichloride, which occurs readily at 180–200°C. in the presence of 8-quinolinol or other chelating agents (Equation 3), again is probably an example of a borderline of Types II and III.



$$(C_6H_5)_2SnCl_2 + 2HCh \xrightarrow{100^\circ\ C.} (C_6H_5)_2Sn(Ch)_2 + 2HCl \quad (2)$$

$$(C_6H_5)_2SnCl_2 + 2HCh \xrightarrow{180^\circ\ C.} Cl_2Sn(Ch)_2 + 2C_6H_6 \quad (3)$$

The kinetics of forming compounds of the type $X_2Sn(Ox)_2$ (X = Cl, Br; Ox^- = 8-quinolinolate) in dimethyl sulfoxide solution have been determined by spectrophotometric and conductometric methods at 180–200°C. (*22*). The pseudo first-order rate law is obeyed, and the observed rate constants, k_ψ, vary as a function of 8-quinolinol. The appropriate rate expression is rate $= k_\psi[(C_6H_5)_2SnX_2] = (k_1 + k_2[HOx]^2)[(C_6H_5)_2SnX_2]$. There is evidence that the two-term rate expression represents the existence of two cleavage paths. One involves as a rate-determining step the formation of a coordination entity which may be represented as $[(C_6H_5)_2SnX\text{-}(C_6H_5)_2SnX_2]^+$ on the basis of a mass-law retarding effect and halide-halide exchange studies. The second path involves nucleophilic attack by the ligand, formation of $[(C_6H_5)_2SnX_2\cdot(HOx)_2]$ and subsequent intramolecular cleavage through the activation of the electrophilic proton and incipient phenyl carbanion. There is considerable uncertainty of the role of solvation in either cleavage path, and the choice of available solvents was severely limited by boiling points which are lower than the minimum temperature for effective cleavage, by poor solubility, or by color which interfered with spectrophotometric determination of rates. However, the rate of tin-phenyl cleavage has been determined by manometric methods in the absence of solvent, and the rate expression is formally the same as that for the dimethyl sulfoxide systems (*21*). A comparison of the ratio data and activation parameters indicates that the dissociative process is essentially not a solvent-assisted one (*21*).

Presumably, because of the enhanced volatility and solubility of organometallic-chelate compounds, it should be possible to carry out mechanistic studies not only in a wide range of solvents but also in the liquid or ansolvous phase and in the gas phase.

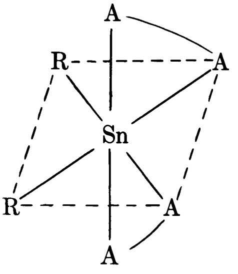
Studies of Stereochemistry and Chemical Bonding

A large number of examples are available, and an adequate coverage is not possible. Certain selected examples, however, may indicate the scope of the field.

One elegant example of the use of a pseudo-metal ion as a central metal ion, and as a probe, is the study (*42*) of the electron distribution in the series of tetrahedral complexes of the type $R_2B(R'COCHCOR'')$. A study of the ^{11}B resonance indicated the pseudo-metal atom demanded electron donation from the chelate ring in a fixed amount which was found to be a function of R but not of R′ and R″. Because an alteration of the structure of the chelate moiety (either ring size or donor atom) caused changes on the ^{11}B and H_1NMR of the R_2B unit, it was possible to evaluate the electronegativity of the ring system composed of the chelate moiety and the boron atom.

A number of organometallic complexes are examples of pentacoordination and are included in an excellent review of pentacoordination by Muetterties and Schunn (*27*). The question of whether nitrogen-metal coordination occurs in 8-quinolinolato(triphenyl)tin(IV) has been a controversial point (*37, 25, 44*).

Several studies have been made of the stereoisomerism of 6-coordinate tin complexes of the type $R_2Sn(Ch)_2$, where Ch is a bidentate ligand. When Ch is a symmetrical bidentate ligand (AA), such as 2,4-pentanedionate, 2,2-bipyridyl, and 1,10-phenathroline, cis (I) and trans (II) isomers are expected; the cis form would be optically active.



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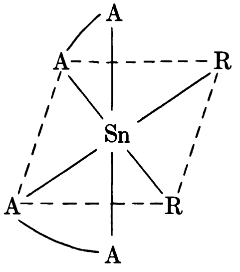

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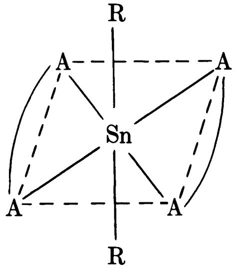

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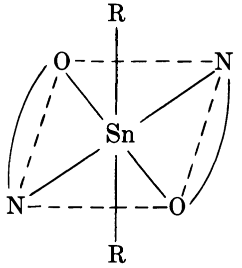

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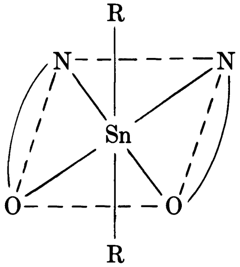
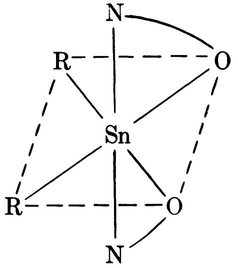


IV



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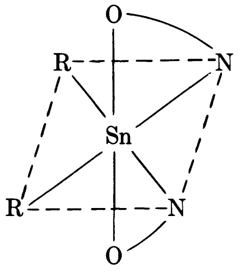

VI

A total of six stereoisomers might be expected when Ch is 8-quinolinolate (O N), including two trans forms (III, IV) and two cis forms (V, VI); both cis forms would exist as an enantiomorphic pair.

Despite these expectations, isomerism has not been observed for $R_2Sn(CH_3COCHCOCH_3)_2$ ($R = CH_3, C_6H_5$). Only the trans form was observed by McGrady and Tobias, who thoroughly studied the structure and bonding of dimethyltin(IV) ion in solution (*24*), followed by the structure and bonding of dimethyl- and diphenyltin(IV) ions with bidentate ligands (*25*). This is in accord with the failure to resolve the diphenyl complex by chromatography, using D-lactose as the absorbant (*28*). On the other hand, Smith and Wilkins (*38*) report high resolution proton magnetic resonance spectra which provide strong evidence that, for complexes of the type $X_2Sn(CH_3COCHCOCH_3)_2$, in which X = Cl, Br, I, the cis form is the stable one. Smith and Wilkins suggest that with two Sn-C bonds of low polarity the sp_z hybrid orbitals (with admixture of $sd_z{}^2$) of tin(IV) are used to give two strong trans bonds, primarily because the *d*-orbitals are too high in energy to be used extensively in bonding. When the six ligands are more nearly comparable in their position in the spectrochemical series, d^2sp^3 hybridization occurs and the cis configuration results owing to smaller splitting between the d_z^2 and $d_{x-y}^{2\ \ 2}$ orbitals. This, of course, might be altered by strong steric effects. It is likely that a mixture of cis and trans isomers would result when the polarity of the C-Sn bond is increased, possibly by the use of perfluoroalkyl groups. Also, the effect of varying the central metal should be examined, and a portion of the series $R_2M(R'COCHCOR'')_2$(R = Cl, M = Ti, Zr, Ge, and Sn) has been prepared (*10*).

It might be well to note that in the study of organometallic-chelate compounds, the uncommon is fairly common. Typically, 2,4-pentanedionate ion is a bidentate ligand but is also bonded to a second platinum atom through the methine group in dimeric $(CH_3)_3Pt(CH_3COCHCOCH_3)$ (*14*) and is bonded to platinum solely through the methine group in 2,2′-bipyridyl(2,4-pentanediono)trimethylplatinum(IV) (*39*). In the complex, $K[Pt(CH_3COCHCOCH_3)_2Cl]$, one 2,4-pentanedionate is bonded conventionally—the other through the methine carbon (*1*).

As a final point it would be useful to have an asymmetric central metal ion for mechanistic studies. One possibility is a complex derived from an optically active compound of tin, $CH_3(C_2H_5)(CH_3CH_2CH_2)SnI$ (*34*). A second possibility would be a heterocyclic ion of the type $\underline{CH_2\text{-}Y\text{-}CH_2\text{-}M}^{+n}$, in which the moiety -Y- contains an asymmetric carbon. A third possibility is an octahedral complex of the type, $\underline{CH_2(CH_2)_5M}(RCOCHCOR)_2$, which would exist as the resolvable cis form. Other possibilities will no doubt be found.

Acknowledgment

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36

Complexes of Some Transition Metals with Polydentate Aliphatic Amines

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The background, chemistry, and steric assignments of aliphatic and cycloaliphatic amines containing three or more coordinating nitrogens are discussed in relation to complex formation of transition metals. Particular attention is focused on the polyethyleneimines and recent work on 5-coordinated structures. Spatial arrangements of many well-known and new complexes are proposed, based on analogy to known ammines, steric ligand requirements, and physical and chemical data. General synthetic methods are outlined according to the number of coordinated nitrogen atoms, including recent work with the new ligand pentaethylenehexamine.

The purpose of this paper is to describe the preparation and properties of coordination compounds containing ligands with three or more aliphatic or cycloaliphatic amino nitrogens.

In this discussion the material will be divided into three major sections:

1) The period 1925–1950
2) Some current work
3) Research carried out in the author's laboratory, including general preparative methods

In order to stress the great potential for further work in this field, the problem of stereoisomerism is treated concurrently with the structures considered.

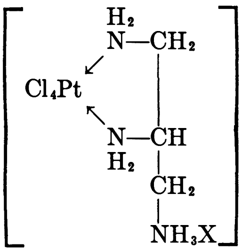
The Early Period

At the time of Werner's premature death in 1919, the three basic geometric configurations of ligands in complexes, the square plane, the tetrahedron, and octahedron had been well-accepted for unidentate and bidentate ligands. The 169 papers written by Werner and his students attest to his painstaking efforts to establish his fundamental stereochemical postulates.

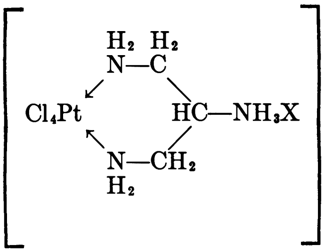
It was obvious to chemists in the early twenties that an extension of Werner's ideas into compounds with polydentate ligands involved the syntheses of suitably constituted, organic substances. Among these were the higher homologs of aliphatic amines related structurally to 1, 2-diaminoethane (en), *dl*-1, 2-diaminopropane (pn), and 1, 3-diaminopropane (tn). Efficient synthetic routes to these "long-chain" bases were at best tedious and frequently very difficult with conventional laboratory equipment.

As a result, rapid preparative progress in this field was hindered until after World War II when many of these amines became commercially available due to their use as cross-linking agents in the polymer and rubber industries.

One of the first tridentate amines studied was 1, 2, 3-triaminopropane (*24*, *25*, *26*, *27*, *28*, *29*, *30*) (ptn) with a large variety of transition metals. The expected 3-coordination was found in all cases except with Pt(IV) where the amine is only bidentate. This produced a demonstrable optical activity due to the preferential formation of a five-membered chelate ring.

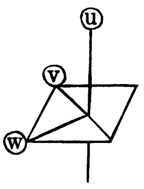


Asymmetric dl form

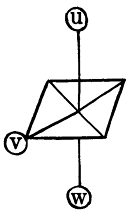


Symmetric—optically inactive

The compound $[Coptn_2]Cl_3$ was also partly resolved into a dextrorotatory form. This was probably the fac-ABA cis B form—the only possible optically-active isomer. The others are mer-ABA and fac-ABA trans B where ptn = ABA, fac = facial or occupying one face of the octahedron, and mer = meridianal or positioned along the edge of the figure (*45*). Stability constants of ptn have been reported (*37*).

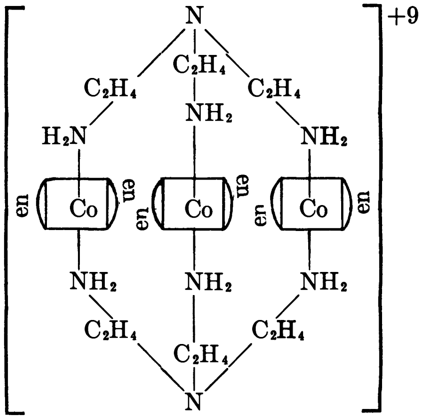


Facial-uvw



Meridianal-uvw

Another amine specifically designed to test Werner's postulates is 2,2′,2″-triaminotriethylamine (*12, 21, 33*) (tate), which can be either tri- or tetradentate. In the latter capacity it can fill four vicinal positions in an octahedron or tetrahedron but not in a square-planar form. With Co(III) it can form the expected octahedral *cis*-$[Co(tate)(SCN)_2]^+$ as well as the tridentate $[Co_3en_6(tate)_2]^{+9}$. The two tate molecules presumably occupy trans positions in the polymeric complexes because attempts at resolution proved fruitless. A possible structure is:



with Ni(II) and Pt(II) tate forms tetrahedral structures due to the restrictive geometry of the ligand. A variety of stability constant data is available (*34*).

Compounds containing diethylenetriamine or 1, 4, 7-triazaheptane (den) have been well studied (*7, 22, 23, 32*). Due to the apparent lack of resolution data and the fact that models show no preferential configurational alignment for the amine, it may be tentatively assumed that the octahedral complexes prepared to date are the fac-ABA trans B or the mer-ABA forms for $[M^{III}(den)_2]^{+3}$ and the latter type alone for structures such as $[M^{III}denX_3]$, where $X =$ any assortment of unidentate groups. This is in analogy to the known trans forms of the analogous triammino complexes (*17*). Because the amine can assume either a planar or tetrahedral geometry, no problem seems to exist with other metals having these steric requirements. Stability data have been determined for den complexes of many transition metals (*9, 13, 14, 36*).

The next member of the "polymeric" ethylenediamine series, triethylenetetramine or 1, 4, 7, 10-tetraazadecane(trien), was used by Basolo (*1*), Jonassen (*15, 16*), and Pearson (*32*) to prepare some Co(III), Ni(II), Pt(II), and Pd(II) complexes. In all cases tetradentate behavior was observed. With Co(III) only *cis*-$[CotrienCl_2]Cl$ could be obtained, which suggested a preferential nonplanar octahedral orientation of the trien—*viz.*, cis-u-trans A (trien = ABBA), or cis-u-trans AB (u = Cl); the compound was resolvable. On the other hand, the diamagnetism and nonresolvability of [Pttrien][$PtCl_4$] and the Pd(II) analog was in accord with a square planar structure. The low values of the instability constants for most trien complexes (*9*, *35*) attest to the ability of the ligand to assume both configurations.

Octahedral complexes of $[M^{III}trienX_2]^{+3}$ (X = unidentate) should exist as (*45*):

a) trans-X b) cis-X trans-A c) cis-X trans-AB with b and c

as *dl* pairs and compounds such as $[M^{III}trien(GG)]^{+3}$ (GG = bidentate) in two optically-active forms—*viz.*, trans A and trans AB (*45*).

Finally, the earlier literature lists (*32*) the preparation of [CotetraenCl] Cl_2, where tetraen = tetraethylenepentamine or 1, 4, 7, 10, 13-pentaazatridecane. It was noted at that time that the compound obtained appeared to be an intractable mixture of two components. This is not surprising in view of the fact that four, optically-active, octahedral stereoisomeric pairs are theoretically predictable—i.e.:

a) trans-A, trans-uC
b) trans-AB′, trans-uC
c) trans-AC, trans-uB′
d) trans-AC, trans-uA′

where tetraen = ABCB′A′ and Cl = u.

Some Current Studies

Very recently (*20*) the three possible stereoisomers of $[CodenIDA]^+$ were prepared by Legg and Cooke ($IDAH_2$ = iminodiacetic acid).

$$[CodenCl_3] + Ag_2IDA + AgNO_3 \rightarrow [CodenIDA]NO_3 + 3AgCl$$

This is the first known example where octahedral compounds of the type $[M^{III}(ABA)(GHG)]$ have been resolved into all predicted forms—*viz.*,

a) mer-ABA b) fac-ABA, trans-BH c) fac-ABA, cis-BH.

It was unfortunate that the resolution of form c), the potentially optically-active one, was not reported. Also, it is interesting to observe that the easy technique of preferential chromatographic elution, developed earlier by Kauffman and co-workers (*18*) for isomer separation, was the method of choice.

A simple route to Cr(III) tridentate monoamines was reported earlier this year (*10*), based on Werner's early work with $CrO_4 \cdot (NH_3)_3$ or $[Cr(NH_3)_3(O_2)_2]$ in the triammine series (*47*, *50*).

Complexes such as [$CrdenCl_3$] were readily made from the analogous [$Crden(O_2)_2$]H_2O and HCl. Again, no apparent attempts at stereochemical resolution were attempted, although compounds such as ($M^{III}ABAu_3$] should exist in two isomeric forms. However, the visible absorption spectrum of [$Crden(H_2O)_3$]$^{+3}$ indicates a fac-ABA conformation in analogy to findings with the ammonia analog (*17*).

The ligand 1, 1, 7, 7-tetraethyldiethylenetriamine (Et_4den) has been employed (*8*) to prepare unusual 5-coordinated species such as [$Co(Et_4den)Cl_2$] and the Ni(II) analog. Because these materials are nonelectrolytes and paramagnetic, they may be regarded as high-spin trigonal bipyramidal complexes. By contrast, [$Rh(Et_4den)Cl_3$] is apparently octahedral, and it is likely that the one of two possible stereoisomers obtained has the mer-ABA structure; the fac-ABA form would involve considerable steric repulsion between the bulky terminal NEt_2 groups.

Sargeson and Searle (*39*) have followed the spatial changes in substitution reactions of the two pairs of *dl* isomers in complexes of trien and Co(III), such as [Cotrien (u_2, uv, or GG)], where $u_2 = Cl_2$, $(H_2O)_2$, $(NO_2)_2$; uv = Cl and H_2O; and GG = CO_3^{-2}. Optical methods such as circular dichroism, and rotary dispersion and absorption were used in addition to polarimetric measurements. Regrettably their paper did not present the synthesis of the enantiomers employed in the work.

A similar series of salts to the above was made by House and Garner (*11*) with Cr(III) as the central ion. However, only the cis-u trans A unresolved forms of [$Crtrienu_2$]$^+$ were prepared, where u = Cl^-, NCS^-, or N_3^- and the trans A form of [$Crtrien(C_2O_4)$]$^+$. Visible and infrared spectra were used to support the above assignments of configuration.

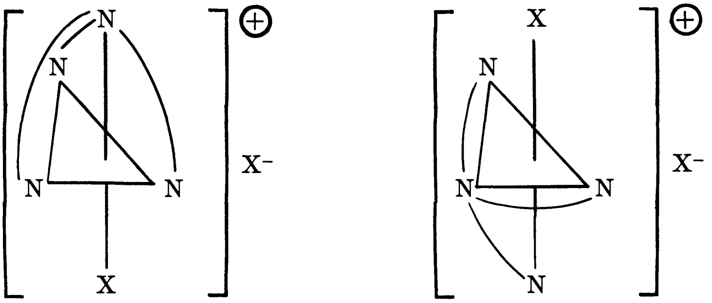
The reaction of the dextrorotatory trans A isomer of [$CotrienCl_2$]$^+$ with liquid ammonia or en (*19*) leads to optical inversion. However, gaseous NH_3 causes extensive racemization with retention of configuration. This was also observed by treatment with 1, 10-phenanthroline in boiling pyridine.

The levorotatory form of the trans AB isomer showed no inversion or appreciable optical activity loss in its reaction with en to form [Cotrien(en)]Cl_3.

The fact that the *l*-trans AB form was obtained from both dichloro isomers indicates that Basolo's [Co(trien)(en)]Cl_3 (*1*) was the racemic form (trans AB) because his [$CotrienCl_2$]Cl was also inactive. Nothing can be said of the structure of this complex which was used as starting material because either possible isomer would have led to the inactive trans AB [Cotrien(en)]Cl_3 above. He was unsuccessful in resolving the latter, owing to the extreme solubilities of the intermediate salts required.

dl-trans A-$[Co(trien)Cl_2]Cl \searrow^{en}$
or *dl-trans* AB-$[Co(trien)en]Cl_3$
dl-trans AB-$[Co(trien)Cl_2]Cl \nearrow_{en}$

Ciampolini and co-workers in Italy have prepared some 5-coordinated complexes with tris (2-dimethylaminoethyl) amine (*4*) (metren) and bis (2-dimethylaminoethyl) methylamine (*5*) (medien). Conductance and spectral data in nonaqueous media for materials such as $M^{II}X_2 \cdot$metren preclude 6-coordinate formulation as a nonelectrolyte but favor rather a trigonal bipyramidal structure such as:



a) b)

$[M^{II}(metren)X]X$

which is a 1:1 ionic type salt; apparently the workers did not consider form b) seriously in their configurational assignment, possibly due to the fact that known 5-coordinate structures are distorted in relation to their axial-trigonal planar, bond distances. This might cause some strain in the N-C-C-N link of the ligand in b) which is shaded above. In a) this would not be expected to occur.

It was noted that largely on the basis of physical evidence, similar compounds of the nonmethylated amine (tate) seem to be on the borderline of compatibility for 5- or 6-coordination, depending on the nature of the metal and the other ligands present. Either formulation, such as $[M^{II}(tate)X]X$ with C.N. 5 (C.N. = coordination number) or $[M^{II}(tate)X_2]$ with C.N. 6 (octahedral), can be written for these complexes. Undoubtedly, crystal-field effects play an important role in these particular cases.

Transition metal compounds with tridentate (medien), such as $[M^{II}(medien)X_2]$, were shown to be 5-coordinate also but showed only small conductivities in nitroethane and, with the exception of $Cu(medien)Cl_2$, were nonconducting in chloroform or nitrobenzene. These products were thus written as nonelectrolytes with a stereochemical arrangement intermediate between a square pyramid and trigonal bipyramid. This appears necessary since the N-Metal-N angle must be equal to or less than 90° for these figures. It should be noted that both geometric forms have been found by x-ray data (*31, 38*).

A series of extremely interesting complexes of Co(III) and Ni(II) has been recently reported by Bosnich and his colleagues (*2, 3*), using tetradentate 1, 4, 8, 11-tetraazocyclotetradecane (cyclam). These substances, made by conventional methods, have the four nitrogens of the ligand more or less in a planar configuration, giving rise to octahedral trans complexes such as $[Co(cyclam)X_2]^{+n}$, where X is a unidentate negative or neutral species. In addition to the trans dichloro compound (green), a small amount of a purple isomer, presumably the cis form, was also obtained.

Octahedral models of the cyclic amine show that four possible *strain-free* planar conformations are possible, as well as two bent arrangements which lead to cis orientation of the remaining two coordination positions. Because each of these six unhindered configurations is distinct from one another, mirror images of each form are possible—even for the trans structures. The latter phenomenon would be without precedent, and further investigation may open a new chapter in inorganic isomerism.

With Ni(II) salts cyclam forms a series of salts which are represented by $Ni(cyclam)X_2$. These behave as 2:1 electrolytes in water and methanol, and the visible absorption spectra are independent of the nature of the anion. However, an x-ray diffraction study of the dichloride (X = Cl) shows a planar ligand arrangement with the two chlorine atoms at the apices of an octahedron but unusually far away (2.5 A.) from the nickel.

At this point, the nature of these unusual compounds is perhaps best formulated as $[Ni(cyclam)X_2]$, which dissociates to $[Ni(cyclam)(Sol)_2]X_2$ (Sol = solvent) in water or methanol. More work is needed to solve the problem unequivocally.

Synthetic Methods and Author's Work

Complexes in this section will be described according to the number of coordinated amino nitrogens per metal atom. Included are preparative techniques which can be generally applied in the area of polydentate coordination chemistry (*40,41,42,43,44*).

Cobalt (III). HEXAMINES. Materials such as $[Coden_2]^{+3}$, $[Codpn_2]^{+3}$, where dpn = dipropylenetriamine or 2, 5-dimethyl-1, 4, 7-triazaheptane, $[Co_2trien_3]^{+6}$ and $[Copenten]^{+3}$, where penten = pentaethylenehexamine or 1, 4, 7, 10, 13, 16-hexaazahexadecane, are most readily prepared from Co(II) salts by the general equation

$$4Co^{+2} + 4X \text{ amine} + 4 \text{ amine } H^{+} + O_2 \rightarrow 4[Co(\text{amine})_{X+1}]^{+3} + 2H_2O \qquad (1)$$

where X, of course, will vary according to the polydentate nature of the amine. The anion of the Co(II) salt and the ligand should be the same if a product is to be isolated; for a solution of the complex cation alone it is immaterial.

Air is generally bubbled through the aqueous mixture although hydrogen peroxide is usually much more rapid in its action and convenience. Aeration times may vary from two or three hours for den to one week for bis(3-aminopropyl)methylamine (medtn).

Methods which start from preformed Co(III) salts are more versatile in synthetic scope but necessitate the prior formation of the intermediate. In these instances solvents such as methyl, ethyl, or isopropyl alcohol are preferred over water due to the ease of product isolation; solubilities in H_2O sometimes cause serious problems in preparation and purification. However, 1-10% (vol.) of water may be desirable in the alcohol as a catalyst. Also, an excess of 10–50% (wt.) of the entering ligand is usually required to ensure rapid and complete conversion. The following equations will summarize the methods employed.

$$[\mathrm{Co(NH_3)_6}]^{+3} + \mathrm{X\ amine} \rightarrow [\mathrm{Co(amine)_x}]^{+3} + 6\mathrm{NH_3} \qquad (2a)$$

$$[\mathrm{Co(NH_3)_5Y}]\ \mathrm{Y_2} + \mathrm{X\ amine} \rightarrow [\mathrm{Co(amine)_x}]\ \mathrm{Y_3} + 5\mathrm{NH_3} \qquad (2b)$$

$$[\mathrm{Co(amine)Cl_3\ or\ (NO_2)_3}] + (\mathrm{amine})^1 \rightarrow [\mathrm{Co(amine)(amine)^1}]\ \mathrm{Cl_3\ or\ (NO_2)_3} \qquad (3a)$$

The first tridentate amine may be the same or different from the second; ammonia (with activated charcoal in water) may even replace the latter to produce salts such as $[\mathrm{Co(den, dpn\ or\ dtn)(NH_3)_3}]^{+3}$, where dtn = 1, 5, 9-triazanonane. The series $[\mathrm{Codtn_2}]^{+3}$ had to be prepared by Equation 3 because Method 1 gave only the red binuclear $[\mathrm{Co_2dtn_2(OH)_3}]^{+3}$. This is a μ-triol complex of which the hexammine analog is long known (*49*). The same result was obtained with the new ligand medtn or 5-methyl-1, 5, 9-triazanonane.

Procedure 3a can be used to prepare complexes with mixed ligands of the widest variety as follows:

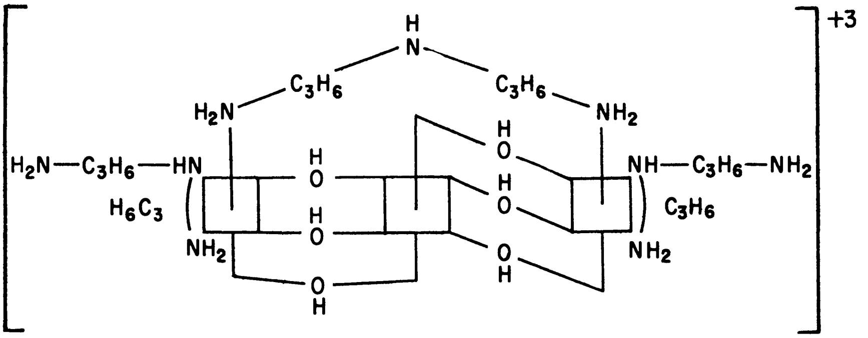
i) $[\mathrm{Co_2den_2(en, pn, tn)_3}]^{+6}$

ii) $[\mathrm{Co_2dpn_2(en, pn)_3}]^{+6}$

$$\text{e.g., } 2[\mathrm{CodenCl_3}] + 3\ \mathrm{en} \rightarrow [\mathrm{Co_2den_2en_3}]\mathrm{Cl_6} \qquad (3b)$$

Tn yielded no analogous product in this case. While $[\mathrm{Codtn(NO_2)_3}]$ gave no hexamine type salts with en, pn, or tn, $[\mathrm{CodtnCl_3}]$ produced the desired $[\mathrm{Co_2dtn_2(en\ or\ pn)_3}]^{+6}$; again tn gave anomalous results.

$[\mathrm{CodenCl_3}]$ reacted with medtn to yield the unexpected product, $[\mathrm{Co_4den_3medtn_3(OH)_6}]^{+6}$ (brown violet), a tetranuclear complex of the μ-hexol type (*48*), where the medtn appears to be unidentate; the possibility that both amine ligands are bidentate cannot be excluded. From the reaction of $[\mathrm{CodtnCl_3}]$ with medtn, purple $[\mathrm{CodtnmedtnCl}]\mathrm{Cl_2}$ (medtn = bidentate) and red $[\mathrm{Co_2dtn_2medtn_2(OH)_3}]^{+3}$ (dtn = bidentate;



Proposed Structure for the $[Co_3\ Medtn_3\ (OH)_6]^{+3}$ *Ion*

medtn = unidentate) were obtained. The last complex also belongs to the μ-triol series above. When excess medtn was refluxed with $[Co(NH_3)_5Cl]Cl_2$ in 2-propanol (99%) for one week (Method 2b), with the hope of obtaining $[Comedtn_2]Cl_3$, two polynuclear products were isolated: brown $[Co_4medtn_4(OH)_6]^{+6}$ (*48*) (medtn = tridentate) and deep olive-green $[Co_3medtn_3(OH)_6]^{+3}$ (medtn = bidentate), which belongs to the relatively little known hexammine-μ-hexol-tricobalt series (*46*).

It is difficult to see how one of the medtn molecules could span the first and third octahedra in this case, except with the two terminal nitrogen atoms, while the other two ligands use their neighboring N atoms. A polymeric constitution seems to be the only alternative.

Apparently medtn has a C.N. of one, two, or three, depending on the geometry of the cation and steric requirements of other ligands present.

The preparation of transition metal complexes with penten marks the last step in mononuclear octahedral complexes begun by Jørgensen and Werner last century with ethylenediamine. Stuart models indicate that the fifth and sixth amine nitrogens are progressively harder to fit into place on the octahedron. If we assume a five-membered ring strain with each tetrahedral nitrogen of 1.5°, the fourth and fifth rings would have a cumulative strain of 6 and 7.5°, respectively. The ion $[Copenten]^{+3}$ should exist in four pairs of optically-active isomers:

a) trans-AC^1	trans-A^1C
b) trans-AC	trans-A^1C^1
c) trans-A	trans-B
d) trans-AB^1	trans-A^1C

where hexen = $ABCC^1B^1A^1$

The stereochemistry of polynuclear complex ions is quite involved and will be mentioned only in passing here. Thus, an ion such as $[M_2^{III}(ABA)_2(GG)_3]^{+6}$, where ABA = tridentate amine and GG = bidentate amine, has 10 isomers, of which four are optically active and five are internally-compensated, meso forms. In this case, one molecule of the amine GG serves to link the two octahedra together.

PENTAMINES. By simply adjusting the molar proportions in Equation 3b to a 1:1 reactant ratio, compounds such as [Co(den or dpn)(en, pn, or tn)Cl]$^{+2}$ may be readily prepared. Ammonia may replace the bidentate amine in the absence of carbon to form [Co(den or dtn)$(NH_3)_2$Cl]$^{+2}$.

When [CodtnCl_3] was heated with en, pn, or tn in 1:1 ratio, only hexamine salts were formed with en and pn—*viz.*, [Co_2(dtn)$_2$(en or pn)$_3$]$^{+6}$, leaving one-third of the nonelectrolyte starting material unreacted as required for a 3 amine: 2 complex stoichiometry. With both 1:1 and 3:2 ratios, tn produced the binuclear "pentamine" compound [Co_2dtn$_2$tn$_3$$Cl_2$]$^{+4}$, where the dtn is bidentate, presumably due to steric requirements. A 3:2 ratio is also involved here: 2[CodtnCl_3] + 3tn → [Co_2dtn$_2$tn$_3$$Cl_2$]$Cl_4$ and unused trichloro complex was recovered when the reaction was carried out in equimolar proportions.

Of particular interest in this section is tetraen, which has not yielded any isolable hexamine-type salts with Co(III) as yet. The pentanuclear structure required is [Co_5tetraen$_6$]X_{15} and should be formed without difficulty. The solubility of salts of this cation appears to be very high in water; more work is currently in progress.

However, this ligand is ideally suited for the facile preparation of purple [CotetraenCl]Cl_2, which can be easily made from [Co$(NH_3)_5$Cl]Cl_2 and the amine by refluxing one day in absolute ethanol. The alcohol-insoluble product is contaminated with a trace of starting material while the mother liquor contains a green basic polynuclear by-product. Attempts to make the tetraen complex in water gave impure substances or mixtures. When aqueous tetraen was heated with Co$(NH_3)_3(NO_2)_3$ (*32*), the final purple "product" was shown to consist of at least three different constituents, of which only about 10% seemed to be the desired material. This was demonstrated by its conversion to [CotetraenNH_3]I_3 with aqueous ammonia and activated carbon.

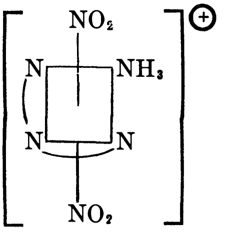
Octahedral complexes of the type [M^{III}(ABA)(GG)u] exist as a) mer-ABA; b) fac-ABA trans-uB; c) fac-ABA cis-uB (*dl* pair). [M^{III}(ABCB^1A^1)u] has four stereoisomeric forms, below, all of which are optically active.

a) trans A	trans uC
b) trans AB^1	trans uC
c) trans AC	trans uA^1
d) trans AC	trans uB^1

TETRAMINES. By careful treatment of triamines such as [Coden$(NO_2)_2$Cl] for short periods of time with dilute aqueous ammonia, one NH_3 molecule displaces a chloride ion to form [Coden$NH_3(NO_2)_2$]$^+$, which is the only example (*6*) of its amine type—*viz.*, [$M^{III}ABAu_2v$], where u = NO_2, v = NH_3, ABA = tridentate amine.

Treatment of the above ion as the chloride with cold concentrated HCl replaces one NO_2 group giving [$CodenNH_3(NO_2)Cl$]Cl represented by [$M^{III}ABAuvw$].

In analogy to the behavior of *trans*-[$Co(NH_3)_4(NO_2)_2$]Cl with HCl, it appears certain that the dinitroamine complex is the inactive mer-ABA (Structure I) trans-u isomer of the four possible ones. The resultant chloronitroamine chloride should then be the inactive mer-ABA trans uw, where w = Cl, u = NO_2, and v = NH_3



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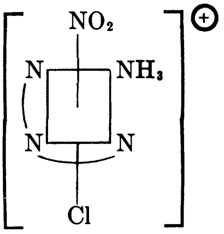


II

For Structure II five other stereoisomers can be written. Of these, three are *dl* pairs.

TRIAMINES. The most useful starting materials in this series are represented by the general formula [$Co(amine)(NO_2)_3$] and can be made, with varying success, by three different routes (*6*).

1) From Co(II) salts:

$$4\,Co^{+2} + 12NO_2^- + 4(amineH)^+ + O_2 \rightarrow 4[Co(amine)(NO_2)_3] + 2H_2O$$

2) From *trans*-trinitrotriammine cobalt (III):

$$Co(NH_3)_3(NO_2)_3 + amine \rightarrow [Co(amine)(NO_2)_3] + 3NH_3$$

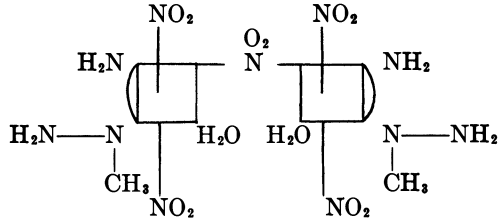
3) From sodium hexanitrocobaltate (III):

$$Na_3[Co(NO_2)_6] + amine \rightarrow [Co(amine)(NO_2)_3] + 3NaNO_2$$

The den and dpn analogs can be made by all three methods, while with dtn Procedure 2 has been used. The latter is the most convenient and rapid preparative technique for all these three amines.

When Method 2 was applied to medtn, a good yield of a brick-red water-insoluble product was obtained. The other trinitro compounds are mustard-yellow by contrast. Analysis of the red substance gave 25.2%C, 5.89%H, and 22.9%N. This checks for [$Co_2medtn_2(NO_2)_5(H_2O)_2$], where medtn is only bidentate.

Upon heating a mixture of the amine with $Na_3[Co(NO_2)_6]$ in absolute ethanol, no reaction occurred until a small amount of water (*ca.* 5% by volume) was added; the identical red nitro compound and colorless sodium nitrite then formed rapidly. A suggested tentative structure is:



Upon treatment with concentrated HCl, the trinitro (den or dtn) complexes form [Co(den or dtn)Cl_3]. However, with 6*M* HCl only one nitro group is replaced to give red-brown [Coden$(NO_2)_2$Cl]; dpn forms the very soluble deep-green [Codpn$(H_2O)Cl_2$]Cl under these conditions.

Similarly, [Codtn$(NO_2)_3$] yields brown [CodtnBr_3] with cold concentrated hydrobromic acid in the presence of urea (to convert HNO_2 to N_2). The above binuclear medtn nitro complex appears to decompose with acids to Co(II) and ligand salts.

The action of oxalic acid on the den or dpn trinitro nonelectrolytes replaces two nitro groups to give [Co(den or dpn)$NO_2(C_2O_4)$], while concentrated nitric acid first produces [Co(den or dpn)$(H_2O)_3$]$[NO_3]_3$ which loses its coordinated water above 100°C. converting to [Co(den or dpn) $(NO_3)_3$].

It seems likely that the trinitro complexes are of the mer-ABA type similar to *trans*-$[Co(NH_3)_3(NO_2)_3]$; this is probably true also for the triaquo, trichloro, and tribromo and nitrooxalato analogs. The chlorodinitro amine, in similar fashion, should be the mer-ABA trans-u isomer of four possible ones.

A new type of triamine complex, [Co(amine)$(SCN)_3$], has been prepared with den (*6*) and dpn (*40, 41, 42, 44*). These substances are only slightly soluble in water with attendant aquation and are tan-colored. They cannot be prepared in aqueous medium as only two thiocyanate groups are introduced to form [Co(amine)$(SCN)_2$OH]; absolute ethanol or 2-propanol must be used. The compound $K_2[Co(SCN)_4]$ is more convenient to use as a starting material than cobalt (II) thiocyanate (*6*).

$$4K_2[Co(SCN)_4] + 4\text{ amine} + 4ROH + O_2(CO_2\text{-free}) \rightarrow 4[Co(\text{amine})(SCN)_3] + 4ROK + 2H_2O + 4KSCN$$

The same procedure, when carried out with dtn, yielded a tan precipitate upon mixing the reagents which turned brown on aeration. Two preparations gave S = 19.55, 15.51%; N = 20.20, 20.28%; calcd. for

$[Codtn(SCN)_3]$: S = 26.4; N = 23.05%. At this writing the nature of these two latter substances is not clear.

Other Transition Metals. COPPER. With den, dpn, trien, tetraen, and penten, Cu(II) forms the interesting series (*40, 41, 42, 44*):

i)	$[Cu_3den_4]$	$[CuI_2]_6$;	olive-green
ii)	$[Cu_3dpn_4]$	$[CuI_2]_6$;	dark olive-green
iii)	$[Cutrien]$	$[CuI_2]_2$;	green-black
iv)	$[Cutetraen]$	$[CuI_2]_2$;	green-black
v)	$[Cu_3penten_2]$	$[CuI_2]_6$;	deep olive-green

by the following sequence of reactions:

$$y\,Cu^{+2} + x\ \text{amine} \rightarrow [Cu_y(\text{amine})_x]^{+2y}$$

$$2yI^- + [Cu_y(\text{amine})_x]^{+2y} + 2y\ CuI \rightarrow [Cu_y(\text{amine})_x][CuI_2]_{2y}$$

The first three compounds have been shown to be nontetrahedral in structure by their reflectance spectra (*40, 41, 42, 43, 44*); presumably they are square planar. With trien this seems to confirm previous findings with Pt(II) and Pd(II) (*15*).

Apparently, the tetraen analog has an uncoordinated ethylamine group in preference to forming a pentanuclear copper complex cation such as $[Cu_5tetraen_4]^{+10}$.

More physical studies are in order for these materials to establish their nature unambiguously.

NICKEL. With tetraen and penten, Ni(II) produces the violet octahedral ions $[Ni_5tetraen_6]^{+10}$ and the expected $[Nipenten]^{+2}$ isolated as the perchlorates. The behavior of copper and nickel with tetraen thus presents an interesting contrast as yet unclarified.

ZINC. Zn(II) forms $[Zntetraen]^{+2}$ and $[Znpenten]^{+2}$ with the same ligands and thus behaves similarly to Cu(II) with tetraen; the stereochemistry of these cations is still in doubt. It is puzzling why zinc reacts in a 1:1 ratio with penten instead of forming a trinuclear complex such as $[Zn_3penten_2]^{+6}$ in analogy to Cu(II).

CADMIUM. This element behaves in the same way as Cu(II) towards tetraen and penten forming $[Cdtetraen]^{+2}$ and $[Cd_3penten_2]^{+6}$, both isolated as the iodides. When the latter compound is recrystallized from a large quantity of boiling water, apparent degradation occurs to produce $[Cd_2pentenI_2]I_2$, tentatively written as a 4-coordinate 2:1 electrolyte.

MERCURY. Upon mixing a solution of mercury(II) chloride in acetone with tetraen and penten in the same solvent, the initially gummy precipitates become crystalline on standing. The molar ratios were $5HgCl_2$: 2 tetraen and $3HgCl_2$: 1 penten. Analytical data gave the following results.

Found		*Calcd.*	
N	Cl	for	
11.75	20.20	$Hg_5tetraen_2Cl_{10}$:	
N:Cl = 3:2		N = 8.08	Cl = 20.4
8.25	11.95	for $Hg_3pentenCl_6$:	
N:Cl = 7:4		N = 8.05	Cl = 20.4

While the chloride value checks for the tetraen complex, the nitrogen analysis is satisfactory for the penten analog.

If the first material is formulated as $Hg_5tetraen_3Cl_{10}$, in which the three ligand molecules use only 10 amino nitrogens to coordinate to mercury, the calculated values become N = 10.9; Cl = 18.4%. Also, assuming an amido-type complex in the case of penten such as $Hg_3(penten\text{-}3H)Cl_3$, where the amine now has the formula $C_{10}H_{25}N_6$, values of N = 9.0 and Cl = 11.4% are obtained.

At best, the whole problem requires considerable further work.

Conclusion

With the ever-increasing variety of organic ligands available and the perfection of synthetic and physical investigative methods, coordination chemistry can systematically expand further into a vast but orderly array of chemical data. We owe all this to the ingenuity and genius of Alfred Werner, as well as to his successors in the scientific tradition he established.

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37

Metal Beta—Ketoenolate Stereochemistry

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The β-ketoenols form coordination compounds with virtually every metal and metalloid in the periodic table. The stereochemistry of these compounds is quite varied. Four-coordinate species may have either a planar or a tetrahedral idealized stereochemistry. Only octahedral tris complexes have been recognized, but both dodecahedral and square anti-prismatic tetrakis species have been studied. Some metals bond to the β-ketoenol through a carbon atom. Polymerization occurs when the coordination number of the metal ion exceeds twice its charge if the β-ketoenolate anion does not interfere sterically. Only a limited number of gross stereochemical arrangements are permitted for transition-metal β-ketoenolate polymers, provided they are formed by a sharing of octahedral edges or faces.

On this occasion of the one-hundredth birthday anniversary of Alfred Werner it is appropriate that the stereochemistry of metal β-ketoenolates, especially the complexes of acetylacetone (Figure 1), should be discussed. Only within the past few years has the solution to an interesting problem in β-ketoenolate stereochemistry, to which Werner addressed himself, finally appeared. In 1901 he attempted to understand (*36*) the structure of certain "peculiar" (merkwürdigen) platinum(II) acetylacetonates of stoichiometry $PtClK \cdot 2CH(COCH_3)_2$ and $PtCl_2Na_2[CH(COCH_3)_2]_2$. He also was fascinated by the metal acetylacetonates

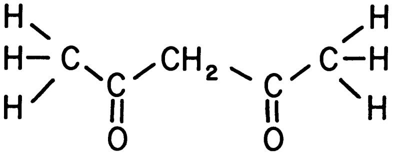


Figure 1. Acetylacetone

generally, especially because these compounds are soluble in organic solvents and also because of their considerable volatility. In his 1901 paper he correctly formulated the species $KPtCl_2(AA)$, which contains both acetylacetonate (AA) oxygen atoms bonded to the platinum.

This paper summarizes the gross stereochemical features which now have been found for β-ketoenolato complexes, placing particular emphasis on those aspects which are most interesting.

Coordination to the β-Ketoenol

There are four different ways in which a β-ketoenolate anion may function as a ligand in bonding to metals and metalloids. These are indicated in Figure 2. By far the most commonly found (*18*) coordination is through the two oxygens of the ligand. However, the coordination through the α-carbon atoms has been established conclusively by x-ray crystallographic methods for a platinum(IV) complex (*34*) and for the Werner complex, $KPt(AA)_2Cl$ (*21*) (Figure 3). Recently, silver ions were shown by crystallographic techniques (*35*) to bond (2.34 A.) with the methylene carbon in the interesting compound, $AgNi(AA)_3 \cdot 2AgNO_3 \cdot H_2O$, first prepared by Ginsberg at Ohio University (*22*, *27*). The silver perchlorate adduct of copper(II) acetylacetonate, $Cu(AA)_2 \cdot 2AgClO_4$ (*22*), presumably also contains silver ions bonded to the methylene carbon atom of the acetylacetonate units. Some interesting rhodium(I) complexes (*28*) also are thought to contain a carbon-metal bond.

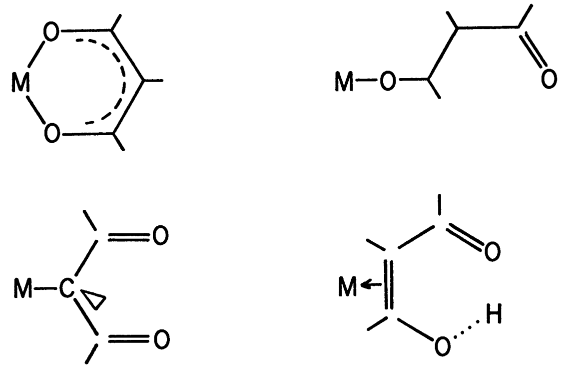


Figure 2. Acetylacetone as a ligand

Bonding of the metal ion to the carbon-carbon double bond of the enol is not crystallographically established as yet, but the elegant work of J. Lewis and co-workers (*1*, *23*, *24*) has proved beyond doubt that a platinum(II)-olefin bond exists in the acidified Werner complex, $HPt(AA)_2Cl$ (Figure 4).

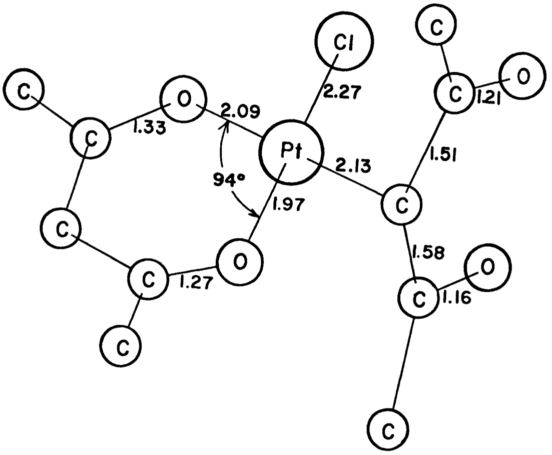


Figure 3. $[Me_3Pt(A)]_2$

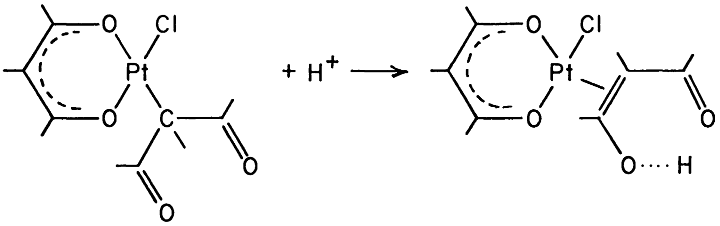


Figure 4. $HPt(AA)_2Cl$

Monomeric Complexes

Since the oxygen atoms as well as the alpha carbon on the β-ketoenolate ring can function as bases to coordinate with metal ions (*3*, *4*, *5*) or to hydrogen bonding solvents (*14*), it should be recognized that β-ketoenolate complexes may have a stereochemistry quite different from that expected—based on the stoichiometry of the complex. However, by a suitable choice of a β-ketoenol ligand, such as 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane), H-DPM, intermolecular effects can be reduced or eliminated with the result that the metal complex formed has the stereochemistry "expected" for the monomeric acetylacetonate complex of that metal ion. For example, nickel(II) acetylacetonate is trimeric as a solid and in solution (*11*), but the dipivaloylmethane complex is a monomeric, undoubtedly planar species, in solution, as well as in the solid state (*37*). This stereochemistry occurs with the monomeric acetylacetonate in dilute solution or in the vapor phase, as indicated by absorption spectra and electron diffraction (*30*).

Four-coordinate monomeric complexes are formed with either tetrahedral or planar stereochemistries. With acetylacetone, the beryllium compound (*2*) has been studied crystallographically and has the expected tetrahedral configuration. Crystalline $Cu(AA)_2$ shows a nearly planar (*13*) arrangement; however, some intermolecular perturbation does occur.

In solution, the monomer of anhydrous $Co(AA)_2$ apparently is tetrahedral (*12*). It is reasonable to expect that the monomeric β-ketoenolate complexes of the alkali earth metals as well as manganese(II), iron(II), zinc(II), cadmium(II), and lead(II) also will be tetrahedral (*18*). However, in the solid state the manganese(II), iron(II) (*19*), and zinc(II) (*6*) complexes with acetylacetone apparently are polymerized (*18*). The cation $B(AA)_2^+$ very likely also contains a tetrahedral BO_4 unit.

With dipivaloylmethane, the zinc(II), cobalt(II) (*12*), and iron(II) complexes (*19*) are all isomorphous. A three-dimensional x-ray structural determination (*12*) of the $Co(DPM)_2$ shows a tetrahedral configuration. The copper(II) complex of this ligand and the nickel(II) derivative are planar. The 3-phenyl-2,4-pentanedione derivative of copper(II) also is planar (*7*).

Monomeric 6-coordinate complexes with trivalent metals appear always to have a nearly octahedral coordination of oxygens about the metal. Structural work has shown this for $Al(AA)_3$ (*34*), $Fe(AA)_3$ (*29*), $Cr(AA)_3$ (*25*), $Mn(AA)_3$ (*26*), and $Rh(AA)_3$ (*31*). The only case that is surprising is that of manganese(III) which should have a ^5E ground state susceptible to Jahn-Teller removal of degeneracy. The x-ray data for $Mn(AA)_3$, which shows six nearly equal Mn-O bond lengths, are not consistent with electronic spectral data available for the β-ketoenolate complexes of manganese(III). The x-ray data possibly may be re-interpreted in terms of a random disordering (*18*) of tetragonally distorted $Mn(AA)_3$ units in the crystal.

No trigonal prismatic structure is known with β-ketoenolate ligands In $AgNi(AA)_3 \cdot 2AgNO_3 \cdot H_2O$, the anionic $Ni(AA)_3^-$ contains (*35*) a nearly octahedral NiO_6 unit. The anionic tris complexes of magnesium(II), zinc(II), cadmium(II), cobalt(II), and manganese(II) presumably also have a similar stereochemistry, although no structural work is available. The cationic silicon(IV), germanium(IV), and titanium(IV) tris complexes also probably are octahedral; however, this has been proved only for $Si(AA)_3^+$ which has yielded optical isomers (*15*).

Four β-ketoenolate ligands about a metal ion produce 8-coordinate complexes in which an anti-prismatic or a dodecahedral arrangement of oxygens about the metal ions is found. The $Zr(AA)_4$ complex is known crystallographically (*32*) to have the $\sim D_2$ symmetry of the Archimedean square anti-prism. Hafnium complexes also are similar, as is the β form of $Th(AA)_4$ and $Pu(AA)_4$ (*16*). The α form of $Th(AA)_4$ and that of $Ce(AA)_4$ and $U(AA)_4$ may be considered somewhat distorted dodecahedra

(*32*). (*See* paper by Matkovic and Grdenic (*24a*).) The esthetically interesting "pinwheel" structure based on the anti-prism, Figure 5, has not been found and, according to Silverton and Hoard (*32*), is not likely to be found.

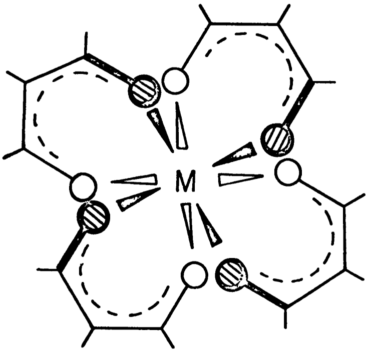


Figure 5. "Pinwheel" structure

Tetrakis anionic complexes have been isolated with certain lanthanides, such as Eu(III), Tb(III), and Gd(III). The structure of the complex, $(NH_4)Eu(F_3AA)_4$, HF_3AA = 1,1,1-trifluoro-2,4-pentanedione, has been completed recently (*31*), but the complete data for the 8-coordinate species are not yet available.

Excluding cases where the complex interacts strongly with solvents or with itself, solution spectroscopic data generally have corresponded well with structural data, except as indicated for $Mn(AA)_3$. The tris chelate complexes of the transition elements appear to remain approximately octahedral in solution. In fact, Fay and Piper (*20*) showed conclusively by NMR and optical activity studies that the trigonal prismatic configuration is not even an intermediate in the isomerization of the unsymmetrical $M(A)_3$ complexes of Al(III), Ga(III), and Cr(III).

Polymeric Complexes

When the coordinating ability of the metal ion is not satiated by the β-ketoenol ligands—i.e., the coordination number exceeds twice the charge, and if the ligands sterically allow it, polymerization (or adduct formation) of the neutral β-ketoenolate complex occurs. Crystallographic evidence is available for the species $[Ni(AA)_2]_3$ (*6*), $[Co(AA)_2]_4$ (*9*), and $[(CH_3)_3Pt(A)]_2$ (*33*), while there is also good evidence for polymerization with $Mn(AA)_2$, $Fe(AA)_2$, $Ln(AA)_3$ Ln = lanthanides), $UO_2(AA)_2$, and $R_2Tl(AA)$ (*18*). The degree of polymerization is variable and, in solution, the species $[Mn(AA)_2]_3$, $[Fe(AA)_2]_6$, $[Ln(AA)_3]_2$, $[UO_2(AA)_2]_2$, and

$[R_2Tl(AA)]_2$ have been suggested. $Zn(AA)_2$ appears to crystallize as a trimer (*3*, *4*, *5*), and $Cr(AA)_2$ (*18*) also appears to be polymeric.

Three basic ways exist in which a neutral $M(AA)_n$ species may polymerize (ignoring specific ring orientations). Two involve using the oxygens, and one, the α-carbon atom pictured in Figure 6. Crystallographic evidence exists for the oxygen bonding, as in 6a, and the carbon bonding, 6c, while spectroscopic data were presented by Colton *et al.* (*8*) for the bridges pictured in 6b for the compound $Re_2(AA)_4Cl_4$.

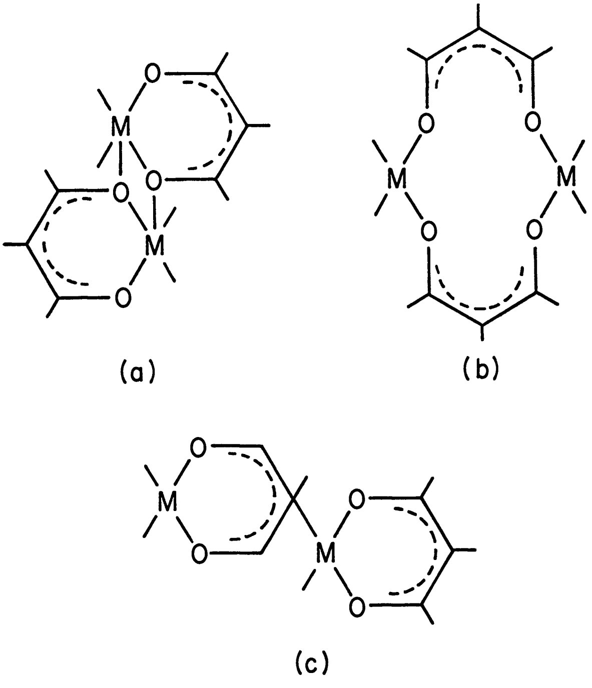
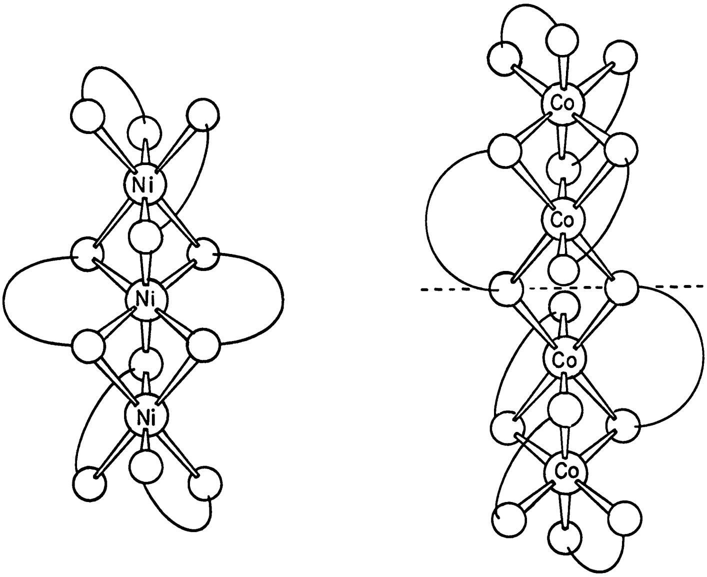


Figure 6. Polymer structures

For polymers of type 6a, octahedra may be joined by faces or by edges, or both, as in $[Co(AA)_2]_4$, shown in Figure 7. If one assumes (a) that each metal ion is surrounded by an octahedron of oxygens, and (b) that polymerization can occur only by joining octahedral faces or edges (points also might be used, but the relative strength of the association would be reduced considerably), it can be shown that up through six $M(AA)_2$ units, only one formal structure has reasonable stability (Table I). (The "formal" structure ignores specific cis-trans arrangements. As Cotton and Elder showed (*10*), there are nine possible trimeric $[Ni(AA)_2]_3$ structures involving shared octahedral faces.) For *N*, the number of metal atoms equal to five and six the formalistic structures pictured in Figure 8, is pre-



Nickel Acetylacetonate Trimer *Cobalt Acetylacetonate Tetramer*

Figure 7. $[Co(AA)_2]_4$

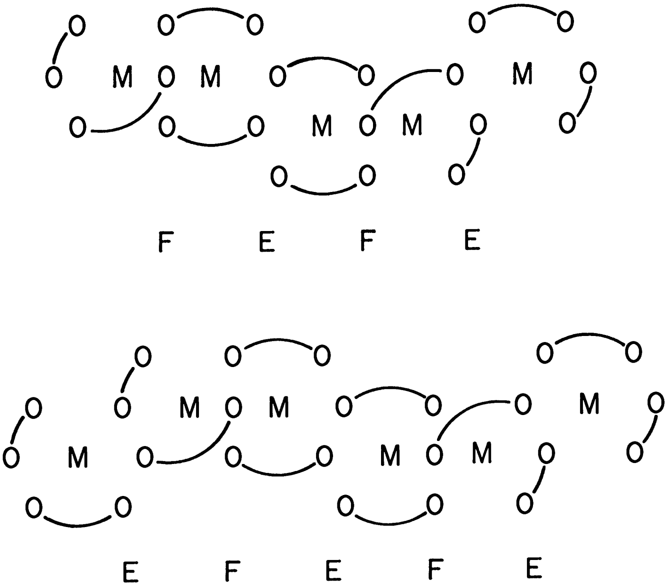


Figure 8. N = 5 and N = 6 polymers

dicted. Unfortunately, the most likely value of N cannot as yet be predicted for the polymeric units. In fact, little differences in energy are expected between certain polymeric forms; hence, it may be possible to find variable polymerization numbers for these species depending on crystallization conditions.

Table I. Possible Numbers of Face (F) and Edge (E) Oxygen Atoms for Polymeric, Octahedral β-Ketoenolates[a]

	N	*O*	*Sites*	*F*	*E*	*Comment*
	2	8	12	0	4	Impossible
*[b]	3	12	18	6	0	Found
	3	12	18	0	6	Impossible
	4	16	24	0	8	Impossible
*	4	16	24	6	2	Found
	5	20	30	0	10	Cyclic
*	5	20	30	6	4	Likely
	6	24	36	12	0	Impossible
	6	24	36	0	12	Cyclic
*	6	24	36	6	6	Likely

[a] F + E + P = 0, P = points, N = No. of metal atoms
2F + 2E + P = S, S = sites = 6N
Thus F + E = S − 0 and 20 − S = P, F = 0, 3, 6, 9 . . ., E = 0, 2, 4, 6 . . . .

[b] Starred species may contain the octahedral face bonded dimeric unit described by Fackler (*17*) and found in $[Co(AA)_2]_4$ and $[Ni(AA)_2]_3$. Cyclic structures are not expected.

Hetero-atom Complexes

Some very interesting structural features exist for neutral β-ketoenolate complexes (*18*) of the type $M(AA)_nL_m$. Adducts with nitrogenous bases or water have yielded a 5-coordinate irregular $Zn(AA)_2 \cdot H_2O$ complex and trans 6-coordinate cobalt(II) and nickel(II) complexes $M(AA)_2 \cdot 2B$, with B = H_2O or pyridine. The vanadyl complex, $VO(AA)_2$, contains a square pyramid of oxygens about the metal, while $UO_2(AA)_2 \cdot H_2O$ shows a pentagonal bipyramidal structure. The anhydrous material is dimeric.

Besides $Zn(AA)_2 \cdot H_2O$, ostensibly 5-coordinate species are known with $Cu(AA)_2 \cdot B$ and $Co(AA)_2 \cdot B$. The cobalt(II) compound with water exists as a dimer containing octahedra which share an edge; however, spectroscopic evidence indicates that a monomeric 5-coordinate adduct can be formed under suitable conditions. Bases generally give a 5-coordinate adduct with $Cu(AA)_2$, although $Cu(F_6AA)_2 \cdot 2H_2O$ presumably is 6-coordinate.

Much additional material could be written about the stereochemistry of β-ketoenolate complexes containing hetero-atoms, particularly with regard to organometallic compounds such as $(CH_3)_2Au(AA)$ or

$(CH_3)_2Sn(AA)_2$. However, significant information currently is being obtained in this area, so that a review of this subject will be more appropriate at a later date.

Acknowledgments

I wish publicly to thank E. C. Lingafelter for helpful information in writing this review. Also, I wish to thank the National Science Foundation, GP-4253, the Public Health Service, and the Petroleum Research Fund for financial support.

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38

Transition Metal Complexes of Alkyl Phosphites.

I. Nitrate Coordination in Some Complexes of Trimethyl Phosphite

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Cobalt(II) perchlorate in the presence of trimethyl phosphite (L) yields the diamagnetic disproportionation products, $[CoL_5]ClO_4$ *and* $[CoL_6](ClO_4)_3$. *The Dq value of 3100 cm.*$^{-1}$ *obtained from the ultraviolet spectrum of the colorless Co(III) complex is comparable with that of the* CN^- *ion. With* $Co(NO_3)_2$, *the complexes* $[CoL_5]NO_3$, $[CoL_5]_2[Co(NO_3)_4]$, *and* $[CoL_5][CoL(NO_3)_2]$ *were isolated. The novel diamagnetic blue anion in the latter compound was also obtained as the* Ph_4As^+ *salt, and infrared evidence is presented which is consistent with a 5-coordinate structure involving bidentate nitrates. Nickel(II) perchlorate with L forms the first reported 5-coordinate diamagnetic complex with five monodentate phosphorus ligands,* $[NiL_5](ClO_4)_2$, *which can be reduced to* $[NiL_4]$ *by heating in aqueous base. In the presence of* $Cu(NO_3)_2$ *or* $Cu(ClO_4)_2$, $[CuL_4]^{+1}$ *is formed, whereas with* $AgClO_4$ *and* $AgNO_3$, $[AgL_4]ClO_4$ *and* $[AgL_2NO_3]$ *are formed, respectively.*

The coordination chemistry of trialkyl phosphites with transition metals (other than with carbonyl or nitrosyl compounds) has received relatively little attention. Table I contains a list of trimethyl phosphite (L) compounds found in the literature. In a report on the reaction of cobalt, nickel, and iron halides, it was concluded that no complexes could be isolated with L in spite of observed color changes (*8*).

Table I. Complexes Containing Trimethyl Phosphite (L)[a]

Compound[b]	*X*	*Reference*[c]
CuX·L	Cl, Br, CN	*35, 36*
CuX·2L	CN	*36*
Ni·4L		*43*
PtX_2·L	Cl	*5*
PtX_2·2L	Cl, F	*39*
AgX·L	Cl	*6*
AuX·L	Cl	*6*
HgX_2·L	Cl	*7*

[a] Nitrosyl and carbonyl compounds are excluded.

[b] Only mole ratios of ligand to metal halide are indicated since some of the complexes seem to be polymeric.

[c] Rather than an exhaustive list of references, only the latest ones to the authors' knowledge are given. Recently Shupack and Wagner (*Chem. Commun.* **1966**, 547) reported the complexes $[CuClL]_4$, $[AgClL]_4$, and AgL_4NO_3. Apparently, the latter compound is formed when $AgNO_3$ and $P(OMe)_3$ react in acetonitrile whereas in this research the reaction was carried out neat with a 10/1 ratio of ligand to metal, producing $[AgL_2NO_3]$. The synthesis of $[AgL_4]NO_3$ may thus involve prior formation of $[Ag(CH_3CN)_4]NO_3$ to effect displacement of the nitrate. This postulate is supported by the conductance of $[AgL_2NO_3]$ as a uni-univalent conductor in acetonitrile.

Because a number of unusual metal complexes have been characterized with polycyclic phosphites (*26*, *28*), it became of interest to reinvestigate some of the reactions of trimethyl phosphite reported in the literature using, in place of halides, anions such as NO_3^- and ClO_4^- which might not be expected to coordinate. Hence, maximum coordination numbers might be attained with only trimethyl phosphite in the coordination sphere. In this paper we report the isolation of the series of diamagnetic species $[CoL_5]^{+1}$, $[CoL_6]^{+3}$, $[NiL_5]^{+2}$, $[CuL_4]^{+1}$, and $[AgL_4]^{+1}$ as perchlorates and/or nitrates. It is shown that the trimethyl phosphite in the $[CoL_6]^{+3}$ complex is a strong-field ligand possessing a *Dq* value comparable with that of CN^-. Evidence is presented which indicates that the polycylic phosphite nickel(II) complexes, previously reported to be 6-coordinate (*28*), are 5-coordinate. Because an excellent review of 5-coordinate species by Muetterties and Schunn has appeared recently (*34*), the subject will not be treated here.

This report also describes two new examples of nitrato-metallate coordination compounds which involve a phosphorus-containing ligand. One is the complex $[AgL_2NO_3]$ and the other the blue diamagnetic cobalt(I) complex anion $[CoL(NO_3)_2]^{-1}$. Of the more than 100 compounds reported in the literature, which are suspected to contain coordinated nitrate, the 12 examined by x-ray diffraction technics are listed in Table II. Two reviews on metal-nitrate interactions have appeared recently (*3*, *19*), so only some general observations will be made here.

Because a pronounced change in symmetry in the nitrate ion accompanies its coordination *via* one or more oxygens to a metal ion, complexes

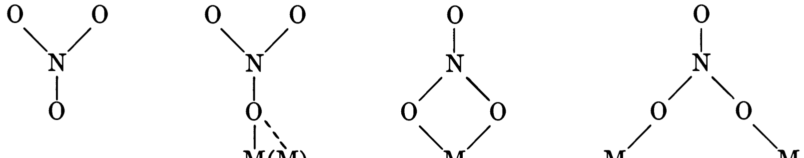
Table II. X-ray Analyses of Compounds Containing Coordinated Nitrate

Compound	*Postulated Coordination Mode of the Nitrate*	*Reference*
$Cu(NO_3)_2$	bidentate[a] and bridging	*45*
$Ti(NO_3)_4$	bidentate	*1*
$[Ph_4As]_2[Co(NO_3)_4]$	bidentate	*10*
$[(Me_3PO)_2Co(NO_3)_2]$	bidentate	*16*
$RbUO_2(NO_3)_3$	bidentate	*46*
$[UO_2(NO_3)_2(H_2O)_2]H_2O$	bidentate	*40*
$Ce_2Mg_3(NO_3)_{12}\cdot 24H_2O$	bidentate	*47*
$[UO_2(NO_3)_2(H_2O)_2]4H_2O$	bidentate	*21*
$Pr(NO_3)_2\cdot 6H_2O$	bidentate	*44*
$UO_2(NO_3)_2(OP(OEt)_3)_2$	bidentate	*20*
$AgC_8H_8NO_3$	monodentate[b]	*33*
$C_7H_8\cdot 2AgNO_3$	bridging	*9*

[a] Bidentate in all cases is meant to imply that two oxygen atoms per nitrate are found to be within bonding distance of the metal.

[b] Because of the nearness of one nitrate oxygen to the metal, it was concluded that some degree of covalency existed.

in which nitrate groups are suspected to coordinate have been investigated extensively by means of near-infrared techniques. Nitrogen-oxygen modes expected for the free nitrate ion (*22*) of D_{3h} symmetry and the monodentate and bidentate forms (C_{2v}) (*4*) are listed in Table III. The data in this table show that although compounds containing ionic or coordinated nitrate can be easily distinguished by examining their infrared spectra, the three possible coordination modes of the nitrate cannot. It is interesting that in Table II all but one of the structures involve bidentate nitrate.



Thus, ascribing infrared bands to monodentate nitrates on the assumption that the metal atom adopts its usual coordination number is somewhat tenuous in the present absence of clear-cut examples of monodentate nitrate structures. Despite the fact that about 30% of the coordinated-nitrate compounds in the literature are suspected from infrared studies to contain monodentate nitrate, a significant portion may on structural analysis be found to possess bidentate nitrate if the ratio of structures in Table II is at all representative.

Attempts have been made to correlate certain infrared spectral features of coordinated compounds with the degree of covalency in the metal-oxygen(s) interaction (*2*, *18*, *32*). Thus, the separation of the ν_3 band in D_{3h} symmetry of ν_4-ν_1 in C_{2v} symmetry has been used in such a study (*18*, *32*), although Katzin has pointed out that this splitting is important only when ν_4-ν_1 is greater than 100 cm.$^{-1}$ because electrical asymmetry in a pure ionic compound can also result in splitting of the ν_3 (D_{3h}) band. In a similar correlation, the frequency of the N-O stretch has been used (*23*) (i.e., ν_1 for NO_3^-(D_{3h}) and ν_2 for a monodentate NO_3 (C_{2v})). Thus, this band might be expected to vary from 1050 cm.$^{-1}$ for ionic nitrate in the Raman spectrum to 854 cm.$^{-1}$ found for CH_3ONO_2 in the infrared region.

Theoretical calculations based on a bond polarization model have proved quite successful in reproducing experimental infrared frequencies for metal-oxygen and nitrogen-oxygen modes in the case of bidentate nitrate (*27*).

The bonding in coordinated nitrate compounds is not well understood. The chemical reactivity of certain coordinated bidentate nitrate groups has led Addison and Simpson (*4*) to assert that there is no basis for considering two sigma metal-oxygen bonds, and that there may be in fact a three-center bond involving orbitals on the metal and both oxygens. It is, however, not unreasonable to suppose that a nitrate group may on some occasions utilize two metal orbitals in traditional bidentate fashion and on others utilize a single metal orbital to form a three-center bond wherein the nitrate is bidentate with respect to a single coordination site. Thus, in some bidentate nitrate systems, where the metal atom apparently has expanded its coordination number, the mean positions of the two nitrate

Table III. Infrared and Raman Modes for Free and Coordinated Nitrate

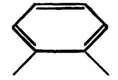
Symmetry	*Type*[a]	*Absorption (cm.$^{-1}$)*		*Assignment*
D_{3h}[22]	A'_1[b]	ν_1(1050)		N-O stretch
	A'_2[c]	ν_2(831)		NO_2 deformation
	E'	ν_3(1390)		NO_2 asym. stretch
	E'	ν_4(720)		planar rocking
		Monodentate	*Bidentate*	
C_{2v}[4]	A_1	ν_1(1290)	ν_2(985)	NO_2 sym. stretch
	A_1	ν_2(1000)	ν_1(1630)	N-O stretch
	A_1	ν_3(740)	ν_3(785)	NO_2 sym. bend.
	B_1	ν_4(1480–1550)	ν_4(1250)	NO_2 asym. stretch
	B_1	ν_5(715)	ν_5(750)	NO_2 asym. bend.
	B_2	ν_6(800)	ν_6(700)	out of plane rock

[a] All modes are infrared and Raman active unless specified otherwise. Within a point group the vibrational modes are numbered from the highest symmetry species and from the highest frequency within any symmetry species.

[b] Infrared inactive.

[c] Raman inactive.

oxygens in question are located approximately at the vertices of a normal coordination polyhedron characteristic of the metal, as in $[Co(NO_3)_4]^{-2}$ (*10, 13*). It is of singular interest that, in contrast to the $[Co(NO_3)_4]^{-2}$ ion, the $[Co(O_2CCF_3)_4]^{-2}$ ion has recently been found to contain monodentate ligands with four oxygens arranged in near tetrahedral geometry around the metal (*11*). Thus, potentially bidentate and isoelectronic ligands do not necessarily coordinate in a similar geometry even though the metal ion is the same. Because of the generally weak donor properties of such ligands, smaller forces due to electronic and steric requirements of the ligand may become dominant in determining geometrical configurations.

The environmental influences which determine whether or not nitrate coordinates and, if so, whether in a monodentate fashion, in one of the bidentate manners, or for that matter perhaps in combinations of these possibilities. Coordinated nitrate has been found with more than 20 metals, most of which are in the transition metal, lanthanide, and actinide series and some with Be, Ca, Zn, Hg, Tl, and Sn. Many examples with other metals are no doubt forthcoming. The type of ligand often found in conjunction with coordinated nitrate does not seem to be restricted to any particular class. Such ligands range from weak to strong sigma donors and monodentate to tetradentate amines. Representative of this group are H_2O, $OP(NMe_2)_3$, $OPMe_3$, $OPPh_3$, $OAsPh_3$, C_5H_5NO, Me_3NO, NH_3, Py, en, and dipy. Well-represented also are ligands which may very well π bond with the metal, such as PEt_3, PPh_3, $SC(NH_2)_2$, P  $PPh_2)_3$ and, as reported in this paper, $P(OMe)_3$ (L).

Experimental

Analyses. Elemental analyses other than those for metals were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. and Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Cobalt analyses were performed on 8–15 mg. samples by decomposing them with 3 ml. conc. HNO_3, heating to near dryness, followed by treatment with 1 ml. 70% $HClO_4$, and evaporating to near dryness again. The remaining solutions were diluted to 50 ml. with a 50% aqueous-acetone solution containing 5 g. of NH_4CNS and were analyzed spectrophotometrically using a molar extinction coefficient of 1842 l. mole^{-1} cm.$^{-1}$ for the $Co(CNS)_4^{-2}$ ion. Nickel analyses were carried out as described previously (*41*). Analytical data are reported in Table IV.

Ultraviolet and Visible Spectra. All solution spectra were scanned in the visible and ultraviolet regions on a Bausch and Lomb Model 505 Spectrophotometer. Reflectance spectra were obtained with a Beckman DU Spectrophotometer equipped with the Beckman 2580 reflectance attachment. Magnesium carbonate used as a reference and diluent were dried at 110°C. in vacuum for 12 hours before use. Spectral data are reported in Table V.

Infrared Spectra. Nujol-hexachlorobutadiene mulls were employed to obtain spectra on a Perkin-Elmer Model 21 Spectrophotometer. Spectral data are reported in Table VI.

Molar Conductivities. Conductivities were obtained as previously described (*42*) and are reported in Table VII.

Preparations. All the complexes were prepared in a similar manner by reaction of an acetone solution of the metal hydrate with an excess of L. Where indicated, the hydrates were dehydrated (*37*) with a 100% excess of 2,2-dimethoxypropane (DMP), previous to adding L.

$[CoL_5]ClO_4$ AND $[CoL_6][ClO_4]_3$. To 0.757 g. (2.07 mmoles) of $Co(ClO_4)_2 \cdot 6H_2O$, dissolved in an acetone-DMP solution, 2.82 g. (22.9 mmoles) of L was slowly added. The solution was allowed to stir for 3 hours, at which time the more insoluble Co(III) compound was filtered from the solution as a nearly colorless powder. It should be noted that the Co(III) complex is shock-sensitive and therefore was handled in mg. quantities. The Co(I) compound was obtained by adding ether to the filtrate to initiate precipitation followed by cooling to 0°C., producing yellow, needle-like crystals. Several recrystallizations were necessary in order to obtain the Co(I) compound free of the Co(III) complex.

$[CoL_5]NO_3$, $[CoL_5]_2[Co(NO_3)_4]$, AND $[CoL_5][CoL(NO_3)_2]$. To 0.944 g. (3.25 mmoles) of $Co(NO_3)_2 \cdot 6H_2O$, dissolved in an acetone-DMP solution, 4.40 g. (35.8 mmoles) of L were slowly added. The dark green solution was allowed to stir for 5 min., after which a small amount of ether (3–5 ml.) was added and the solution cooled to 0°C. The solid that soon formed was removed by filtration and more ether added. This process was repeated with cooling over a 4–5 day period. First precipitated was a dark violet solid, $[CoL_5][CoL(NO_3)_2]$, followed by a dark red solid, $[CoL_5]_2$-$[Co(NO_3)_4]$, and lastly the yellow solid, $[CoL_5]NO_3$. Throughout these precipitations a small amount of white solid was a persistent contaminant. This may be the $[CoL_6](NO_3)_3$ which co-precipitates with the compounds. Thus far it has not been possible to obtain this compound in sufficient quantity for analysis. The complexes were purified by recrystallizing several times from an acetone-ether mixture.

$[CoL_5]_2[Co(NO_3)_4]$ was also prepared by dissolving 0.096 g. (0.13 mmole) of $[CoL_5]NO_3$ in acetone and adding to it an acetone-DMP solution containing 0.039 g. (0.13 mmole, 100% excess) of $Co(NO_3)_2 \cdot 6H_2O$. The dark red complex was obtained by adding ether and cooling the solution to 0°C.

$[Ph_4As][CoL(NO_3)_2]$. To 0.12 g. (0.17 mmole) of $[CoL_5][CoL(NO_3)_2]$ dissolved in 3 ml. acetonitrile, 1.6 ml. of 0.10 *M* acetonitrile solution of Ph_4AsNO_3 (0.16 mmole) were added with stirring. Addition of ether produced a dark blue solid which was recrystallized from CH_2Cl_2 and ether to give well-formed azure blue crystals.

$[NiL_5](ClO_4)_2$. A total of 1.45 g. (3.83 mmoles) of $Ni(ClO_4)_2 \cdot 6H_2O$ was slowly added to 24.8 g. (200 mmoles) of L. The orange solid which formed after stirring the solution 1 hr. was filtered under nitrogen and recrystallized from a methanol-ether mixture.

Table IV. Analyses

Compound	*C* Calcd.	*C* Found
[CoL$_5$]ClO$_4$	23.15	22.97
[CoL$_6$](ClO$_4$)$_3$[b]		
[CoL$_5$]NO$_3$	24.27	24.17
[CoL$_5$]$_2$[Co(NO$_3$)$_4$]	21.61	21.68
[CoL$_5$][CoL(NO$_3$)$_2$]	21.92	21.96
[Ph$_4$As][CoL(NO$_3$)$_2$]		
[NiL$_5$](ClO$_4$)$_2$	20.52	20.30
[CuL$_4$]ClO$_4$	21.85	21.65
[CuL$_4$]NO$_3$	23.19	22.97
[AgL$_4$]ClO$_4$	20.48	20.32
[AgL$_2$NO$_3$]	17.25	17.72
[Ni(P(OCH)$_3$(CH$_2$)$_3$)$_5$](BF$_4$)$_2$	34.88	34.59
[Ni(P(OCH$_2$)$_3$C(CH$_2$)$_4$CH$_3$)$_5$](ClO$_4$)$_2$	42.23	42.67

[a] Q = Cl.
[b] Compound is explosive.
[c] Q = metal.
[d] Q = N.
[e] Q = B.

Table V. Ultraviolet and

Compound	*Solvent*
[CoL$_5$]ClO$_4$	CH$_2$Cl$_2$
[CoL$_6$](ClO$_4$)$_3$[b]	CH$_3$CN
[CoL$_5$]NO$_3$	CH$_2$Cl$_2$
[CoL$_5$]$_2$[Co(NO$_3$)$_4$]	CH$_2$Cl$_2$
[CoL$_5$][CoL(NO$_3$)$_2$][c]	CH$_2$Cl$_2$
[Ph$_4$As][CoL(NO$_3$)$_2$][d]	
[Ph$_4$As]$_2$[Co(NO$_3$)$_4$]	CH$_3$NO$_2$
[NiL$_5$](ClO$_4$)$_2$	CH$_2$Cl$_2$
[Ni(P(OCH)$_3$(CH$_2$)$_3$)$_5$](BF$_4$)$_2$	CH$_2$Cl$_2$
[Ni(P(OCH$_2$)$_3$C(CH$_2$)$_4$CH$_3$)$_5$](ClO$_4$)$_2$	CH$_2$Cl$_2$
[Co(Me$_3$PO)$_2$(NO$_3$)$_2$][f]	CHCl$_3$

[a] Extinction coefficients in units of 1 mole^{-1} cm.$^{-1}$ appear in parentheses.
[b] Bands were resolved by Gaussian analysis.
[c] Bands for the anion were resolved by Gaussian analysis.
[d] Spectrum in CH$_2$Cl$_2$ was identical to [CoL$_5$][CoL(NO$_3$)$_2$] except for the yellow band due to [CoL$_5$]$^{+1}$.
[e] Reflectance spectrum.
[f] *See* Reference *15*.

of Complexes

H		*Q*		*P*	
Calcd.	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
5.78	5.78	4.52	4.55[a]	19.91	19.82
		5.38	5.47[c]		
6.08	6.02			20.93	20.75
5.41	5.67	3.37	3.46[d]	18.63	18.84
5.48	5.64	2.84 11.9	2.93[d] 11.7 [c]	18.88	18.78
		8.54	8.49[c]		
5.17	5.16	8.07	7.99[c]	17.65	17.76
5.50	5.56	5.38	5.60[a]	18.83	18.57
5.79	5.70	2.25	2.48[d]		
5.16	5.22	5.02	4.99[a]	17.62	17.70
4.31	4.31	3.35	3.19[d]		
4.36	4.73	2.11	2.35[e]	15.00	14.53
6.64	6.97	5.55 4.58	5.64[a] 4.44[c]	12.13	11.69

Visible Spectra of Complexes

Wave Length (mμ)[a]

230(1.3×10^4), 253(1.6×10^4), 382(1.0×10^3)
261(4.4×10^4), 285(7.5×10^3), 306(1.7×10^3), 340(1.1×10^3)
230(1.4×10^4), 253(1.2×10^4), 382(1.0×10^3)
230(1.5×10^4), 253(1.2×10^4), 382(1.0×10^3), 538(102)
230(1.5×10^4), 253(1.2×10^4), 382(1.0×10^3), 525(67), 573(120), 615(59)

538(135)
259(1.6×10^4), 404(2.5×10^3)
265[e] 425[e]
— 365(2.6×10^3)
250[e] 400[e]
367(2.1×10^3)
525(*sh*), 560(144)

$[NiL_4]$. A total of 0.88 g. (1.00 mmole) of $[NiL_5](ClO_4)_2$ was added to a solution of 0.14 g. (1.00 mmole) of K_2CO_3 in 10 ml. H_2O. A colorless solid formed with noticeable CO_2 evolution. The solid was filtered off and washed with water. The nuclear magnetic resonance spectrum was found to be identical to that of an authentic sample of $[NiL_4]$ prepared by the method of Vinal and Reynolds (*43*).

$[Ni(P(OCH)_3(CH_2)_3)_5](BF_4)_2$, $[Ni(P(OCH_2)_3CCH_3)_5](ClO_4)_2$, $[Ni(P(OCH_2)_3CCH_2CH_3)_5](ClO_4)_2$, $[Ni(P(OCH_2)_3C(CH_2)_4CH_3)_5](ClO_4)_2$. All the above compounds were prepared in a manner analogous to that described for $[NiL_5](ClO_4)_2$ by adding acetone solutions of $Ni(ClO_4)_2 \cdot 6H_2O$ or $Ni(BF_4)_2 \cdot 6H_2O$ to a 100% excess of the ligand (*24, 28*) dissolved in acetone. In each case a yellow solid precipitated almost immediately, which was repeatedly recrystallized from an acetone-ether mixture.

$[CuL_4]ClO_4$. A total of 1.48 g. (4.00 mmoles) of $Cu(ClO_4)_2 \cdot 6H_2O$ was slowly added in 0.20 g. quantities over a period 1.5 hr. to a stirred suspension of 0.28 g. (2.00 mmoles) of K_2CO_3 in 25 ml. of L (200 mmoles). The resulting solution was stirred for 10 hrs., after which a large volume of ether was added, producing a white powdery solid.

$[CuL_4]NO_3$. To 0.665 g. (2.76 mmoles) of $Cu(NO_3)_2 \cdot 3H_2O$, dissolved in an acetone-DMP solution, were slowly added 3.42 g. (27.6 mmoles) of L. The light blue solution first turned dark blue but became colorless when all the ligand was added. The solution was slightly diluted with ether and cooled to 0°C. producing colorless crystals. The solid was recrystallized from an acetone-ether mixture.

$[AgL_4]ClO_4$. To 25 ml. of L (200 mmoles) was very slowly added 0.83 g. (4.00 mmole) of $AgClO_4$. After the mildly exothermic reaction ceased, a large volume of ether was added, producing a white solid which was recrystallized from methanol at 0°C. Adding the $AgClO_4$ too rapidly caused the reaction mixture to burst into flames.

$[AgL_2NO_3]$. To 5 ml. of L (40 mmole) was very slowly added 0.61 g. (3.6 mmole) of $AgNO_3$. After the exothermic reaction ceased the solution was stirred for ½ hr. Adding a large volume of ether to the solution produced a white solid which was recrystallized from an acetone-ether mixture. The molecular weight of 436 measured in acetone on a Mechrolab Model 301 A Osmometer agreed within 4.5% of the calculated monomeric weight of 418.

Discussion

The formulations of the complexes herein reported, as shown in Tables IV–VII, are supported by the conductivity data reported in Table VII, as well as the analytical data in Table II. All of the complex species are diamagnetic (except those containing the $[Co(NO_3)_4]^{-2}$ ion), as shown by the normal proton chemical shifts to be published later. The disproportionation reaction of $Co(ClO_4)_2$ with L reported previously to form $[CoL_5]ClO_4$ and $[CoL_6](ClO_4)_3$ (*29*) is similar to that reported for polycyclic phosphites (*28*). The strong-field nature of L in the cobalt(III) complex is demonstrated by the diamagnetism of the complex and a calculated *Dq*

Table VI. Infrared Data in the Nitrate Region[a]

Compound	ν_3		ν_1	ν_2
Ionic Nitrate[b]	1360		1020	820
$[CoL_5]NO_3$	1368			828
$[CuL_4]NO_3$	1350			828
$[Ag(Ph_3P)_4]NO_3$[c]	1343			
	ν_4	ν_1	ν_2	ν_6
$[CoL_5]_2[Co(NO_3)_4]$[d]	1462	1320, 1285	1022	812
$[Ph_3AsMe]_2[Co(NO_3)_4]$[e]	1462	1285	1022	807
$[Ph_4As]_2[Co(NO_3)_4]$[d]	1478, 1462, 1435	1305, 1285	1015	810
$[CoL_5][CoL(NO_3)_2]$[d]	1490, 1462	1305, 1285	1018	807
$[Ph_4As][CoL(NO_3)_2]$[d]	1500, 1479, 1435	1305, 1285	1018	808
$[Co(Me_3PO)_2(NO_3)_2]$[f]	1517, 1492, 1469	1312, 1304, 1282	1024	812
$[AgL_2NO_3]$	1448, 1423	1350, 1285	1025	818
$[Cu(Ph_3P)_2NO_3]$[c]	1475	1275	1022	810

[a] Values are in cm.$^{-1}$
[b] *See* Reference *17*.
[c] *See* Reference *14*.
[d] Resolution was not sufficient to observe shoulder peaks.
[e] *See* Reference *38*.
[f] *See* Reference *15*.

Table VII. Molar Conductances[a]

Compound	*Molar Conductance (mhos cm.$^{-1}$ mole^{-1})*	*Solvent*
$[CoL_5]ClO_4$	113	Acetone
$[CoL_6](ClO_4)_3$	460	Acetonitrile
$[CoL_5]NO_3$	146	Acetone
$[CoL_5]_2[Co(NO_3)_4]$	253	Acetone
$[CoL_5][CoL(NO_3)_2]$	118	Acetone
$[Ph_4As][CoL(NO_3)_2]$	142	Acetonitrile
$[NiL_5](ClO_4)_2$	307	Acetonitrile
$[CuL_4]ClO_4$	159	Acetonitrile
$[CuL_4]NO_3$	113	Acetone
$[AgL_4]ClO_4$	147	Acetonitrile
$[AgL_2NO_3]$	13	Acetone
$[AgL_2NO_3]$	167	Acetonitrile
$Cu(PPh_3)_2NO_3$[b]	~0	Nitrobenzene
$[Ag(PPh_3)_4]NO_3$[b]	19.3	Nitrobenzene

[a] The following compounds and their molar conductivities were used for comparison: $(n\text{-}C_4H_9)_4NBr$, 123(acetone); $[Ph_4As]_2[Co(NO_3)_4]$, 252(acetone); $(n\text{-}C_4H_9)_4NNO_3$, 158(acetonitrile); $[Ni(en)_3](ClO_4)_2$, 312(acetonitrile), $[Co(P(OCH)_3(CH_2)_3)_6](ClO_4)_3$, 430(acetonitrile) (*28*).
[b] *See* Reference *14*.

value similar to that employed for polycylic phosphites (*28, 41*). If it can be assumed that the spin-allowed transitions, $^1A_{1g}(t_{2g})^6 \rightarrow {}^1T_{1g}(t_{2g})^5(e_g)$

and ${}^1A_{1g}(t_{2g})^6 \rightarrow {}^1T_{2g}(t_{2g})^5(e_g)$ correspond to the bands at 340 and 306 mμ, respectively (Table V), then *Dq* is 3100 cm.$^{-1}$ (The unexpectedly high intensities of these bands may be due to an intense ultraviolet absorption tail occurring with them.) This value is somewhat lower than *Dq* for polycylic phosphites (*ca.* 3250–3350 cm.$^{-1}$) (*28*) but can still be compared with that for $Co(CN)_6^{-3}$ (3350 cm.$^{-1}$) (*25*). Ligand-ligand repulsions are not prohibitive in $[CoL_6]^{+3}$, although they may cause the lower *Dq* value for L, compared with constrained polycyclic phosphites. It may be, however, that the L molecules undergo some constraint of the alkoxy moieties in order to minimize ligand-ligand repulsions. Such constraint would also increase the dipole moment of the ligand because of greater directional character of the oxygen lone pairs (*12*).

In addition to forming a nitrate of $[CoL_5]^{+1}$, a $[Co(NO_3)_4]^{-2}$ and the new $[CoL(NO_3)_2]^{-1}$ derivatives are also formed. The $[Co(NO_3)_4]^{-2}$ derivative is not unexpected in view of the large size of the $[CoL_5]^{+1}$ cation. The presence of the $[Co(NO_3)_4]^{-2}$ ion is confirmed by comparing the spectral data for this ion in Tables V and VI with those of Drago *et al.* (*38*) for similar compounds. The diamagnetic $[CoL(NO_3)_2]^{-1}$ ion, however, presents some interesting structural possibilities. The complex $[CoL_5]$ $[CoL(NO_3)_2]$ contains both an anionic and a cationic complex cobalt(I) atom bound to L. Although the structures of the two ions cannot be determined until x-ray studies are completed, the infrared data in Table VI indicate nitrate coordination (*15, 17*). If the anion like the cation is also 5-coordinate, employing the bidentate nature of the NO_3^- ion, some form of trigonal bipyramid or square pyramid might be anticipated. Structures involving bidentate nitrates for $[CoL(NO_3)_2]^{-1}$ derive some tentative support from the very similar nitrate infrared bands observed by Cotton for the complex $[Co(Me_3PO)_2(NO_3)_2]$ (*15*) (Table VI) which, according to x-ray analysis (*16*), possesses a bidentate nitrate structure. Furthermore, the visible spectrum of the $[CoL(NO_3)_2]^{-1}$ ion resembles that of $[Co(Me_3PO)_2(NO_3)_2]$ (Table V). The lack of $[CoL_6](NO_3)_3$ in isolable amounts may reflect an instability of such a complex in contrast to the perchlorate salt which forms in appreciable quantities. Difficulties were also noted in storing the analogous $[Co(P(OCH_2)_3CCH_3)_6](NO_3)_3$, which could only be obtained in a metathetical reaction with the perchlorate (*41*).

The excellent reproducible analytical results for $[NiL_5](ClO_4)_2$ cause substantial doubt to be cast on the formulation of the analogous polycyclic phosphite complexes as 6-coordinate (*28*). The relatively high molecular weights of the polycyclic phosphite nickel(II) complexes did not permit facile distinction between a 5:1 and 6:1 ligand-metal ratio on the basis of elemental analyses. Because the reflectance and solution spectral data in Table V are similar, it can be tentatively concluded that the $[NiL_5]^{+2}$ and $[Ni(P(OCH)_3(CH_2)_3)_5]^{+2}$ ions are essentially 5-coordinate in the solid and solution states. The absence of a band near 260 mμ in the case of the solution spectrum of $[Ni(P(OCH)_3(CH_2)_3)_5]^{+2}$, however, is unexplained. Preliminary results of an x-ray examination (*30*) of $[Ni(P(OCH)_3(OCH_2)_3)_5](ClO_4)_2$ reveal an axially compressed trigonal bipyramidal configuration for the cation. Substantiating evidence for postulating a 5-coordinate nickel(II) species stems from the striking similarity in the visible spectra of these complexes to those of the isoelectronic and probably isostructural cobalt(I) complexes of L (Table V) and of the polyclic phosphites (*28*). To the best of our knowledge, these compounds represent the first 5-coordinate nickel(II) complexes containing five monodentate phosphorus ligands in the coordination sphere.

The perchlorate complexes of $[CuL_4]^{+1}$ and $[AgL_4]^{+1}$ exhibit maximum coordination numbers with L as previously found with polycyclic phosphites (*31*, *42*). Neither of these perchlorate compounds was shock-sensitive in our hands. Although the nitrate complexes of these metals also contain four polycyclic phosphites (*31*, *42*), $[CuL_4]NO_3$ and $[AgL_2(NO_3)]$ are formed with L. The low conductivity of the latter compound in acetone (Table VII) and the infrared spectrum in the nitrate region confirm the presence of coordinated nitrate. Because the complex is monomeric in acetone, polymers involving bridging nitrates are ruled out in solution. Unless the silver is 3-coordinate and therefore bonded to a monodentate nitrate—or perhaps a bidentate nitrate involving a three-center bond—a tetrahedral structure containing a normal bidentate nitrate is expected. Because of the coordinating ability of acetonitrile, it is not surprising that the nitrate is displaced from $[AgL_2NO_3]$, thereby resulting in a conductivity corresponding to a 1:1 electrolyte. That NO_3^- is able to compete with L in the silver(I) compound indicates that L is a somewhat weaker ligand than polycylic phosphites because nitrate coordination was not observed when the latter ligands were used. Using Ph_3P, Cotton has shown (*14*) that four Ph_3P ligands are attached to either Ag^{+1} or Cu^{+1} in the perchlorates, whereas in the nitrates the Ag^{+1} was bound to four Ph_3P molecules while the Cu^{+1} was bound to two Ph_3P ligands and one nitrate. In our compounds, using L instead of Ph_3P causes a reversal in the behavior of the two metal ions for some reason as yet unexplained.

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39

Transition Metal Complexes of Alkyl Phosphites

II. Metal Coordination Involving Isomerizeration of a Phosphorous Acid Ester

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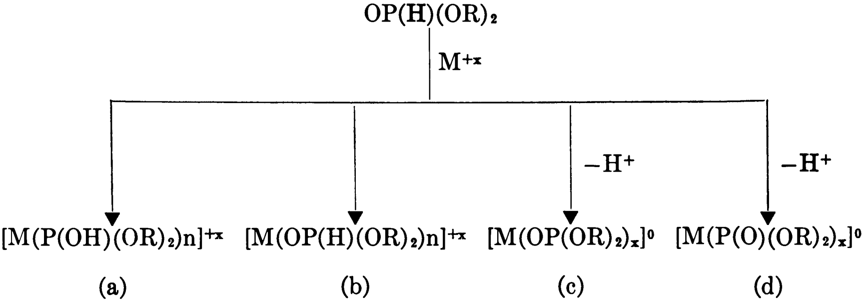
The rapid, acid-catalyzed hydrolysis of the polycyclic phosphite 2,8,9-trioxa-1-phosphaadamantane (L) produces two isomeric hydrolysates, 3-α-oxo-3-β-hydrido-7-β-hydroxy-2,4-dioxa-3-phosphabicyclo (3.3.1) nonane (Isomer A), and 3-β-oxo-3-α-hydrido-7-β-hydroxy-2,4-dioxa-3-phosphabicyclo (3.3.1) nonane (Isomer B), the configurations of which were tentatively postulated on the basis of infrared and PNMR spectra. Each isomer dehydrates to L under vacuum at 120°C., as well as in the presence of Cu^{+2} *or* Ph_3C^{+1} *ions to give* $[CuL_4]^{+1}$ *and* $[Ph_3CL]^{+1}$*, respectively. With hydrated metal ions, L forms complexes of the general formula* $[M(L\cdot H_2O)_4](X^2)$*, where* $X = BF_4^-$ *or* ClO_4^- *and* $M = Mn^{+2}, Zn^{+2}, Fe^{+2}$*, and* Cd^{+2}*. Of the isomers, only A forms the identical complexes with these ions as well as* Ni^{+2}*. Infrared evidence is presented which is consistent with the postulate that* $L\cdot H_2O$ *is an enol form of A bound to the metal through phosphorus.*

Very few investigations of the ligand properties of phosphorous acid diesters $OP(H)(OR)_2$ have been reported, as shown in Table I. Molecules of this type are potentially interesting in that several coordination reactions with transition metals may be possible—depending perhaps mainly on the metal:



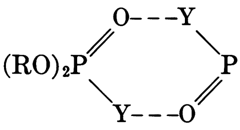
Modes (c) and (d) could conceivably be extended to include anionic complexes if the number of ligands capable of coordinating is in excess of the charge on the metal. It might be pointed out that the well-known tendency of rare-earth and actinide metals to form phosphoryl-oxygen bonds is exemplified by uranyl ion in the presence of $(EtO)_2P(O)H$ (*4*). Proton NMR studies, in which only a change in J_{PH} occurs on complexing (*4*), support a linkage of the type $MOP(H)(OEt)_2$ as in (b). Mode (c) was found for $[AgOP(OR)_2]$ (*7, 12, 13*) from infrared and x-ray studies, and mode (d) was claimed for $[XHgP(O)(OR)_2]$ (*3, 8*) and $[Hg(P(O)(OR)_2)_2]$ (*8, 15*) from chemical and infrared studies. (Molecular weights obtained in benzene indicated that $[XHgP(O)(OR)_2]$ was dimeric. Species of the form  (where Y = HgX) were suggested to account for the data (*3*).) The former compound, however, is also postulated to be $[XHgOP(OR)_2]$ on the basis of other infrared evidence (*12*). In the case of $[Pt(P(OR)_2OH)_2(P(OR)_2O)_2]$ (*14*) the neutral $P(OR)_2OH$

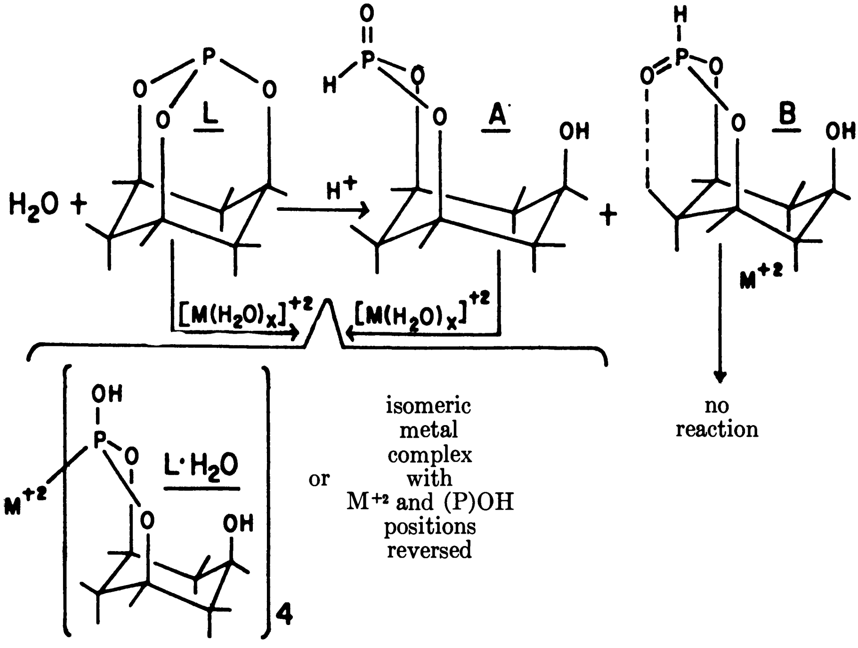
Table I. Complexes Containing Phosphorous Acid Diesters $OP(H)(OR)_2$

Compound[a]	*R*	*Reference*
$(OP(OR)_2)HgX$ (X = Cl, Br, I, SCN, OAc)	Et, *n*-Pr, *i*-Pr *n*-Bu, *i*-Bu, *n*-Pent, *n*-Hept	*3, 8, 12*
$(OP(OR)_2)_2Hg$	Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu	*8, 15*
$OP(OR)_2Ag$	Et	*7, 12, 13*
$(OP(H)(OR)_2)_2(OP(OR)_2)_2Pt$	Me, Et, *n*-Pr, *n*-Bu	*14*

[a] *See* text for discussion of ligand-metal link.

ligands may coordinate as in (a) or (b), and the anionic $P(OR)_2O^-$ ligands could employ mode (c) or (d).

We wish to report several metal complexes formed from a phosphorous acid diester of the type $OP(H)(OR)_2$ which underwent isomerization to form a metal-phosphorus bond as in (a). In the course of our investigations on the complexing properties of polycylic phosphites (*9*, *17*), it was found that 2,8,9-trioxa-1-phosphaadamantane (L) undergoes a rapid, acid hydrolysis in acetone to form two colorless, crystalline hydrolysates, A and B. Only isomer A or L complexed with divalent hydrated metal ions, and it is concluded from infrared evidence that A has isomerized as shown in the following reaction sequence. Supporting infrared and PNMR evidence is presented for the tentatively postulated structures of A and B.



Experimental

Solvents. All solvents were reagent grade. Acetone was dried over Linde 4-A Molecular Sieve.

Measurements. Infrared spectra in the sodium chloride region were obtained in Nujol and hexachlorobutadiene mulls on a Perkin-Elmer Model 21 Spectrometer. Proton NMR spectra were obtained on approximately 20% by weight solutions at 14,100 gauss on a Varian HR-60 NMR Spectrometer, and are shown in Figure 1. Irradiation of the two POCH methine protons at 294 cps reduced the quartet in C (obtained by expansion of the 821 cps PH peak) to the doublet in A. Irradiation at 114 cps in the methylene region reduced the quartet to the triplet in B. In dimethyl sulfoxide, using Me_4Si as an internal standard, the POCH doublet

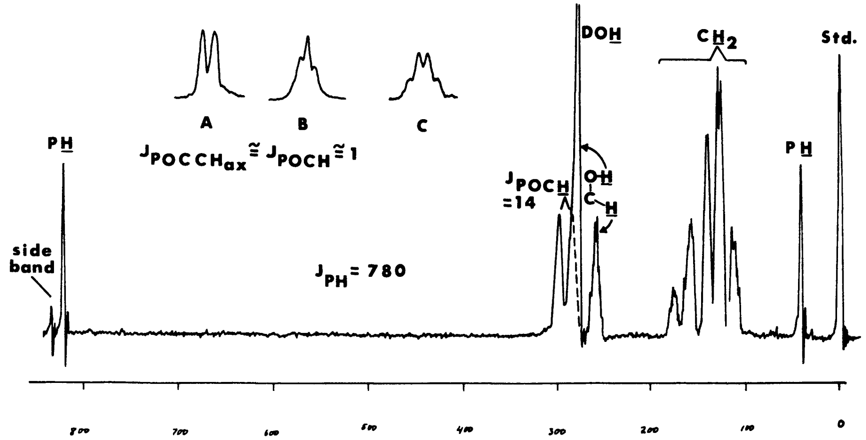


Figure 1. Proton NMR spectrum of isomer B in D_2O using Tier's salt as an internal standard

was well resolved due to the absence of the DOH peak in the spectrum shown. Furthermore, the COH peak was observed at 223 cps. With but minor shifts, the spectrum of isomer A was very similar to that of B except for the PH peaks. Expansion of the PH doublet (66.5 and 796 cps) revealed no observable coupling to other protons.

Microanalyses in Table II were performed by Galbraith Laboratories, Inc.

2,8,9-Trioxa-1 Phosphaadamantane (L). The tricyclic phosphite was prepared by a method described previously (*16*).

Hydrolysis of L. PREPARATION OF 3-α-OXO-3-β-HYDRIDO-7-β-HYDROXY-2,4-DIOXA-3-PHOSPHABICYCLO [3.3.1] NONANE; (ISOMER A) AND 3-β-OXO-3-α-HYDRIDO-7-β-HYDROXY-2,4-DIOXA-3-PHOSPHABICYLO [3.3.1] NONANE; (ISOMER B). To a stirred solution of 6.40 g. of L (40.0 mmole) and 0.72 ml. of water (40.0 mmole) in 20 ml. of acetone was added 1 drop of 70% perchloric acid. A colorless solid formed after 40 sec. The reaction mixture was stirred for 1 hr. and the resulting solid filtered under nitrogen, washed with acetone and ether, and then dried under vacuum at room temperature. A second fraction of solid was collected by adding ether to the acetone supernatant. A total of 7.03 g. (99% yield) of isomeric mixture was collected. The isomers were separated by fractional crystallization from absolute ethanol. Isomer A, the less soluble, was purified by recrystallization from boiling acetone. The more soluble isomer, B, was purified by recrystallization from methanol. A total of 2.3 g. (33% yield) isomer A and 1.8 g. (26% yield) isomer B was collected.

Dehydration of Isomer A. Isomer A (0.20 g.) was heated to 120°C. under vacuum. The dehydration product, L, was sublimed out and collected in 70% yield.

Dehydration of Isomer B. This was carried out in a similar manner to that of isomer A, and a 70% yield of L was collected.

Table II. Analyses

	C	
Compound	*Calc.*	*Found*
$Mn(L \cdot H_2O)_4(ClO_4)_2$	29.80	29.95
$Fe(L \cdot H_2O)_4(H_2O)_2(ClO_4)_2$	28.80	28.62
$Ni(L \cdot H_2O)_4(BF_4)_2$	30.50	30.28
$Ni(L \cdot H_2O)_4(ClO_4)_2$	29.72	29.47
$Zn(L \cdot H_2O)_4(BF_4)_2$	30.28	30.02
$Zn(L \cdot H_2O)_4(ClO_4)_2$	29.48	29.89
$Cd(L \cdot H_2O)_4(ClO_4)_2$	28.10	27.77
$[CuL_4]NO_3$	37.70	37.71
$[CuL_4]ClO_4$	36.00	35.58
$[AgL_4]NO_3$	35.60	34.55
$[AgL_4]ClO_4$	34.05	34.01

[a] Q = P.
[b] Q = N.
[c] Q = Cu.
[d] Q = Ag.

Phosphonium Salts of L from Isomer A and Isomer B. 1-TRIPHENYLMETHYL-4-METHYL-2,8,9-TRIOXA-1-PHOSPHAADAMANTANE PERCHLORATE FROM ISOMERS A AND B. To a suspension of 0.52 g. of isomer A (2.92 mmoles) in acetone (15 ml.) was added 1.00 g. (2.92 mmoles) of triphenylmethyl perchlorate. After 3 hrs., a pale yellow precipitate formed which was filtered off and dried under vacuum at room temperature. Recrystallization of the product from acetonitrile gave 0.82 g. (56% yield) of a colorless solid which was shown to be identical with an authentic sample of 1-triphenylmethyl-4-methyl-2,8,9-trioxa-1-phosphaadamantane perchlorate (*16*) by infrared spectroscopy and elemental analysis. A similar procedure with isomer B gave the same product in 53% yield.

1-TRIPHENYLMETHYL-4-METHYL-2,8,9-TRIOXA-1-PHOSPHAADAMANTANE TETRAFLUOROBORATE FROM ISOMERS A AND B. To 1.00 g. (5.12 mmoles) of silver tetrafluoroborate in acetone (10 ml.) was added a solution of 1.43 g. (5.12 mmoles) of triphenylmethyl chloride in acetone (15 ml.). After 5 min., the filtered solution was added to a stirred suspension of 0.90 g. (12 mmoles) of isomer A in acetone (20 ml.). After 4 hrs., a colorless precipitate formed which was filtered off and dried under vacuum at room temperature. The colorless solid (0.52 g., 30% yield), was shown to be identical with an authentic sample of 1-triphenylmethyl-4-methyl-2,8,9-trioxa-1-phosphaadamantane tetrafluoroborate (*16*) by infrared spectroscopy. A similar procedure with isomer B gave the same product in 31% yield.

Complexes of $L \cdot H_2O$ from L. Since the method of preparation was similar in all cases, a typical example is given.

TETRAKIS ($L \cdot H_2O$)ZINC(II) PERCHLORATE. Fifteen ml. of an acetone solution containing 0.64 g. (4.0 mmoles) of L were added to 0.38 g. (1.0 mmoles) of zinc perchlorate hexahydrate dissolved in 10 ml. of acetone, and the solution was stirred for 7 hrs. The colorless precipitate which formed

of Complexes

H		*Q*		*Cl*	
Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
4.55	4.76			7.35	6.98
4.83	4.95			7.10	6.89
4.67	4.80	13.11	12.84[a]		
4.54	4.78			7.31	7.25
4.66	4.88	13.01	12.82[a]		
4.54	4.75			7.26	7.37
4.33	4.20			6.92	6.65
4.74	4.80	1.83	1.88[b]		
4.49	4.52	7.92	8.34[c]	4.42	4.27
4.48	4.56	15.30	15.50[a]		
4.28	4.30	12.71	12.45[d]	4.19	4.10

was filtered off, washed with ether, and dried under vacuum at room temperature. A 65% yield was realized.

This technique was also used to prepare tetrakis(L·H_2O)cadmium(II) perchlorate, tetrakis(L·H_2O)iron(II) perchlorate dihydrate, and tetrakis(L·H_2O)manganese(II) perchlorate in similar yields.

Complexes of L·H_2O from Isomer A. Since the method of prepaeration was similar in all cases, a typical example is given.

TETRAKIS(L·H_2O)NICKEL(II) TETRAFLUOROBORATE. To a suspension of 0.80 g. (4.5 mmoles) of Isomer A in acetone (20 ml.) was added a solution of 0.40 g. (12 mmoles) of nickel tetrafluoroborate hexahydrate in acetone (5 ml.). The solution was stirred for 1 hr., after which the resultant pale green precipitate was filtered off, washed with acetone, and dried under vacuum at room temperature. A yield of 100% was realized.

This technique was also used to prepare the following complexes: tetrakis(L·H_2O)cadmium(II) perchlorate, tetrakis(L·H_2O)zinc(II) perchlorate, tetrakis(L·H_2O)zinc(II) tetrafluoroborate, tetrakis(L·H_2O)nickel(II) perchlorate, tetrakis(L·H_2O)iron(II) perchlorate dihydrate, and tetrakis(L·H_2)manganese(II) perchlorate.

TETRAKIS(L)COPPER(I) PERCHLORATE FROM L. To a stirred solution of 0.37 g. (1.0 mmole) of $Cu(ClO_4)_2 \cdot 6H_2O$ in 10 ml. of absolute ethanol was added a solution of 1.60 g. (19.0 mmoles) of L in 25 ml. of absolute ethanol. A colorless solid formed immediately. The solution was cooled to 0°C. for 1 hr., after which the solid was filtered off under nitrogen, washed with ethanol and anhydrous ether, and dried under vacuum at room temperature. A total of 0.75 g. (94% yield) was collected. The nitrate derivative in 99% yield was obtained in a similar manner using $Cu(NO_3)_2 \cdot 6H_2O$.

TETRAKIS(L)SILVER(I) PERCHLORATE. To a stirred solution of 0.21 g. (1.0 mmole) of $AgClO_4$ in 10 ml. of absolute ethanol was added a solution of 0.96 g. (6.0 mmoles) of L in 20 ml. of the same solvent. The colorless solid which formed immediately was filtered under nitrogen, washed with cold ethanol and ether, and dried under vacuum at room temperature. The yield was 100%. Similarly, the nitrate derivative was obtained in 99% yield from $AgNO_3$.

TETRAKIS(L)COPPER(I) OR SILVER(I) PERCHLORATE FROM ISOMERS A AND B. To a suspension of 0.7 g. (4 mmoles) of isomer A or B in 25 ml. of acetone was added 1 mmole of copper(II) perchlorate hexahydrate or anhydrous silver(I) perchlorate, and the suspension was stirred for 18 hrs. The colorless copper complex was filtered off and dried under vacuum at room temperature. Some reduction to silver metal occurred in the reaction of silver perchlorate. The precipitate was therefore extracted with ethanol, and the extract was filtered and concentrated to obtain the complex. Approximately 30% yields of both compounds were obtained.

Dissociation of ($L \cdot H_2O$) Complexes. The complex $[Zn(L \cdot H_2O)_4][ClO_4]_2$, for example, in D_2O gave an NMR spectrum very similar to that of free isomer A in D_2O. Addition of further isomer A to that solution produced no change in chemical shifts but caused an increase in line intensities.

Conversion of Tetrakis($L \cdot H_2O$)nickel(II) Perchlorate and Tetrafluoroborate to Pentakis(L)nickel(II) Perchlorate and Tetrafluoroborate. Three-tenths gram (0.3 mmoles) of the pale green complex $[Ni(L \cdot H_2O)_4][ClO_4]_2$ was heated under nitrogen for 10 min. at a temperature of 140°C. The resulting yellow solid was washed with absolute ethanol and dried under vacuum at room temperature. The solid (62% yield) was shown to be identical with an authentic sample of $[NiL_5][ClO_4]_2$ (*5*) by infrared spectroscopy. A similar reaction with $[Ni(L \cdot H_2O)_4][BF_4]_2$ gave $[NiL_5][BF_4]_2$ (*5*) in 65% yield.

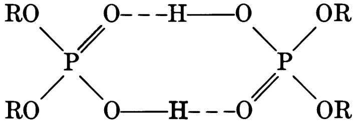
Discussion

Structural Considerations of Isomers A and B. Proton NMR spectra of isomer A and B are shown in Figure 1. The only major difference in the spectra is the appearance of each member of the PH proton doublet as an apparent 1331 quartet in B, in contrast to the single line for each member observed in A. From our recent work on the influence of geometrical factors in long-range proton-proton spin-spin interactions (*2*), it was shown that a favorable condition for coupling over a distance of five bonds is opposing collinear CH bonds. Thus, the PH proton in B is collinear and opposed to the axial methylene proton beneath. Coupling of the PH proton with the axial methylene and with each of the two identical methinyl protons could produce an overlapping doublet of triplets appearing as a 1331 quartet in each member of the PH proton doublet. Tentative assignment of the OH group on the carbon ring to the axial position in each isomer arises from the lack of any substantial coupling of the equatorial proton geminal to the alcohol group to the vicinal axial and equatorial protons. If the OH groups were equatorial, the geminal axial proton might have been expected to couple to the trans vicinal protons with a magnitude of about 12 cps, as was found for an Arbuzov product of L in which the halide was postulated to be equatorial on the basis of NMR and infrared evidence (*1*). That the two isomers differ only in the arrangement of the groups around phosphorus is supported by the observation that the OH stretching frequencies are the same (3450 cm.$^{-1}$) for both isomers, whereas the PH and P=O modes occur at 2440 and 1241 cm.$^{-1}$, respectively, in A and 2510 and 1208 cm.$^{-1}$, respectively, in B. It is not possible to conclude from the infrared spectra of the isomers whether either isomer possesses an enol form of the type $HOP(OR)_2$ in the free state because the COH band at 3450 cm.$^{-1}$ might mask the POH stretching mode. The integrations of the PH and CH proton resonances leave no doubt, however, that little if any enol exists in D_2O. It is of some interest that Daasch (*7*) reports a band at *ca.* 3500 cm.$^{-1}$ in $HP(O)(OR)_2$ (where R = Et and *n*-Bu) which is not ascribed to a POH mode, however, since its intensity did not reduce upon addition of Et_3N.

Dehydration of Isomers A and B to L. Both isomers are dehydrated to L at 120°C. under vacuum or in the presence of triphenylmethyltetrafluoroborate or perchlorate in acetone at room temperature to form the phosphonium salts $[Ph_3CL][X]$ ($X = BF_4^-$ or ClO_4^-) obtained previously from L directly (*16*). Both isomers also react with $Cu(ClO_4)_2 \cdot 6H_2O$ in acetone at room temperature to lose water in the formation of the copper(I) complex $[CuL_4]ClO_4$. This complex can also be obtained as a reduction product in the reaction of L with $Cu(ClO_4)_2 \cdot 6H_2O$ under the same conditions. The relative ease of the dehydration reactions further supports the postulate that the COH group is axial, for it is difficult to visualize a reasonable mechanism involving an equatorial OH which must produce an axially situated oxygen when L is formed. The mechanisms of the hydrolysis of L and the reverse dehydration will be discussed in a future publication.

Complexes of $L \cdot H_2O$. The $L \cdot H_2O$ complexes shown with their analyses in Table II can be formed from the metal hydrates in acetone upon reaction with L or A, except the Ni^{+2} complexes which form only with A. L in the presence of $Ni(BF_4)_2 \cdot 6H_2O$ or $Ni(ClO_4)_2 \cdot 6H_2O$ yields the 5-coordinate $[NiL_5]^{+2}$ ion (*5*). It is interesting that heating the $[Ni(L \cdot H_2O)_4]^{+2}$ complexes also yields some of the $[NiL_5]^{+2}$ compounds. In no reaction of L or A with a metal hydrate was any B detected. The complexes dissociate in CH_3OH, H_2O and CH_3CN to yield only A and solvated metal ion and are insoluble in most organic solvents.

Infrared studies of the complexes containing $L \cdot H_2O$ reveal that in all cases the PH stretching mode disappears and an additional, somewhat broad OH band in the range 3300–3400 cm.$^{-1}$ appears. In free acids of the type $OP(OH)(OR)_2$, the consistent appearance of the OH stretching mode between 2500 and 2700 cm.$^{-1}$ (*6*, *11*) has been attributed to the presence of hydrogen-bonded dimers on the basis of cryoscopic measurements (*11*). The dimer is postulated to involve an eight-member ring as shown below.



It is not surprising that a different situation obtains in the metal complexes of L·H_2O because the complexes are not analogous to systems of the type $OP(OH)(OR)_2$. A is an ester of the type $OP(H)(OR)_2$ which we suggest forms complexes of the type $[M(P(OH)(OR)_2)_4]^{+2}$. Hence, the possibilities for hydrogen bonding are severely limited, and a free OH stretch is observed at higher frequencies as expected.

Further, albeit somewhat weaker, evidence for the suggestion that L·H_2O is an enol form of A in the complexes stems from the replacement of a very strong band at 1248 cm.$^{-1}$ in free isomer A by two narrow bands of medium intensity which vary slightly in position among the complexes. This region of the spectrum is quite rich in bands in both A and the complexes. Thus, it is highly likely that the $P=O$ stretching absorption assigned at 1248 cm.$^{-1}$ disappeared, unmasking two weaker bands characteristic of either the complex or ligand. If no rearrangement about phosphorus had taken place and the metal had coordinated to the phosphoryl oxygen in A, it would be somewhat difficult to explain satisfactorily an apparent splitting and reduction in intensity of the $P=O$ band and no significant shift of its position to lower frequencies. Furthermore, the disappearance of the narrow PH band would be highly improbable upon coordination of a metal to the phosphoryl oxygen. The plausibility of another band at 3350 cm.$^{-1}$, arising from a stretching mode of a free OH on phosphorus, further reduces the attractiveness of coordination via a phosphoryl oxygen. It can be concluded with fair certainty that coordination of the type shown in (a) obtains in these complexes rather than (b). Possibilities (c) and (d) involving an anionic ligand and expulsion of a proton are definitely excluded on the basis of the analyses since the ClO_4^- and BF_4^- anions are retained.

It is not at all clear why divalent Mn, Fe, Zn, and Cd prefer to coordinate to phosphorus in the L·H_2O complexes, especially because the phosphoryl oxygen in A is available, and the steric requirements of A are lower. Yet efforts to form compounds of these metal ions with L have thus far failed. Interestingly, neither Cu^{+2} nor Ag^{+1} forms an L·H_2O complex under our conditions but rather cause dehydration of A and formation of the $[CuL_4]^{+1}$ and $[AgL_4]^{+1}$ ions, respectively, which can also be obtained from a reaction of Cu^{+2} and Ag^{+1} with L. Apparently, an intermediate situation is reached with Ni^{+2} which forms $[Ni(L \cdot H_2O_4]^{+2}$ when A is employed, and $[NiL_5]^{+2}$, when L is used or if the $L \cdot H_2O$ complex is heated. At the opposite extreme, Co^{+2} does not react with A but does disproportionate in the presence of L to form $[CoL_5]^{+1}$ and $[CoL_6]^{+3}$ (*10*).

The molar conductances of the copper(I) and silver(I) complexes of L in Table III are evidence for their formulation as 1:1 electrolytes. The $L \cdot H_2O$ complexes were either too insoluble or disproportionated in the various solvents employed for meaningful conductances to be obtained. The role, if any, of the COH group in the $L \cdot H_2O$ complexes and the structures of these coordination compounds is not known at this time because of lack of suitable crystals for structural analysis. Attempts to synthesize isomer A with a proton in place of the alcoholic OH are in progress, as well as coordination experiments with more simple ligands of the type $OP(H)(OR)_2$.

Table III. Molar Conductance Values of Complexes in Acetonitrile

Compound	*Molar Conductance (mhos/cm. mole)*
$(t\text{-Bu})_4NO_3$	158
$[CuL_4]ClO_4$	150
$[AgL_4]NO_3$	147
$[AgL_4]ClO_4$	160

All attempts to form metal complexes with B failed. This observation is tentatively rationalized on the basis of the higher (by 70 cm.$^{-1}$) stretching frequency of the PH link in B, compared with A, which may indicate a higher PH bond order. Consequently, PH bond rupture necessary for the migration of the proton to the oxygen (or perhaps insertion of the oxygen in the PH link) may be more difficult for B. Furthermore, the lower P=O stretching frequency (by 33 cm.$^{-1}$) for B compared to A may reflect a lower P=O bond order because of hydrogen bonding with the equatorial proton immediately below. Such a hydrogen bond might have significant stability because it would form one of the bridges in a bicyclic system of stable six-member rings. It should be noted that these structural arguments are consistent with the observation of long-range coupling of the bridgehead protons discussed above. It is interesting, however, that heat or the presence of Cu^{+2}, Ag^{+1}, or Ph_3C^{+1} ions at room temperature is sufficient to disrupt the stable structure of B and cause dehydration. Evidently the enol ($L \cdot H_2O$) readily formed from A is not formed from B under the conditions employed. Thus, B either dehydrates, dehydrates and coordinates as L, or does not react. Table IV contains a summary of the reactions discussed in this paper.

Table IV. Summary of Reactions of L, A, and B with Various Ions

	L	*A*[a]	*B*[a]
[b]M = Mn^{+2}, Fe^{+2}, Zn^{+2}, Cd^{+2}	$[M(L\cdot H_2O)_4]^{+2}$	$[M(L\cdot H_2O)_4]^{+2}$	N.R.
[c]Ni^{+2}	$[NiL_5]^{+2}$	[d]$[Ni(L\cdot H_2O)_4]^{+2}$	N.R.
[c]Cu^{+2}	$[CuL_4]^{+1}$	$[CuL_4]^{+1}$	$[CuL_4]^{+1}$
[e]Ag^{+1}	$[AgL_4]^{+1}$	$[AgL_4]^{+1}$	$[AgL_4]^{+1}$
Ph_3C^{+1}	$[Ph_3CL]^{+1}$	$[Ph_3CL]^{+1}$	$[Ph_3CL]^{+1}$
[c]Co^{+2}	$[CoL_5]^{+1}$, $[CoL_6]^{+3}$	N.R.	N.R.

[a] A or B upon heating dehydrate to L.
[b] Metals in hydrated form. In anhydrous form, L does not react.
[c] Metals in hydrated form.
[d] Forms $[NiL_5]^{+2}$ upon heating.
[e] Metal in anhydrous form.

Note: Recently Chatt and Heaton described (Proceedings, IX International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, 1966, p. 440) several platinum(II) complexes of $R_2P(O)H$, in which bonds of the type $PtP(OH)R_2$ and $PtP(R)_2OPt$ were postulated on the basis of chemical, infrared, and NMR evidence. Thus, acids of the class $OP(H)R_2$ also seem to utilize mode (a) upon coordination to a single platinum. Furthermore, simultaneous use of modes (a) and (c) leads to bridge bonding of the ligand between platinum atoms.

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40

Solvational Control in Spin-State Variations among Nickel(II) Complexes

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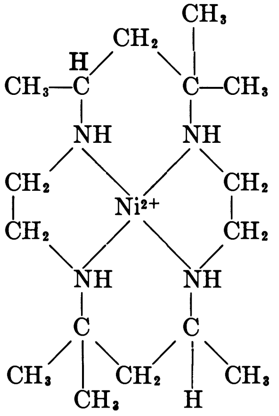
The various modes of interaction with molecules of solvents that govern the spin states of nickel(II) ions are both subtle and potent. The best known examples involve direct metal ion-solvent coordination. In certain cases, these processes represent poised equilibria with comparable amounts of the 6-coordinate triplet and lower coordinate singlet present. Such systems are particularly sensitive to minor variations in the character of the solvent. With bulky organic ligands, the complexes themselves probably act as solvent-structuring solutes. The effects of other solutes and other variables on solvent structure may be reflected in shifts in the equilibrium. The stoichiometric interaction of complex and solvent molecule via a hydrogen bonding process is also well documented and subject to similar variations. Apparently, in some nonprotonic solvents the dielectric properties support ionization equilibria that are associated with a spin-state change but, from the direction of the change, coordination of the solvent is not important.

Early references (*2*, *16*, *17*) to the variation of spin state for nickel(II) with the coordination environment consider two most plausible situations—the conversion of square-planar diamagnetic nickel(II) to octahedral paramagnetic nickel(II) by the addition of the fifth and sixth ligands above and below the plane of the first four ligating atoms, and the possibility of the existence of either a ground state triplet or a singlet for nickel(II) in square-planar, 4-coordinate structures or tetragonal, 6-coordinate structures. Indeed, the recurrent hypothesis has been offered that in certain poised systems the singlet and triplet states might have very nearly the same energies and, therefore, might coexist. Extensive study has been dedicated to those systems that were suspected of illustrating this phenomenon (*18*).

That the role of solvent in affecting spin-state variations deserves closer attention may be shown by summarizing a number of compelling phenomena. Though the nature of these effects has many aspects and might be variously described, three particular facets are explored here. In the case of certain nickel(II) systems poised equilibria occur with comparable amounts of 6-coordinate triplet and lower coordinate singlet present. Such systems are particularly sensitive to minor variations in the character of the solvent. With bulky organic ligands, the complexes themselves probably act as solvent-structuring solutes, thereby lowering the activity of solvent molecules and making them less available for coordination. The effects of other solutes and other variables on solvent structure may be reflected in shifts in the singlet-triplet equilibrium. The second set of phenomena involves stoichiometric interaction between nickel complex and solvent molecules without direct coordination by the solvent. In a number of instances it appears that hydrogen bonding in these definite solvates determines the spin state of the nickel(II) atom. Finally, in some nonprotonic solvents, the dielectric properties support ionization equilibria that are associated with a spin-state change but, from the direction of the change, coordination of solvent is not important.

Solute Character and Solvent Activity

It is instructive to begin with a consideration of systems that are not necessarily poised but may be shifted far toward a single, spin state. The macrocyclic ligand reported by Curtis (*5*), 2,4,4,9,11,11-hexamethyl-1,5,8,12-tetraazacyclotetradecane (Ni^{2+} complex, Structure I, hereafter



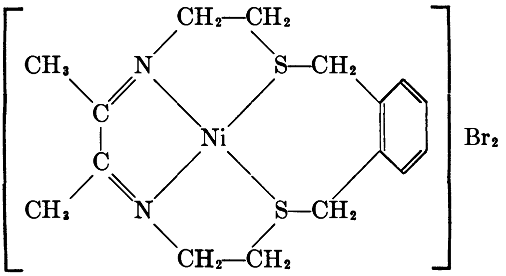
I

abbreviated as CT), is constrained by stereochemistry to coordination in a single plane. This constraint is most pronounced with the meso isomer, and discussion is confined to derivatives of that form. A series of salts and tetragonal complexes Ni(CT)X_2 has been reported (*6*). The anhydrous chloride and bromide, for example, are violet in color and exhibit the normal magnetic behavior expected of 6-coordinate nickel(II) complexes having triplet ground states (*6, 11*). When dissolved in nonpolar solvents, such as $CHCl_3$, the complexes remain 6-coordinate and paramagnetic (*11*).

In contrast, when Ni(CT)Cl_2 or Ni(CT)Br_2 is dissolved in water, it converts to a planar, diamagnetic complex which acts as a di-univalent electrolyte. Also, the nickel(II) ion in Ni(CT)$^{2+}$ will not combine with NH_3 when dissolved in aqueous solution (*11*). These observations present a number of disturbing features. The failure of H_2O and NH_3 to coordinate is inferred from the fact that the solution properties are typical of planar nickel(II). Both NH_3 and H_2O occupy positions much higher in the spectrochemical series than Cl^- or Br^-. Consequently, if either of these neutral molecules were coordinated, the nickel atom would surely exist in its paramagnetic triplet state.

The nagging question remains—why do these excellent ligands fail to coordinate? The most convenient molecular explanation would be of a steric nature; however, H_2O and NH_3 molecules are substantially smaller than Br^- so that spatial restrictions are not involved. It is tempting to seek some model based on specificity of the axial sites on nickel, perhaps for donors prefering B-type metals; however, quantitative studies (*12*) show that the spectrochemical series for the X groups in Ni(CT)X_2 is normal (CN^- (> CT) > NCS^- > ONO^- > F^- > N_3^- > $NO_3^- \sim Cl^-$ > Br^- > I^-). It therefore becomes necessary to seek the cause in factors external to the complexes in question. That such factors are readily recognized will be evident shortly.

A second example of failure of certain solvents to exhibit their expected coordinating abilities is found in the solution behavior of dibromo(*S,S'*-*o*-xylyl-2,3-pentanedione-bis-mercaptoethylimine)nickel(II) (*3, 4*) (Structure II, hereafter abbreviated as Ni(PEX)Br_2). From the work of Imhof and Drago (*9*), we know that the ligand, field-splitting parameters for $Ni(CH_3OH)_6^{2+}$ in methanol and $Ni(dmf)_6^{2+}$ in dimethylformamide are virtually identical. However, Ni(PEX)Br_2 shows sharply dissimilar behaviors in the two solvents (*3, 4*). In dmf it dissolves to form a paramagnetic, 6-coordinate, di-univalent electrolyte which is formulated as $[Ni(PEX)(dmf)_2]^{2+}$, $2Br^-$. In methanol solution, at equilibrium, it is a diamagnetic, di-univalent electrolyte. Also, it should be pointed out that Ni(PEX)Br_2 exists in simple paramagnetic, 6-coordinate form in nonpolar solvents, such as $CHCl_3$. As in the case of Ni(CT)X_2, it must be inferred that CH_3OH does *not* coordinate with the nickel atom in Ni(PEX)$^{2+}$, although there is no obvious steric or electronic reason for this fact.



II

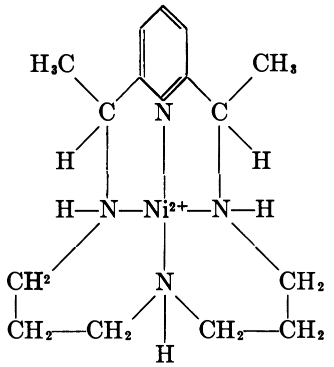
Systems involving poised equilibria provide equally pertinent data. An early and particularly revealing set of observations arises from Jørgensen's study (*10*) of the visible spectra of aqueous solutions of Ni(trien)$^{2+}$. In dilute solution in pure water, equal molar concentrations of nickel(II) salts and triethylenetetraamine exhibit properties typical of pseudo-octahedral structure. In fact, the correspondence of the spectra to the octahedral prescription is so close that Jørgensen suggested the hydrated ion to exist in the cis form—i.e., *cis*-Ni(trien)(H_2O)$_2^{2+}$. Now, as increasing amounts of certain salts are dissolved in this solution, a new, intense absorption band appears in the visible region of the spectrum and increases as a function of the salt concentration. Perchlorates are particularly effective. The new absorption band corresponds to the appearance of planar nickel(II) and is accompanied by loss of octahedral nickel. The dissolving of, for example, $NaClO_4$ shifts the equilibrium of Equation 1 to the right.

$$\underset{\text{(triplet)}}{\mathrm{Ni(trien)(H_2O)_2{}^{2+}_{(aq)}}} \rightleftharpoons \underset{\text{(singlet)}}{\mathrm{Ni(trien)^{2+}_{(aq)}}} + 2H_2O \qquad (1)$$

Obviously, the added salt decreases the activity of the solvent in order to affect this poised equilibrium.

Karn (*11*) has recently found that the magnetic moment of aqueous (2,11-dimethyl-3,7,11,17-tetraazabicyclo(11.3.1)heptadeca-1(17), 13, 15-triene)nickel(II) (Structure III, hereafter abbreviated as Ni(KN)$^{2+}$) is indicative of a mixture of spin states. From the study of the temperature dependence of the magnetic susceptibility of the solution, the equilibrium of Equation 2 is deduced.

For the reaction as written, $\Delta H = +4.5$ kcal./mole, and $\Delta S = 16$ eu. These values are concentration dependent because of the effect of the complex on the activity of water. Two facts are particularly notable. The large, positive entropy change associated with the formation of the diamagnetic species is consistent with the desolvation model. Also, this is a rare



III

$$\underset{\text{(triplet)}}{Ni(KN)(H_2O)_2{}^{2+}_{(aq)}} \rightleftharpoons \underset{\text{(singlet)}}{Ni(KN)^{2+}_{(aq)}} + 2H_2O \qquad (2)$$

instance in which the singlet is at higher energy than the triplet in a system involving nickel(II) in a singlet-triplet equilibrium.

The complex behavior of certain of the Lifschitz salts probably arises from similar causes. The work of Higginson, Nyburg, Wood (*8*), and Nyburg and Wood (*19*) is sufficiently detailed to lead to interesting speculations. In acetone solution, $Ni(m\text{-}stein)_2(Cl_2CHCO_2)_2$, where m-stein represents meso-stilbenediamine, exists as a blue, presumably paramagnetic, material; however, portionwise addition of water leads to incremental formation of a diamagnetic yellow form. It would be most comfortable to conclude that the enhanced dielectric constant of water merely leads to a progressive shift of the equilibrium of Equation 3 to the right. The trouble is the blue crystals isolated from acetone contain the ion (x-ray crystal structure) $Ni(m\text{-}stein)_2(H_2O)_2{}^{2+}$. This suggests the

$$\underset{\text{(triplet)}}{Ni(m\text{-}stein)_2(Cl_2CHCO_2)_2} \rightleftharpoons \underset{\text{(singlet)}}{Ni(m\text{-}stein)_2{}^{2+}} + 2Cl_2CHCO_2{}^- \qquad (3)$$

alternative and fascinating process given in Equation 4. Note that this requires the coordination of water to be most extensive when water is in low abundance.

$$Ni(m\text{-}stein)_2(H_2O)_2{}^{2+} \underset{+\text{acetone}}{\overset{+H_2O}{\rightleftharpoons}} Ni(m\text{-}stein)_2{}^{2+} + 2H_2O \qquad (4)$$

The most readily apparent factor common to these several processes is their dependence on the availability of water (or other solvent) molecules for coordination. A second, equally important factor is the large bulk of organic matter in the ligands. In fact, these complexes may be thought of as irregular doughnut shaped masses of hydrophobic material with positively charged Lewis acids occupying the "hole." As a consequence of this structural character, a water molecule must be largely separated from the bulk of the solvent in order to coordinate. Thus, the fulcrum of the poised equilibrium has as its supporting bases the processes of Equations 5 and 6.

$$H_2O_{(aq)} \rightleftharpoons H_2O_{(vap)} \tag{5}$$

$$2H_2O_{(vap)} + NiL^{2+} \rightleftharpoons NiL(H_2O)_2{}^{2+} \tag{6}$$

The general hydrophobic character of the ligands has a major effect on the first equilibrium—i.e., on the availability of the water, and it is this factor that requires attention. It is well-recognized that hydrophobic solutes, such as hydrocarbons, dissolve with sizeable negative ΔH and ΔS of solutions. This and other data have led to theories explaining how such solutes cause the degree of structuring, or ice-like character, of water to increase (*14*).

In the flickering cluster model of water, an adiabatic condition is marked by rapid, random fluctuation of partially structured regions throughout the volume, with the total fraction of the fluid that is structured a constant. The nature of the structuring is presumed to involve hydrogen bonding, as in ice, and a given water molecule at any instant might be characterized in terms of the number of hydrogen bonds it has formed. Nonpolar, structure-making solutes increase the degree of structuring of the water by stabilizing "Frank-Evans icebergs" adjacent to themselves. The hydrophobic character of these solute particles may be considered to cause an interface of structured water to be formed that is not unlike a surface. The structuring presumably is transmitted through a number of layers of solvent molecules.

In contrast to this behavior, ions of modest electrostatic fields reduce the degree of structuring of the solvent water. The solvent molecules in such cases can be sorted into three regions—the inner sphere, where they are strongly oriented; a structure-broken region; and the bulk of the solvent where the molecules are normal. Apparently, strongly hydrated cations may behave quite differently. There is reason to believe that these species may not only alter but also increase the extent of structuring of water. Thus, an ion having a coordination sphere belonging to the cubic system might induce structure on the solvent through perpetuation of its own ligand array into the bulk of the solution by means of strong hydrogen bonds.

Returning to the case at hand, these complexes probably act as hydrophobic solutes and influence the structure of water so that the solvent molecules are less available than they otherwise would be. The presence of a positive charge is probably not effective in affecting solvent structure because the charge is buried in the large hydrophobic structure. One can envision a Frank-Evans iceberg enclosing one of the complex ions with the ice-like structure bridging over the "hole" containing the metal ion. Therefore, in the first example cited, $Ni(CT)^{2+}$ decreases the activity of water because it is a structure-making solute, thereby making the solvent unavailable for coordination. The example of $Ni(KN)^{2+}$ illustrates an essential aspect of this theory. Because it is the hydrophobic character of the complex itself that is causing the nickel atom to have to relinquish its coordinated water molecules, the relative concentration of singlet at equilibrium should be enhanced as the total concentration of complex is increased. This is indeed the case. Further, a critic must point out the fact that the concentration of water decreases as the concentration of complex increases. This cannot be the cause of the observed effect, for the range of concentrations is small and all solutions are dilute so that the concentration of water is essentially constant throughout the range.

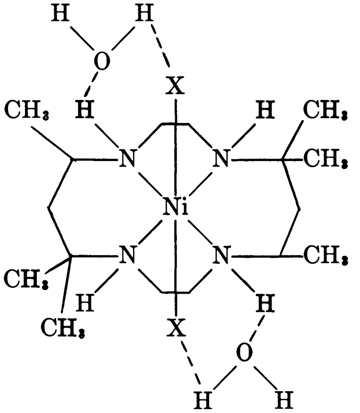
Similarly, the role of acetone in the case of $Ni(m\text{-stein})_2^{2+}$ *might* be to disrupt the structure of water, thereby counteracting the effect of the complex which, again, is structure-making. The distinction between the behavior of CH_3OH and dmf toward Ni^{2+} and $Ni(PEX)^{2+}$ suggests that CH_3OH has a hydrogen-bonded partial structure analogous to that of water. In such a case, the cubic Ni^{2+} ion might readily be incorporated into the solvent structure, while coordination of CH_3OH to $Ni(PEX)^{2+}$ requires removal of that solvent molecule from interaction with the rest of the solvent.

Specific Hydrogen Bonding Effects

Despite the considerable coordinating ability of the water molecule (or CH_3OH), other intermolecular associations sometimes take precedence under conditions where coordination to a metal ion would otherwise be expected. This is well-illustrated by the behavior of systems containing water in solvent quantities, as described in the preceding section. There also exist well-documented examples of related processes in which only stoichiometric amounts of water or related material are involved.

Perhaps the most clearly defined example involves the macrocyclic complex of Curtis, $Ni(CT)X_2$. The solid, violet, paramagnetic, anhydrous chloride and bromide must be carefully protected from moisture for they readily revert to yellow, diamagnetic dihydrates. The fact that two molecules of water are taken up to produce a diamagnetic nickel(II) ion is especially interesting for displacement of the halide, and coordination by the water molecules would surely produce a violet, paramagnetic species in view of the relative positions of H_2O, Br^-, and Cl^- in the spectrochemical series. The most reasonable supposition is that the water molecule interacts with the complex in such a way that the ligand field of the axially-oriented halides is diminished. Clearly, this may be accomplished by hydrogen bonding of the water molecule to the coordinated halide. Curtis first offered this explanation (*6*). Such a model had been offered earlier to explain the variation in properties with hydration of the *N*,*N*-dialkylethylenediamine complexes of nickel halides (*7*).

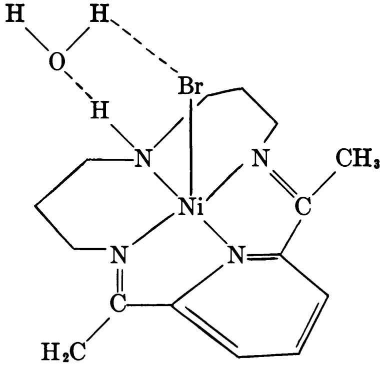
The macrocyclic complex Ni(CT)Br_2 exhibits a similar effect in solution in nonpolar solvents (*11*). If dissolved in freshly purified chloroform, it has the expected molecular weight (osmometer) for a monomeric, 6-coordinate structure and retains the color and spectrum of a typical pseudo-octahedral nickel(II) complex having a triplet ground state. However, if a hydroxylic solute is added or, in fact, if the stabilizer (C_2H_5OH) is not removed from the chloroform, the nickel atom exhibits the spectrum of square-planar, diamagnetic nickel(II), but still shows a normal molecular weight. It is suggested that hydrogen bonding, as shown in Structure IV, weakens the bond between the metal atom and the halide ion, thereby producing the singlet state.



IV

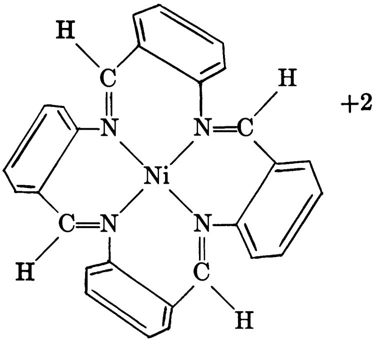
Recently, a closely related model has been invoked (*13*) to explain the role of a single water molecule in promoting 5-coordination. The diamagnetic, complex ion is bromo(2, 12-dimethyl-3, 7–11, 17-tetraazabicyclo(11.3.1)heptadeca-1, (17), 2, 11, 13, 15-pentaene)nickel(II) (hereafter abbreviated as Ni(CU)Br^+). This ion forms only monohydrated salts, and the water of hydration is not removed at 100°C. *in vacuo.* The proposed function of the water molecule is shown in Structure V.

A similar role has been suggested for water molecules in systems exhibiting more complex, magnetic behavior. In the case of the nickel(II)



V

complexes of the tetradentate ligand tetrabenzo[b, f, j, n][1, 5, 9, 13]tetraazacyclohexadecine (Structure VI, hereafter abbreviated as TAAB), Ni(TAAB)X_2, three classes of behavior were observed (*18*). For X^- = ClO_4^-, BF_4^-, or $B\phi_4^-$, the nickel(II) is planar and diamagnetic. For X^- = I^-, NO_3^-, or NCS^-, μ = 3.2 BM, and the complexes exhibit electronic spectra consistent with a 6-coordinate, tetragonal structure (*12*). Both the chloride and bromide are anomalous in three ways: (a) Only they exist as monohydrates, Ni(TAAB)$X_2 \cdot H_2O$, and the water is held tenaciously; (b) The magnetic moments are 1.7 (Cl^-) and 1.5 (Br^-) BM at room temperature; (c) The occurrence of low magnetic moments with these ligands, while iodide yields a fully paramagnetic compound, is inconsistent with the usual spectrochemical series for nickel(II)—i.e., Dq(Cl^-) > Dq(Br^-) > Dq(I^-). As in other cases, the water cannot profitably be assumed to be coordinated for it is a stronger ligand than the halides, and it should surely produce the triplet ground state. The system can be satisfactorily explained as a result of detailed magnetic (*18*) and spectral (*11, 12*) studies. The temperature variation of the magnetic



VI

susceptibility agrees nicely with a model based on an equilibrium between singlet and triplet states, and the thermal parameters are $\Delta H = +800$ cal./mole, $\Delta S = +0.57$ eu for $\mathrm{Ni(TAAB)Cl_2 \cdot H_2O}$ and $\Delta H = +700$ cal./mole, $\Delta S = -0.45$ eu for $\mathrm{Ni(TAAB)Br_2 \cdot H_2O}$. The strict, linear graphs of $\ln K$ *vs.* $1/T$ reveal that ΔH is independent of temperature over the brief 200°C. range studied, thus sustaining the two-state model. The values of ΔS differ from that expected for a change in spin state alone. This demonstrates the superposition of at least one additional, structural change involving a negative entropy change. The first spectral band has been assigned to the transition ${}^3B_{1g} \rightarrow {}^3E_g$, and the energy of this transition depends in part on the axial ligands (*1*). Consequently, its position should reflect the position of the anion in the spectrochemical series. The observed frequencies are $\mathrm{Cl^-}$, 8800 cm.$^{-1}$; $\mathrm{Br^-}$, 8300 cm.$^{-1}$; and $\mathrm{I^-}$, 8100 cm.$^{-1}$, as expected on the basis of the usual behavior of nickel(II). It is therefore concluded that the portions of the samples present as triplets are normal. It follows then that the occurrence of the singlet-triplet equilibrium probably should not be attributed to the destabilizing of the triplet but to stabilizing of the singlet. Such a situation can be envisioned in terms of the equilibrium of Equation 7. The energy of hydrogen bonding is presumed to stabilize the singlet isomer. In view of the poor hydrogen bonding ability of the iodide ion, the distinction between the iodide, on the one hand, and the chloride and bromide derivatives, on the other, is readily understood.

$$\begin{array}{ccccccc} [\mathrm{Ni(TAAB)X_2}] & + & \mathrm{H_2O} & \rightleftharpoons & [\mathrm{Ni(TAAB)X}]^+ & + & \mathrm{X^-\cdots HOH} \\ \text{(octahedral,} & & \text{(interstitial} & & \text{(5 coord.,} & & \text{(hydrogen bonded} \\ \text{triplet)} & & \text{water)} & & \text{singlet)} & & \text{anion)} \\ & & & \text{or} & [\mathrm{Ni(TAAB)}]^{2+} & + & \mathrm{X^-\cdots HOH\cdots X^-} \\ & & & & \text{(planar,} & & \text{(hydrogen bonded} \\ & & & & \text{singlet)} & & \text{anion)} \end{array} \qquad (7)$$

A more subtle example of the role of hydration is found in the properties of solid $\mathrm{Ni(PEX)Br_2}$ (*3*, *4*). For the related compounds, $\mathrm{Ni(PEX)Y_2}$, where $\mathrm{Y^-} = \mathrm{ClO_4^-}$ or $\mathrm{I^-}$, the nickel atom is in its singlet state, while the triplet state occurs for $\mathrm{Y^-} = \mathrm{Cl^-}$, $\mathrm{N_3^-}$, and $\mathrm{NCS^-}$. The bromide complex has a magnetic moment of 1.57 BM, and the magnetic susceptibility obeys the Curie-Weiss law with only a small Weiss constant. This result suggests the possibility of nonequivalent nickel(II) atoms in the unit cell, some being diamagnetic and some paramagnetic. Precedents are found in the structure of bis(diphenylbenzyl phosphine)nickel(II) bromide (*15*), which contains two paramagnetic tetrahedral molecules and one isomeric diamagnetic planar molecule per unit cell and in the structure of a yellow form of bis(*m*-stilbenediamine)nickel(II) dichloroacetate which contains two paramagnetic octahedral nickel(II) complexes and one planar diamagnetic complex per unit cell. In such cases, the moment calculated per paramagnetic ion is normal.

If Ni(PEX)Br_2 contains both paramagnetic, pseudo-octahedral, and diamagnetic species in the unit cell, the ratio must be three diamagnetic for each paramagnetic ion because the squares of the moments average. This assumption leads to the assignment of $\mu_{eff} = 3.14$ BM for the paramagnetic species present.

The relationships just described apply to samples carefully protected from moisture. Ni(PEX)Br_2 slowly absorbs water, apparently approaching a limit of ½ mole of H_2O per mole of complex. This change in composition is accompanied by a parallel decrease in μ_{eff}, approaching a small limiting residual value typical of spin-paired nickel(II). It is concluded that the one molecule in four of Ni(PEX)Br_2 that was in the paramagnetic, triplet state has combined with two molecules of water and changed into a planar, diamagnetic form. Again, the hydrogen bonding role of water is apparent.

Spin-state Variations in Nonhydroxylic Solvents

In CH_3NO_2, Ni(PEX)Cl_2 behaves essentially as a nonelectrolyte, retaining coordination of the two chlorides and displaying triplet, magnetic and spectral properties, closely related to those observed for the solid (*3*, *4*). In contrast, Ni(PEX)I_2 is diamagnetic both in the solid state and in CH_3NO_2 solution, having very similar spectra in the two states. Molar conductance in nitromethane shows the compound to be a uni-univalent electrolyte ($\lambda_M = 75$ ohm^{-1} at $C = 10^{-3}M$), thereby strongly suggesting the cation to be 5-coordinate, Ni(PEX)I^+.

Ni(PEX)Br_2 is intermediate in properties and behavior. In nonpolar solvents, such as dichloroethane, the compound exists as a neutral, molecular, 6-coordinate species having a normal, triplet, ground state, as inferred from molecular weight, magnetic moment, and electronic spectra. However, in nitromethane, at room temperature, the substance exhibits intermediate values for molar conductance (58 ohm^{-1} at 10^{-3} M) and magnetic moment (2.65 BM at 9.44 x 10^{-3} M). Dilution experiments yield values for the molar conductance that are consistent with an equilibrium constant of 1.66 x 10^{-3} (T = 25°C.) for the process given in Equation 8.

$$\underset{\text{(triplet)r}}{\text{Ni(PEX)B}_2} \rightleftharpoons \underset{\text{(singlet)}}{\text{Ni(PEX)Br}^+} + \text{Br}^- \qquad (8)$$

Ni(PEX)Br^+ is assumed to be a diamagnetic, 5-coordinate complex in analogy to Ni(PEX)I^+. The validity of the treatment is verified by the predicted moment of the solution showing 2.65 BM; theory predicts 2.60 BM, which is in excellent agreement. This appears to be a satisfactory example of the variation of spin state in response to the dielectric properties of solvent, for there is no reason to assume coordination by the nitromethane. This example contrasts to the cases cited for water solutions, because the strong coordinating ability of water requires that solvent molecules complex or that there be a complicating reason this does not occur. It has always been the temptation of the coordination chemist to presume that the dissociation of a bound group in solution leaves a coordination site vacated, even in solvents that can readily provide ligands. Present orientation of the field would lead the investigator to presume exactly counter to that old difficulty and always assume that the ionization process involves displacement by solvent molecules rather than dissociation under the action of the dielectric property of the solvent. Clearly neither assumption is generally valid, and a substantial number of appropriate examples must be subjected to careful experimentation.

Acknowledgment

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Coordination Chemistry of Selected Elements of Group III

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The sequence $[H_4B]^-$, $[H_3BNH_3]$, $[H_2B(NH_3)_2]^+$, $[HB(NH_3)_3]^{+2}$, *and* $[B(NH_3)_4]^{+3}$ *can be described as a sequence in which the hydride ion ligand is replaced systematically by* NH_3 *molecules. The last two members of this sequence have not been established as yet, but the first and third members result from the direct reaction of* B_2H_6 *and* NH_3. *When* NR_3 *is used as a ligand instead of ammonia in direct reaction with* B_2H_6, *the displacement of the hydride is less complete and the sole product is the non-ionic* H_3BNR_3. *The result is similar to that found when metal halides form coordination compounds with* NH_3 *or* NR_3. *Ammonia tends to give ionic products and trimethylamine usually produces non-ionic complexes. The complexes of the form* $H_2B(Base)_2{}^+$ *can be treated as true coordination compounds which: 1) undergo displacement reactions of both hydride and base and 2) show the chelate effect. Evidence has also been presented to suggest that coordination can stabilize a lower oxidation state of boron. Synthesis of an optically active cation of the form* $[B\ a,\ b,\ c,\ d]^+$ *now appears practical. Coordination theory can also be extended to complexes of* Al^{+3} *and* Ga^{+3}.

The recognition of the tetrahedral carbon atom by Le Bel and van't Hoff was probably one of the most spectacular advances in stereochemistry. It gave rise to the theoretical concept of a two atom bond and provided an easy method for rationalizing the geometry of both doubly and triply bonded structures. In view of the success of the carbon models, it was not strange that the early coordination models of Wurtz, Graham, Jørgensen, and Blomstrand followed the chain and ring arrangements of carbon very closely and made minor allowances for valence differences in atoms. Werner's major contributions were twofold; he recognized that 1) the geometry of octahedral cobalt compounds can differ spectacularly from the geometry of tetrahedral carbon compounds, and the geometry of planar platinum compounds can differ from that of both carbon and cobalt, and 2) that in order to rationalize these experimentally observable differences in geometry a new kind of bonding, or "secondary valence," was required.

An analogous situation, which in retrospect bears a fascinating resemblance to Werner's contribution, can be found in the unravelling of the geometry and bonding patterns of the boron hydrides and their derivatives. Recognition by Lipscomb, Kasper, Longuet-Higgins, and their co-workers of the fundamental geometry of the boron hydrides can be compared with Werner's recognition of octahedral and planar arrangements in metal complexes. A break with a well-entrenched carbon analogy was required. Furthermore, like Werner's system, it required a new bonding concept. Werner created the donor acceptor or coordinate bond; the new geometry of the boron hydrides required the recognition of the multicenter bond, which had not been a part of the lore of carbon chemistry. Such a bond can, however, like the coordinate covalent bond, be considered as a logical extrapolation of the carbon system. One starts with a triple bond, six electrons between two atoms; goes to a double bond, four electrons between two atoms; goes to a single bond, two electrons between two atoms; then proceeds to a three-center bond, two electrons among three atoms; goes to a multicenter bond, two electrons among many atoms; and finally goes to the metallic bond, two electrons among an infinite number of atoms (or complete delocalization). It is not surprising that boron falls on the metallic side of carbon in its bonding patterns.

It is not my purpose to introduce this completely foreign concept of boron hydrides into this symposium. Rather, it is my purpose to explore the application of classical Werner coordination concepts to the chemistry of the Group III elements—boron, aluminum, and gallium. These concepts serve a most useful correlative and predictive function in interpreting the behavior of many of the compounds of these elements.

Such a correlation seems worth considering because developments in these systems have been rapid and significant. In 1964, a book which included discussions of coordination chemistry noted the following in referring to complexes of B, Al, Ga, In, and Tl: "In aqueous solution the coordination chemistry of these elements is almost exclusively that of the complexes of fluoride and oxygen donor ligands." In just these past two years an exciting broader chemistry for the elements of Group III has been recognized and is developed herein.

Werner's Concepts in Boron Chemistry

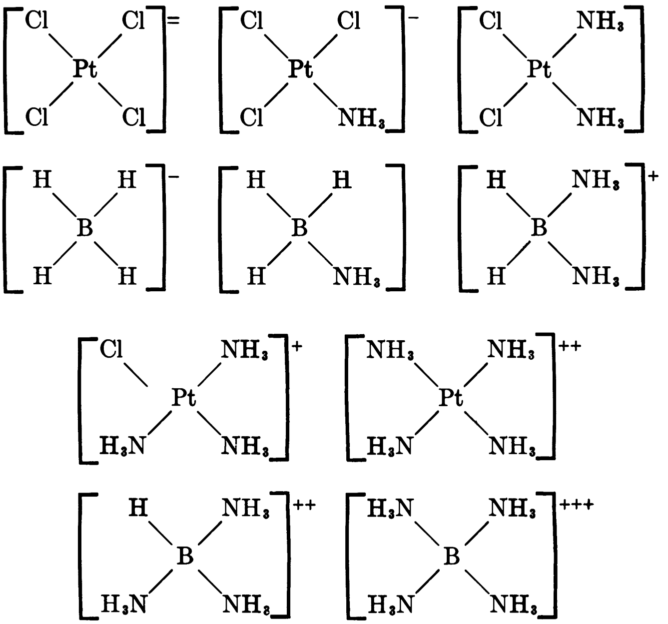
If one restricts attention to those boron compounds containing only a single boron atom, a striking comparison to the simplest coordination compounds can be made. If, on the other hand, one considers the higher boron hydrides containing boron-boron bonds, one finds analogies to modern metal-metal bonded systems and to the organometallic complexes, the structures of which are being elucidated by studies of Dahl and others.

Diborane-ammonia Systems. Consider the formal analogy between the chloroammines of platinum and the ammonia adducts of diborane. It is useful to consider the hydrogen atoms attached to boron in the ammonia addition compounds of diborane as negative hydridic ligands, comparable to the chloride ions found in coordination chemistry. Although this concept may have been considered heresy some years ago, it was made easier to accept when Chatt (*2*) and his colleagues demonstrated the reaction:

The presence of hydridic hydrogen and its ability to replace a chloride ligand was clearly demonstrated by this process. With the recognition of the analogy, a formal comparison between the complexes of $PtCl_2$ and NH_3 and the complexes of B_2H_6 and NH_3 can be drawn. The analogy is shown at the top of the following page.

The ammonia addition complexes of diborane are revealed as true coordination compounds of boron in which hydride ligands are replaced systematically by ammonia molecules. It is worthwhile to note that the analogy is a formal one and has no implications relative to geometry. It simply demonstrates the similar formulas of members of two substitution series. The particular divalent and trivalent cations $[HB(NH_3)_3]^{+2}$ and $[B(NH_3)_4]^{+3}$ have not, to the best of my knowledge, been reported as yet, but I confidently predict that both a trivalent and divalent cation of boron will be prepared in the near future. Chelation phenomena, as described in subsequent discussions, may well be helpful in achieving this goal. An earlier, tentative report (*19*) from my laboratory of the divalent cation $[HB(NH_3)_3]^{+2}$ was later shown by us to be in error. More sophisticated methods of synthesis appear to be required.

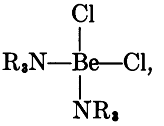
Diborane-alkylamine Systems. The nature of the base is important in determining the type of product obtained from the direct interaction of diborane and base. For example, when B_2H_6 is allowed to react directly



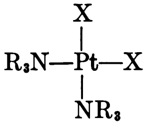
with $N(CH_3)_3$, the product is almost 100% $H_3BN(CH_3)_3$. On the other hand, when B_2H_6 is allowed to react with NH_3 the product is almost exclusively $[H_2B(NH_3)_2^+][BH_4^-]$ (*19*). Beachley (*1*) showed that with methylamine the principal product is $[H_2B(NH_2CH_3)_2^+][BH_4^-]$, while Shore, Hickam, and Cowles, in a quantitative study (*20*), showed that in reactions with B_2H_6 ammonia gives almost exclusively the ionic compound $[H_2B(NH_3)_2^+][BH_4^-]$. With methylamine the product is principally $[H_2B(NH_2CH_3)_2][BH_4^-]$, but measurable amounts of $H_3BNH_2CH_3$ are formed; with dimethylamine the product is principally $H_3BNH(CH_3)_2$ with smaller amounts of the ionic solid $[H_2B(N(CH_3)_2H)_2]^+[BH_4^-]$, while with trimethylamine the product was exclusively $H_3BN(CH_3)_3$, and no ionic solid is formed.

It is interesting to speculate on reasons for the decreasing tendency to form the ionic product as one goes from ammonia to trimethylamine. The answer undoubtedly lies in the nature of one of the transition states in the process, because the ion $[H_2B(NR_3)_2]^+$ can be prepared by other procedures and is known to be very stable. Detailed speculation on this question goes beyond the present discussion; it is, however, significant to note that the key differences lie in the bases, not in any pecularities of diborane. When $CoCl_2$ is allowed to react in the same sequence, the products are $[Co(NH_3)_6]Cl_2$, $[Co(NH_2CH_3)_6]Cl_2$, $[Co(NH_2C_2H_5)_4Cl_2]$, and $CoCl_2 \cdot N(CH_3)_3$ and $CoCl_2 \cdot N(C_2H_5)_3$ (*28*). When $BeCl_2$ reacts, the products are principally $[Be(NH_3)_4]Cl_2$, $[Be(NH_2CH_3)_4]Cl_2$,

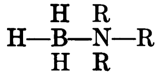
$BeCl_2(N(C_2H_5)_2H)_2$, and $BeCl_2(N(CH_3)_3)_2$ (*28*). Similarly, with platinum, the complex ion $[Pt(NH_3)_4]^{+2}$ is known but *not* the corresponding $[Pt(NR_3)_4]^{+2}$ ion. Only $[PtCl_2(NR_3)_2]$ has been reported. The basic process in each case seems to be the systematic replacement of halide ions from the original structure by coordinating molecules of the base. This process was indicated earlier for platinum. A directly comparable replacement series for hydride ion can be formulated for diborane. Cationic species containing NH_3 or H_2O such as $[Be(NH_3)_4]^{+2}$, $[Co(H_2O)_6]^{+2}$, $[Co(NH_3)_6]^{+2}$, $[Pt(NH_3)_4]^{+2}$, and $[H_2B(NH_3)_2]^+$ represent more extensive replacement of halide or hydride ligands than is found in the nonelectrolyte species containing tertiary amines and phosphines.



$R_3N\text{—}\overset{\displaystyle Cl}{\underset{\displaystyle NR_3}{Be}}\text{—}Cl,$



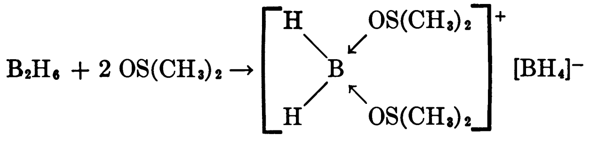
$R_3N\text{—}\overset{\displaystyle X}{\underset{\displaystyle NR_3}{Pt}}\text{—}X$



$H\text{—}\overset{\displaystyle H}{\underset{\displaystyle H}{B}}\text{—}\overset{\displaystyle R}{\underset{\displaystyle R}{N}}\text{—}R$

For example, in each of the above formulas replacement of the halide or hydride ligand is less extensive than in the corresponding ammonia complexes. These facts lead to the generalization that those bases favoring ionic coordination products, through extensive ligand displacement in direct reaction with metal halides, are the very ones favoring ionic coordination products (boron cations) and more extensive hydride replacement in reactions with boron hydrides. The rule is rather broadly applicable and suggests that, in water, diborane should give the cation $[H_2B(H_2O)_2]^+$ and the BH_4^- anion. Evidence for reaction of diborane with aqueous solutions of KOH to give almost 50% yields of KBH_4 was presented years ago by Winternitz (*27*), whereas evidence for the unstable cation $[H_2B(H_2O)_2]^+$ in aqueous solutions of B_2H_6 was presented in a paper by Jolly (*10*) given before the Inorganic Division of the ACS.

The foregoing correlation leads to some interesting comparisons. Cotton (*3*) and his students have found that $CoCl_2$ reacts with dimethylsulfoxide to give $[CoCl_2 \cdot 3OS(CH_3)_2]_n$. Structural studies show that the compound is a dimer of formula $[Co(OS(CH_3)_2)_6][CoCl_4]$. The analogy developed earlier for NH_3 would suggest that diborane should react with $OS(CH_3)_2$ to give an ionic solid comparable to $[H_2B(NH_3)_2{}^+][BH_4{}^-]$ because the ion $[Co(OS(CH_3)_2)_6]^{+2}$ can be compared to $[Co(NH_3)_6]^{+2}$. The work of McAchran and Shore (*12*) shows that the reaction of B_2H_6 with dimethyl sulfoxide can be described by the equation shown below.



The direct comparison of the above with the ammonia reaction is obvious.

Displacement Reactions in Complexes of the Boron Hydrides. One of the most vigorously investigated areas of coordination chemistry is the study of ligand substitution reactions. Distinguished men have sharp differences of opinion on mechanisms, and ingenious methods for testing models of various types have been devised. While mechanistic studies on substitution reactions in boron cations have not yet reached this degree of sophistication, substitution reactions which create boron cations or transform them, are now well recognized, and mechanisms are becoming of interest.

AMINE DISPLACEMENT REACTIONS. Miller and Muetterties (*14*), Dupont, and Moews (*15*), working in the laboratories of the University of Michigan, demonstrated base displacement processes independently. Base displacement processes involve the displacement of a given donor molecule by a stronger donor molecule and may be represented by the general equation:

$$[H_2B(\text{Base A})_2] + 2(\text{Base B}) \rightarrow [H_2B(\text{Base B})_2]^+ + 2(\text{Base A})$$

As one might surmise from the well-known chelate effect in transition metal chemistry, bidentate ligands can replace two comparable monodentate ligands. For example, ethylenediamine replaces two molecules of ammonia in $[H_2B(NH_3)_2]^+$ to give $[H_2B(en)]^{+10}$ and *N,N,N′, N′*-tetramethylethylenediamine replaces two molecules of trimethylamine in $[H_2B(N(CH_3)_3)]^+$ to give $[H_2H(TMED)]^+$. Finally, 2,2′-bipyridine will also coordinate to the two-position on boron. The effects of tri- and tetradentate ligands are being studied now in our laboratory. Miller and Muetterties (*14*) reported the following as the experimentally observed displacement order: diamines > amines > phosphines, arsines > sulfides. This order parallels roughly the σ-donor properties of these compounds; it is significant, however, that amines will replace phosphines from complexes of the form $[H_2B(PR_3)_2]^+$, but phosphines will replace amines from the nonionic H_3BNR_3. The foregoing facts suggest that steric factors reduce the stability of the bis-phosphine complex $[H_2B(PR_3)_2]^+$ more than they do the stability of the bis-amine complex, $[H_2B(NR_3)_2]^+$. In the absence of these steric factors, where only one phosphine molecule is involved (i.e., H_3BPR_3), the phosphine coordinates more strongly than does the amine. Other rather severe steric limitations were found by Miller and Muetterties (*14*) to apply to the base displacement process. Trimethylamine and bipyridine displace dimethyl sulfide in $[H_2B(S(CH_3)_2)_2]^+$, but ethyldimethylamine and *N*-methylpiperidine do not.

HYDRIDE DISPLACEMENT. The first preparation of H_3BNH_3 was effected by hydride displacement using BH_4^- and an NH_4^+ salt (*19*). The appropriate equation is: $BH_4^- + NH_4^+ \rightarrow H_3BNH_3 + H_2$. Further replacement of H^- to produce cations can be effected by carrying out the process at a higher temperature (*14*):

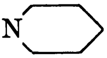
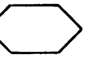
$$H_3B\text{ Base} + [\text{Base H}]^+X^- \xrightarrow{100\text{-}180^\circ\text{C.}} [H_2B(\text{Base})_2]^+X^- + H_2.$$

The anion, X^-, must be reasonably stable toward reduction and must be large enough so that it does not compete with the amines for coordination positions on the boron atom. Anions tending to give H_2BX(base) are undesirable. Iodide and $B_{12}H_{12}^{-2}$ ions work well, but chloride salts give the process:

$$H_3B\cdot\text{Base} + [\text{Base H}^+]Cl^- \rightarrow H_2BCl(\text{Base}) + H_2 + \text{Base}$$

instead of the desired process:

$$H_3B\cdot\text{Base} + [\text{Base H}]^+X^- \rightarrow [H_2B(\text{Base})_2]^+X^- + H_2 \qquad (14)$$

Steric factors are also of importance here. When tertiary amines are used in the above process, the tertiary amine must have at least one methyl group, and the other hydrocarbon groups must not be branched at the α-carbon atom. Thus, $(C_2H_5)_2CH_3N$ and CH_3N can be incorporated into the bis-amine cation, but $N(C_2H_5)_3$ and $(CH_3)_2N$— will not give the cationic product. The hydride displacement reaction can be used to prepare cations containing two different amines coordinated to the same boron atom if steric limitations are observed:

$$H_3B(\text{Base A}) + [\text{Base BH}]^+X^- \rightarrow [H_2B(\text{Base A})(\text{Base B})]^+X + H_2$$

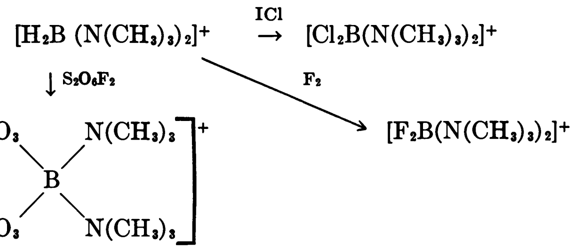
Typical compounds reported by Miller and Muetterties (*14*) are listed in Table I. The boron cations listed have properties dependent upon the nature of the base molecules attached. In general, stability to hydrolysis or oxidation increases with the strength of the base in the displacement series. Salts of the bis-amine cations (the most stable in the series) have been recovered without noticeable change from concentrated H_2SO_4, HCl, HNO_3, and 10% NaOH held near 100°C. for prolonged periods. Strong oxidizing agents such as salts of gold (III) and silver (I) and 30% H_2O_2 are ineffective at 100°C. Aqua regia converts the bis-amine cation to the monochloro derivative $[HClB(NR_3)_2^+]$. Cations in which the base is a tertiary phosphine are stable to boiling acid and strong oxidizing agents, but are slowly degraded in hot, aqueous base. The arsine cations are hydrolyzed in boiling water, and the dimethylsulfide cations are hydrolyzed in cold water. Most salts are quite stable thermally but, in cases where the anion will coordinate, it may enter the coordination sphere on heating:

$$[H_2B(N(CH_3)_3)_2]Cl^- \xrightarrow{195°C.} H_2BCl\,N(CH_3)_3 + N(CH_3)_3$$

The unusual stability of the above complexes is clearly analogous to the formerly unexpected stability of the metal amine complexes; even the tendency of the anion to enter the coordination sphere on heating is clearly reminiscent of the same type of process in metal complexes:

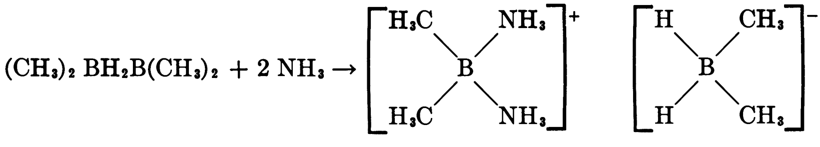
$$[Co(NH_3)_6]\,Cl_3 \xrightarrow{\Delta} [Co(NH_3)_5Cl]\,Cl_2 + NH_3$$

More Complete Hydride Displacement. Miller and Muetterties (*14*) found that complete hydride displacement could be effected by several different anions. Typical reactions are summarized below:



A related difluoro complex involving tetrakis (dimethylamino) ethylene as a base was reported by Wiberg and Buchler (*26*). Dichloro cations were also reported by Nöth and his students (*18*).

Cationic species containing organic groups in place of the hydrogen atoms have been reported by several workers (*4*, *5*, *13*, *15*, *16*, *17*). Work of Moews (*15*) on $(CH_3)_2BH_2B(CH_3)_2$ shows that this molecule is cleaved by NH_3 just like diborane to give alkylated cations and anions of boron:

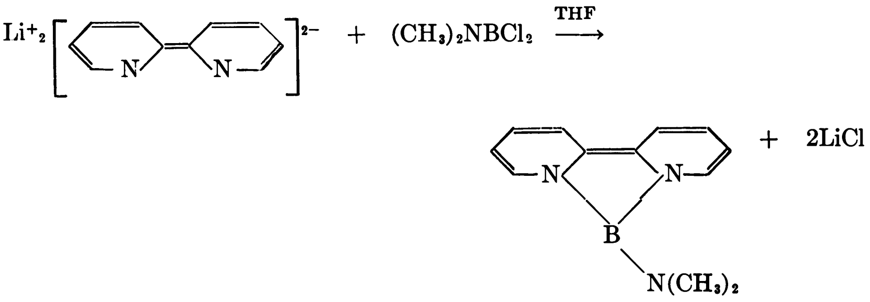


A chelate containing ethylenediamine in place of ammonia can also be prepared.

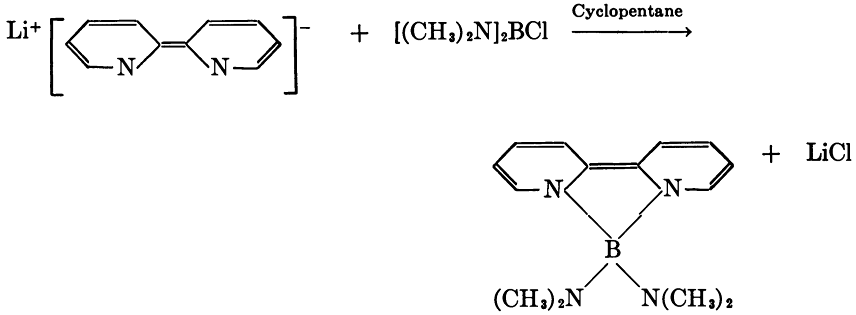
Expected Optical Activity in Boron Cations. Through procedures outlined earlier, boron cations can be synthesized containing four different ligands. Miller and Muetterties reported $\{HXB[N(CH_3)_3][N(C_2H_5)(CH_3)_2]\}^+$.

This ion should be optically active, as should the chelate $\{HXB[(CH_3)_2N\text{-}CH_2\text{-}CH_2CH(CH_3)N(CH_3)_2]\}^+$. Attempts to resolve these cations are indicated in the literature.

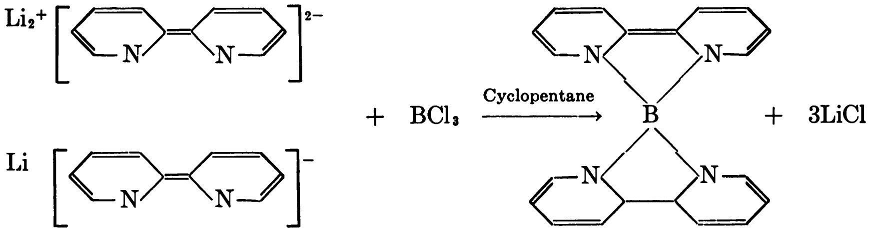
Stabilization of Lower Oxidation States of Boron by Coordination. One of the most dramatic results of the coordination process with many metals is the stabilization of formerly unexpected oxidation states. Within the last few months, the stabilization by coordination of states which appear in a formal sense to be B^+ and B^{+2} has been reported by Kuck and Urry (*11*), who used dilithium 2,2′-bipyridine. The reactions are represented as:



Deep red solid stable in *absence* of air. Diamagnetic.

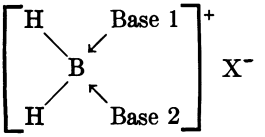


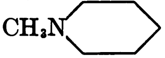
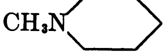
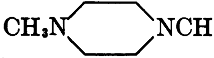
Red, paramagnetic



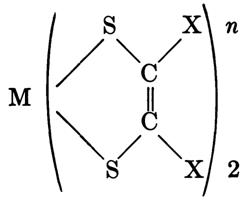
Red oil
very reactive

Table I. Boron Cations with Two Hydrides (*14, 15*)



Base₁	*Base₂*	X^-	*m.p.*
$N(CH_3)_3$	$N(CH_3)_3$	$B_{12}H_{12}^{-2}$	260-270
$N(CH_3)_3$	$N(CH_3)_3$	PF_6^-	200-205
$N(CH_3)_3$	$N(CH_3)_3$	ICl_2^-	150
$N(CH_3)_3$	$N(CH_3)_3$	$AuCl_4^-$	—
$N(CH_3)_2(C_2H_5)$	$N(CH_3)_2(C_2H_5)$	$B_{12}H_{12}^{-2}$	218°C.
$N(CH_3)_2(C_2H_5)$	$N(CH_3)_2(C_2H_5)$	PF_6^-	65°C.
$N(CH_3)(C_2H_5)_2$	$N(CH_3)(C_2H_5)_2$	PF_6^-	135-136
		PF_6^-	108-109
Tetramethylethylenediamine		$B_{12}H_{12}^{-2}$	340-350
Tetramethylethylenediamine		Cl^-	—
Tetramethylethylenediamine		PF_6^-	240-244
		PF_6^-	240-250
$N(CH_3)_3$	$N(C_2H_5)(CH_3)_2$	PF_6^-	
$P(CH_3)_3$	$P(CH_3)_3$	PF_6^-	178
$(CH_3)_2P\text{-}CH_2CH_2\text{-}P(CH_3)_2$		PF_6^-	240-260

It is perhaps debatable whether or not one should assign a lower oxidation number to boron in these complexes because the extra negative charge is delocalized over the organic moiety, but the situation appears to be comparable in many ways to that found by Gray (*6, 25*) for compounds of the transition metals in unusual oxidation states. These square-planar complexes have the general formulation,



where n can range from 0 to -2. The compounds have been described by Gray as electronically delocalized with the negative charge distributed over the organic moiety. The same kind of description may be appropriate for the boron systems of Kuck and Urry, and facile electrolytic oxidation and reduction may well be anticipated.

Summary of Werner Concepts in Boron Chemistry

The treatment of boron cations as typical coordination compounds has been proposed. The following features characteristic of coordination compounds may be listed.

1) A typical substitution sequence, in which hydride ligands are replaced by amines or other ligands, exists.

2) Bases which give ionic products in reactions with metal halides tend to give ionic products in direct reactions with diborane and tetraborane.

3) Complexes formed have unusual stability, a fact which is reminiscent of many of the amine coordination compounds.

4) Ligand substitution reactions of many types can be effected.

5) The chelate effect is apparent in boron chemistry, as it is in transition metal chemistry.

6) "Unusual valence states" resulting from probable delocalization of charge over organic ligands appear in both transition metal and boron chemistry.

7) Optical isomerism for boron cations of the form [B a b c d]$^+$ is predicted but, to the best of the author's knowledge, resolution of such complexes into optical isomers has not yet been reported.

Base-addition Complexes of Aluminum Hydrides and Related Compounds

Because the aluminum(III) cation is larger than the boron(III), the simplest arguments would suggest a larger coordination number for both the ammonia and trimethylamine adducts of aluminum(III). The cation $[Al(NH_3)_6]^{+3}$ is obtained when AlI_3 is dissolved in liquid ammonia (*24*), indicating complete displacement of iodide ligands. The reactions of AlH_3 with NH_3 are less well-defined, but solvolysis and H_2 loss are to be anticipated. On the other hand, the reaction of AlH_3 with $N(CH_3)_3$ has been studied in considerable detail. X-ray diffraction data (*9*) indicate clearly a structure wherein a linear N-Al-N arrangement exists. Although the hydrogens were not directly and unequivocally located, distances in the lattice are such that the only reasonable place for these atoms would be in an equilateral triangle around the aluminum atom in a plane perpendicular to the N-Al-N axis. A coordination number of 5 for aluminum(III) is indicated by these data. An aluminum hydride complex containing only one trimethylamine has also been prepared as a monomer in a number of solvents (*8*). It is logical to assume that this compound contains Al(III) with a coordination number of 4. As in the case of boron hydrides and metal halide systems, ammonia tends to give maximum replacement of halide or hydride ligands to produce a cationic species containing aluminum(III). Trimethylamine again gives less complete ligand replacement and promotes formation of a non-electrolyte of coordination number 4 or 5.

Base-addition Complexes of Gallium Compounds

Gallium, in much of its chemistry, seems to fall between boron and aluminum despite the fact that it falls below the latter in the periodic table. This is true even though Ga^{+3} is assigned a slightly larger radius than Al^{+3} by many authors. Cations of the form $[Ga(NH_3)_6]^{+3}$ would be expected, though little definitive structural information on the gallium halide complexes of ammonia is available (*7*). Complexes of the general formula $GaX_3 \cdot nNH_3$ are recognized (*7*), where n can have values of 1,3, 5, 6, 7, and 14 for X = Cl. In complexes containing six or more NH_3, the cation is probably $[Ga(NH_3)_6]^{+3}$. In other cases the quantity of NH_3 used was not adequate to displace the halide completely.

Other complexes of gallium have been more exhaustively studied. Gallium hydride, GaH_3, forms with trimethylamine a 1:1 solid complex which melts at 69°C. and decomposes slowly even at room temperature (*23*). X-ray diffraction studies of the 1:1 complex show the presence of $H_3GaN(CH_3)_3$ units with two molecules per unit cell. A coordination number of 4 for gallium is indicated (*21*).

At −45°C. a second molecule of the amine is picked up by $H_3GaN(CH_3)_3$ to give $GaH_3(N(CH_3)_3)_2$. Comparison of this diadduct (dissociation pressure 6.1 mm. at −45°C.) with the similar aluminum diadduct $((CH_3)_3N)_2AlH_3$, which can be sublimed at room temperature with only slight decomposition, clearly demonstrates the greater stability of the aluminum complex with coordination number 5. From the monomeric nature of $((CH_3)_3N)_2GaH_3$ in trimethylamine solution, it is inferred that gallium in this compound is 5-coordinate (*23*).

Finally, one other gallium complex, the structure of which has been studied recently (*22*), is of significance in this discussion. The compound $(CH_3)_2GaCl \cdot 2NH_3$ has been shown to have the structure $[(CH_3)_2Ga(NH_3)_2]^+Cl$. Treatment of this complex with ethylenediamine gives $[(CH_3)_2Gaen]^+$. The analogy to the comparable boron ions, $[(CH_3)_2B(NH_3)_2]^+$ and $[(CH_3)_2Ben]^+$, is clear.

Summary

A review of the chemistry of Group III complexes shows that many of the concepts of Werner's coordination chemistry may be applied to these elements. Furthermore, the differences observed in the complexing behavior between ammonia and trimethylamine reflect fundamental differences in the amines. Ammonia tends to give ionic compounds, whereas trimethylamine tends to give non-ionic products. Trends observed with the metal halides can be extrapolated into hydrides of boron, aluminum, and gallium. An extension of Werner's concepts provides a significant

framework within which much of the new "simple" chemistry of the Group III elements can be correlated.

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42

Trigonal-Prismatic Coordination

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Recently several 6-coordinate metal complexes have been shown to exhibit a trigonal-prismatic rather than an octahedral structure. The events leading to the discovery of the new coordination geometry are placed in historical perspective. The evidence which led to assigning the trigonal-prismatic structure to many of the complexes is summarized. At present, at least 14 complexes definitely possess the unusual geometry and, furthermore, the structure is highly likely for many other species. The bonding in trigonal-prismatic complexes is described in molecular orbital language. Electronic structural considerations show that it is not meaningful to assign definite oxidation states to the central metal in these extremely covalent systems. Finally, the possible reasons for the occurrence of trigonal-prismatic coordination are discussed, and some speculation is offered as to its scope.

In a brilliant paper published in 1893 (*38*), Alfred Werner established octahedral stereochemistry for the 6-coordinate transition metal ion. In his deliberations Werner also considered both the hexagonal-planar and trigonal-prismatic structures but successfully eliminated these in the cases he investigated. It is a great tribute to Werner that in the 70-odd years since his historic work, countless structural investigations have failed to reveal a truly nonoctahedral, molecular, 6-coordinate complex. It has only been in the past year that an authentic example of nonoctahedral stereochemistry has been found.

Werner's experiments were performed in liquid solutions, and the complexes he worked with maintain their basic octahedral structure in the

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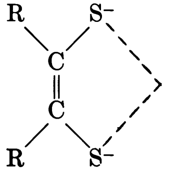
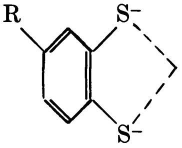
solid state. Our main interest, as was Werner's, is in molecular complexes, but it should be noted that a 6-coordinate geometry other than octahedral has been known in certain crystals for many years. For example, in 1923, Dickinson and Pauling (*11*) found S_6 trigonal-prismatic coordination in molybdenite (MoS_2) and tungstenite (WS_2). Since then, the NiAs structure has been found to possess, in part, a trigonal-prismatic array of atoms (*40*). In these compounds the lattice structure is infinite and three-dimensionally extended, and it is clear that crystal packing is a principal determinant of the stereochemistry.

The first molecular, 6-coordinate complexes which proved to adopt a nonoctahedral structure contain the bidentate, sulfur-donor ligands of the general structures, I and II:



I

Ia R = CN(mnt)
Ib R = Ph(sdt)
Ic R = CF_3
Id R = H
Ie R = CH_3

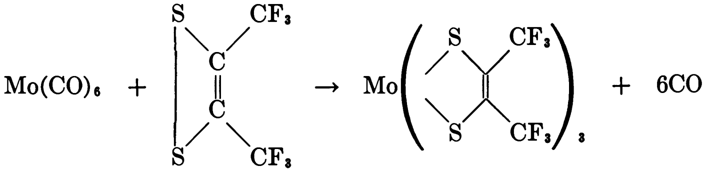


II

IIa R = H(bdt)
IIb R = CH_3(tdt)

The first of these ligands to be used was toluene 3,4-dithiolate (tdt) (IIb). Clark used this ligand (*6*, *7*) in 1936 for determining tin. Since that time, tdt has been used by several investigators (*3*, *5*, *23*, *28*) as a qualitative test for such metals as Mo, W, and Re, but no attempts were made to isolate any of the complexes (much less establish their geometry). The first actual isolation of a complex was by Gilbert and Sandell who made $Mo(tdt)_3$ (*22*). However, these workers were not able to prepare an analytically pure sample.

In 1963, the first well-characterized tris complex in the I series was prepared by King (*24*) in the reaction of $Mo(CO)_6$ with bis(trifluoromethyl)dithietene to give $Mo(S_2C_2(CF_3)_2)_3$.



Shortly before this time a substantial interest had developed in these ligands for a very different reason (*10, 31, 39*). With the metals in the Fe through Cu families in the transition series, these ligands form bis complexes with two very unusual properties. Firstly, the square planar geometry is stabilized over a large range of metals including Fe, Co, Rh, Ni, Pd, Pt, Cu, Ag, and Au. Secondly, for any given metal and ligand the complex is capable of stable existence in more than one oxidation state. The various oxidation states are simply related by one-electron transfer reactions. For example, $Ni(sdt)_2^{-n}$ has been isolated as $n = 0$, 1, and 2. Because of the unusual nature of these complexes, several workers sought to extend the square planar geometry by producing bis complexes of metals which lie farther to the left in the periodic table. At one point (*33*) it was reported that bis planar complexes of sdt with V, Cr, Mo, W, Re, Ru, and Os had been synthesized. On closer examination, however, it turned out that these were not unusual 4-coordinate complexes but were instead 6-coordinate systems. The 6-coordinate nature of these complexes was firmly established in several different studies (*8, 30, 37*), and many other 6-coordinate complexes of the bidentate sulfur-donor ligands were synthesized and characterized (*9, 26*).

In one of these studies (*26*), it was observed that $Co(mnt)_2^-$ reversibly adds one mole of ligand to form the complex $Co(mnt)_3^{-3}$. The tendency of the square planar $Co(mnt)_2^-$ anion to form readily 6-coordinate adducts with bidentate ligands and only 5-coordinate species with monodentate ligands led to the suggestion that the tris complexes might possess a trigonal-prismatic structure.

Langford (*25*), in an attempt to confirm or disprove this possibility, tried unsuccessfully to resolve the $Co(mnt)_3^{-3}$ complex into optical isomers. Octahedral complexes containing bidentate ligands are reduced to D_3 symmetry and should be resolvable because of the absence of mirror planes or symmetry centers. At the same time, Archer (*2*) tried to resolve the neutral $Mo(S_2C_2(CF_3)_2)_3$ complex, but he too was unsuccessful. The inability to resolve the tris complexes, $Co(mnt)_3^{-3}$ and $Mo(S_2C_2(CF_3)_2)_3$, raised some doubts concerning the conventional octahedral formulation of these systems.

In an x-ray structural investigation (*15, 16*) of the 6-coordinate $Re(sdt)_3$ complex, rhenium was found to be surrounded by the six sulfur atoms in a nearly perfect, trigonal-prismatic coordination. The sides of the prism are square with no significant difference between the average intra- and closest interligand S-S distances. A perspective drawing of the coordination geometry is shown in Figure 1. Only the twisting of the phenyl rings out of the planes of the five-membered, metal-chelate rings prevents this molecular complex from having rigorous D_{3h} symmetry. Unlike the hexagonal lattices of MoS_2 and WS_2, the crystal structure of

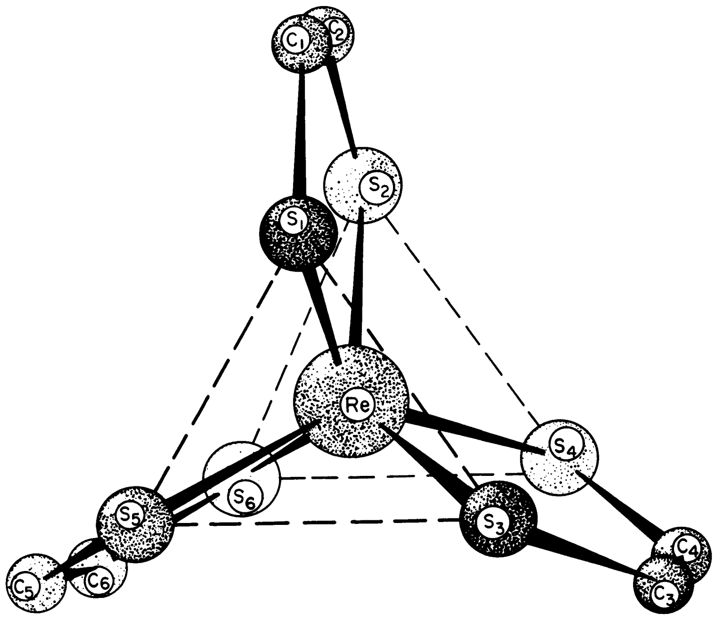


Figure 1. Coordination geometry of the Re(sdt)$_3$ complex

Re(sdt)$_3$ consists of the packing of discrete, well-separated, molecules, the closest Re-Re approach being approximately 9.5 A.

With this structure determination, it became important to establish the generality of trigonal-prismatic coordination in the tris complexes of the bidentate sulfur ligands. First, however, it had to be shown that the molecular geometry found for Re(sdt)$_3$ in the crystal was maintained in solution. This problem was easily solved by a comparison of the solid state and solution properties of Re(sdt)$_3$. It was found (*36*) that the electronic and electron spin resonance spectra of the complex remain essentially unchanged on dissolution in nonpolar solvents such as $CHCl_3$ and CCl_4. Thus, the trigonal-prismatic coordination remains in solution. The main feature of the electronic spectrum consists of an intense, two-band pattern in the visible region which gives both the solution and the crystals their dark green color.

Now the probe began as to whether the trigonal-prismatic coordination was limited to this particular ligand, or to rhenium, or perhaps to just this particular complex. In checking for other possible ligands, it was realized from previous experience that a neutral complex would most likely be produced using tdt as a ligand. Thus, toluene 3,4-dithiol reacted with $ReCl_5$ in CCl_4 and Re(tdt)$_3$ was prepared (*36*). A comparison of the electronic spectra, ESR spectra in solution, frozen glass ESR spectra, and polarographic behavior revealed the Re(tdt)$_3$ complex to be amazingly similar to the Re(sdt)$_3$ complex. The new geometry was thus strongly confirmed for the tdt complex, and we see that the "non-classical" structure is not limited to the sdt ligand.

The next step was to show that this geometry is not limited to Re alone, for it is well known that Re forms a multitude of quite unusual complexes, not the least of which is ReH$_9^{-2}$ which has the geometry of a face-centered trigonal-prism (*21*). It was first found that W(sdt)$_3$ and Re(sdt)$_3$ are isomorphous (*15, 16, 36*), as shown by their x-ray powder patterns, indicating the probability of trigonal-prismatic coordination for W(sdt)$_3$. The spectrum of W(sdt)$_3$ is the same in solid and solution (*35*) and, significantly, the dominant feature of the spectrum is again an intense, two-band pattern in the visible region much like that found in the Re complexes. This pattern has now been found (*35*) in all of the neutral complexes of Re, W, and Mo with the bidentate sulfur-donor ligands. The first band always occurs at $\sim$14,000 cm.$^{-1}$ with ϵ $\sim$20,000, and the second always occurs at $\sim$24,000 cm.$^{-1}$ with ϵ $\sim$15,000. We consider these bands as characteristic of the trigonal-prismatic MS$_6$ chromophore for second- and third-row transition elements. It is this pattern which gives all of the complexes their characteristic green to blue-green color. Further evidence for the occurrence of the trigonal-prismatic coordination in Mo complexes was supplied by an x-ray study of Mo(S$_2$C$_2$H$_2$)$_3$ by Smith and coworkers (*34*), which showed this complex to have an MS$_6$ framework almost identical to that found in Re(sdt)$_3$. Thus, there is good evidence that all the neutral complexes of Mo, W, and Re with these sulfur-donor ligands are trigonal-prismatic.

The coordination geometry of the tris complexes containing first-row transition metals still had to be established. While isomorphism studies indicated the possibility of trigonal-prismatic coordination for V(sdt)$_3$ and Cr(sdt)$_3$, direct proof of this unusual geometry was clearly needed. To this end, the molecular structure of V(S$_2$C$_2$Ph$_2$)$_3$ was determined (*13, 17*). Once again, the metal is found at the center of a trigonal-prismatic array of sulfur atoms. The average intra- and interligand S-S distances are approximately equal (3.058 and 3.064 A., respectively), but there is a slight distortion of the prism about the three-fold axis. The dimensions of the prism are strikingly similar to those found for Re(sdt)$_3$ and Mo(S$_2$C$_2$H$_2$)$_3$. It is quite remarkable that in going from the first-row complex V(S$_2$C$_2$Ph$_2$)$_3$ to analogous second- and third-row systems the closest interligand sulfur-sulfur distance does not change significantly (3.050 A. in Re(sdt)$_3$ and 3.11 A. in Mo(S$_2$C$_2$Ph$_2$)$_3$), and that the metal-sulfur distance is effectively constant (V-S, 2.337 A.; Mo-S, 2.33 A.; Re-S, 2.325 A.). The implications of the near constancy of the S-S distances in these complexes are discussed below.

On the basis of its isomorphism with V(sdt)$_3$, the chromium complex is assumed to be trigonal-prismatic. A comparison of the spectra of the isoelectronic species $Cr(sdt)_3$ and $V(sdt)_3^-$ shows them to be quite similar and indicates that the trigonal-prismatic coordination extends to $V(sdt)_3^-$.

It is now of interest to look at the polarographic behavior of all of these complexes. As in the bis series, it is found that reversible one-electron transfers occur (*8*, *9*, *35*, *36*), corresponding to the reductions $ML_3 \rightarrow ML_3^-$, $ML_3^- \rightarrow ML_3^{-2}$, and (often) $ML_3^{-2} \rightarrow ML_3^{-3}$. In addition, there is a reversible, one-electron oxidation for the ReL_3 complexes. These indicate at least the transient existence of reduced (and oxidized) species which probably also possess the trigonal-prismatic geometry. However, there is considerable uncertainty as to the structure these complexes will adopt when they are isolated as salts. Certain of the reduced forms have already been isolated with the ligands mnt, Ia, and tdt (IIb), and it is possible that one or more of them will exhibit a conventional octahedral structure (*13*, *17*). More will be said on this point later.

We would now like to reach some kind of an understanding as to the bonding in these complexes. Based on past experience, it is obvious that a molecular orbital treatment is the best way to describe the bonding because of the thoroughly delocalized nature of the electronic systems and because of the significant role the ligand plays in the electronic structure. Molecular orbital calculations were performed (*35*) on $Re(sdt)_3$ in D_{3h} symmetry which corresponds to the coordination geometry as found in the original structure determination.

The principal electronic energy levels are shown in Figure 2. The levels labeled $2a_2''$, $3e'$, and $3e''$ are mainly combinations of in-plane, π functions on the ligands. These levels are filled with 10 electrons in the complexes under consideration. The level $4e'$ is a delocalized combination of the $3\pi_v$ ligand functions with the $d_{x^2-y^2}$ and d_{xy} metal functions. This level is filled with four electrons in the complexes. The next higher molecular orbital is $2a_2'$, which is nonbonding in the complex and localized on the ligands. It is strictly composed of ligand $3\pi_v$ functions. The next three levels are of d symmetry, and may be considered the ligand field levels in trigonal-prismatic complexes. In order of increasing energy they are $3a_1'(z^2) < 5e'(x^2 - y^2, xy) < 4e''(xz, yz)$.

According to the energy levels shown in Figure 2, the ground state electronic structure for $Re(S_2C_2Ph_2)_3$ is ...... $(4e')^4(2a_2')^2(3a_1')^1 = {}^2A_1'$. This ground state is compatible with the gross features of the ESR and magnetic susceptibility results for $Re(sdt)_3$. Another recent molecular orbital calculation (*32*) for these systems predicts a ${}^2E'$ ground state for the neutral Re complex, but this state is inconsistent with the observed magnetic properties.

The oxidation state assignment problem stems from the nature of the filled $4e'$ level. The classical case of Re(VI) and a ligand unit of L_3^{-6} corresponds to $4e'$ being designated a ligand level. If $4e'$ is more properly identified with the metal, the four electrons should be included with the

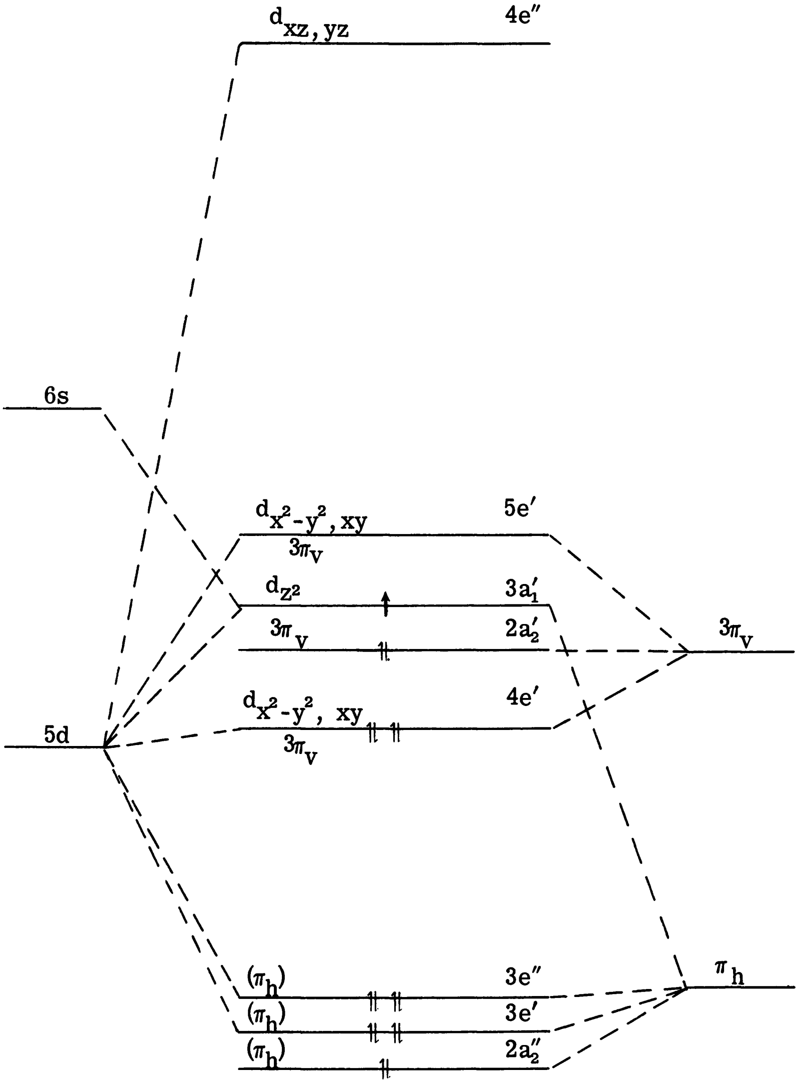


Figure 2. Suggested molecular orbital energy levels for Re(sdt)$_3$

metal and the oxidation state assignment is [Re(II)][L$_3^{-2}$]. However, it is not possible to state unequivocally the "ownership" of 4*e*′, owing to its highly delocalized nature. The various calculations on these systems and the optical spectral and polarographic experiments tend to confirm this uncertain state of affairs. Therefore, we are left with the general molecular orbital model as the only realistic means of describing the ground state electronic structures of the MS$_6$-type, trigonal-prismatic systems.

The neutral W and Mo complexes contain one less valence electron, and we expect the highest filled orbitals to be ...... $(4e')^4(2a_2')^2$ or a

${}^1A_1'$ ground state. We do not expect the molecular orbitals to change greatly in going from Re to W or Mo, and thus the limiting oxidation-state formulations are still M(II)[L_3^{-2}] and M(VI)[L_3^{-6}], with neither isolated configuration providing a true picture of electronic structure.

We are now in a position to speculate on factors which contribute to the stabilization of the trigonal-prismatic geometry. It is important while doing this to keep in mind that x-ray and other evidence have been presented that establishes square planar coordination for 4-coordinate complexes containing structurally-related sulfur-donor ligands.

From the nine x-ray structural determinations (*12, 13, 14, 15, 16, 17, 18, 19, 20, 29, 34*) on various complexes containing these bidentate sulfur-donor ligands, it is an interesting and significant result that, independent of the coordination geometry or the central metal, the S-S distance always takes a value close to 3.05 A. We take this relatively short, nominally "nonbonded" S-S distance to indicate that there are interligand bonding forces present in these complexes which are considerably stronger than in classical octahedral, tetrahedral, or planar complexes. It is the compromise between these S-S bonding interactions and the S-S nonbonded repulsions which leads to the ubiquitous 3.05 A. separation and to the stability of the nonclassical structures. Assuming this argument is sound, we extrapolate it and suggest that 8-coordinate complexes containing these sulfur-donor ligands in a state of oxidation comparable to Re(sdt)$_3$ should exhibit cubic (or approximately cubic) coordination, with each edge of the S_8 cube being 3.0–3.1 A. This requires an M-S distance of 2.6 A., which may possibly be attained using actinide central metals.

A contributing factor to the stability of trigonal-prismatic coordination may be the effective use of the three valence d orbitals not involved in strong σ bonding. For example, involvement of the sulfur π_h orbitals and the metal d_{z^2} leads to a stable bonding orbital ($2a_1'$), which is occupied in all the complexes. Another possible stabilizing influence for trigonal-prismatic coordination is the large interaction of the d_{xy}, $d_{x^2-y^2}$ orbitals with the thoroughly delocalized ligand $3\pi_v$ level. This leads to a particularly stable $4e'$ level, which is occupied in all of these complexes. A stabilizing σ interaction in the e' molecular orbitals has also been put forward (*21*) as an explanation of trigonal-prismatic stability. In this respect, it is pertinent to note that ReH_9^{-2} has the structure (*1*) of a face-centered trigonal prism, with the three face-centered hydrogens strongly σ bonded to the metal, presumably through extensive interaction with the d_{xy}, $d_{x^2-y^2}$ orbitals. In the Re(sdt)$_3$ trigonal prism, the ligand π_v orbitals may play a stabilizing role similar to that of three face-centered hydrogens in ReH_9^{-2}. Further investigations should help elucidate whether or not π_h-d_{z^2} bonding, strong π_v-d_{xy}, $d_{x^2-y^2}$ bonding, and S-S bonding are essential features of trigonal-prismatic coordination.

The next step in determining the overall structural patterns in the tris-bidentate-sulfur complexes is to investigate by x-ray methods one or more of the species reduced to at least the dianionic stage. It is a fact that the three available structures are all on the highly oxidized, neutral ML_3 complexes and, aside from some physical evidence on certain of the ML_3^- complexes, nothing is known about the structures of the anionic systems.

If S-S bonding is a strong contributing factor to the stability of the trigonal-prismatic complexes, the reduced species ML_3^{-2} and ML_3^{-3} may prefer to adopt an octahedral (D_3) configuration. Presumably, this is because the reduced species must accommodate electrons in *antibonding* molecular orbital levels (such as $5e'$) which possess a high degree of sulfur-orbital character. Placing electrons in these levels will tend to decrease the S-S bonding and therefore favor an octahedral (staggered) arrangement of donor atoms.

Recent work (*4, 21*) has afforded a number of new complexes, the structures of which should be of great interest. These complexes and their magnetic ground states are $Mn(mnt)_2^{-2}$ (S = 3/2), $Fe(mnt)_3^{-2}$ (S = 1), $Mo(mnt)_3^{-2}$ (S = 0), $W(mnt)_3^{-2}$ (S = 0), and $Re(mnt)_3^{-2}$ (S = 1/2). Structural studies on several of these systems are now in progress (*27*).

Acknowledgment

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INDEX