

A millennial overview of transition metal chemistry

F. Albert Cotton

Laboratory for Molecular Structure and Bonding, Department of Chemistry,
Texas A&M University, PO Box 30012, College Station, Texas 77842-3012, USA

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The present state of transition metal chemistry (restricted largely to the d-block elements) is surveyed with an eye to the history of the subject. With the coordination chemistry of Alfred Werner as a base of reference, there are (evolutionary) developments that may be considered as evolving naturally therefrom and (revolutionary) developments that seem not to have been adumbrated by the Wernerian concepts.

1. Introduction

In this last year of the second millennium (I note that the year 2000 is *not* the first year of the third millennium, no matter what the arithmetically-challenged of this world may like to think) it is fitting to look back at what has been accomplished in chemistry up to now. My concern is with the chemistry of the transition elements. The broadest definition¹ of this term is “elements that have partly filled d or f shells as elements or in

any of their commonly occurring oxidation states.” However, I shall restrict myself mainly to a subset of these elements, the so-called d-block elements, as shown in Fig. 1.

The chemistry of the transition elements is differentiated from that of the other (so-called main group) elements in several ways, of which the following three are perhaps most important.

(1) The transition elements typically form compounds in two or more oxidation states, and redox chemistry, including electrochemistry, is of major importance.

(2) The majority of transition element compounds have visible spectra (which is why they are colored) and the interpretation of these spectra provides a wealth of information concerning their electronic structures. A classic example is provided by the spectra of tetrahedral and octahedral complexes of cobalt(II), as shown in Fig. 2.

(3) A great many transition element compounds have one or more unpaired electrons and therefore have interesting and often useful magnetic properties.² These magnetic properties range from simple Curie paramagnetism to those associated with high-temperature superconductivity.

At the beginning of the first millennium (*i.e.*, six days after the birthday arbitrarily assumed for Jesus) only the following transition elements were known: iron, copper, silver and gold. By the end of the first millennium these were still the only ones known. Indeed it was not until the 18th century that three more were discovered,³ all by Swedish chemists. While cobalt appears to have been known, more or less, at an earlier date it was only in the period 1735–1739 that Georg Brandt published the first truly scientific studies of this element. In 1751 Axel Fredrik Cronstedt announced that he had discovered a new metal which he called nickel. In 1774 Johan Gottlieb Gahn isolated metallic manganese by reducing pyrolusite with carbon.

During the 19th century most of the remaining transition metals were recognized and a considerable amount of their chemistry developed. The only transition elements remaining to be discovered in the century that ends this year are europium (1901), lutetium (1907), promethium (1943), hafnium (1923), rhenium (1925) and technetium (1939).

While the development of transition element chemistry occurred slowly throughout the 19th century, it was in the last two decades, with the work of Sophus Mads Jorgensen in Denmark and Alfred Werner in Switzerland, that the heart and soul of this discipline, namely, transition metal *complexes* took shape. Both of these men made massive contributions to the “data base” but it was Werner who supplied the conceptual firepower that made history.

Probably the greatest conceptual contribution to inorganic chemistry—comparable in both direct and indirect impact to the concept of the tetrahedral carbon atom in organic chemistry—is Alfred Werner’s concept of coordination compounds and his general theory of how they behave. Since its promulgation and general acceptance over the decades between 1890 and 1910, it has provided a central trunk from which many

F. Albert Cotton was born in Philadelphia, PA in 1930 and received his A.B. and Ph.D. degrees from Temple and Harvard Universities, respectively. He was on the faculty of MIT from 1955 to 1971 and has been at Texas A&M since 1972. He has been recognized by both ACS awards in inorganic chemistry, the ACS Priestley Medal, the AIC Gold Medal, the Robert A. Welch Prize, the King Faisal Prize, the Paracelsus Prize, the Wolf Prize and the National Medal of Science. His interests have been in inorganic, organometallic and structural chemistry. He discovered the existence of quadruple bonds, as well as related triple, double and single bonds in a similar structural context, and has explored their chemistry extensively.



F. Albert Cotton

Periodic Table of the Elements

GROUP 1																		18					
1 H 1.0079	2																	2 He 4.0026					
3 Li 6.941	4 Be 9.0122																	5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
11 Na 22.990	12 Mg 24.305	3	4	5	6	7	8	9	10	11	12	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948						
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80						
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc 98.906*	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29						
55 Cs 132.91	56 Ba 137.33	57 La 138.91*	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.8	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po 209.98*	85 At 209.99*	86 Rn 222.02*						
87 Fr 223.02	88 Ra 226.03*	89 Ac 227.03*	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (269)	109 Mt (266)	110 (273)	111 (272)	112 (294)												

*Lanthanide series													
58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 146.92*	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97

▲Actinide series													
90 Th 232.04*	91 Pa 231.04*	92 U 238.03	93 Np 237.05*	94 Pu 239.05*	95 Am 241.06*	96 Cm 244.06*	97 Bk 249.08*	98 Cf 252.08*	99 Es 252.08*	100 Fm 257.10*	101 Md 258.10*	102 No 259.10*	103 Lr 262.11*

Fig. 1 A Periodic Table with the d-block elements in darker red and the other transition metals, the lanthanides and actinides, in light red.

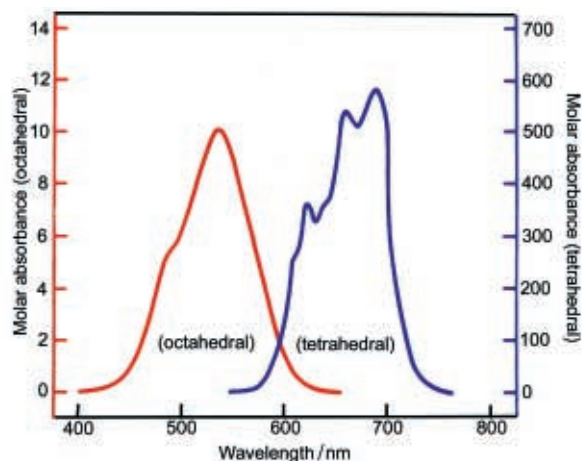


Fig. 2 Spectra of tetrahedral and octahedral Co^{II} complexes. Note the fifty-fold difference in intensities.

fruitful branches of transition element chemistry have grown and flourished.

The central ideas of Werner's theory have been summarized by one of his distinguished students, Paul Pfeiffer, as follows:⁴

According to Werner's hypothesis, inorganic molecular compounds contain single atoms which function as central nuclei around which are arranged in simple, spatial geometrical patterns a definite number of other atoms, radicals, and other molecules capable of independent existence. The figure expressing the number of atoms grouped around one central atom of a molecular compound was designated by Werner as the coordination number of this atom. The concept of coordination number, to which are also joined the concepts of "auxiliary valence number and force" and "indirect linking," forms the central point of the Wernerian system. Only a few coordination numbers come into consideration, the most important being 3, 4, 6, and 8. The number 6 occurs especially often. Thousands of

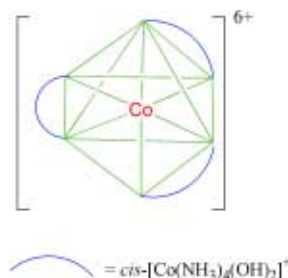


Fig. 3 Alfred Werner's ingenious optically active cation containing no carbon atom.⁵

molecular compounds of cobalt, chromium, platinum, *etc.*, correspond to the 6 type. In all of these as Werner pointed out in his first paper, the spatial configuration is octahedral in that around the central metal atom lie the six coordinated atoms in the corners of an octahedron."

Let me outline, in somewhat more contemporary terminology, the vital points of the Wernerian view of coordination chemistry:

(a) A metal ion or atom was a discrete center about which a set of ligands is arranged in a definite way.

(b) The number and arrangement of ligands were generally either 4 (tetrahedron or square), or 6 (octahedron), with others being rare.

(c) The general concept of a (unidentate) ligand was the passive one of a nonmetal atom donating an electron pair to the central metal atom.

(d) Polynuclear complexes were recognized (indeed Werner's famous "totally inorganic" optically active complex, Fig. 3, is one) but the important point is that the metal atoms were conceived of as independent centers, each with its own set of ligands. Two or more metal atoms could be held in the same molecule solely through bridging ligands, each of which used a separate electron pair for each of the two (or more) metal atoms to which it is coordinated.

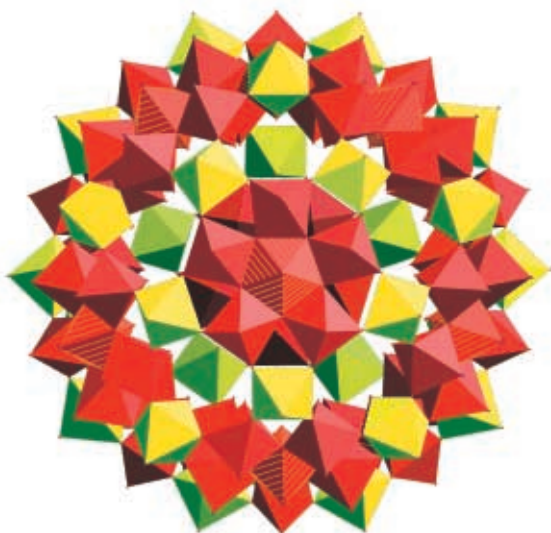


Fig. 4 A schematic representation of the structure of $[\{ \text{OMo}(\text{H}_2\text{O}) \}_{30} \{ (\text{Mo})\text{Mo}_5\text{O}_{21}(\text{CH}_3\text{CO}_2)(\text{H}_2\text{O})_4 \}_{12}]$; $\text{OMo}(\text{H}_2\text{O})$ units are in red. This drawing was prepared by Dr Hartmut Bögge of Bielefeld University.

(e) Ligands were regarded essentially as immutable entities that attached themselves to the metal atom and did nothing more.

2. Evolutionary developments since Werner

(a) Structural characterization

Without a direct means of structure determination, Werner, and for many years those who followed him, necessarily restricted themselves to considering essentially only octahedral six-coordination and the two forms, square and tetrahedral, of four-coordination. While a great number of important and interesting compounds are included in these categories, transition metal chemistry would finally have reached an impasse had X-ray crystallography not become a practical tool. Today, of course, the ready availability of structural information has revolutionized the transition element chemist's *modus operandi*. We can now determine the shape and dimensions of any coordination polyhedron, however irregular it may be.

In general, we can nearly always, except in the rarest cases, take it for granted that the structures of our complexes will be known to us, usually in quantitative detail. With this in mind, we tend both to design and to solve our research problems in different ways.

Outside the realm of Wernerian coordination chemistry, the advent of fast and powerful X-ray methodology has also had a huge impact. There are so many examples that could be cited that I must choose only two, quite arbitrarily, to illustrate the point. In some cases the major goal of the X-ray work is simply to find out the qualitative nature of the product. An extreme and beautiful example of this would be one of A. Müller's huge polymolybdate "wheels",⁶ shown in Fig. 4. In other cases the major goal is to track quantitatively the effects of electronic structure changes on the metrical parameters of a molecule. An example of this sort of thing is provided by studies of the dependence of Cr–Cr distances on the ligands surrounding a Cr_2^{4+} core,⁷ as shown in Fig. 5.

(b) Thermodynamics and kinetics

There has been an enormous burgeoning of knowledge about the thermodynamic and kinetic aspects of the formation and transformation of complexes. While mechanistic problems, by nature, defy ultimate solution, a great deal of progress has been made. At the very least, kinetic data have allowed us to narrow the number of mechanistic possibilities for many reactions

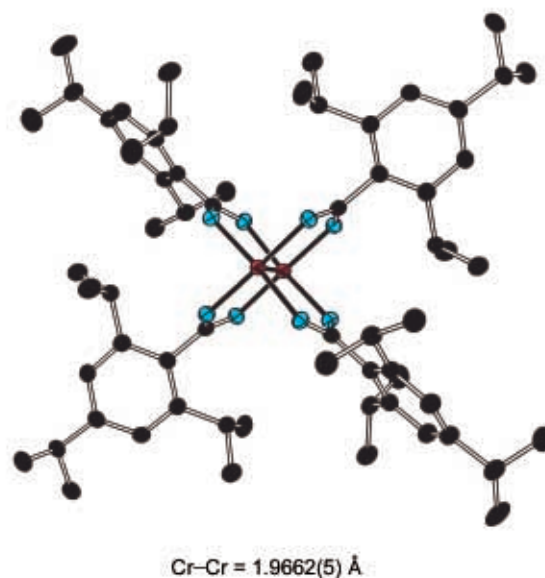
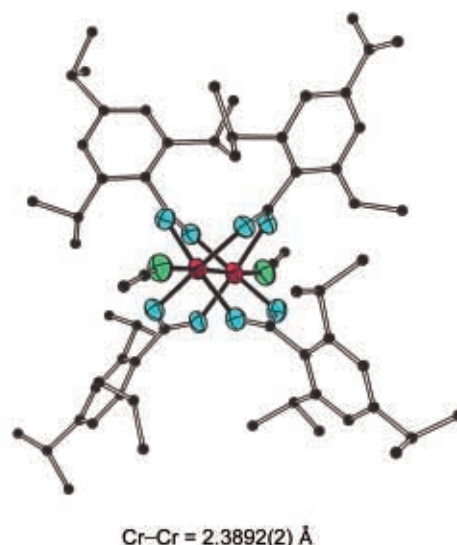


Fig. 5 The structures of a $\text{Cr}_2(\text{O}_2\text{CR})_4$ molecule with (upper) and without (lower) axial ligands. $\text{R} = 2,4,6\text{-}[(\text{CH}_3)_2\text{CH}]\text{C}_6\text{H}_2$ and the axial ligands are CH_3CN .

and classes of reactions to the point where useful predictive thinking is feasible. Also, very complicated, specially designed ligands have been invented and used to achieve special and selective modes of complexation. In this respect there has recently been useful give and take between the coordination chemist and the biochemist, with the former producing model systems of interest in biochemical problems and Nature revealing a considerable flair for evolving special purpose ligands.

In connection with the kinetics and mechanisms of reactions of coordination compounds of transition metals, special mention must be made of the work of Taube⁸ whose ingenious experiments in the 1950's and Marcus⁹ whose theory laid the foundations of systematic study of electron transfer reactions.

(c) Metal carbonyls and similar compounds

A few of these were known in Werner's time but they did not attract his attention so far as I am aware. It was only with the pioneering work of Walter Hieber, commenced a few years after the death of Werner, that this area began its transformation from being a small collection of chemical oddities to being a major branch of modern chemistry. Hieber himself stated¹⁰ that at the time he commenced serious research on metal carbonyls they were "far from being firmly categorized as a class of compounds, and were considered by many as curiosities."

Metal carbonyls are important for both direct and indirect reasons. Their direct importance comes from their reactivity and the many chemical processes, including catalytic ones, in which they participate.¹¹ Of course, it is not only metal carbonyls *per se* that are important but all of the many related low-valent complexes with ligands such as NO, phosphines, isocyanides, and so forth.

The major indirect reason for the importance of metal carbonyls and similar complexes was the impetus they gave to the development of valence theory. In Werner's own time the forces by which ligands were attached to metal ions were simply referred to as "secondary valences." Later the concept of electron pair donation, *e.g.*, by NH₃, H₂O or Cl⁻ to Co³⁺, evolved and was eventually articulated in considerable detail by Pauling.¹² But this "plug and socket" picture of bonding was considered to be inadequate for the known metal carbonyls, since simple donation from the extremely weak Lewis base, CO, to a neutral metal atom failed to explain their stability and properties. Thus the well-known symbiotic interplay of σ -donation plus π -acceptance became the accepted explanation for M-CO bonding. It is a wonderful example of how science advances to note that within only the last decade this seemingly be-all-and-end-all theory of M-CO bonding has been shown not to encompass all the facts. Metal carbonyls are now known (more than 200!) in which the π -acceptance part of the conventional picture is of little or no importance.¹³

(d) Electronic structures

Transition metal chemistry was handicapped for many years by the inability of theory to deal quantitatively with the electronic structures of the compounds. During the 1930's and 1940's Pauling devised ultra-simple approaches based on valence bond theory. These were widely accepted and certainly represented an advance. Their most obvious shortcoming was a total inability to explain the electronic spectra. In the early 1950's chemists rediscovered the symmetry-based approach originally devised by Bethe (crystal field theory) and extended significantly by Van Vleck. With allowance for covalence but with retention of all the help that symmetry arguments could provide, chemists developed this into the ligand field theory.¹⁴ This was extremely useful, but worked only for mononuclear complexes of high (O_h , T_d , D_{4h}) or relatively high symmetry.

The availability of fast computers on the one hand and very powerful and subtle spectroscopic tools on the other have now led to enormous progress in our comprehension of how ligands are bound to metal atoms and how the entire electronic structure of the complex gives rise to the magnetic, spectroscopic and chemical properties of the complex. This is not to say that we do not still have challenging problems, but high quality calculations can now be done on compounds of whatever nuclearity or symmetry. The best rigorous methods are based on Hartree-Fock and density functional theory. The former is reliable for transition metal complexes only when supplemented by large amounts of configuration interaction, which is very costly to calculate; the latter is less rigorous but can in many cases predict molecular structure. In addition, in any method of calculation it is necessary (but not simple) to include relativistic effects for all complexes of the elements in the third transition series. Still, the progress that has been made is phenomenal and we can expect further advances.

3. Revolutionary developments since Werner

Over the course of time there have been developments and discoveries that were, partly or even totally, outside the conceptual pattern laid down by Werner. These developments, therefore, cannot be said to have merely evolved out of Wernerian coordination chemistry, or to have been latent therein. Several

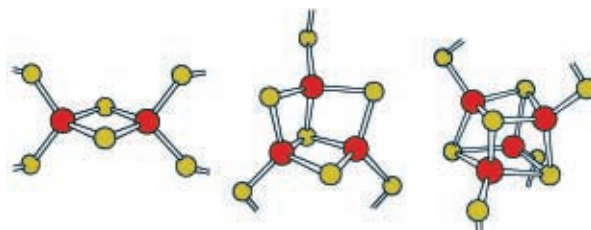


Fig. 6 The Fe₂S₂, Fe₃S₄ and Fe₄S₄ cores (each with cysteine(s) attached to each iron atom).

of these will be mentioned here, more or less in order of increasingly revolutionary (*i.e.*, non-evolutionary) character.

(a) Biometallic chemistry

It has been realized in recent years, that, as Wilkinson and I put it in *Basic Inorganic Chemistry*,¹⁵ "biochemistry is not merely an elaboration of organic chemistry, ... (but) ... involves, in an essential ... way, many of the chemical elements, including metals." No fewer than 9 transition elements, V, Cr, Mn, Fe, Co, Ni, Cu, Mo and W are known to be involved in life processes. Though relatively small quantities are present, life as we know it would not exist without them. Thus, the recognition and study of many biologically essential coordination compounds, *e.g.*, hemoglobin, vitamin B₁₂ coenzyme, scores of metalloenzymes, "blue" copper proteins, to name some principal ones, has been exciting and important.¹⁶ However, in all of those just cited, it is not unfair to say that they contain "Werner" complexes in a biological setting. The biological setting itself is, of course, quite a departure from classical coordination chemistry since it is only in very recent years that the importance of metal ions in biological systems has been recognized. It is noteworthy, also, that in certain cases (*e.g.*, the blue copper proteins) very distorted coordination geometries occur and the contribution that distortion or strain may make to the action of a metalloenzyme (Vallee and Williams' entatic state concept¹⁷) would have to be considered at least somewhat outside the framework of the Wernerian concepts.

The only well-known area of biometallic chemistry that seems to me to be unequivocally non-Wernerian, in a basic chemical sense, is the chemistry of the ferredoxins of the 2-, 3- and 4-iron types.¹⁸ Here we have polynuclear complexes in which electronic coupling of the metal atoms through the bridging sulfur atoms is so strong that the Fe₂S₂, Fe₃S₄ or Fe₄S₄ (Fig. 6) group behaves as a unit.

(b) Organo-transition-metal chemistry

It is, perhaps, a moot point whether this field should be included in the list of evolutionary developments. Certain types of organo compounds seem not entirely discontinuous from the Werner complexes. Zeise's anion is an example, provided we recognize that electrons can be donated (and back-accepted) by two atoms in concert. It is also pertinent that in one¹⁹ of the two seminal papers^{19,20} on ferrocene chemistry, the molecule was specifically conceptualized as a species not unlike [Fe(CN)₆]⁴⁻ (Fig. 7). While this idea has some shortcomings and was quickly superseded by more sophisticated descriptions, it served as a theoretical as well as historical bridge from Werner complexes to the metallocene chemistry. However, from a knowledge of Werner type complexes, *e.g.*, [Fe(CN)₆]⁴⁻, there would be no realistic possibility of *predicting* the existence of ferrocene, or other metallocene compounds. The enormous range and complexity of organo-transition-metal complexes now known and the many modes of reaction that have no true analogs among either the classical Werner complexes or among main group organometallic compounds provide further grounds for arguing that this field, in general, was not latent in the pre-existing concepts of Wernerian coordination chemistry.

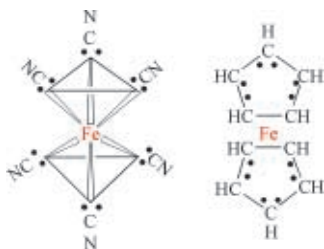
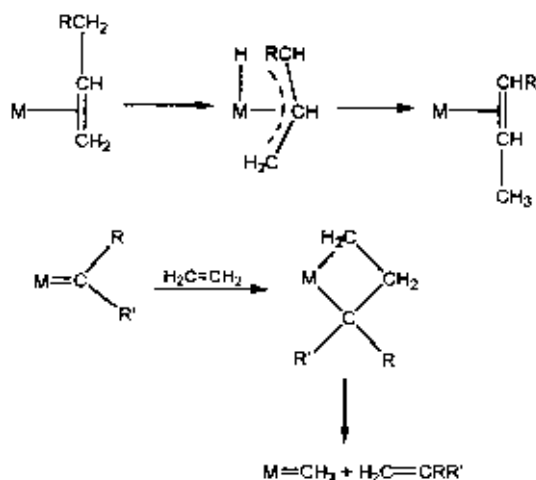


Fig. 7 The $\text{Fe}(\text{CN})_6^{4-}$ ion and ferrocene.

Certainly, there is one aspect of organo transition metal chemistry that is revolutionary, namely, the reactivity of the ligands. In Wernerian chemistry, ligands usually play a passive role, functioning as donors to the metal ion but not otherwise having any “life of their own.” One of the most fascinating aspects of organo-transition-metal chemistry is the way in which the organic ligands are rearranged and transformed. This, indeed, is the basis for the enormously important catalytic activity of transition metals. Consider, for example, the mechanisms for olefin isomerization and olefin metathesis shown in Scheme 1.



Scheme 1 Ligand reactivity of these types was not latent in Wernerian coordination chemistry.

(c) Catalytic activity of transition metals

A chemical industry without transition metal catalysts would bear no resemblance to the chemical industry that actually exists today. The earliest industrial catalysts were mainly heterogeneous, for example, transition metal particles supported on intrinsically inert materials such as α -alumina. Such catalysts were mainly discovered by empirical methods and developed largely by trial and error, although today surface science²¹ has progressed to a stage where at least some rational basis can be supplied for the action of heterogeneous catalysts. Perhaps the earliest important one was the Haber catalyst (a form of iron) for the high-temperature, high-pressure reaction of H_2 and N_2 to form ammonia. Another landmark heterogeneous catalyst was the form of TiCl_3 used in the Ziegler–Natta process for olefin polymerization. There is also the tonnage scale conversion of ethylene to ethylene oxide over a catalyst of Ag supported on α - Al_2O_3 .

In the 1960's the rational development of homogeneous catalysts based on transition metals began and has since resulted in a number of enormously important processes.²² By and large the basis for these developments is the fundamental understanding of the organometallic chemistry of the transition elements. Among the top performers in this class (and the elements involved) are the Wilkinson catalyst for the hydroformylation reaction (Rh), the Monsanto acetic acid process



Fig. 8 One of the molecules devised by E. N. Jacobsen for chiral catalysis of olefin oxide formation.

(Rh), the conversion of ethylene to acetaldehyde (Pd), and olefin polymerization (Zr, Ni); there are many others too numerous to mention.

It should also be noted that one of the greatest recent advances in organic chemistry, asymmetric synthesis, depends entirely upon transition metal atoms as the catalytic centers. In this connection it is pertinent to mention the names of Knowles and Jacobsen²³ and Sharpless²⁴ in the US and Kagan²⁵ in France. The metals involved are principally Rh, Ti, Os and Mn, and the key idea is to complex them with appropriate chiral ligands. As an example, Fig. 8 shows one of Jacobsen's epoxidation catalysts.

(d) Stereochemical nonrigidity or fluxionality

As noted earlier, the Wernerian concept of a coordination shell implied a fixed spatial arrangement of ligands, with a single, well-defined geometry, about the central ion. During the mid-1960's, it began to become clear^{26–28} that there are important exceptions to this idea. It is true that octahedral arrangements tend to be rigid, but for all higher coordination numbers and for coordination number 5, nonrigidity is the normal situation.²⁶ Moreover, for many organometallic compounds²⁷ and most polynuclear metal carbonyls²⁸ fluxionality, nonrigidity or ligand scrambling form an essential part of their character.

(e) Metal–metal bonding

The discovery that transition elements form complexes, and other compounds, in which the *metal atoms combine not only with ligands but with one another* is a revolutionary break with Wernerian coordination chemistry. This is a concept that lies entirely outside the scope of Werner's ideas, and it did not begin to assume any major position in transition metal chemistry until after about 1965—*i.e.*, about half a century after Werner's death. Although a few scattered examples existed in the literature earlier it was only in the early 1960's that the importance of metal atom clusters (a term only coined in 1964²⁹) and pairs of strongly (multiply) bonded metal atoms was recognized and the deliberate, purposeful study of their compounds undertaken. The concept of a central pair or cluster of metal atoms rather than a single central atom is the basis of a new, non-classical transition metal chemistry in basic contrast to the classical or Wernerian chemistry. We note, explicitly, that Werner was well aware of the existence of polynuclear complexes;³⁰ indeed, he pioneered in their study. However, the compounds he dealt with were correctly regarded as simply the conjunction of two or more mononuclear complexes through shared ligand atoms and their properties were assumed to be understandable in terms of the properties of the component individual metal atoms and their local sets of ligands.

As early as 1907 we find a compound, “ $\text{TaCl}_2 \cdot 2\text{H}_2\text{O}$,” now known to be $\text{Ta}_6\text{Cl}_{14} \cdot 7\text{H}_2\text{O}$ with an octahedral cluster of Ta atoms, reported whose behavior could not be understood in Wernerian terms. During the 1920's several lower halide complexes of molybdenum were studied and these, too, were not understandable as classical coordination compounds.

It was with the structural work of Brossset³¹ showing the occurrence of Mo_6 clusters that this non-conformity became

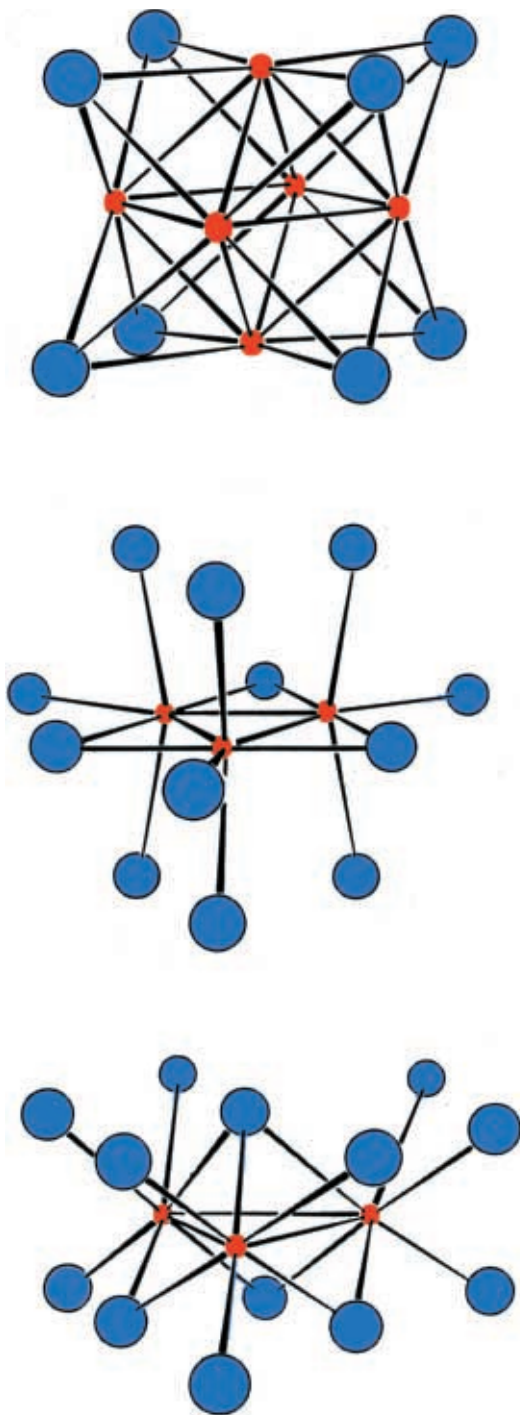


Fig. 9 Three landmark metal atom cluster species: the Mo_6Cl_8 unit discovered by Brosset (top), the $\text{Re}_3\text{Cl}_{12}^{3-}$ ion (center), and the $\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9^{3+}$ ion (bottom), where the water molecules are the three non-bridging ligands on each metal atom.

understandable. However, neither this work, nor a subsequent study of tantalum clusters led to any comprehensive recognition of the existence of a new area of transition metal chemistry (Fig. 9). It was only with the discovery that “ ReCl_4^- ” compounds really contain triangular Re_3 groups with very short (*ca.* 2.47 Å) Re–Re bonds,^{32,33} and the proposal³² that these are not only direct metal–metal bonds but double bonds that the field of metal–metal bonds and clusters became a recognized, non-Wernerian field of inorganic chemistry.

Since then, events have moved rapidly, with the highlights being the recognition of triple and quadruple bonds³⁴ and the rapid extension of this type of chemistry to include all of the transition elements except for manganese. Many phases of the field are still only superficially explored, and there is no doubt

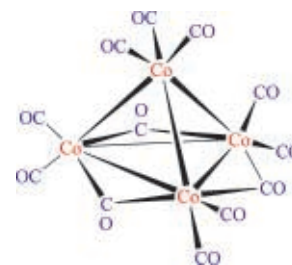


Fig. 10 The $\text{Co}_4(\text{CO})_{12}$ structure, with a tetrahedron of metal atoms forming the core.

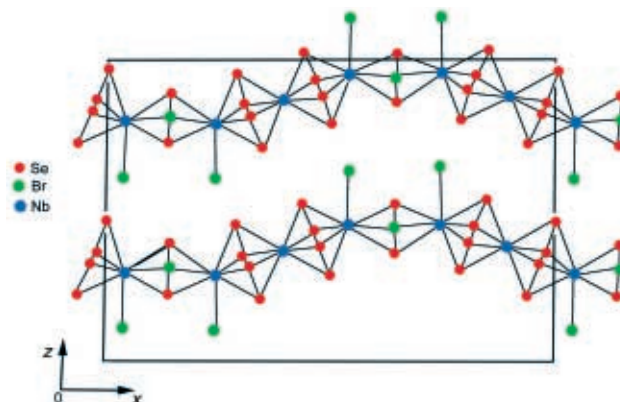


Fig. 11 The $\text{Nb}_6\text{Se}_{20}\text{Br}_6$ structure, adapted from ref. 34.

that the chemistry of compounds containing clusters of transition metal atoms as well as M–M multiple bonds is still a growing field although already one of broad and well-established importance.

In addition to the type of cluster chemistry involving metal atoms in positive oxidation states from +2 to +4, it is also important to draw attention to the very important chemistry of metal carbonyl type cluster compounds, a typical example being $\text{Co}_4(\text{CO})_{12}$ (Fig. 10).

(f) Solid state chemistry

There are, of course, a great many solid compounds of the transition elements that are neither molecular nor simple ionic salts. Structurally, they consist of infinite chains, sheets or three-dimensional networks that exist only in the solid state. It was not until the advent of X-ray crystallography, and more particularly of the modern, efficient era of X-ray crystallography, that this area could undergo significant development. Physicists have always been interested in the simplest solid state compounds, *e.g.*, oxides and sulfides, that require little or no synthetic skill to make. However, chemists have now shown that there is a rich variety of solid state compounds that display highly varied physical, spectroscopic and magnetic properties and structures of the most elaborate (yea bizarre) types. However, in one instance where things are not so simple, it must be admitted that physicists led the way; that was the discovery of copper oxide based high-temperature superconductors.³⁵ The work of the late Jean Rouxel on one-dimensional structures displaying remarkable charge-density waves³⁶ is another example that can be mentioned; one of these compounds is shown in Fig. 11. There is little doubt that the solid state chemistry, which is essentially non-Wernerian, is still at an early stage of development.

4. Supramolecular chemistry

The transition metals are playing a major role in this relatively new and expanding realm. To a large degree it is an evolutionary extension of Wernerian chemistry, but its emergence has occurred nearly a century after Werner's work.

While some supramolecular assemblies are based on hydrogen bonds, many very remarkable and beautiful ones are based on the use of transition metal complexes as structure-directing elements. Again, among the host of possibilities I choose just two as illustrations. One³⁷ is a molecular compound based on Pd^{II} or Pt^{II}, Fig. 12. Another is a substance containing infinite sheets of tubes (made in my own laboratory by Dr Chun Lin). A simplified view of this structure is shown on the cover of this issue, while a detailed picture is displayed in Fig. 13. Supramolecular compounds, whether consisting of discrete giant molecules or extended arrays (1-, 2- or 3-dimensional) are of interest as microporous or mesoporous materials, and I believe this is a field that will continue to unfold for many years to come.

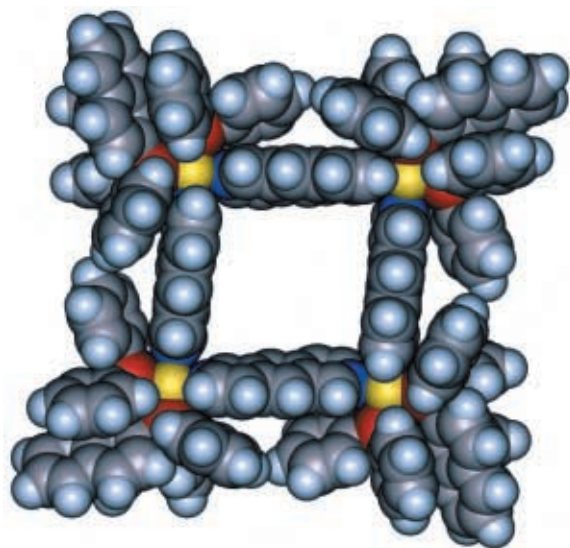


Fig. 12 An example of the use of Pt²⁺ ions (shown in yellow) to direct the formation of supramolecular squares. This drawing was supplied by Professor Peter Stang of the University of Utah.

Closely related to supramolecular chemistry is the field of molecular topology, in which catenanes and rotaxanes play a major role.³⁸ In the assembly of such molecules, the key factor is the use of transition metal ions, most often Cu⁺ and Cu²⁺, as templates. By exploiting the redox properties (Cu⁺ ↔ Cu²⁺) and the accompanying changes in preferred coordination number of the metal ion, a kind of molecular machine in which one ring of a catenane is caused to rotate relative to the other has been constructed, as shown in Fig. 14.

Concluding remarks

For the transition elements, the chemistry of the past has been brilliant and that of the future is also likely to be brilliant. The variety of behavior of which these elements are capable is immense, each element being capable of doing things no other

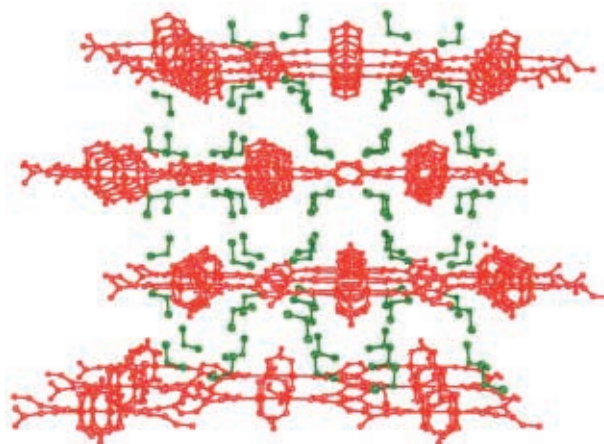


Fig. 13 A detailed drawing of the structure shown schematically on the cover. The layers of Rh₂⁴⁺ connected tubes are in red and the inter-layer molecules of CH₂Cl₂ are in green (with H atoms omitted). The complete formula for the ligands bridging the pairs of rhodium atoms is (*p*-CH₃OC₆H₄N)₂CH.

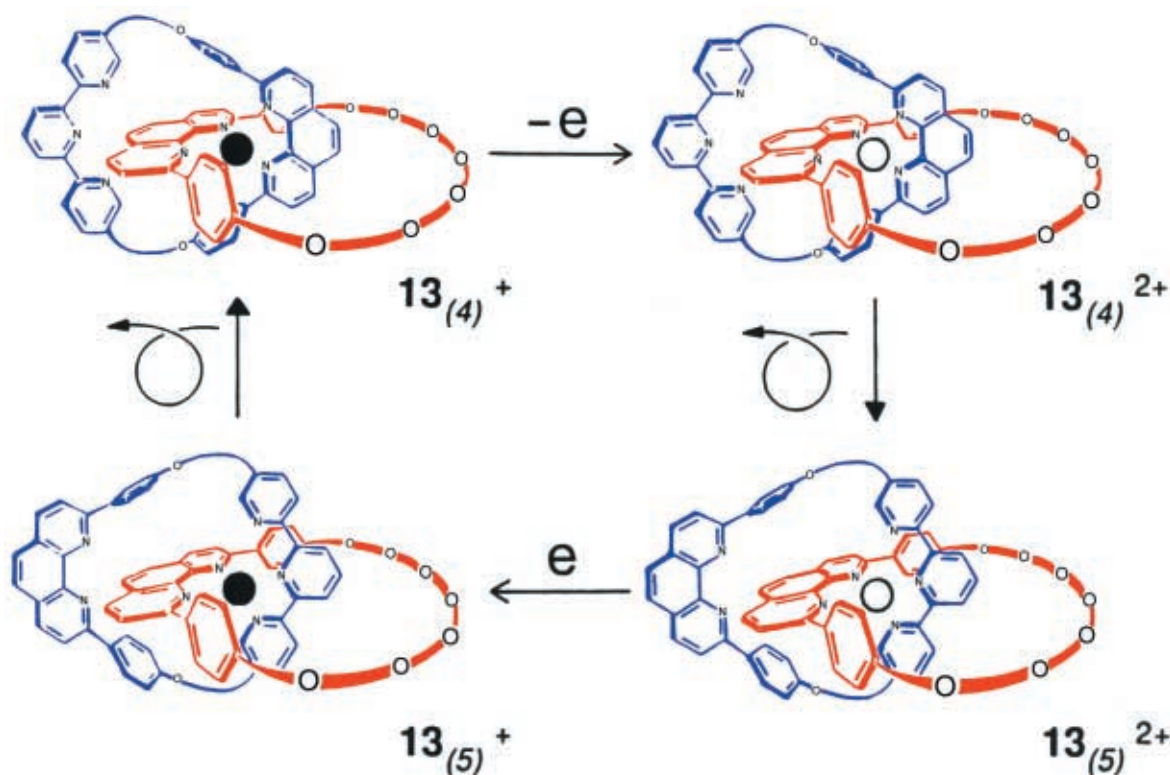


Fig. 14 Electronically induced molecular rearrangements undergone by the copper catenane $13^{2+/+}$. The subscript 4 or 5 indicates the number of nitrogen atoms coordinated to the metal. Adapted from ref. 36.

one can do. Even neighboring elements (whether horizontally, *e.g.*, Ni, Co, or vertically, *e.g.*, Ni, Pd) have vastly different chemical properties. Much as we already know about their chemistry, I am sure there is even more that we do not yet know. There will still be a lot of fun, intellectual satisfaction and profit to be had from advancing the chemistry of the transition elements in the third millennium.

Finally, I must acknowledge that this survey is incomplete and, no doubt, disproportionately reflects some of my personal interests. Despite these shortcomings, I hope it gives a reasonable impression of the fascination and accomplishments of transition metal chemistry as the second millennium comes to its end. I look forward to seeing what the next generation can do with these elements.

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