STEREOCHEMISTRY AND REACTION MECHANISMS OF HEXACOVALENT INORGANIC COMPLEXES

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I. INTRODUCTION

An observation made in 1798 by Tassaert (199) during the analysis of some cobalt compounds was the beginning of a new and important branch of inorganic chemistry. This analysis was carried out by the precipitation of cobalt hydroxide with sodium hydroxide. However, on one occasion ammonium hydroxide was employed in excess and it was observed that the usual precipitate dissolved in the excess base. Upon standing overnight, the reaction mixtures yielded an orange crystalline material with the composition $CoCl_3 \cdot 6NH_3$. The six ammonia molecules were very firmly held in the solid; thus a new and different type of compound had been discovered. The "valence" theories that existed at the time were completely inadequate to account for compounds of this type, so they became known as *complex compounds*. During the hundred years that followed, considerable work was done and numerous theories were proposed to explain the structure of these compounds. However, it was not until 1893, when Werner (225) suggested the possible existence of two types of valence, that the real nature of the complex compounds began to become apparent. Werner's Coordination Theory was soon followed by the concept of an electron pair as a covalent bond by Lewis (126), and finally Pauling (166) introduced the present orbital picture. Although the term "complex compound" is still used in reference to these substances, it is generally agreed that their fundamental structures are now understood.

The researches of coördination chemists have in many respects been analogous to those of the organic chemist in his study of the reactions of carbon compounds, which have been investigated by the accumulation of stereochemical and kinetic data. The organic chemist has been rather successful with his interpretation of the data in terms of probable reaction mechanisms. That this task for the coördination chemist is expected to be somewhat more difficult, can be ascertained from the following statement of Bailar (6):

> "The complexity of the stereochemistry of inorganic compounds makes it difficult to establish generalizations and to formulate theories on the basis of observations of these compounds. On the other hand, we have here an extremely useful tool for testing theories of the organic stereochemist. A theory may describe the behavior of a tetrahedral molecule very well, but if it cannot predict behavior in molecules of other structures, it is in error in some particular. Moreover, when working with the complex inorganic compounds, it is possible to achieve conditions which cannot be achieved with carbon compounds. Thus, it is possible to compare the stereochemical properties of analogous compounds of different elements; it is possible to vary the valence of the central atom of the complex; and it is possible to achieve optical activity when the center of asymmetry is attached to two or more identical univalent groups."

In spite of the numerous difficulties encountered in studies of coördination compounds, there now exists considerable information on their stereochemistry; also, several kinetic observations have been reported. It is felt therefore that the time is opportune to review these findings and the proposed reaction mechanisms. Recent reviews have included excellent discussions on tetracovalent complexes (153, 177), the stability of complexes (24, 137), and the lability or bond type of complex ions (69, 200). Therefore, in order to avoid needless repetition, this review will consist of a discussion of hexacovalent complex compounds with emphasis on stereochemical and kinetic studies and the interpretation of these results on the basis of probable reaction mechanisms. The compounds discussed here are of the *inert* type (200) and, as most of this work has been done with cobalt(III), much of the review will deal with its complexes. Furthermore, it is well known that these hexacovalent complexes have an octahedral configuration.

II. KINETICS OF SUBSTITUTION REACTIONS

It will become apparent from the discussion in Sections III and IV that stereochemical results alone will not define the reaction mechanisms of hexacovalent complexes. Therefore it is essential to utilize both kinetic and stereochemical data in any attempt to elucidate the mechanisms of these reactions. The kinetic studies, it will be seen, at least allow one to eliminate certain reaction paths from consideration. Although most reactions in which a coördinated ligand is replaced by another group proceed at moderate rates, relatively few such reactions have been studied kinetically. No attempt will be made to review the literature on this subject completely. Instead, a few typical examples will be cited to illustrate the difficulties encountered, particularly in attempts to determine the molecularity of these reactions.

A. Acid hydrolysis

The substitution reaction that has been investigated most by kinetic methods is that generally referred to as *aquation*[1] and illustrated by the stoichiometric equation:

$$[Co(NH_3)_5Cl]^{+2} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{+3} + Cl^-$$

Several investigators (31, 73, 124) have shown that reactions of this type follow first-order kinetics. There is a first-order dependence on the concentration of the complex, and, as water is the solvent, this is said to be a pseudo-first-order reaction. Unfortunately these salts are generally soluble only in water and the application of other solvents has not been practical; indeed, there has been no report of a kinetic study of the reaction between a complex ion and water in a non-aqueous system. Therefore, the kinetic data collected in aqueous solutions have shed no light on the role played by water in such reactions.

Although rates of acid hydrolysis are for the most part independent of ionic strength (2, 123, 124), Garrick (74) has shown that the rate with $[Co(NH_3)_5Cl]^{+2}$ is definitely accelerated in the presence of nitrate or sulfate ions. He observed a specific catalytic effect, the sulfate ion being a much better catalyst for the reaction than the nitrate ion. It was suggested that this could be due to either the intermediate coördination of the sulfate ion,

$$[Co(NH_3)_5Cl]^{+2} + SO_4^{-2} \rightarrow [Co(NH_3)_5SO_4]^+ + Cl^- \qquad (1a)$$

$$[Co(NH_3)_5SO_4]^+ + H_2O \rightarrow [Co(NH_3)_5H_2O]^{+3} + SO_4^{-2} \qquad (1b)$$

or the formation of an ion-pair:

$$[Co(NH_3)_5Cl]^{+2}\cdot SO_4^{-2} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{+3} + Cl^- + SO_4^{-2} \qquad (2)$$

Adell's (2) recent discovery that the forward rate of reaction 1b is even slower than that of the overall acid hydrolysis of $[Co(NH_3)_5Cl]^{+2}$ would appear to rule out mechanism 1. In any case, it is doubtful that the molecularity of an acid hydrolysis reaction could be ascertained solely on the basis of the ionic strength effect.

In addition, the rate of acid hydrolysis of ammine complexes in an acid medium (pH range of approximately 0.5 to 3) is independent of the hydrogen-ion concentration (124). However, the rate of aquation of an acidoaquoammine complex varies inversely with the concentration of hydrogen ion (31). This phenomenon was demonstrated by Brønsted with the complex ions $[Co(NH_3)_5NO_3]^{+2}$ and $[Co(NH_3)_4H_2ONO_3]^{+2}$; data for these compounds are represented graphically in figure 1. Brønsted explains the behavior of the aquoammine complex on the

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[1] The term "aquation" has been applied to reactions that involve the replacement of a group by a water molecule, whereas hydrolysis has been used to mean the replacement of a ligand by a hydroxide ion. Since both involve reactions with water, it would appear more appropriate to refer to these as hydrolysis reactions. Therefore in this review the terms "acid hydrolysis" and "base hydrolysis" will be adopted to mean replacement with water and with hydroxide ion, respectively.

basis of the fact that equilibria of the type

$$[Co(NH_3)_4H_2ONO_3]^{+2} + H_2O \rightarrow [Co(NH_3)_4OHNO_3]^{+} + H_3O^{+}$$

are known to exist in aqueous solution (83). Because of its smaller positive charge, the hydroxo complex would be expected to lose the nitrate more readily than would the corresponding aquo complex of higher positive charge. Thus

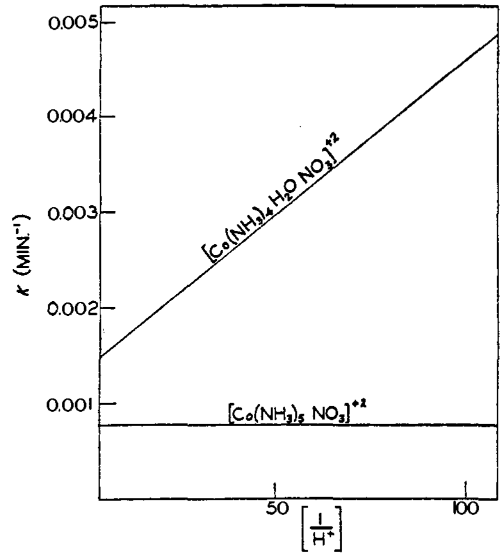


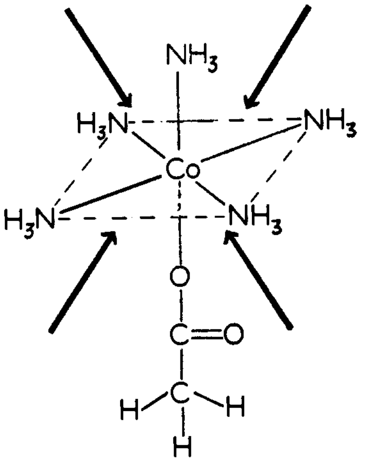
Fig. 1. Dependence of rates of acid hydrolysis of $[Co(NH_3)_5NO_3]^{+2}$ and $[Co(NH_3)_4H_2ONO_3]^{+2}$ on the hydrogen-ion concentration.

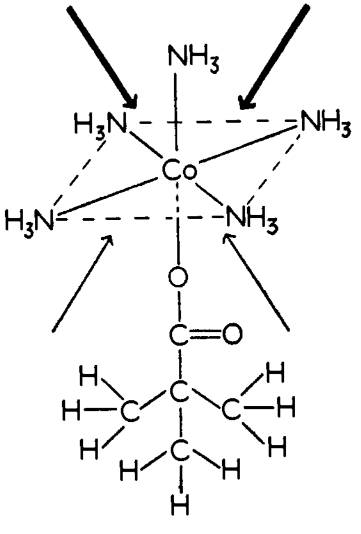
Brønsted suggests that the observed pH dependence can be accounted for on the basis of the following reaction mechanism:

$$\begin{array}{ccccccc} [Co(NH_3)_4H_2ONO_3]^{+2} & + & H_2O & \xrightleftharpoons{\text{slow}} & [Co(NH_3)_4(H_2O)_2]^{+3} & + & NO_3^- \\ \updownarrows & & & & \updownarrows & & \\ [Co(NH_3)_4OHNO_3]^{+1} & + & H_2O & \xrightleftharpoons{\text{fast}} & [Co(NH_3)_4OH(H_2O)]^{+2} & + & NO_3^- \\ + H^+ & & & & + H^+ & & \end{array}$$

Since the acid-base equilibria are established instantaneously, it is seen from the above equations that the rate of reaction will be greater the larger the concentration of $[Co(NH_3)_4OHNO_3]^{+1}$, or, as observed, the rate of acid hydrolysis is expected to increase with decreasing hydrogen-ion concentration. Brønsted suggests that this mechanism receives additional support from the fact that the rate of reaction of the corresponding pentammine, $[Co(NH_3)_5NO_3]^{+2}$, is independent of pH in this acid region. In other words, under these conditions there is no appreciable acid dissociation of the pentammine complex (see page 467).

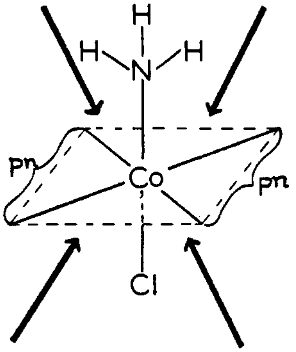
This problem regarding the molecularity of acid hydrolysis reactions has been approached recently (19) by a study of the rates of reaction of analogous complex ions which vary in the amount of steric hindrance in the complex. In the first of these studies the rates of both acid and base hydrolysis were determined for some *C*-substituted acetatopentamminecobalt(III) ions, $[\text{Co}(\text{NH}_3)_5\text{X}]^{+2}$. The rates of reaction were found to vary with the acidity of the corresponding substituted acetic acid, as shown in table 1. There was no indication that different steric requirements had any influence on the rates. The conclusion is drawn that the reactions proceed either by a dissociation ($\text{S}_\text{N}1$) process or by a displacement ($\text{S}_\text{N}2$) mechanism with the incoming group approaching the complex ion from a position opposite to that of the outgoing group. The latter point is apparent when one considers molecular models which clearly show that the front of the complex becomes less readily accessible with increasing size of the acetato group, whereas the back remains unchanged. This is shown below for the complex ions $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}]^{+2}$ and $[\text{Co}(\text{NH}_3)_5(\text{CH}_3)_3\text{CCOO}]^{+2}$; the heaviness of the arrow designates the relative accessibility of the central cobalt(III) to the incoming group.

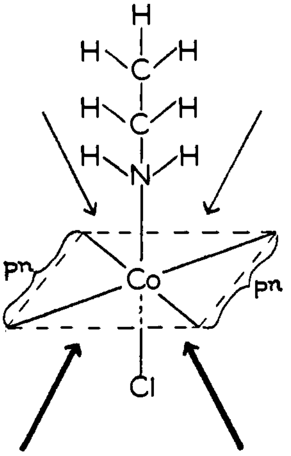




In a recent extension of this work (22), the steric hindrance at the front of the complex was kept constant whereas that of the rear was changed. This study utilized a series of complex ions of the type *trans*-$[\text{Copn}_2\text{aCl}]^{+2}$.[2] Preliminary results indicated that the rate of aquation actually increases with an increase in the size of the group opposite the outgoing chloride ion. A consideration of molecular models suggests that if this reaction proceeds *via* a bimolecular process with an attack from the rear, the rate of reaction is expected to decrease with increasing size of group a.

[2] a = NH_3, CH_3NH_2, $\text{C}_2\text{H}_5\text{NH}_2$, and $\text{C}_5\text{H}_5\text{N}$; pn = propylenediamine.





The fact that such a decrease was not observed suggests that there must be no appreciable approach of the incoming group from the rear of the complex. These results, along with those from the study of the *C*-substituted acetatopentamminecobalt(III) systems, indicate that the acid hydrolysis reaction in these

TABLE 1

Rates of acid and base hydrolysis of acetatopentamminecobalt(III) ions

$[Co(NH_3)_5X]^{+2}$ X^-	DISSOCIATION CONSTANT OF HX	ACID HYDROLYSIS (70°C.) *k*	BASE HYDROLYSIS (25°C.) *k*
		min.$^{-1}$	*liters mole*$^{-1}$ *min.*$^{-1}$
CF_3COO^-	5×10^{-1}	3.3×10^{-3}	4.4
CCl_3COO^-	2×10^{-1}	3.2×10^{-3}	4.3
$CHCl_2COO^-$	5×10^{-2}	9.6×10^{-4}	1.6
CH_2ClCOO^-	1.4×10^{-3}	3.5×10^{-4}	2.5×10^{-1}
CH_2OHCOO^-	1.5×10^{-4}		7.0×10^{-2}
CH_3COO^-	1.8×10^{-5}	4.9×10^{-4}	4.2×10^{-2}
$CH_3CH_2COO^-$	1.4×10^{-5}	1.9×10^{-4}	2.7×10^{-2}
$(CH_3)_2CHCOO^-$	1.5×10^{-5}	1.6×10^{-4}	3.4×10^{-2}
$(CH_3)_3CCOO^-$	1.0×10^{-5}	2.6×10^{-4}	1.8×10^{-2}

systems is unimolecular or proceeds by a dissociation (S_N1) mechanism. The increase in rate that was actually observed may be due to several factors such as base strength, possible resonance structures with pyridine, and perhaps even a steric acceleration of reaction rate.

Additional support is afforded the dissociation (S_N1) mechanism as a result of kinetic studies on the acid hydrolysis of several *trans*-$[Co(AA)_2Cl_2]^+$ cations (167). As shown in table 2, the complex ions containing *C*-substituted ethylenediamine undergo hydrolysis more rapidly than the corresponding ethylenediamine complex. The fact that increased crowding around the central ion does not decrease the rate would indicate that these reactions do not involve the approach of an incoming group or proceed through a seven-coördinated activated complex, that is, by an S_N2 mechanism. A more probable interpretation is that a pentacoördinated intermediate is involved or, in other words, the acid hydrolysis reaction proceeds by a dissociation (S_N1) process.

As will be discussed in more detail later (page 511), the stereochemical evidence on these reactions likewise supports the dissociation mechanism. For example, it has been demonstrated that several optically active complex ions of the type[3] $[Coen_2aCl]^{+1(or+2)}$ yield the corresponding aquo complexes $[Coen_2aH_2O]^{+2(or)+3}$ with complete retention of configuration (140). Furthermore, Mathieu (141) has found that the rate of change in optical rotation as $[Coen_2Cl_2]^{+1}$ is transformed into optically active $[Coen_2H_2OCl]^{+2}$ is the same as the rate of formation of chloride ion. A possible intermediate which may be postulated to account for this retention of configuration would be one with a tetragonal pyramid structure (table 7) resulting from a dissociation of the hexacovalent complex.

TABLE 2

Rates of acid hydrolysis of $[Co(AA)_2Cl_2]^+$ *ions*

$[Co(AA)_2Cl_2]^+ + H_2O \rightarrow [Co(AA)_2H_2OCl]^{+2} + Cl^-$

DIAMINE (AA)	SYMBOL	$k \times 10^3$	TEMPERATURE	E_a
		min.$^{-1}$	°*C.*	*kcal./mole*
$NH_2CH_2CH_2NH_2$	en	1.9	25	28
$NH_2CH_2CH(CH_3)NH_2$	pn	3.7	25	28
dl-$NH_2CH(CH_3)CH(CH_3)NH_2$	*dl*-bn	8.8	25	26
meso-$NH_2CH(CH_3)CH(CH_3)NH_2$	meso-bn	250	25	24
$NH_2CH_2C(CH_3)_2NH_2$	iso-bn	130	25	26
$NH_2C(CH_3)_2C(CH_3)_2NH_2$	tet-me	Instantaneous	10	
$NH_2CH_2CH_2NHCH_3$	Me-en	1.0	25	27
$NH_2CH_2CH_2NHC_2H_5$	Et-en	5.9	25	29
$NH_2CH_2CH_2NH(n\text{-}C_3H_7)$	*n*-Pr-en	7.1	25	27
$NH_2CH_2CH_2CH_2NH_2$	tn	600	10	
$NH_2CH_2C(CH_3)_2CH_2NH_2$	dan	180	25	24

B. *Base hydrolysis*

Next in order of the most extensively studied substitution reactions in complex ions is that known as *base hydrolysis* and illustrated by the equation:

$$[Co(NH_3)_5Cl]^{+2} + OH^- \rightarrow [Co(NH_3)_5OH]^{+2} + Cl^-$$

Qualitative observations indicate the extreme rapidity with which these reactions occur as compared to the corresponding aquation reaction. Indeed, the reaction of hydroxide ion is unique in its rapidity (72). As will become apparent shortly, this behavior may perhaps be associated with the rapid attainment of acid–base equilibrium.

The base hydrolysis reactions that have been studied kinetically were found to be of the second order (19, 32, 174) but of the first order with respect to both the complex ion and the hydroxide ion. This first-order dependence on hydroxide-

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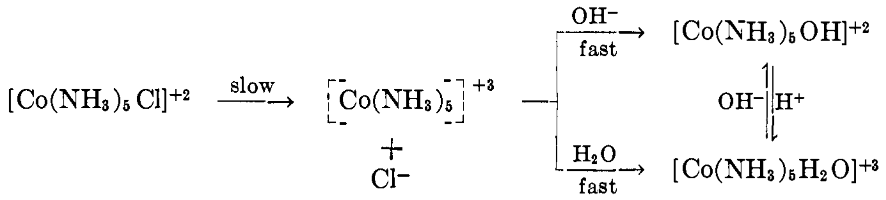
[3] a = Cl^-, NO_2^-, NCS^-, or NH_3.

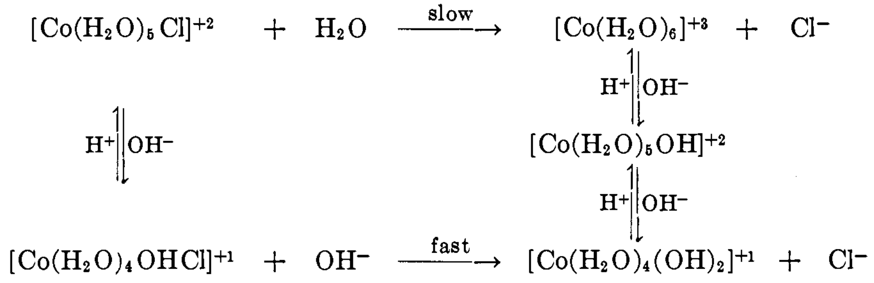
ion concentration suggests a bimolecular process. Thus, a unimolecular process would be expected to follow the following reaction paths:



$$\begin{tikzcd}
 & & {[Co(NH_3)_5OH]^{+2}} \arrow[d, shift left, "H^+"] \\
{[Co(NH_3)_5Cl]^{+2}} \arrow[r, "slow"] & {[Co(NH_3)_5]^{+3} + Cl^-} \arrow[ur, "OH^-", "fast"'] \arrow[dr, "H_2O", "fast"'] & \\
 & & {[Co(NH_3)_5H_2O]^{+3}} \arrow[u, shift left, "OH^-"]
\end{tikzcd}$$

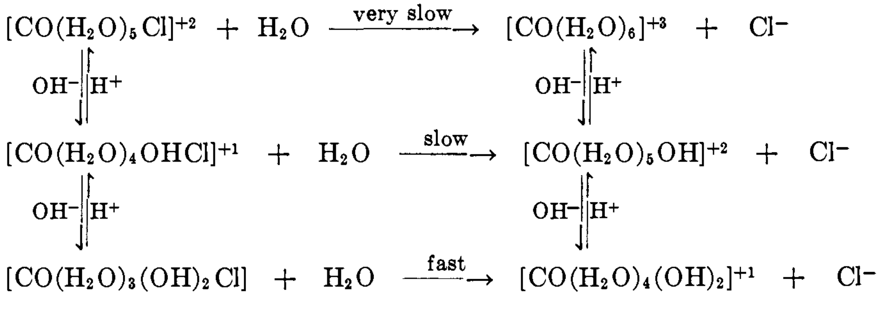
With the slow, or rate-determining, step being that of dissociation, either hydroxide ion or water could enter the coördination sphere of the pentacovalent intermediate with the same net result. Therefore such a mechanism cannot be operating, as the rate of the above sequences of reactions would show no dependence on the concentration of hydroxide ion.

With complex compounds that contain labile hydrogen atoms, an additional complication is introduced and it becomes impossible to draw any conclusion as to the molecularity of the reactions. For example, it has already been mentioned that in the acid region Brønsted (31) observed no pH dependence for the rate of acid hydrolysis of $[Co(NH_3)_5NO_3]^{+2}$ but with the corresponding $[Co(NH_3)_4H_2ONO_3]^{+2}$ there is an inverse relationship to the hydrogen-ion concentration. This has been adequately accounted for on the basis of the acid-base equilibrium of the aquo complex (page 462). Bjerrum (26) likewise found that the rate of acid hydrolysis of the aquo complex, $[Cr(H_2O)_5Cl]^{+2}$, has a second-order dependence on the hydroxide-ion concentration. This second-order dependence likewise suggests a mechanism involving an acid–base equilibrium. However, it is not clear from the available data whether only one proton is removed, followed by a bimolecular reaction with additional hydroxide ion,



$$\begin{tikzcd}
{[Co(H_2O)_5Cl]^{+2} + H_2O} \arrow[rr, "slow"] \arrow[dd, shift left, "OH^-"] & & {[Co(H_2O)_6]^{+3} + Cl^-} \arrow[d, shift left, "OH^-"] \\
 & & {[Co(H_2O)_5OH]^{+2}} \arrow[u, shift left, "H^+"] \arrow[d, shift left, "OH^-"] \\
{[Co(H_2O)_4OHCl]^{+1} + OH^-} \arrow[uu, shift left, "H^+"] \arrow[rr, "fast"] & & {[Co(H_2O)_4(OH)_2]^{+1} + Cl^-} \arrow[u, shift left, "H^+"]
\end{tikzcd}$$

or whether the complex behaves as a dibasic acid such that



$$\begin{tikzcd}
{[CO(H_2O)_5Cl]^{+2} + H_2O} \arrow[r, "very slow"] \arrow[d, shift left, "H^+"] & {[CO(H_2O)_6]^{+3} + Cl^-} \arrow[d, shift left, "H^+"] \\
{[CO(H_2O)_4OHCl]^{+1} + H_2O} \arrow[u, shift left, "OH^-"] \arrow[r, "slow"] \arrow[d, shift left, "H^+"] & {[CO(H_2O)_5OH]^{+2} + Cl^-} \arrow[u, shift left, "OH^-"] \arrow[d, shift left, "H^+"] \\
{[CO(H_2O)_3(OH)_2Cl] + H_2O} \arrow[u, shift left, "OH^-"] \arrow[r, "fast"] & {[CO(H_2O)_4(OH)_2]^{+1} + Cl^-} \arrow[u, shift left, "OH^-"]
\end{tikzcd}$$

In view of these two possibilities the molecularity of the rate-determining step is not known.

Although the acidity of aquo complexes has long been recognized, similar behavior of ammine compounds in water was not well defined until the work of Anderson, Spoor, and Briscoe (4). These workers found that hexamminecobalt(III) cation exchanges hydrogen with deuterium oxide. Since this complex is known to be very stable with regard to loss of ammonia, it was proposed that the exchange is accomplished by the following ionization:

$$[Co(NH_3)_6]^{+3} + D_2O \rightleftharpoons [Co(NH_3)_5NH_2]^{+2} + HD_2O^+$$

This view is substantiated by the fact that the rate of exchange varies inversely as the hydrogen-ion concentration. Furthermore, salts of complex ions of the type $[Pt(NH_3)_4NH_2Cl]^{+2}$ and $[Pt(NH_3)_5NH_2]^{+3}$ have indeed been isolated (212). On the basis of these results, Garrick (72) proposed a mechanism to explain the rapid basic hydrolysis of ammine complexes. The suggested reaction path may be outlined as follows:

$$\begin{tikzcd}
{[CO(NH_3)_5Cl]^{+2}} \arrow[d, shift right, "OH^-"'] & & & & & \\
{[CO(NH_3)_4NH_2Cl]^{+1}} \arrow[u, shift right, "H^+"'] & + & H_2O \arrow[r] & {[CO(NH_3)_4NH_2H_2O]^{+2}} \arrow[d] & + & Cl^- \\
& & & {[CO(NH_3)_5OH]^{+2}} & &
\end{tikzcd}$$

With such a reaction mechanism the rate of hydrolysis would be of the first order in hydroxide-ion concentration, as this controls the amount of amido complex, $[Co(NH_3)_4NH_2Cl]^{+1}$, available for reaction. With the possibility of this type of mechanism for basic hydrolysis reactions, it becomes apparent that, as with the corresponding acid hydrolysis reactions, the molecularity here is likewise not known.

On the basis of charge separation alone one would expect the base hydrolysis of an ammine complex, $[Co(NH_3)_5Cl]^{+2}$, to be slower than that of the corresponding amido ion, $[Co(NH_3)_4NH_2Cl]^{+1}$. However, even if the mechanism suggested by Garrick were not correct, the more nucleophilic hydroxide ion may still be expected to react more rapidly than does water, as is the case with carbon compounds containing no acid hydrogens (91). Furthermore, the negative hydroxide ion should approach a positively charged ion more readily than would the negative dipole of a neutral water molecule. It would therefore be of interest to compare the rates of reaction, using complexes which contain no labile hydrogens, so that the hydrolysis mechanism suggested by Garrick would not be possible. Preliminary studies have been made on complexes of this type, but as yet only qualitative observations are possible. Unfortunately, the known complexes that contain no acid hydrogen are not numerous, and most of these were found to react even with water too rapidly to follow. The only information available at present is that the base hydrolysis of the complex ions $[Co(dipy)_2OHCl]^{+1}$ and $[Co(dipy)_2OHNO_2]^{+1}$ is faster than the acid hydrolysis

(195). It may of course be argued that the hydrogen on the hydroxo group is still sufficiently acidic to allow for its removal in alkali; more definitive experiments must be designed before it is possible to exclude either of these mechanisms.

C. Substitution reactions other than hydrolysis

Some kinetic studies have been made on the reverse reaction of acid hydrolysis; these have been referred to as *anation reactions* (123).[4]

$$[Co(NH_3)_5H_2O]^{+3} + Cl^- \rightarrow [Co(NH_3)_5Cl]^{+2} + H_2O$$

Lamb and Fairhall (123) investigated the reactions of $[Co(NH_3)_5H_2O]^{+3}$ and $[Ir(NH_3)_5H_2O]^{+3}$ with chloride ion to yield the corresponding chloropentammine complexes. Since the kinetic data agreed with a first-order process, it was suggested that the combination of the aquo complex with the chloride ion is not the slow or rate-determining change. Instead it would appear that some other slow change is involved which is monomolecular. Brønsted and Livingston (32) suggest that the apparent first-order kinetics may be caused by the continual change in ionic strength during the course of reaction. Lamb (122) agreed that the application of the Brønsted correction (30) for this effect in the kinetic equation for opposed first- and second-order reactions gives a modified kinetic equation practically indistinguishable from the simple equation for opposed first-order reactions. Adell (2) and Garrick (73) have found that the reaction of $[Co(NH_3)_5H_2O]^{+3}$ with either sulfate or chloride ion is of the second order. This first-order dependence on the concentration of chloride ion does not necessarily indicate a displacement process. The same dependence would be observed with the following dissociation mechanism:

$$[Co(NH_3)_5H_2O]^{+3} \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} [Co(NH_3)_5]^{+3} \xrightarrow{Cl^-} [Co(NH_3)_5Cl]^{+2}$$

In such a scheme an equilibrium is set up between the aquo compound and the pentacovalent activated complex, but the rate of formation of $[Co(NH_3)_5Cl]^{+2}$ will still be dependent upon the concentration of chloride ion. Therefore once again the second-order kinetics is insufficient to distinguish between a unimolecular and a bimolecular process.

However, if the dissociation mechanism is involved there should be some high concentration of the anion at which the rate of replacement of water would have a zero-order dependence upon the anion concentration. This limiting rate would be equal to the rate of water exchange as measured with the aid of water containing O^{18}. Consider the reaction sequence

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B; \quad B + C \xrightarrow{k_3} D$$

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[4] The term "anation" will not be used in this review, as it would not appear necessary to restrict discussion to replacement of water by anions. In fact, it is possible for water to be replaced by other neutral groups, for neutral groups other than water to be replaced by anions, for direct replacement of one anion by a different anion, and, finally, for exchange involving the same neutral groups or anions. One may even visualize reactions involving coördinated positively charged groups or replacement by such groups.

If B is an unstable intermediate, the steady-state approximation may be used for its rate of formation.

$$\frac{d[B]}{dt} = 0 = k_1[A] - k_2[B] - k_3[C][B]$$

giving

$$[B] = \frac{k_1[A]}{k_2 + k_3[C]}$$

at the steady state. The rate of formation of the final product D is given by

$$\frac{d[D]}{dt} = k_3[B][C] = \frac{k_1k_3[A][C]}{k_2 + k_3[C]}$$

In our case this equation becomes

$$\frac{d[Co(NH_3)_5Cl^{+2}]}{dt} = \frac{k_1k_3[Co(NH_3)_5H_2O^{+3}][Cl^-]}{k_2 + k_3[Cl^-]}$$

which in the limit of high chloride-ion concentration becomes:

$$\frac{d[Co(NH_3)_5Cl^{+2}]}{dt} = k_1[Co(NH_3)_5H_2O^{+3}]$$

Rutenberg and Taube (184a) have made some measurements on the system $[Co(NH_3)_5H_2O]^{+3}$–SO_4^{-2}. Their results indicate that the sulfate ion enters the coördination sphere by way of a dissociation mechanism. The situation, however, is complicated by the formation of an ion-pair between the aquo complex and sulfate ion (130a, 201). Recent studies in our laboratory (22, 195) on the reaction of *cis-* and *trans*-aquonitrobis(ethylenediamine)cobalt(III) ion with nitrite ion also support a dissociation process. As illustrated in figure 2, the first-order dependence on nitrite-ion concentration starts to drop off at concentrations greater than 0.5 *M* and a zero-order dependence is reached beyond 1.0 *M*. If this effect is due to the operation of the dissociation mechanism as outlined above, it should follow that the *same* limiting rate (equal to the rate of dissociation of the aquo complex to the pentacovalent intermediate) would be reached independent of the nature of the anion which enters the coördination sphere. Thiocyanate ion has also been studied, but since it reacts more slowly, the rate does not reach the limiting value at any reasonable value of the concentration.

There are numerous examples of reactions in which the overall process involves the replacement of one anion by a different anion as, for example, the preparation of $[Co(NH_3)_5NO_2]^{+2}$ by the reaction of $[Co(NH_3)_5Cl]^{+2}$ with nitrite ion. Although many of these reactions proceed at a conveniently measurable rate, few detailed kinetic studies have been made. However, on the basis of present evidence, it would appear that when these reactions take place in water, the first step is always hydrolysis (68, 195).

Some studies have been made on the rate of ligand exchange in complex ions, using radioactive isotopes as tracers. One of the first studies of this type was made by Ettle and Johnson (68) during an investigation of *cis–trans* interconversion of $[Coen_2Cl_2]^{+2}$ (page 493). It was shown with the aid of radiochlorine that there was no direct replacement of chloro groups by chloride ion. Instead, the results showed that all of the chlorine exchange occurred through the intermediate formation of aquo complexes. A more recent study by Adamson, Welker, and Wright (1) on the rate of cyanide exchange in the system $[Mn(CN)_6]^{-3}$–CN^- has been interpreted on the basis of an intermediate formation of a heptacovalent aquo complex:

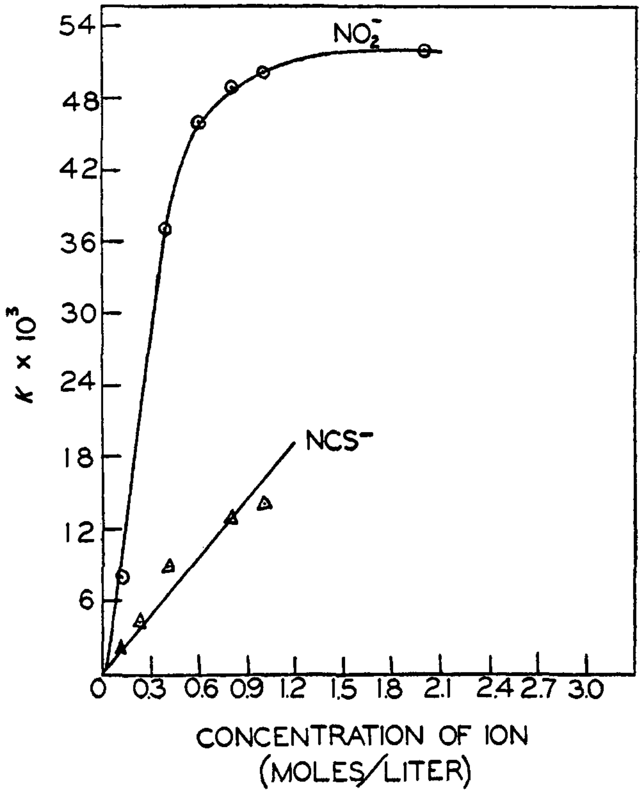


Fig. 2. Variation of rate of reaction of *cis*-$[Coen_2NO_2H_2O]^+$ with concentration of nitrite and thiocyanate ions at a pH of 5.4 and at 35°C.

$$[Mn(CN)_6]^{-3} + H_2O \rightleftharpoons [Mn(CN)_6H_2O]^{-3} \rightleftharpoons [Mn(CN)_5H_2O]^{-2} + CN^-$$

This mechanism was suggested as being preferable to a dissociation process because for a unimolecular case the activation energy was much too low to account for the observed rate. Charonnat (38) has also suggested an expanded coördination number for the activated complex, $[Cr(C_2O_4)_3(H_2O)_2]^{-3}$, to account for the racemization of $[Cr(C_2O_4)_3]^{-3}$ (page 505). Harris and Stranks (86) have made a detailed study of the kinetics of exchange between free carbonate ion and $[Co(NH_3)_4CO_3]^+$, making use of carbon-14. The results obtained are said to be consistent with the following equilibria:

$$[Co(NH_3)_4CO_3]^+ + H_3O^+ \rightleftharpoons [Co(NH_3)_4H_2OHCO_3]^{+2} \qquad (1)$$

$$[Co(NH_3)_4H_2OHCO_3]^{+2} + H\overset{*}{C}O_3^- \rightleftharpoons [Co(NH_3)_4H_2OH\overset{*}{C}O_3]^{+2} + HCO_3^- \qquad (2)$$

$$[Co(NH_3)_4H_2OHCO_3]^{+2} + H_2O \rightleftharpoons [Co(NH_3)_4(H_2O)_2]^{+3} + HCO_3^- \qquad (3)$$

$$[Co(NH_3)_4(H_2O)_2]^{+3} + H\overset{*}{C}O_3^- \rightleftharpoons [Co(NH_3)_4H_2OH\overset{*}{C}O_3]^{+2} + H_2O \qquad (4)$$

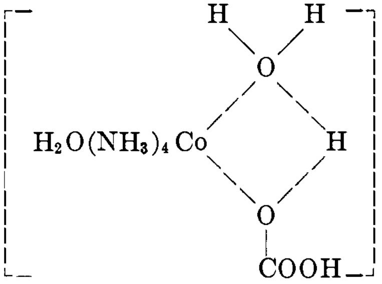
$$[Co(NH_3)_4H_2OH\overset{*}{C}O_3]^{+2} \rightleftharpoons [Co(NH_3)_4\overset{*}{C}O_3]^+ + H_3O^+ \qquad (5)$$

The acid decomposition was also studied and found to occur by way of the following reactions.

$$[Co(NH_3)_4CO_3]^+ + H_3O^+ \rightleftharpoons [Co(NH_3)_4H_2OHCO_3]^{+2} \qquad (1)$$

$$[Co(NH_3)_4H_2OHCO_3]^{+2} + H_3O^+ \rightleftharpoons [Co(NH_3)_4(H_2O)_2]^{+3} + CO_2 + H_2O \qquad (2)$$

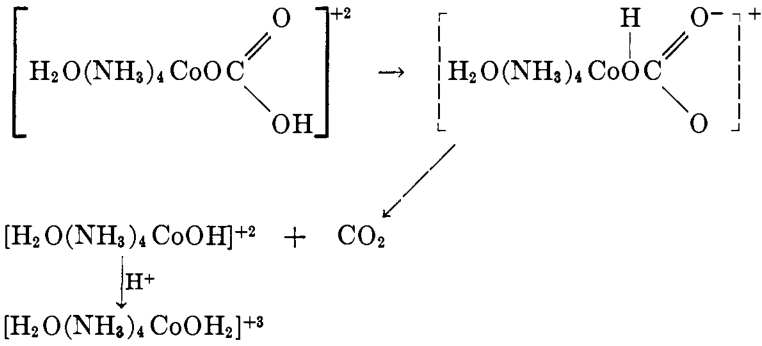
reaction 2 being rate-determining. The activated complex is visualized as the heptacovalent intermediate:



Strank and Harris state that the experimental results are not in accord with the formation of a dissociated entity, $[Co(NH_3)_4H_2O]^{+3}$. It is also of interest that Hunt, Rutenberg, and Taube (92) find that the analogous reaction

$$[Co(NH_3)_5CO_3]^+ + 2H_3O^+ \rightleftharpoons [Co(NH_3)_5H_2O]^{+3} + 2H_2O + CO_2$$

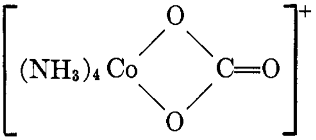
proceeds with at least 99 per cent of the cobalt(III)-oxygen bond remaining intact. Furthermore, the carbon dioxide liberated had not equilibrated with the O^{18}-enriched water used as solvent. The mechanism is therefore said to be of the type observed in the hydrolysis of organic esters (173). On the basis of these results, Harris (85) suggests as an alternative mechanism for the acid decomposition of $[Co(NH_3)_4H_2OHCO_3]^{+2}$ an attack by hydrogen ion on the oxygen atom bonded to the cobalt and carbon atoms. The reaction sequence may be designated as follows:



Similarly, studies on the kinetics of exchange of isotopic carbon between $[Co(NH_3)_5C_2O_4]^+$ and oxalate ion have been reported by Kant and Kohman (114). They find that the total rate, given by

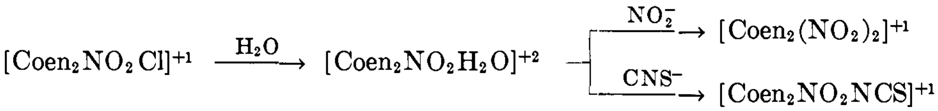
$$R = R_1 + R_2 = k_1[Co(NH_3)_5C_2O_4^+] + k_2[Co(NH_3)_5C_2O_4^+][C_2O_4^{-2}]$$

is independent of ionic strength but increases with increasing concentration of hydrogen ion, thus suggesting that $H_2C_2O_4$ is probably the principal exchanging oxalate species. The rate of exchange of carbonate ion and $[Coen_2CO_3]^+$ has also been investigated (85, 273). Although an appreciable isotope effect was observed during the exchange experiments involving $[Co(NH_3)_4CO_3]^+$, there was no such effect with the corresponding complex $[Coen_2CO_3]^+$. Harris (85) is of the opinion that this difference may be explained on the basis that in aqueous solution the ethylenediamine complex exists as $[Coen_2H_2OCO_3]^{+2}$, where the carbonato group behaves as a monodentate and is therefore similar to HCO_3^-. However, the large isotope effect observed with the tetrammine complex suggests that this ion exists in solution as



so that the carbonato group acts as a bidentate and therefore differs appreciably from HCO_3^-. It would be of interest to check this hypothesis, using the complex ions $[Co(NH_3)_5CO_3]^+$ and $[Coen_2NH_3CO_3]^+$.

A detailed study of the rate of formation of $[Coen_2(NO_2)_2]^{+1}$ and $[Coen_2NO_2NCS]^{+1}$ by the reaction of $[Coen_2NO_2Cl]^{+1}$ with nitrite and thiocyanate ions in aqueous solution has recently been completed (195). It was found that the rate of formation of these complexes is less than the rate of aquation of the chloronitro complex employed. Furthermore, the rate at which the chloronitro complex liberates chloride ion is independent of the nitrite-ion concentration. Finally, the rate of change of the absorption spectrum for the reaction mixture, calculated on the basis of a two-step reaction mechanism, is in good agreement with the experimentally observed changes. Therefore it can be concluded that these reactions proceed by way of acid hydrolysis according to the following reaction scheme:



$$[Coen_2NO_2Cl]^{+1} \xrightarrow{H_2O} [Coen_2NO_2H_2O]^{+2} \begin{cases} \xrightarrow{NO_2^-} [Coen_2(NO_2)_2]^{+1} \\ \xrightarrow{CNS^-} [Coen_2NO_2NCS]^{+1} \end{cases}$$

It would be of interest to investigate reactions of this type in non-aqueous solvents, particularly in solvents that have little or no tendency to coördinate.

III. GEOMETRICAL ISOMERISM

Although the discussion in this review is concerned primarily with the chemistry of geometrical and optical isomers, it is significant that other types of isomerism exist in complex compounds. The different types of isomers have been summarized in table 3, even though they generally are well known.

Numerous complications arise in connection with the study of the stereochemistry of hexacovalent complex compounds. At present one of the most difficult tasks is that which involves the synthesis of a desired geometrical isomer. Since our knowledge of these reactions is still very limited, the usual approach in such a synthesis is largely empirical or, at best, is based on analogy to a supposedly similar system. Unfortunately neither of these approaches is entirely satisfactory, as illustrated, for instance, by the fact that *trans*-$[Coen_2Cl_2]^{+1}$ reacts with aqueous ammonia to yield *cis*-$[Coen_2NH_3Cl]^{+2}$ (241), whereas the same reaction with the analogous propylenediamine complex yields *trans*-$[Copn_2NH_3Cl]^{+2}$ (163). It follows that the configuration of the compound cannot be deduced from its method of preparation alone but must be established by some independent approach. It is not surprising that only the simplest of these complexes have been synthesized and adequately characterized. For this reason the geometrical isomers most intensively studied have been those containing two like or unlike groups which are different from the other four, i.e.,

$$[Ma_4b_2], \quad [Ma_4bc], \quad [M(AA)_2a_2], \quad \text{and} \quad [M(AA)bc]^5$$

Some of the compounds for which all of the theoretically possible geometrical isomers have been isolated are shown in table 4. A limited amount of work has been done with more complicated compounds and some such systems will be described, but in general the discussion will pertain primarily to the simpler and better defined structures.

A. *Synthesis of cis–trans isomers*

Reactions involved in the preparation of complex compounds are of the generalized acid–base type, in which generally a less basic group is replaced by one that is more basic for the particular system involved. These reactions are regularly encountered in the qualitative scheme of cation analysis where, for

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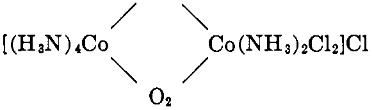
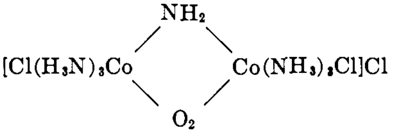
[5] M = central metal atom; a, b, c = monodentate ligand; AA = symmetrical bidentate ligand.

example, a very common observation is the deep blue coloration obtained by the addition of ammonia to an aqueous solution of copper(II) ions. This instantaneous color change results from the replacement of coördinated water by the more basic ammonia. Other, more stable complexes react similarly but often at measurable rates. For instance, upon dissolution of *trans*-$[Coen_2Cl_2]Cl$ in water the solution gradually changes from green to pink as one chloro group is replaced by water to yield the corresponding chloroaquo complex, $[Coen_2H_2OCl]^{+2}$ (111).

TABLE 3

Isomerism in complex compounds (154)

ISOMERISM	EXAMPLE
Geometrical	*cis*- and *trans*-$[Coen_2Cl_2]Cl$
Optical	*d*- and *l*-$[Coen_3]Cl_3$
Ionization	$[Coen_2ClBr]Cl$ and $[Coen_2Cl_2]Br$
Linkage*	$[Co(NH_3)_5ONO](NO_3)_2$ and $[Co(NH_3)_5NO_2](NO_3)_2$
Coördination	$[Coen_3][Cr(C_2O_4)_3]$ and $[Cren_3][Co(C_2O_4)_3]$
Polymerization	$[Pt(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_2Cl_2]$
Coördination position	 and 
Miscellaneous†	$[Co(NH_3)_5ClO_3]Br_2$ and $[Co(NH_3)_5BrO_3]ClBr$ $[Coen_2$(*i*-propylamine)$Cl]Cl_2$ and $[Coen_2$(*n*-propylamine)$Cl]Cl_2$ $[Pt^{IV}(NH_3)_2(SO_3)_2]$ and $[Pt^{II}(NH_3)_2S_2O_6]$ $Ce^{IV}[Fe^{II}(CN)_6]$ and $Ce^{III}[Fe^{III}(CN)_6]$

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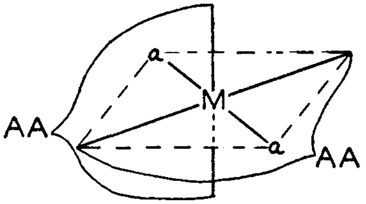
* There appears to be some question as to the existence of the nitrito complex $[Co(NH_3)_5ONO](NO_3)_2$ (3, 125).

† The examples given of platinum(II) and platinum(IV) complexes and of cerium(III) and cerium(IV) salts are not known but merely hypothetical.

Coördination compounds in which all of the ligands attached to the central atom are the same, $[Ma_6]$ or $[M(AA)_3]$, can in general be prepared very readily by the reaction of the metal ion with an excess of the donor material. However, no steadfast rule can be made for the synthesis of complexes containing two or more different ligands. Even greater difficulties are usually encountered in attempts to obtain both the *cis* and the *trans* isomers of a particular complex. A flow-sheet for the synthesis of some geometrical isomers of cobalt(III) complexes illustrates some of the approaches to this problem (see table 5).

Except for the interconversions of *cis*- and *trans*-$[Coen_2Cl_2]^{+2}$ and the reaction of *cis*-$[Coen_2(H_2O_2)]^{+3}$ with alkali to yield *trans*-$[Coen_2H_2OOH]^{+2}$, the reactions outlined in table 5 all proceed with retention of configuration. That rearrangements do occur during the reaction of complex ions constitutes a sizable portion of the discussion in this review (page 485).

A common technique for the preparation of a *cis* isomer involves the replacement of a bidentate group with two monodentate ligands and is of course successful only if there is no rearrangement to the *trans* configuration. This principle was first recognized by Werner (226), who compared chelation to the formation of maleic but not fumaric anhydride. He also pointed to the similarity in the behavior of metal and carbon atoms in forming five- and six-membered rings more readily than larger rings. That a bidentate group cannot reach across opposite positions in a complex is readily apparent from a consideration of atomic dimensions. Tress (209) has made an interesting stereochemical observation which supports the well-established fact that a bidentate group must span adjacent positions. He points out that the existence of *cis* and *trans* isomers of [M(AA)$_2$a$_2$] complexes is proof that groups AA span adjacent positions, since if these were attached at *trans* positions there would exist only a racemate.



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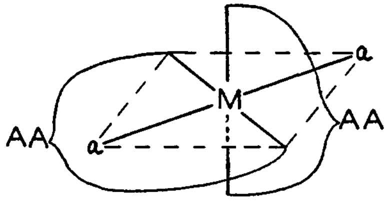

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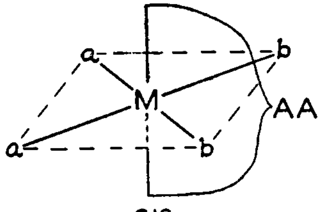
Furthermore, if AA did span *trans* positions and were free to rotate past groups a and b in the complex [MAAa$_2$b$_2$], it would exist only in two optically inactive forms.



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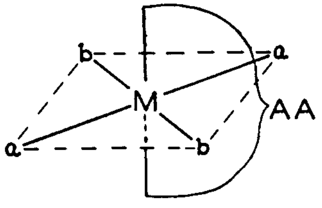

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Since complexes of this type have been shown to be optically active, the bidentate group must span *cis* positions.

In this connection it should be mentioned that attempts have been made to produce large chelate rings with coördination across opposite positions. For example, polymethylenediamines have been employed, but these reacted with metal ions to yield oils believed to be polymeric cations resulting from the coördination of the two nitrogens in the same diamine to different central atoms (172, 210). However, recently Pfeiffer (170) has succeeded in preparing seven- and even nine-membered chelate rings by the reaction of polymethyl-

TABLE 4

*Geometrical isomers**†

Chromium(III)	
$[Cren_2(H_2O)_2]^{+3}$ (169)	$[Cren_2H_2O(OH)]^{+2}$ (169)
$[Cren_2Br_2]^{+}$ (168)	$[Cren_2Cl_2]^{+}$ (232)
$[Cren_2(NCS)_2]^{+}$ (168)	$[Cr(H_2O)_2(C_2O_4)_2]^{-}$ (250)
Cobalt(III)	
$[Coen_2(NH_3)_2]^{+3}$ (268)	$[Coen_2NH_3H_2O]^{+3}$ (230, 238)
$[Coen_2(H_2O)_2]^{+3}$ (261)	$[Co(NH_3)_3(H_2O)_3]^{+3}$ (145)
$[Coen_2NH_3Br]^{+2}$ (266)	$[Coen_2NH_3Cl]^{+2}$ (262)
$[Coen_2NH_3F]^{+2}$ (188)	$[Coen_2NH_3NCS]^{+2}$ (5)
$[Coen_2NH_3NO_3]^{+2}$ (242)	$[Coen_2NH_3NO_2]^{+2}$ (271)
$[Coen_2(CH_2{=}CHCH_2NH_2)Cl]^{+2}$ (150)	$[Coen_2(C_6H_5CH_2NH_2)Cl]^{+2}$ (151)
$[Coen_2H_2O(OH)]^{+2}$ (228)	$[Coen_2H_2OCl]^{+2}$ (70, 152)
$[Coen_2H_2ONO_2]^{+2}$ (233)	$[Coen_2H_2ONCS]^{+2}$ (236)
$[Coen_2F_2]^{+}$ (56, 188)	$[Coen_2Cl_2]^{+}$ (111, 235)
$[Coen_2Br_2]^{+}$ (260)	$[Coen_2(ONO)_2]^{+}$ (227)
$[Coen_2(NO_2)_2]^{+}$ (231)	$[Coen_2(NCS)_2]^{+}$ (258)
$[Coen_2OHCl]^{+}$ (70, 152)	$[Coen_2NO_2Cl]^{+}$ (234)
$[Coen_2ClBr]^{+}$ (270)	$[Coen_2NCSCl]^{+}$ (217)
$[Coen_2NCSBr]^{+}$ (240)	$[Coen_2OHNCS]^{+}$ (239)
$[Coen_2NCSNO_2]^{+}$ (271)	$[Coenpn(NO_2)_2]^{+}$ (256)
$[Coen(NH_3)_2Cl_2]^{+}$ (13)	$[Copn_2(NO_2)_2]^{+}$ (93, 221)
$[Copn_2Cl_2]^{+}$ (259)	$[Cocptdin_2Cl_2]^{+}$ (104)
$[Cobn_2Cl_2]^{+}$ (41a)	$[Costien_2Cl_2]^{+}$ (272)
$[Co(NH_3)_4Cl_2]^{+}$ (75)	$[Co(NH_3)_4(NO_2)_2]^{+}$ (112)
$[Co(NH_2CH_2COO)_3]$ (128)	$[Co(CH_3CH(NH_2)COO)_3]$ (127, 130)
$[Co(NH_3)_2C_2O_4(NO_2)_2]^{-}$ (183)	$[Co(NH_3)_4(SO_3)_2]^{-}$ (87)
Iridium(III)	
$[Irpy_3Cl_3]$ (52)	$[Ir(C_2H_5SC_2H_5)_3Cl_3]$ (178)
$[Irpy_2Cl_4]^{-}$ (47)	$[Irpy_2OHCl_3]^{-}$ (52)
$[Irpy_2NO_3Cl_3]^{-}$ (52)	$[Irpy_2(C_2O_4)_4]^{-}$ (48)
$[Ir(C_2O_4)_2Cl_2]^{-3}$ (46)	

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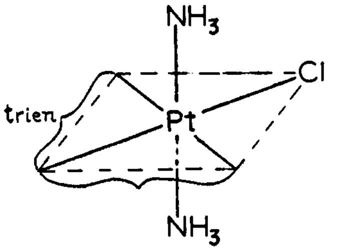
* Table 4 contains some hexacovalent complexes for which all of the theoretically possible geometrical isomers have been reported. Although most of the examples reported are listed, the author makes no claim as to the completeness of this table.

† The following symbols are used in tables 4 and 11 as well as in the text:
$BigH^{+}$ = biguanidinium ion,
bn = 2,3-diaminobutane,
CH_3-ophen = 5-methyl-1,10-phenanthroline,
chxn = *trans*-1,2-diaminocyclohexane,
cptdin = *trans*-1,2-diaminocyclopentane,
dipy = 2,2′-bipyridine,
DMG = dimethylglyoxime (ion),
en = ethylenediamine,
ophen = 1,10-phenanthroline,
pn = propylenediamine,
py = pyridine, and
tart = tartrate ion.

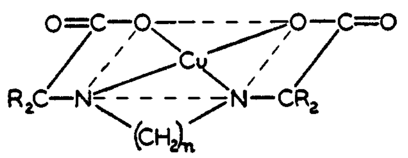
TABLE 4 (*Continued*)

Platinum(IV),(II)	
$[Pt(CH_3CN)_2(NH_3)_4]^{+2}$ (211)	$[PtenNH_3NO_2Cl_2]^+$ (40)
$[Pt(NH_3)_2Br_4]$ (27)	$[Pt(NH_3)_2Cl_4]$ (42)
$[Pt(NH_3)_2I_4]$ (110)	$[Ptpy_2Cl_4]$ (113)
$[Pt(NH_3)_2(NO_2)_2Br_2]$ (42)	$[Pt(NH_3)_2(NO_2)_2Cl_2]$ (42)
Rhodium(III)	
$[Rhpy_2H_2OCl_3]$ (49)	$[Rhpy_2Cl_4]^-$ (49)
$[Rhpy_2OHCl_3]^-$ (49)	$[Rhpy_2NO_3Cl_3]^-$ (49)
$[Rh(C_2O_4)_2Cl_2]^{-3}$ (50)	
Ruthenium(III)	
$[Ru(NH_3)_4Cl_2]^+$ (77)	$[Ru(NH_3)_4Br_2]$ (76)

enediamines with divalent metal ions in alcohol solutions. A new approach (146) to this problem was made by using 2-chloro-1,6-diammine-3,4,5-diethylenetriamine platinum(IV) ion, $[Pt\ trien\ (NH_3)_2Cl]^{+3}$.



Removal of the middle nitrogen from the coördination sphere of the tridentate group would result in an eight-membered ring spanning *trans* positions. This might be achieved either by making use of the tetracovalency of platinum(II) or by the replacement of one group for another in the coördination sphere. Both of these techniques have been successfully employed by Chernyaev and Fedorova (41) to prepare monodentate compounds of ethylenediamine. However, Mattern (146) was unable to obtain conclusive evidence that the middle amine of the tridentate was displaced to leave the end amines spanning opposite positions. He suggests that perhaps a tridentate with a poorer coördinating group in the middle may give the desired results. It is claimed that a large ring has been formed across *trans* positions of the planar tetracovalent copper(II) ion. Schlesinger (185) prepared complexes of copper(II) with numerous amino acids and assigned the following structures:



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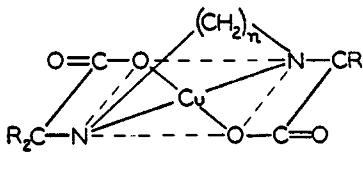

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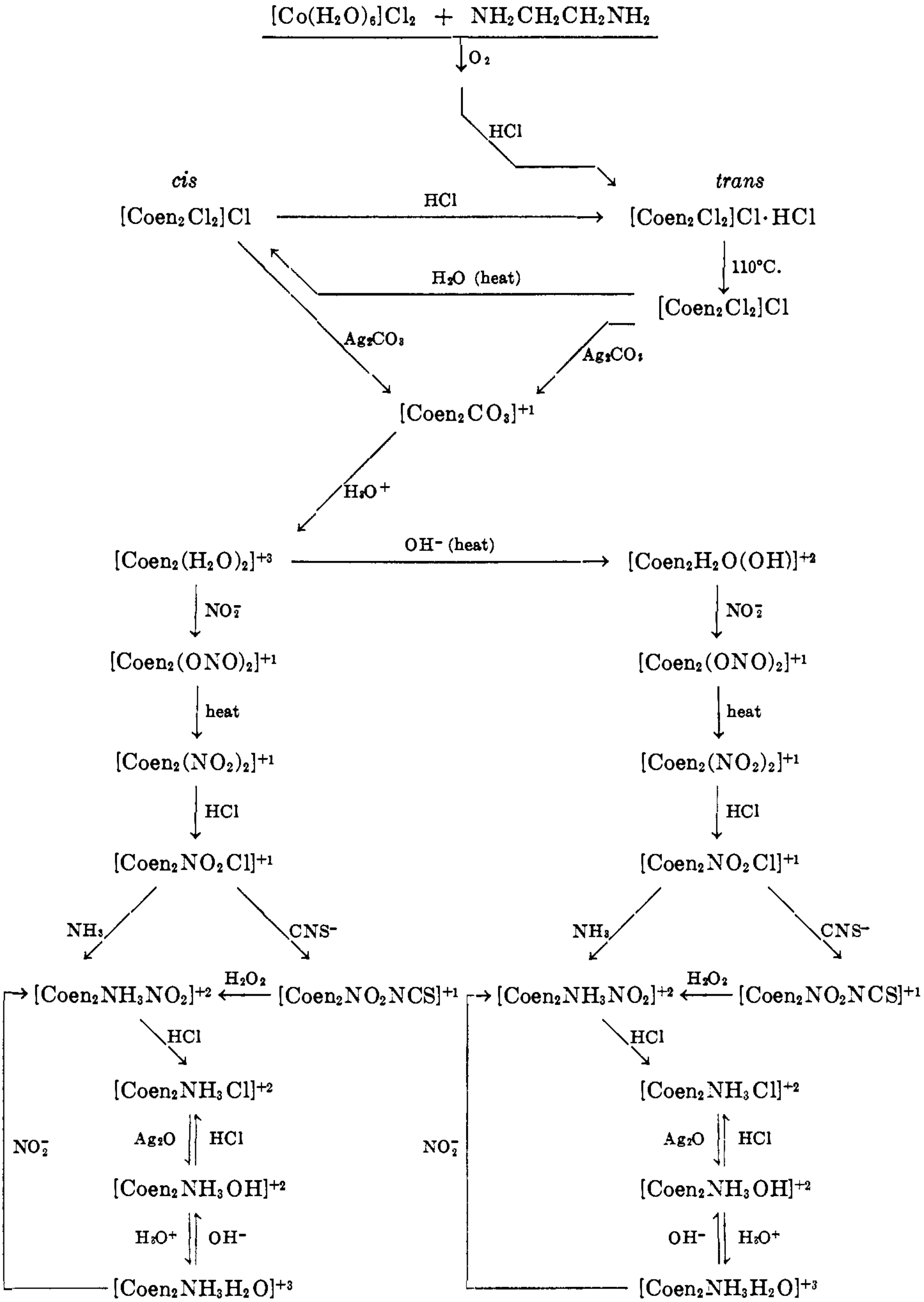
TABLE 5

*Flow-sheet for the preparation of geometrical isomers of some cobalt(III) complexes**



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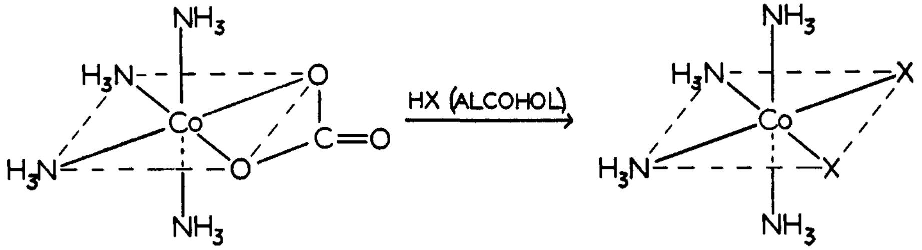
* References for the synthesis of specific compounds are available in table 4.

For $n = 2$ or 3 and for $n = 10$ only one isomer was formed but for intermediate values of n, two modifications were obtained; these were believed to be *cis* and *trans* forms. Schlesinger believed that the blue complex obtained when $n = 2$ or 3 is the *cis* isomer, whereas the violet form with $n = 10$ is the *trans* complex. Reihlen (180) has challenged this interpretation and is of the opinion that the existence of the two forms is perhaps due to the methylene groups lying "inside" or "outside" the coördinated nitrogen atoms.

Since bidentate groups span only adjacent positions, the replacement of such groups is generally used in the synthesis of *cis* isomers. For example, a very common starting material for the preparation of *cis*-diacidotetrammincobalt(III) complexes is carbonatotetramminecobalt(III) nitrate. This red salt can be readily obtained by air oxidation of cobalt(II) nitrate hexahydrate in the presence of ammonium carbonate (219). The carbonato radical does not precipitate upon the addition of barium chloride but carbon dioxide is liberated when acid is added.

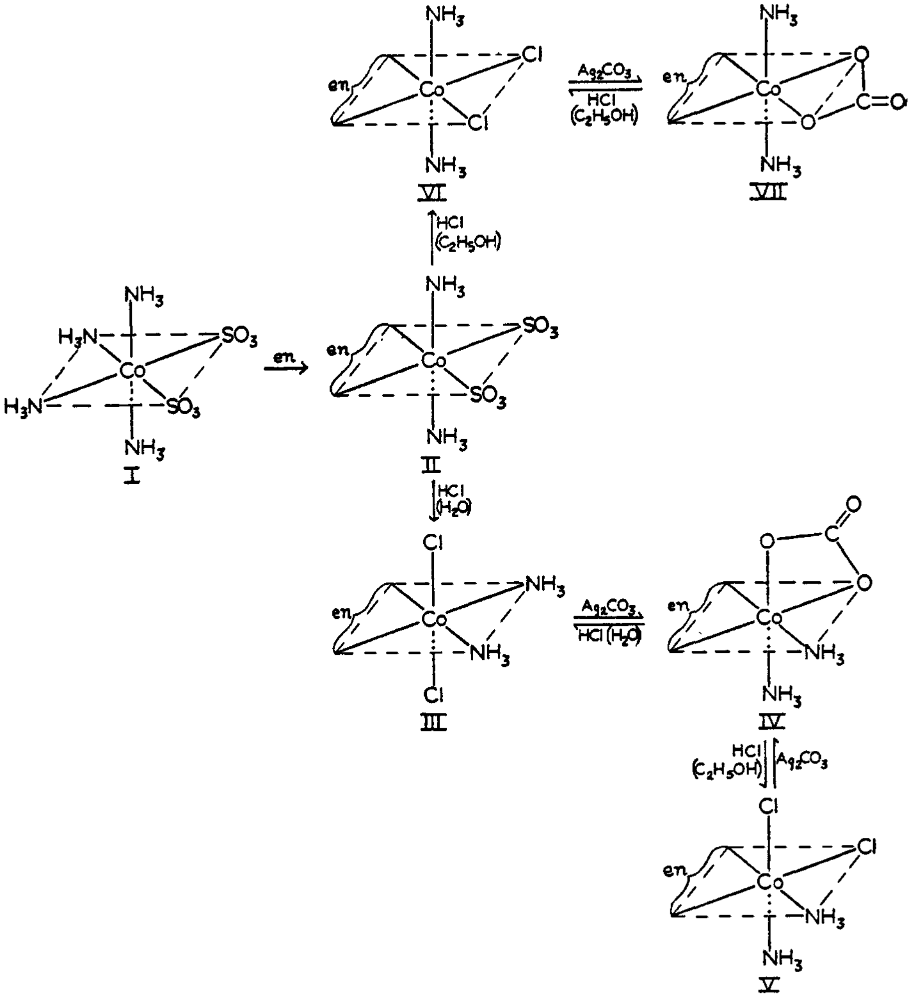


On the assumption that no rearrangement takes place during this reaction, the resulting product has a *cis* configuration. In these reactions rearrangement to the *trans* salt is kept at a minimum if the solid complex is allowed to react with an alcoholic solution of the desired acid. Bailar and Peppard (13) have successfully employed this technique for the preparation of the three stereoisomers of dichlorodiammine(ethylenediamine)cobalt(III) ion, $[Coen(NH_3)_2Cl_2]^{+1}$. The reaction of complex II (shown in table 6) with aqueous hydrochloric acid results in rearrangement to the *trans*-dichloro product (III), whereas when this same reaction is carried out in alcohol there is a retention of configuration and the *cis*-dichloro complex (VI) is obtained. Furthermore, treatment of III with silver carbonate results in the formation of the carbanato complex IV, which necessitates a rearrangement to allow the carbonate ion to span adjacent positions. Complex IV, if allowed to react with aqueous hydrochloric acid, yields the original *trans*-dichloro compound (III), but with alcoholic hydrogen chloride there is retention of configuration and the *cis*-dichloro (V) is obtained.

It should also be mentioned that the first reaction shown in table 6, where the two ammonia molecules opposite the sulfito groups have been preferentially replaced by a molecule of ethylenediamine, has been attributed to a phenomenon known as the "*trans* effect." Quagliano and Schubert (177) have recently written an excellent review on this effect, which was first proposed in 1926 by Chernyaev (39). The *trans* effect stipulates that the bond holding a group *trans* to an electronegative or other labilizing group is weakened. Werner (225) had employed this phenomenon to determine the configuration of platinum(II) complexes but apparently did not recognize its generality. A considerable amount of work has been reported, primarily by Russian chemists, in which the *trans* effect was utilized for the synthesis of specific platinum(II) complexes. Although it has been used successfully in the synthesis of planar tetracovalent compounds, no systematic attempt has been made to see whether it might be extended to the preparation of hexacovalent complexes. However such a study would be of considerable interest, since it was recently shown by Yatsimirskiĭ and Pankova

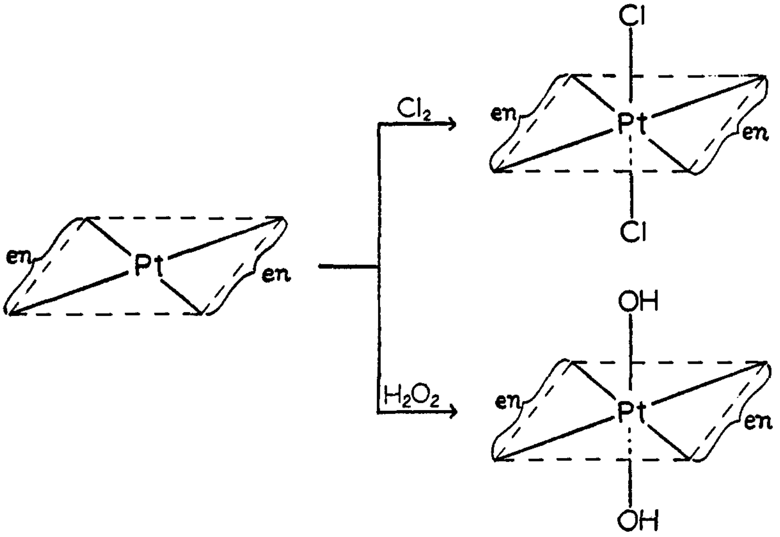
TABLE 6

Synthesis of geometrical isomers of $[Coen(NH_3)_2Cl_2]^{+1}$

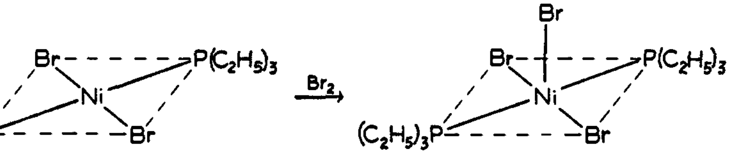


(274), who measured the heats of formation of numerous cobalt(III) complexes, that a *trans* effect seems to exist in these compounds.

With one exception the synthesis of complexes with a *trans* structure is still entirely empirical. The exception has to do with an increase in the oxidation state of the central metal atom accompanied by an increase in coördination number. There are several examples of such a reaction in which a planar tetracovalent complex of platinum(II) is oxidized to a hexacovalent platinum(IV) compound (18, 121).



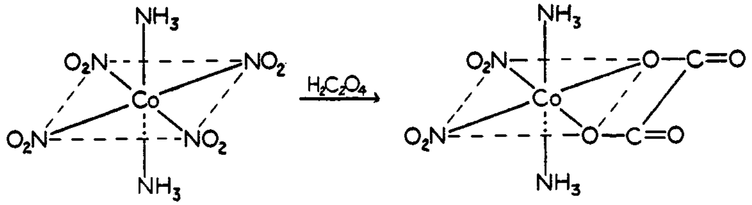
Unfortunately, this procedure for the preparation of *trans* complexes is applicable only to systems that undergo the changes in oxidation states and coördination number outlined here for platinum. Furthermore, it may be that the *trans* configuration is obtained with platinum complexes, as these generally react with retention of configuration, whereas a similar scheme of reactions on some other system might well result in rearrangement to the *cis* product. On the basis of the limited amount of information available it is impossible to attempt any broad generalizations on the nature of these reactions. Jensen (106, 107) has reported a reaction in which nickel(II) was oxidized to nickel(III) with an accompanying increase in coördination number from 4 to 5:



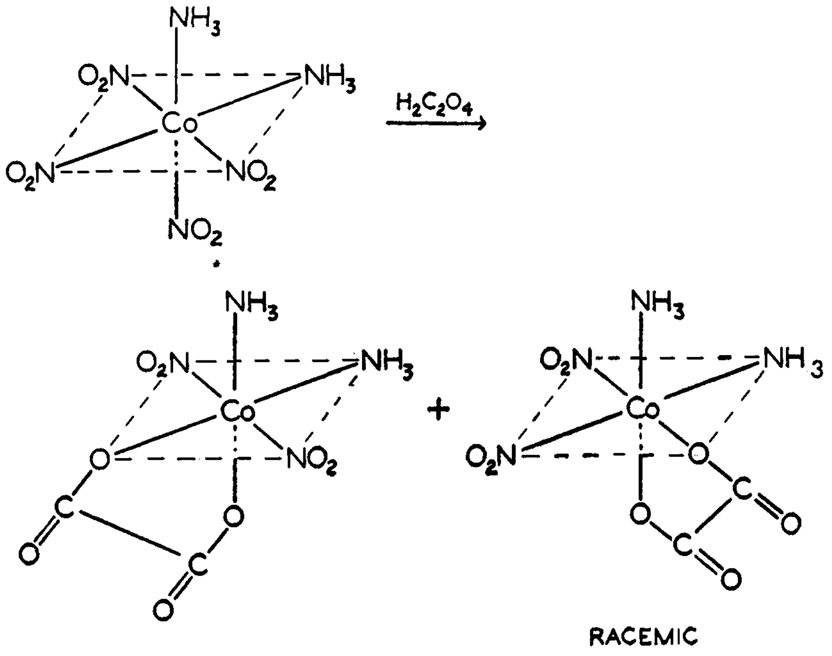
It is of interest to note that the groups which were originally planar maintain their positions and the additional bromo group lies immediately above the plane. This is analogous to the first step in the transformation of [Pten$_2$]$^{+2}$ to *trans*-[Pten$_2$Cl$_2$]$^{+2}$ or [Pten$_2$(OH)$_2$]$^{+2}$.

B. The determination of the configuration of cis–trans isomers

The configuration of complex compounds is usually not known from the method of preparation. Consequently, numerous techniques have been utilized to establish the spatial arrangement of the atoms in a complex ion. The procedure which makes use of a reaction with a bidentate molecule has not been as successfully applied with hexacovalent complexes (204) as it has with the planar tetracovalent (80, 81) compounds. This may be attributed to the fact that hexacovalent compounds rearrange more readily during reaction than do the planar tetracovalent complexes. A good illustration of such a difficulty is found in the work of Thomas (204) on the structure of Erdmann's salt, $NH_4[Co(NH_3)_2(NO_2)_4]$. Thomas allowed the complex to react with oxalic acid in equal molar ratios and reasoned that if the complex had a *trans* configuration only one product would result;



a *cis* configuration would be expected to yield two products, one of which should be optically active.



Thomas isolated two products from this reaction, one of which he was able to resolve. He, therefore, concluded that Erdmann's salt must be the *cis* isomer. Wells (223) has since made a complete x-ray analysis of the silver salt of this anion, $Ag[Co(NH_3)_2(NO_2)_4]$, and has found that the ammonia groups are in *trans* positions. He is of the opinion that the *trans* complex must rearrange during its reaction with oxalic acid to yield the two products obtained by Thomas. An alternative explanation perhaps may be that when isolated as the silver salt the complex has a *trans* configuration, whereas the ammonium salt obtained from an analogous reaction mixture is indeed the *cis* form (page 493).

Other chemical approaches not involving a bidentate molecule have been used, but these have not been entirely successful. For example, the *cis* and *trans* isomers of $[Co(NH_3)_4(NO_2)_2]^{+1}$ react differently with boiling hydrochloric acid (23) and can be readily distinguished by this reaction. Dissolution of the *cis* isomer yields a purple solution from which green cystals of the *trans*-dichloro complex slowly separate, whereas with the *trans* isomer an immediate red precipitate of the *trans*-chloronitro compound is formed. The corresponding ethylenediamine isomers, $[Coen_2(NO_2)_2]^{+1}$, undergo the same reactions (227). On the basis of this reaction with hydrochloric acid Hurlimann (93) assigned a *cis* configuration to the complex $[Co(l\text{-pn})_2(NO_2)_2]Br$, obtained from the reaction of $[Co(NH_3)_3(NO_2)_3]$ and *l*-propylenediamine. O'Brien, McReynolds, and Bailar (163) have shown, by means of rotatory dispersion curves, that the salt which Hurlimann (93) isolated was in reality a mixture of *cis* and *trans* isomers and furthermore that *trans*-$[Co(l\text{-pn})_2(NO_2)_2]^+$ does not form a red precipitate when boiled with concentrated hydrochloric acid.

Proof of structure of hexacovalent complexes on the basis of chemical reactions alone is therefore usually open to some question. However, the *cis* isomers of certain types of complexes ($[M(AA)_2a_2]$, $[M(AA)_2ab]$, $[MAAa_2b_2]$, etc.) are capable of being resolved into optically active antipodes and the resolution of such a compound is definite proof of a *cis* structure. This procedure has been used more than any other to establish the configuration of these compounds. When an optically active ligand is attached to the central metal atom, the resulting complex is optically active regardless of geometrical configuration. In such a case the *cis* and *trans* isomers can be distinguished only if the optical rotation is determined at several different wave lengths (163). The *cis* isomer will give an anomalous dispersion curve, while the curve for the *trans* form will resemble that for the optically active ligand.

Two different physicochemical methods have been used to determine the geometrical configurations of hexacovalent complexes. These utilize x-ray and absorption spectra. The laborious process involved in an x-ray analysis has no doubt been one reason why the method has not been used more extensively for this purpose, even though it is capable of giving the definite spatial arrangements of the atoms. In some instances the colors of geometrical isomers are greatly different, as is true with *violeo*(*cis*) and *praseo*(*trans*) dihalotetrammine cobalt (III) ions. The absorption spectra of these complexes have been extensively studied, in both the visible and the ultraviolet wave-length regions. As early as 1915, Shibata (189) made numerous generalizations with regard to these spectra. One of his statements was that "stereoisomers in general absorb differently." He also noticed that cobalt(III) complexes always have two absorption maxima,—one in the visible and the other in the near ultraviolet. It was observed that in addition to these two absorption bands *trans*-$[Co(NH_3)_4(NO_2)_2]^{+1}$ has another band in the near ultraviolet, which Shibata referred to as the "third band" and which he believed to be characteristic of negative ligands in *trans* positions. The work on this characteristic "third band" has been extended by Tsuchida (215), who has also given a theoretical interpretation for each of the absorption maxima. However, some question has been raised (15, 16) as to the complete reliability of the appearance of a third band for the determination of geometrical structures. Sueda (196) has assigned configurations to cobalt(III) and chromium(III) complexes on the basis of relative absorptions in the near ultraviolet region. Recent studies (16, 192) further substantiate the fact that geometrical isomers can generally be distinguished by means of a comparison of their absorption spectra. It is interesting that these studies are now being extended into the infrared region (125, 176).

Other physicochemical techniques, such as Raman spectra, electron diffraction, dipole moments, etc., have not been used to distinguish between geometrical isomers of hexacovalent coördination compounds. Many of these techniques would not be readily applicable to compounds of this type, which usually are highly colored, non-volatile, and soluble only in the more polar solvents. Measurement of dipole moments of the isomers should, however, furnish a direct approach to their configurations, as the unsymmetrical *cis* form would have a large moment as compared to that of the symmetrical *trans* isomer. It is difficult to determine dipole moments accurately in an aqueous medium, but recently two indirect approaches have been made to this problem, based on the electrical symmetry of the geometrical isomers. Holtzclaw (88) has attempted to find a method of distinguishing between *cis*- and *trans*-$[Co(NH_3)_4(NO_2)_2]^{+1}$ by a comparison of their half-wave potentials. The *cis* isomer was reduced at a lower potential than the *trans* under all conditions tried. Holtzclaw suggests two factors which may account for the greater ease of reduction of the *cis* isomer: (*1*) The unsymmetrical structure of the *cis* isomer affords the possibility of greater orientation in the field around the dropping mercury electrode and (*2*) the greater thermodynamic stability of the *trans* isomer as compared with the corresponding *cis* isomer. These researches have been extended to other complex systems and in every case the *cis* isomer was found to be more readily reduced than the corresponding *trans* form (89). A recent report by King and Walters (116) reveals that geometrical isomers can be conveniently separated with the aid of cation-exchange resins. The elution curve obtained for a mixture of *cis*- and *trans*-$[Co(NH_3)_4(NO_2)_2]^+$ salts shows that the *trans* isomer is more easily removed from the resin than is the corresponding *cis* ion. This has been the case with all of the complexes studied to date (115) and would appear to be attributed to the larger dipole moment of the *cis* complex. Additional studies are required to establish the validity of this generalization. It would also be of interest to investigate the behavior of anionic isomers on anion-exchange resins.

C. Substitution reactions of cis–trans isomers

There are numerous examples of substitution reactions in geometrical isomers of hexacovalent complexes. Since most of these reactions have been reported for cobalt(III) complexes, the discussion that follows will deal primarily with compounds of cobalt(III). However, it may be mentioned that the general considerations are expected to be analogous with any hexacovalent complex.

In 1912 Werner (237) gave a detailed account of some observations made on several pairs of *cis*- and *trans*-cobalt(III) complexes. His qualitative data were tabulated to illustrate the ratio of *cis* and *trans* products obtained from the reaction of either a *cis* or a *trans* isomer with a particular reagent. In his attempt to find a correlation among these reactions, Werner was originally of the opinion that they may be of three different types. Thus it was suggested that they be considered as follows:

(1) Addition reactions

These reactions include the replacement of a negative group by a neutral group such as ammonia or water.

$$[\mathrm{Coen_2NCSBr}]^{+1} + \mathrm{NH_3} \rightarrow [\mathrm{Coen_2NH_3NCS}]^{+2} + \mathrm{Br}^-$$

$$[\mathrm{Coen_2Cl_2}]^{+1} + \mathrm{H_2O} \rightarrow [\mathrm{Coen_2H_2OCl}]^{+2} + \mathrm{Cl}^-$$

(2) Displacement reactions

This category is the reverse of (1), or the replacement of a neutral molecule by a negative ligand.

$$[\mathrm{Coen_2NH_3Cl}](\mathrm{NO_2})_2 \rightarrow [\mathrm{Coen_2NO_2Cl}]\mathrm{NO_2} + \mathrm{NH_3}$$

$$[\mathrm{Coen_2H_2OCl}]\mathrm{Cl_2} \rightarrow [\mathrm{Coen_2Cl_2}]\mathrm{Cl} + \mathrm{H_2O}$$

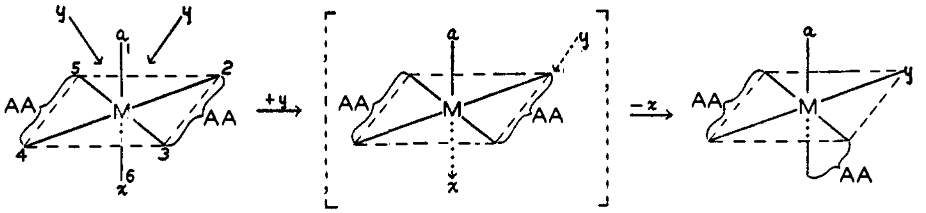
(3) Substitution reactions

Reactions listed here involve the replacement of a negative group by a different negative group.

$$[\mathrm{Coen_2Cl_2}]^{+1} + \mathrm{NO_2^-} \rightarrow [\mathrm{Coen_2NO_2Cl}]^+ + \mathrm{Cl}^-$$

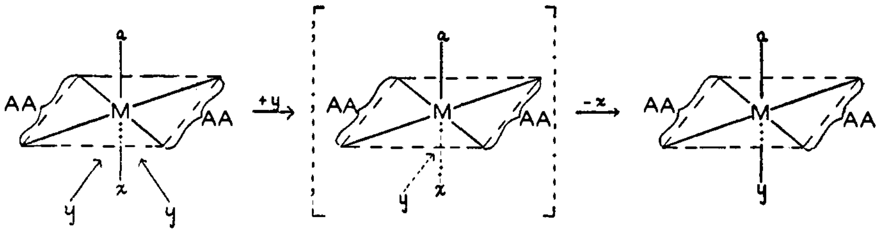
Werner later stated that on the basis of the available data, it appeared that the same phenomena were involved in all of the reactions and that it was perhaps unwise to think of them as separate types. He then suggested that since in several instances the reactions take place with retention of configuration, the rearrangements that occur may be attributed to the fact that the more stable isomer will be formed in the larger concentration. However, this supposition was likewise later abandoned, as it did not appear to be in accord with the experimental observations. For instance, the reaction of liquid ammonia with *trans*-$[\mathrm{Coen_2NCSCl}]^{+1}$ yields $[\mathrm{Coen_2NH_3NCS}]^{+2}$ in a ratio of two parts of the *cis* isomer to one of the *trans*. This suggests that the *cis* isomer is more stable than the *trans* and that this accounts for the partial rearrangement. On this basis it would be anticipated that the reaction of *cis*-$[\mathrm{Coen_2NCSCl}]^{+1}$ under the same conditions would yield exclusively *cis*-$[\mathrm{Coen_2NH_3NCS}]^{+2}$, but experiments reveal that the product is a 1:1 mixture of the *cis* and *trans* isomers. Furthermore, the formation of two parts *trans*- and one part *cis*-$[\mathrm{Coen_2NO_2Cl}]^{+}$ by the reaction of *trans*-$[\mathrm{Coen_2Cl_2}]^{+}$ with one equivalent of nitrite ion would suggest that *cis*-$[\mathrm{Coen_2NO_2Cl}]^{+}$ is more stable than the *trans* isomer. However, it is known that when a solution of *cis*-$[\mathrm{Coen_2NO_2Cl}]^{+}$ is evaporated to dryness, the salt is almost quantitatively converted to the *trans* isomer. Moreover, a solution of *cis*-$[\mathrm{Coen_2NH_3Cl}]^{+}$ containing one equivalent of sodium nitrite, when concentrated to dryness, yields primarily *trans*-$[\mathrm{Coen_2NO_2Cl}]^{+}$. Results of this type indicate that rearrangements do not occur as a consequence of the relative stability of the isomers in question.

Werner finally accounted for the stereochemical changes by assuming that the central atom or entire complex, although completely coördinated, may still exert a directive influence upon the group entering the complex. In his discussion the ligands directly attached to the central atom were referred to as members of the first coördination sphere; it was suggested that a second sphere of ions or molecules surrounds the complex. The orientation of the groups in this second sphere is dependent upon the group as well as on the nature of the complex. If the incoming group in the second sphere is directed to a position opposite the group being replaced (outgoing), the configuration of the reaction product will differ from that of the starting material:



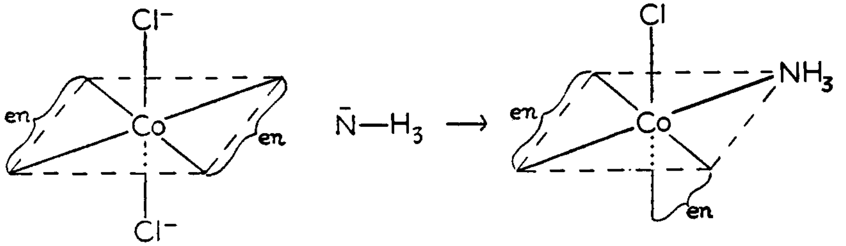
Here it is seen that group y will become attached to the central atom at a position other than that being vacated by x. If y occupies a position in the plane perpendicular to the paper (2, 3, 4, or 5) a rearrangement with one end of the bidentate group moving down to occupy position 6 can be visualized. However, if y stays at 1, then group a will move in the plane perpendicular to the paper and the bidentate group will again shift to the vacated position. In other words, the *trans* isomer will yield a *cis* product.

On the other hand, Werner was of the opinion that if the incoming group is fixed in the second coördination sphere in the vicinity of the group being replaced, the configuration of the reaction product is the same as that of the reactant.



Why then do reactions yield a mixture of *cis* and *trans* products? Werner was of the opinion that in some instances the orientation of the incoming group in the second sphere was not well defined, so that an isomeric mixture of the product might be expected. On the basis of this interpretation Werner concluded that there was no obvious relation between the position occupied by the incoming group and that vacated by the group being replaced.

It has also been suggested (144) that the charge distribution in the complex is an important factor with regard to rearrangements during substitution reactions. For example, the reaction of *trans*-$[Coen_2Cl_2]^+$ with ammonia to yield *cis*-$[Coen_2NH_3Cl]^{+2}$ has been explained on the basis that the negative dipole of the ammonia molecule will approach the complex at a position as far removed from the negative chloro groups as possible.

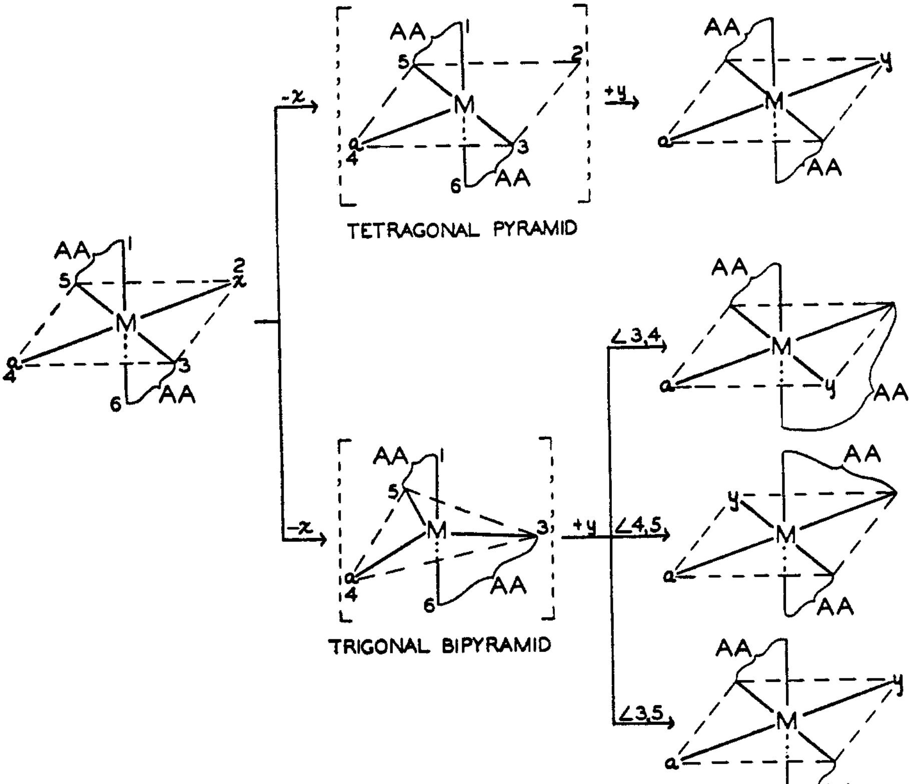


Hence the approach of the ammonia will be from a position perpendicular to Cl—Co—Cl and the complex must rearrange in such a way as to yield a *cis* product. Although such factors may be important, it should be kept in mind that they cannot be the only parameter to be considered. In such a case this same argument would lead to the conclusion that *cis*-$[Coen_2Cl_2]^+$ would react with ammonia to yield *trans*-$[Coen_2NH_3Cl]^{+2}$. However, the product of this reaction is likewise the *cis* isomer. Furthermore it is known that the analogous propylenediamine compound *trans*-$[Copn_2Cl_2]^+$ yields *cis*-$[Copn_2NH_3Cl]^{+2}$ (163). Drew and Pratt (53) had still another suggestion, according to which they proposed to account for rearrangements in complexes of the type $[M(AA)_2a_2]$ on the basis that one of the chelate rings is opened and then reclosed. That this mechanism is not tenable has been rather elegantly demonstrated by Ettle and Johnson (68) (page 493).

Substitution reactions with tetrahedral carbon have been shown to progress essentially by either S_N1 (ionization) or S_N2 (displacement) mechanisms (181) and recently Swain (198) has extended this to include a push-pull mechanism. An attempt has been made (17, 20) to apply much the same approach to the octahedral structure. It was suggested that the *dissociation* (S_N1) *process* would yield a pentacovalent intermediate with either a tetragonal pyramid or a trigonal bipyramid structure. As indicated in table 7, if it is assumed that the incoming group will approach the activated complex at the most accessible position (position of largest angle) in the *trans* complex $[M(AA)_2ax]$, then some estimate of the probable configuration of the reaction product can be made. If the intermediate structure is a tetragonal pyramid, then the approach of y perpendicular to the plane 1,3,6,5 will yield exclusively a *trans* product. The trigonal bipyramid configuration possesses three 120° angles; a *cis* product is obtained if y approaches at either ∠3,4 or ∠4,5, but the *trans* isomer results from an approach at ∠3,5. The same scheme has been used for the analogous *cis* isomer. The *displacement* (S_N2) *process* has been considered to give a heptacovalent

TABLE 7

Dissociation process (S_N1) *for trans*-$[M(AA)_2ax]$



intermediate, probably of pentagonal bipyramid structure. The diagrams in table 8 show expected products for the reaction of *trans*-[M(AA)$_2$ax] depending on whether the incoming group approaches from the front or the rear of the complex. If the rear is defined as the side of plane 1,3,6,5, that is, adjacent to group *a*, then the approach of *y* from this side will yield a *cis* product, whereas approach from the front or the side adjacent to *x* will give rise to a *trans* product.

TABLE 8

Displacement (S_N2) *process for trans*-[M(AA)$_2$ax]

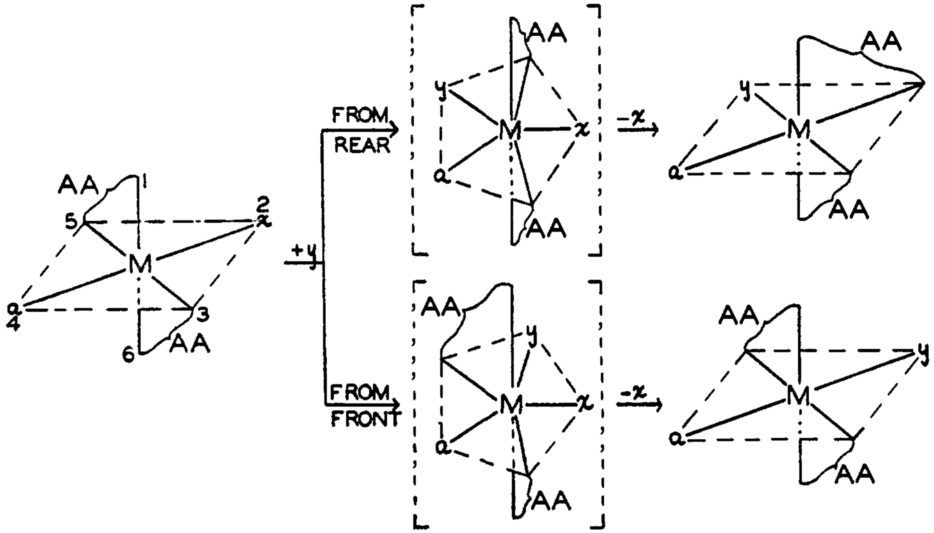


TABLE 9

Relative amounts of geometrical isomers anticipated on the basis of various reaction mechanisms for substitutions in octahedral complexes of the type [M(AA)$_2$ax]

[M(AA)$_2$ax]	DISSOCIATION (S_N1)				DISPLACEMENT (S_N2)			
	Tetragonal pyramid		Trigonal bipyramid		Rear		Front	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Trans................	0	100	66.6	33.3	100	0	0	100
Cis...................	100	0	66.6	33.3	66.6	33.3	100	0

In the same way estimates were made as to the probable reaction of the analogous *cis* isomer. A summary of the structures anticipated on the basis of these reaction processes applied to the octahedral complex [M(AA)$_2$ax] is given in table 9. It should be remembered that with the reaction paths designated to yield 66.6 per cent *cis* and 33.3 per cent *trans* products, this is only a statistical estimate based upon the different plausible approaches of the incoming group to the central atom. However, it is to be expected that in most instances specific factors such as the steric hindrance or inductive effect of the coördinated groups may greatly alter these theoretical ratios of geometrical isomers.

Attempts to find some correlations in the experimental results of Werner (237) by making use of the mechanistic approach just described were not successful. Basolo, Stone, and Pearson (20) suggest that because of the experimental technique employed by Werner, rearrangements may occur during the isolation of the reaction product or the estimate of relative isomeric ratios. That the interconversion of *cis–trans* isomers does occur, particularly with cobalt(III) complexes, is discussed in the next section (page 491). In an attempt to avoid any secondary rearrangements, the reactions of the geometrical isomers [Coen$_2$NH$_3$Cl]$^{+2}$, [Coen$_2$NO$_2$Cl]$^{+}$, and [Coen$_2$NCSCl]$^{+1}$ with reagents H_2O, OH^-, NO_2^-, and NCS^- were investigated spectrophotometrically. The general conclusion based on these studies was that more than one reaction path is involved in these reactions. It is of interest that the *trans* complexes reacted with hydroxide ion to yield predominantly the corresponding *cis* hydroxo complex, suggesting either an S_N2 reaction with primarily an approach from the rear or an S_N1 process with a trigonal bipyramid intermediate.

TABLE 10

Reactions of cis- and trans-[Coen$_2$NO$_2$Cl]$^+$

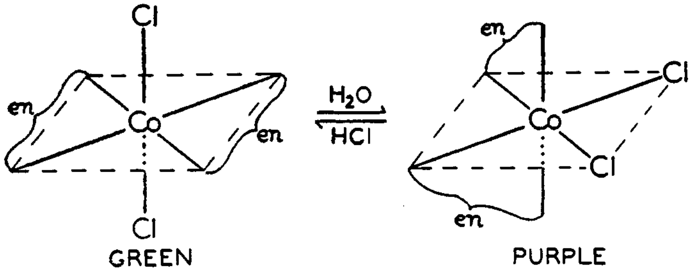
CONFIGURATION	REAGENT	PRODUCT	*Cis*	*Trans*
			per cent	*per cent*
Cis	H_2O ($HClO_4$)	[Coen$_2$H$_2$ONO$_2$]$^{+2}$	100	0
Trans	H_2O ($HClO_4$)	[Coen$_2$H$_2$ONO$_2$]$^{+2}$	0	100
Cis	Ag^+ ($H_2O + HClO_4$)	[Coen$_2$H$_2$ONO$_2$]$^{+2}$	100	0
Trans	Ag^+ ($H_2O + HClO_4$)	[Coen$_2$H$_2$ONO$_2$]$^{+2}$	0	100
Cis	OH^-	[Coen$_2$NO$_2$OH]$^{+1}$	90	10
Trans	OH^-	[Coen$_2$NO$_2$OH]$^{+1}$	60	40
Cis	NO_2^- (90% CH_3OH)	[Coen$_2$[NO$_2$)$_2$]$^{+1}$	100	0
Trans	NO_2^- (90% CH_3OH)	[Coen$_2$(NO$_2$)$_2$]$^{+1}$	0	100
Cis	NCS^- (90% CH_3OH)	[Coen$_2$NO$_2$NCS]$^{+1}$	Largely	
Trans	NCS^- (90% CH_3OH)	[Coen$_2$NO$_2$NCS]$^{+1}$		Largely

The only complex to give essentially consistent results was [Coen$_2$NO$_2$Cl]$^+$ and here, except for the reaction with hydroxide ion, there was generally retention of configuration (table 10). It is of interest to note that the aquation reactions give the same products in water as they do in the presence of silver ion, although the latter may be expected to have a tendency to pull the chloro group from the complex. Kinetic studies (195) have shown that the reactions of [Coen$_2$NO$_2$Cl]$^+$ with nitrite ion and with thiocyanate ion do not take place by direct substitution but instead go by way of the aquonitro complexes. Furthermore, as the reaction of $[Coen_2H_2ONO_2]^{+2}$ with nitrite ion appears to take place by a dissociation (S_N1) mechanism (page 469) and as there is retention of configuration during this reaction it would appear to involve a tetragonal pyramid intermediate. Additional support is afforded this mechanism by the fact that the optical activity of an active *cis* aquonitro complex is not lost even after standing in solution for as long as two months. Since the rate of dissociation of *cis*-$[Coen_2H_2ONO_2]^{+2}$ is measurable, if the configuration of the pentacovalent activation complex is that of a trigonal bipyramid, the racemization of the optically active compound would be expected to occur at a comparable rate. It becomes apparent from this that stereochemical studies alone are of little value in the elucidation of the reaction mechanism of octahedral complexes. Combined with kinetic data they give considerable insight into these reaction paths.

D. *Interconversion of cis–trans isomers*

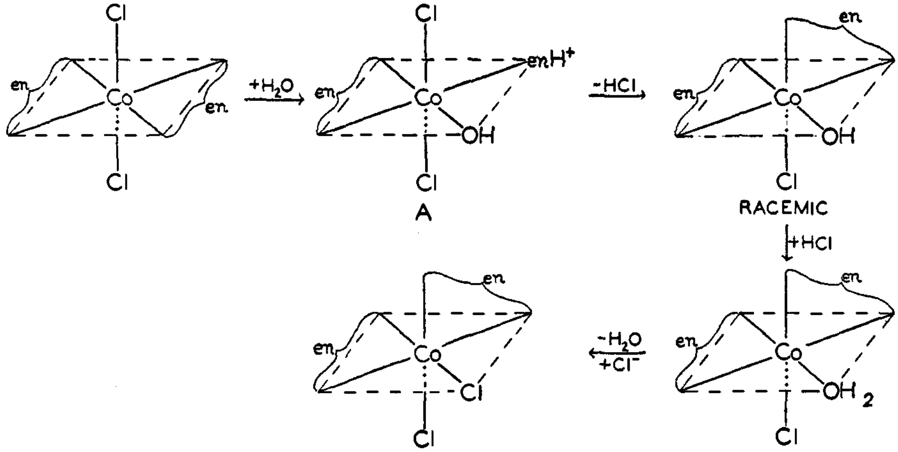
It was realized as early as 1889 (111) that interconversion of geometrical isomers of complex compounds is possible. Because of rearrangements of this type, techniques employed for the preparation of supposedly *cis* complexes by replacement of a chelate group or the proof of structure by the reaction with such a group have been criticized (224). These changes in configuration, although of rather common occurrence in octahedral complexes, are less pronounced with planar compounds (143). In several instances prolonged boiling or evaporation to dryness of the *cis* salts yields the corresponding *trans* isomers. Examples are furnished by $[Coen_2NO_2Cl]Cl$ (234), $[Coen_2(NO_2)_2]NO_3$ (231), $K_3[Ir(C_2O_4)_2Cl_2]$ (46), and $K_3[Rh(C_2O_4)_2Cl_2]$ (50).

The best-known example of *cis–trans* interconversion is that between the *praseo* and *violeo* cobalt complexes, discovered by Jorgensen (111).

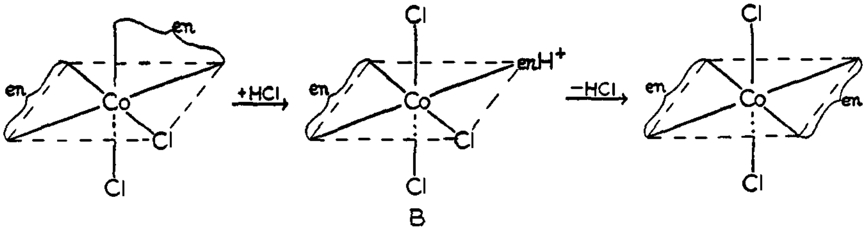


When an aqueous solution of the green *trans*-$[Coen_2Cl_2]Cl$ is concentrated on a steam bath, the crystals that separate are purple and consist largely of *cis*-$[Coen_2Cl_2]Cl$. The *cis* complex can in turn be transformed into the *trans* isomer by evaporation of a hydrochloric acid solution of the *cis* salt to yield the *trans* hydrochloride, $[Coen_2Cl_2]Cl \cdot HCl$. Some studies have been made to elucidate the mechanism of these transformations. In fact, this is the only example of *cis–trans* interconversion which has been investigated in any detail.

Drew and Pratt (53) suggested that *trans*-[Coen$_2$Cl$_2$]Cl is converted to the *cis* isomer by the following sequence of reactions:



Transformation of the *cis* isomer in hydrochloric acid to the *trans* salt is said by Drew and Pratt to occur as follows:



No direct experimental evidence was cited to support this hypothesis. The authors make the suggestion primarily on the supposition that the structure of the hydrochloride generally designated as *trans*-[Coen$_2$Cl$_2$]Cl·HCl is that represented above as B. It is stated that such a structure is in accord with the observation that the ethylenediamine chelate ring in platinum(II) complexes is opened by digestion with hydrochloric acid (41, 54). Although Drew and Pratt have postulated structures A and B for complexes believed to be *cis*-[Coen$_2$Cl$_2$]Cl·H$_2$O and *trans*-[Coen$_2$Cl$_2$]Cl·HCl, there is no direct evidence in support of their "open-ring" structure. In fact, on the basis of the purple and green colors of these isomers, as well as the fact that neither dehydration nor removal of hydrogen chloride markedly alters their respective colors, it would appear that the structure of the complex is not markedly changed by the presence of either water or hydrogen chloride. Furthermore, if acid hydrolysis of [Coen$_2$Cl$_2$]Cl were to yield a structure of the type designated by A, such a reaction would result in the production of racemic mixtures. Mathieu (141) has shown, however, that optically active [Coen$_2$Cl$_2$]Cl undergoes mutarotation to [Coen$_2$H$_2$OCl]Cl$_2$ at a rate the same as that of chloride-ion formation, and in addition the aquo complex appears to have the same configuration as the original dichloro compound.

Ettle and Johnson (68) employed radiochlorine in a detailed study of this system and were able to demonstrate that the reaction mechanism was not that proposed by Drew and Pratt (53). They observed that the interconversion in the presence of radiochloride ion is accompanied by a complete random distribution of chloride ion with coördinated chloro groups, so intramolecular rearrangement can be disregarded. Furthermore, direct replacement of cöordinatively bound chloro groups by chloride ion was not observed with any of the complex ions. It is of interest in this connection that the initial rate of change of rotatory power of optically active $[\mathrm{Coen_2Cl_2}]^+$ in aqueous solution is somewhat accelerated by potassium chloride. Since there is no direct exchange of chlorine, the catalytic influence of potassium chloride cannot be attributed to a process of inversion by replacement analogous to that proposed by Olsen (164) and by Meer and Polanyi (147) for carbon compounds.

In the absence of either intramolecular rearrangement or direct replacement of chloride, it is plausible to suspect interaction with the solvent, and the facts are in accord with the following equilibria:

$$[\mathrm{Coen_2\,Cl_2}]^+ \underset{(d)}{\overset{(a)}{\rightleftharpoons}} \underset{+\ \mathrm{Cl}^-}{[\mathrm{Coen_2\,H_2O\,Cl}]^{+2}} \underset{(c)}{\overset{(b)}{\rightleftharpoons}} \underset{+\ \mathrm{Cl}^-}{[\mathrm{Coen_2(H_2O)_2}]^{+3}}$$

Reactions (a) and (b) take place during the initial stages of the concentration at steam bath temperatures. The reverse reactions, (c) and (d), occur as the solutions become more concentrated, and the concentration of chloride ion increases. The slowness of reactions (c) and (d) is responsible for failure to achieve more than partial isomerization by evaporation at room temperature, under which conditions the products invariably contain appreciable quantities of the aquo complex ions.

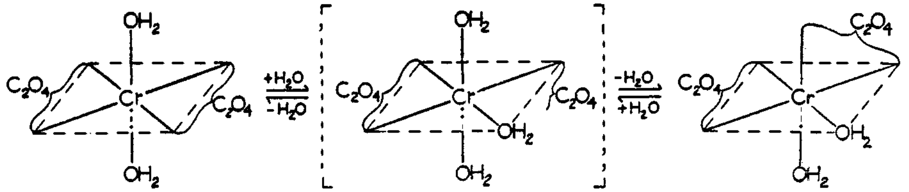
The relative amounts of the isomeric chlorides obtained appear to be largely or entirely controlled by differences in solubility. Although *cis*-$[\mathrm{Coen_2Cl_2}]\mathrm{Cl}$ is the less soluble isomer and separates from an aqueous solution, the *trans* salt forms a slightly soluble addition compound, $[\mathrm{Coen_2Cl_2}]\mathrm{Cl\cdot HCl}$, and is the isomer isolated from a hydrochloric acid solution. The less soluble *trans*-$[\mathrm{Coen_2Cl_2}]\mathrm{NO_3}$ is always the isomer isolated whenever either water or acid solutions of the *cis*- or *trans*-nitrates are evaporated. Furthermore, that the role played by hydrochloric acid is that of a precipitant and is not that suggested by Drew and Pratt was demonstrated by employing the radioactive complex *trans*-$[\mathrm{Coen_2\overset{*}{C}l_2}]$-Cl. This salt was dissolved in cold water and hydrochloric acid was added immediately to precipitate $[\mathrm{Coen_2\overset{*}{C}l_2}]\mathrm{Cl\cdot HCl}$; this, when heated to 110°C., lost hydrogen chloride that was found to contain no radioactivity.

Ettle and Johnson (68) found that a mechanism consistent with their observations may be the following:

$$\begin{array}{rcl}
cis\text{-}[\mathrm{Coen_2Cl_2}]^+ + \mathrm{H_2O} & \rightleftharpoons & cis\text{-}[\mathrm{Coen_2H_2OCl}]^{+2} + \mathrm{Cl}^- \\
 & & \upharpoonleft\!\downharpoonright \\
trans\text{-}[\mathrm{Coen_2Cl_2}]^+ + \mathrm{H_2O} & \rightleftharpoons & trans\text{-}[\mathrm{Coen_2H_2OCl}]^{+2} + \mathrm{Cl}^-
\end{array}$$

No mention is made by the authors as to how the rearrangement may occur between the *cis*- and *trans*-chloroaquo complexes. Mathieu (141) suggests that optically active *cis*-$[Coen_2H_2OCl]^{+2}$ undergoes racemization by way of a pentacovalent intermediate (page 511) and this may be expected to have a trigonal bipyramid structure. Mathieu (140) has demonstrated that *cis*-$[Coen_2Cl_2]^+$ undergoes aquation with retention of configuration, but there is no direct evidence on this point in the case of the *trans* isomer. Studies on the absorption spectra of aqueous solutions of aquo complexes of cobalt(III) reveal that these isomers generally undergo rearrangement with considerable ease (16, 25, 43a, 84a, 218). Basolo (16) reports the rapid rearrangement of *cis*- and *trans*-$[Coen_2H_2O(OH)]Br_2$ in aqueous solution, whereas in a dilute solution of bromic acid (pH 0.7) the respective diaquo complexes do not appear to undergo rearrangement so rapidly. Bjerrum (25) is making an extensive study of the rates of rearrangement of compounds of this type in aqueous acidic and basic solutions. The rearrangements with *cis*- and *trans*-$[Coen_2H_2ONO_2]^{+2}$ are slow (20) compared to the rates of aquation of *cis*- and *trans*-$[Coen_2NO_2Cl]^+$, so in this system it was possible to determine the configurations of the aquation products and these were found to be the same as those of the reactants.

Hamm (84a) has recently reported the results of a kinetic investigation on the conversion of *trans*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ into the *cis* isomer. The rate of isomerization was found to be of the first order with respect to the complex, independent of hydrogen-ion concentration at pH values below 4.5, and only slightly dependent upon ionic strength. The reaction has a negative entropy of activation ($\Delta S^\ddagger = -15.3$ cal./degree) and a value of 17.5 kcal. for the heat of activation. Hamm suggests that these data are in accord with the following mechanism:



However, it should be mentioned that although the above mechanism is consistent with the experimental observations, these may also be interpreted on the basis of some other reaction process. Direct evidence in support of the mechanism proposed by Hamm must await a study of water exchange making use of water containing oxygen-18.

IV. OPTICAL ISOMERISM

Asymmetric hexacovalent complex ions of different types varying from $[M(AA)a_2b_2]$ to $[M(ABCCBA)]^6$ have been resolved into their optically active antipodes. Some of the complexes that have been resolved are shown in table 11. Whenever the information was given, the ease of racemization is noted.

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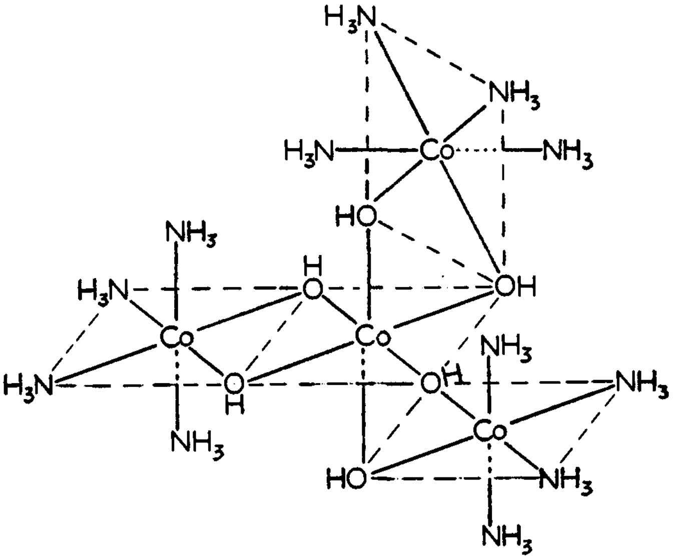
[6] (ABCCBA) = sexadentate group with three different atoms attached to the central atom.

Of all the complex compounds which have been resolved, only two contain no carbon. In 1914, when it was still believed that only carbon compounds could be optically active, it was significant that Werner was able to effect the resolution of the tris(tetramminecobalt(III)-μ-diol)cobalt(III) ion (255).



The chloride of this ion was synthesized by the reaction of ammonia with chloroaquotetramminecobalt(III) chloride. The resulting cation was resolved by fractional crystallization of the dextrorotatory α-bromocamphor-π-sulfonate salt to yield optical antipodes with rotations of $[M]_D^{25°} = \pm 47{,}600°$. The other completely inorganic complex ion which has been resolved to date is the anion *cis*-$[Rh(NHSO_2HN)_2(H_2O)_2]^-$ (135). The optical isomers have a rotation of $[M]_{5780}^{25°} = \pm 33°$ and are optically stable, showing no tendency to undergo racemization in solution.

A. Resolution

The problems encountered and methods employed in the resolution of complex compounds are much the same as those in the resolution of organic compounds. One of the biggest differences is that biochemical processes as employed for the resolution of organic compounds have not been applied to coördination compounds. The method generally used involves the conversion of the racemic mixture into diastereoisomers by means of an optically active resolving agent and the separation of the diastereoisomers by fractional crystallization. Cationic complexes are often resolved by way of the *d*-tartrate, the *d*-α-bromocamphor-π-sulfonate, the *d*-camphor-π-sulfonate, or the antimonyl *d*-tartrate salts, whereas anionic complexes are converted to salts of the optically active bases such as strychnine, brucine, cinchonidine, or α-phenethylamine. Optically active complexes can themselves be used to resolve other complexes, as illustrated in the

TABLE 11

Optical isomers(a)(b)

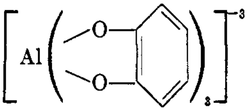
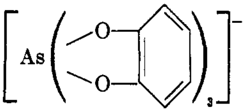
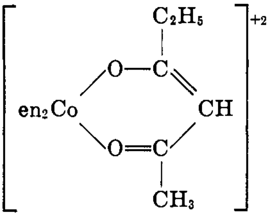
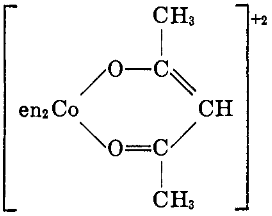
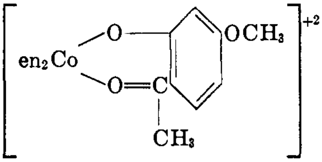
Aluminum(III)	
$[Al(C_2O_4)_3]^{-3}$ (34, 220)(c)(d)	 (208)
Arsenic(V)	
 (222)	
Cadmium(II)	
$[Cden_3]^{+2}$ (160)(c)(e)(f)	
Chromium(III)	
$[Cren_3]^{+3}$ (245)	$[Cren_2Cl_2]^{+}$ (232)(i)
$[Cren_2C_2O_4]^{+}$ (36)(g)	$[Crpn_2Cl_2]^{+}$ (163)
$[Crpn_2(NCS)_2]^{+}$ (163)	$[Cren(C_2O_4)_2]^{-}$ (36, 254)(h)
$[Cr(C_2O_4)_3]^{-3}$ (36, 96, 247)(e)(h)	$[Cr(OOCCH_2COO)_3]^{-3}$ (97)
Cobalt(III), (IV)	
$[Coen_3]^{+3}$ (136, 243)(g)	$[Copn_3]^{+3}$ (214)
$[Co(cptdin)_3]^{+3}$ (104)	$[Co(NH_2CH_2CH(NH_2)CH_2NH_2)_2]^{+3}$ (136)
$[Coen_2cptdin]^{+3}$ (104)	$[Coen_2ophen]^{+3}$ (99)
$[Coen_2pn]^{+3}$ (94)	$[Coen_2(NH_3)_2]^{+3}$ (268)
$[Copn_2(NH_3)_2]^{+3}$ (163)	$[Coen_2NH_3H_2O]^{+3}$ (141, 230)(g)
$[Coen_2H_2OCl]^{+2}$ (141, 152)(h)	$[Co(BigH^{+})_3]^{+3}$ (179)(h)
$[Coen_2H_2ONO_2]^{+2}$ (141, 233)(g)	$[Coen_2H_2ONCS]^{+2}$ (141, 236)(g)
$[Coen_2NH_3Br]^{+2}$ (141, 266)(i)	$[Coen_2NH_3Cl]^{+2}$ (262)
$[Coen_2NH_3NCS]^{+2}$ (5)	$[Coen_2NH_3NO_2]^{+2}$ (271)
$[Coen_2CH_3NHCH_2COO]^{+2}$ (149)	$[Coen_2NH_2CH_2COO]^{+2}$ (149)
 (267)	 (267)
$[Copn_2NH_3Cl]^{+2}$ (163)	 (171)

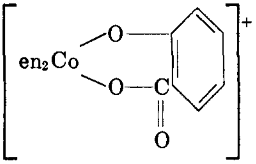
TABLE 11—*Continued*

Cobalt(III), (IV)—*Continued*

$[Coen_2Cl_2]^+$ (141, 235)[h][i][j]
$[Coen_2NCSCl]^+$ (141, 217)[i]
$[Coen_2NO_2Cl]^+$ (141, 234)[i]
$[Coen_2NO_2Br]^+$ (44)
$[Coen_2CO_3]^+$ (265)
$[Coen(NH_3)_2Cl_2]^+$ (13)

$[Coen_2NO_2NCS]^+$ (271)
$[Coen_2OHCl]^+$ (70)
$[Coen_2ClBr]^+$ (270)
$[Coen_2(NO_2)_2]^+$ (231)
$[Coen_2C_2O_4]^+$ (36, 257)[g]
$[Coenpn(NO_2)_2]^+$ (256)

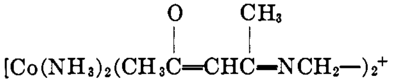
$[Copn_2Cl_2]^+$ (163, 259)



(156)

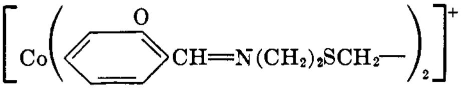
$[Copn_2(NCS)_2]^+$ (163)
$[Copn_2CO_3]^+$ (12)
$[Co(cptdin)_2Cl_2]^+$ (104)
$[Cobn_2Cl_2]^+$ (41a)

$[Copn_2(NO_2)_2]^+$ (93, 221)
$[Copn_2SO_3]^+$ (163)
$[Copn_2tart]^+$ (109)
$[Costien_2Cl_2]^+$ (272)$_2$

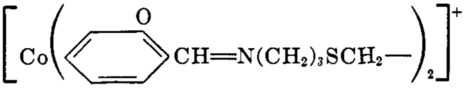


$$[Co(NH_3)_2(CH_3\overset{\overset{\displaystyle O}{|}}{C}{=}CH\overset{\overset{\displaystyle CH_3}{|}}{C}{-}NCH_2{-})_2]^+$$

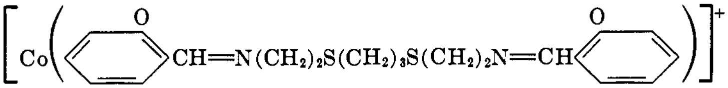
(157)



(67)



(66)



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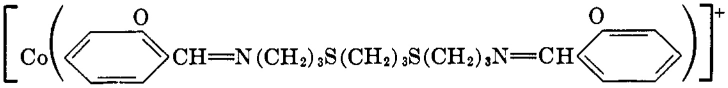

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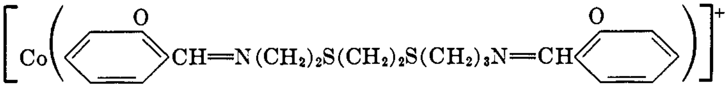

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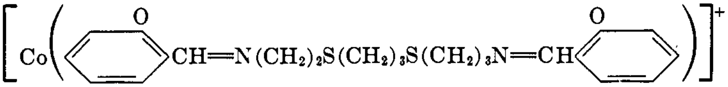


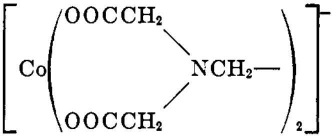
(57)

$[CoNH_3(DMG)Cl]$ (216)

$[Co(NH_3)_2C_2O_4(NO_2)_2]^-$ (204)

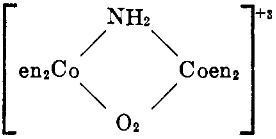
TABLE 11—*Continued*

Cobalt(III), (IV)—*Continued*

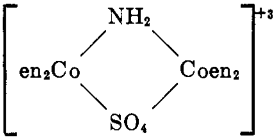


(57)

$[Co(C_2O_4)_3]^{-3}$ (36, 95)



(207, 263)



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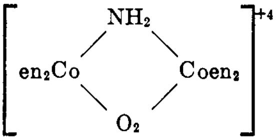
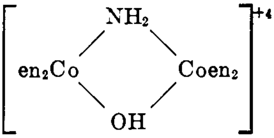
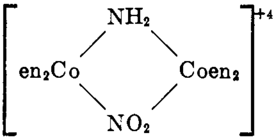


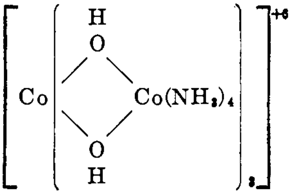
(264)



(252)



(249)



(255)

Gallium(III)

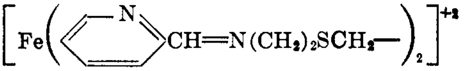
$[Ga(C_2O_4)_3]^{-3}$ (158)(c)

Iridium(III)

$[Iren_3]^{+3}$ (269)
$[Iren_2(NO_2)_2]^{+}$ (269)
$[Ir(C_2O_4)_2Cl_2]^{-3}$ (46)
$[Ir(chxn)_3]^{+3}$ (102)
$[Ir(C_2O_4)_3]^{-3}$ (45)

Iron(II), (III)

$[Fe(dipy)_3]^{+3}$ (65)(e)
$[Fe(dipy)_3]^{+2}$ (65, 244)(h)
$[Fe(ophen)_3]^{+3}$ (63)(e)
$[Fe(ophen)_3]^{+2}$ (63)(b)



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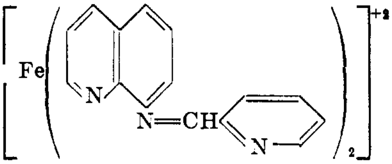


(57)

$[Fe(C_2O_4)_3]^{-3}$ (203)(c)(d)

TABLE 11—*Concluded*

Nickel(II)

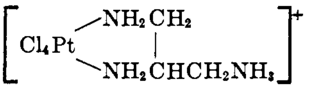
$[Ni(dipy)_3]^{+2}$ (155, 186)(h)
$[Ni(CH_3\text{-}ophen)_3]^{+2}$ (197)(h)
$[Ni(ophen)_3]^{+2}$ (62)(h)

Osmium(II), (III)

$[Os(dipy)_3]^{+3}$ (35)
$[Os(dipy)_3]^{+2}$ (35)(g)
$[Os(ophen)_3]^{+3}$ (65)
$[Os(ophen)_3]^{+2}$ (58, 65)(g)

Platinum(IV)

$[Pten_3]^{+4}$ (98)
$[PtenNH_3NO_2Cl_2]^{+}$ (40)
$[Ptpn_3]^{+4}$ (194)



$$\left[Cl_4Pt\begin{matrix}\diagup NH_2CH_2\\ \quad\quad |\\ \diagdown NH_2CHCH_2NH_3\end{matrix}\right]^{+}$$

(134)

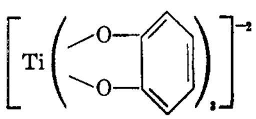
Rhodium(III)

$[Rhen_3]^{+3}$ (246)
$[Rh(chxn)_3]^{+3}$ (102)
$[Rh(NHSO_2NH)_2(H_2O)_2]^{-}$ (135)
$[Rh(OOCCH_2COO)_3]^{-3}$ (97)
$[Rh(cptdin)_3]^{+3}$ (103, 105)
$[Rh(CH_3CH(NH_2)CH_2CH(NH_2)CH_3)_3]^{+3}$ (55)
$[Rh(C_2O_4)_3]^{-3}$ (251)

Ruthenium(II), (III)

$[Ru(dipy)_3]^{+3}$ (61)(c)
$[Ru(dipy)_3]^{+2}$ (61)(g)
$[RupyNO(C_2O_4)_2]^{-}$ (37)
$[Ru(ophen)_3]^{+3}$ (59, 60)(c)
$[Ru(ophen)_3]^{+2}$ (59, 60)(g)

Titanium(IV)



(184)

Zinc(II)

$[Znen_3]^{+2}$ (161)(c)(e)(f)

(a) See footnote to table 4.

(b) Although most of the examples reported are listed here, the author makes no claim as to the completeness of this table.

(c) An aqueous solution of the optically active complex is completely inactive after standing only a few hours at room temperature.

(d) Attempts to repeat the resolution have not been successful.

(e) Racemization occurs in the solid state.

(f) Attempts to resolve analogous complexes, $[Cdpn_3]^{+2}$ and $[Znpn_3]^{+2}$, were not successful (159).

(g) An aqueous solution of the optically active complex remains active for several months at room temperature.

(h) Kinetics of racemization has been investigated.

(i) The complex undergoes certain substitution reactions without loss in optical activity and essentially with retention of configuration (table 12).

(j) Inversion reaction observed in the conversion to $[Coen_2CO_3]^{+}$ (8) and $[Coen_2(NH_3)_2]^{+3}$ (9).

resolution of the ethylenediaminetetraacetatecobaltate(III) anion by way of the *d*-tris(ethylenediamine)cobalt(III) salt (57). Removal of the resolving agent from the desired antipode has been accomplished in various ways, depending upon the property of the individual complex as well as that of the resolving agent.

If the asymmetric complex is non-ionic, diastereoisomeric salts cannot be formed. It was demonstrated by Tsuchida, Kobayashi, and Nakamura (216) that one of the enantiomorphs may be preferentially adsorbed on optically active quartz. They have applied this technique to the resolution of the non-ionic complex $(Co(DMG)_2NH_3Cl]$ as well as to other compounds. This same method has been used successfully by Bailar and Peppard (13) and very recently by Kuebler and Bailar (120).

TABLE 12

Substitution reactions in optically active complexes (140, 248)

(Retention of configuration)

COMPLEX	REAGENT	PRODUCT
l-$[Coen_2Cl_2]^+$	H_2O	*d*-$[Coen_2H_2OCl]^{+2}$
	$K_2CO_3(H_2O)$	*d*-$[Coen_2CO_3]^+$
	$(NH_4)_2C_2O_4$	*d*-$[Coen_2C_2O_4]^+$
l-$[Coen_2NO_2Cl]^+$	H_2O	*d*-$[Coen_2H_2ONO_2]^{+2}$
	$NaNO_2$	*d*-$[Coen_2(NO_2)_2]^+$
	KCNS	*l*-$[Coen_2NCSNO_2]^+$
l-$[Coen_2NCSCl]^+$	H_2O	*l*-$[Coen_2H_2ONCS]^{+2}$
	NH_3	*d*-$[Coen_2NH_3NCS]^{+2}$
	$NaNO_2$	*d*-$[Coen_2NCSNO_2]^+$
l-$[Coen_2NH_3Br]^{+2}$	H_2O	*d*-$[Coen_2NH_3H_2O]^{+3}$
l-$Cren_2Cl_2]^+$	$(NH_4)_2C_2O_4$	*d*-$[Cren_2C_2O_4]^+$

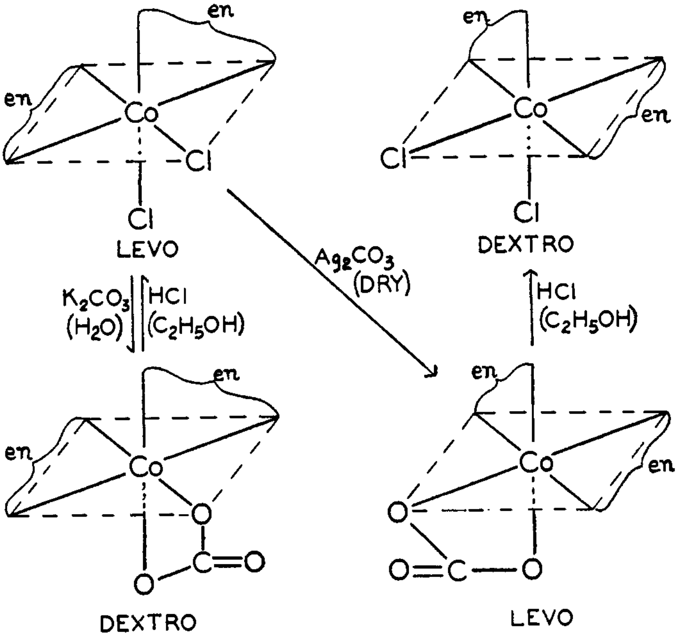
It has also been demonstrated that other special methods are applicable to the resolution of complex compounds. The mechanical separation of crystals used by Pasteur (165) in 1848 is known to work with $K_3[Cr(C_2O_4)_3]$ (96) and $[Rh(cptdin)_3](ClO_4)\cdot 12H_2O$ (103). Werner and Basshart (257) separated the optical antipodes of $[Coen_2C_2O_4]^+$ and of $[Cren_2C_2O_4]^+$ by preferential crystallization, using a seed crystal of the optically active complex. Delepine (51) used a method referred to as "the method of active racemates" and by this process claimed to be able to relate the generic configurations of analogous compounds.

Jonassen, Huffman, and Bailar (109) have obtained optically active $[Coen_3]^{+3}$ by means of a partial asymmetric synthesis (page 515). Jaeger and Berger (101) were not successful in an attempt to produce optically active $[Co(C_2O_4)_3]^{-3}$ by radiation with dextrorotatory and levorotatory circularly polarized light.

B. Substitution reactions of optical isomers

In addition to his study of substitution reactions in geometrical isomers, Werner (248) investigated some reactions not accompanied by complete racemization. There was complete retention of configuration in the optically active product (table 12). The assignment of relative generic configuration by Werner was based on his assumption that for analogous complex ions, the antipodes which form the least soluble salts with the same resolving agent have the same generic configuration. Jaeger (100) was quick to criticize this method but later became convinced that the assumption appeared to be valid and actually employed the method in some of his studies. Mathieu (139) has repeated some of Werner's work and, by correlating the absorption spectra and rotatory dispersion curves of the complexes, has agreed with Werner that these reactions take place with retention of configuration. Although the method of Mathieu appears to have some theoretical support, neither method can be taken as absolute proof of generic configuration.

Only two examples are known in which inversion of configuration takes place during the reaction of optically active complex compounds. The first of these was discovered by Bailar and Auten (8) with the conversion of $[Coen_2Cl_2]^+$ to $[Coen_2CO_3]^+$ by the reaction with aqueous potassium carbonate and with dry silver carbonate. On the basis of the work by Werner and Mathieu, which indicates a retention of configuration in the reaction with aqueous potassium carbonate, the relative configurations may be designated as follows:



The above reaction scheme also receives some support from the fact that the liberation of carbon dioxide by the suspension of the carbonate complex in an alcoholic solution of hydrogen chloride is expected to take place with retention of configuration. This system has been studied in some detail and it has been shown that the solvent plays an important role in these reactions. Bailar, Jonelis, and Huffman (11) observed that mercurous carbonate gave the same results as did potassium carbonate and furthermore that an excess of silver carbonate yielded the levo salt but that at equivalent concentrations or less the dextro complex was obtained. Bailar and Peppard (14) allowed a solution of *l*-$(Coen_2Cl_2]Cl$ to stand for various periods of time before allowing it to react with silver carbonate and found that the freshly prepared solution gave the levo complex, whereas the aged solutions gave the dextro salt. In addition it was observed that if the dry *l*-dichloro complex is intimately mixed by grinding with dry potassium or silver carbonate, and water is then added, the product shows levorotation. It was concluded on the basis of these studies that the conversion of *l*-$[Coen_2Cl_2]^+$ to *d*-$[Coen_2CO_3]^+$ proceeds by way of an aquated intermediate and that conversion to *l*-$[Coen_2CO_3]^+$ proceeds directly.

TABLE 13

Conversion of l-$[Coen_2Cl_2]^+$ *into optically active* $[Coen_2(NH_3)_2]^{+3}$

REAGENT	TEMPERATURE	$[\alpha]^{25°}_{5270}$
	°C.	
Liquid NH_3	-77	-32
	-33	-22
	$+25$	$+29$
Gaseous NH_3	$+80$	$+43$
NH_3 in CH_3OH	$+25$	$+31$
NH_3 in C_2H_5OH	$+25$	$+29$

This is in accord with results obtained by Werner (248) and Mathieu (140) to the effect that acid hydrolysis reactions generally proceed with retention of configuration. Furthermore, Basolo, Stone, and Pearson (20) report that the aquonitro complexes, *cis*- and *trans*-$[Coen_2H_2ONO_2]^{+2}$, are converted to $[Coen_2(NO_2)_2]^+$ and $[Coen_2NCSNO_2]^+$ with retention of configuration. That substitution reactions in aqueous solutions of moderate concentrations generally proceed by way of aquation (14, 68, 195) may account for the retention of configuration observed with optically active complexes. On the basis of the fact that inversion takes place in the reactions that occur in the absence of water, it should be of interest to investigate the kinetics of analogous systems either at higher reagent concentrations or in solvents other than water. One may anticipate that if a direct displacement reaction is observed it would be accompanied by rearrangement. Since *trans* complexes appear to react with hydroxide ion (20) to yield primarily *cis* hydroxo complexes, it would be of interest to know the molecularity of these reactions. Brown (33) has additional evidence to support the hypothesis that every direct substitution in octahedral complexes involves a rearrangement of configuration.

The second example of inversion with optically active compounds (9) is the reaction of *l*-$[Coen_2Cl_2]^+$ with ammonia. In this case the optical rotation of the reaction product, $[\text{Coen}_2(\text{NH}_3)_2]^{+3}$, appears to be dependent upon the temperature at which the reaction is carried out (table 13). It was also determined that in no case did the *luteo* product contain more than 10 per cent of the *trans* isomer. Bailar, Haslam, and Jones (9) suggest that inversion in this instance shows that an even number of substitutions on an octahedral atom does not necessarily lead to retention of configuration, as has been postulated for a tetrahedral atom (147, 164). Since the reaction

$$[\text{Coen}_2\text{Cl}_2]\text{Cl} \xrightarrow{\text{NH}_3} [\text{Coen}_2\text{NH}_3\text{Cl}]\text{Cl}_2 \xrightarrow{\text{NH}_3} [\text{Coen}_2(\text{NH}_3)_2]\text{Cl}_3$$

proceeds stepwise, it was anticipated that the same mechanism would function in the replacement of each chloro group from the complex, and the conversion of the dichloro salt to the diammine salt would necessarily take place in an even number of steps. However, the authors mention that replacement of a negative chloro group by a neutral ammonia molecule may produce such a profound change in the complex ion that the second step of the reaction does not follow the same mechanism as the first. It is likewise possible that the reaction paths are quite different under the different experimental conditions.

C. Racemization of optical isomers

The racemization of optically active complex compounds in most instances takes place readily when compared to that of carbon compounds. Generally there appears to be a rather good correlation between the rate of racemization of a complex ion and the type of bond involved (108). The greater the ionic character of the bond, the greater the tendency for the optically active substance to lose its activity. In fact, it is generally agreed that the resolution of a complex is a good indication that the chemical bonds involved are at least largely covalent. However, it should be mentioned that the resolution of certain labile complexes such as $[\text{Al}(\text{C}_2\text{O}_4)_2]^{-3}$ (34, 220), $[\text{Ga}(\text{C}_2\text{O}_4)_3]^{-3}$ (158), $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{-3}$ (202), $[\text{Cden}_3]^{+2}$ (160), and $[\text{Znen}_3]^{+2}$ (161) has been reported. Attempts to repeat the resolution of the aluminum(III) and iron(III) complexes have not always been successful (51, 187). These metal ions are known to establish equilibrium rapidly with the donor groups and therefore it has been suggested (200) that if these complexes are indeed resolvable, it must be possible for the interconversion of dextro and levo forms to be slow even though the coördinated groups undergo rapid substitution or exchange.

Essentially two different mechanisms have been proposed to account for the racemization of complexes of the type $[\text{M}(\text{AA})_3]$: (*1*) dissociation[7] and (*2*) intramolecular rearrangement. The discussion that follows will deal primarily with the tris(oxalato) complexes, $[\text{M}(\text{C}_2\text{O}_4)_3]^{-3}$, as these have been subjected to ex-

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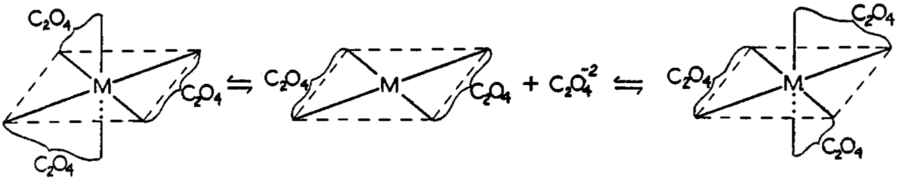
[7] Thomas (202) referred to this process as ionization, and this is generally the term used in the literature. However, it would appear more appropriate to speak of it as dissociation, in order to include systems that do not involve the production of ions, i.e.:

$$[\text{Ni}(\text{ophen})_3]^{+2} \rightleftharpoons [\text{Ni}(\text{ophen})_2]^{+2} + \text{ophen}$$

tensive study. It would appear from the data gathered on these systems that the interconversion is not due to a dissociation process, but rather must involve an intramolecular rearrangement. However, there is at present no conclusive evidence in support of a particular type of intramolecular process.

Thomas (202) suggested that the racemization of $[M(C_2O_4)_3]^{-3}$ can be accounted for on the basis of a dissociation process:



He was of the opinion that the removal of an oxalate ion from the hexacovalent complex would yield a planar tetracovalent intermediate, which upon recombination would revert with equal probability to the original configuration or its mirror image. Since the planar intermediate is not asymmetric, the optical activity is lost as a result of dissociation. Since these racemizations occur in aqueous solutions, a more probable intermediate would be $[M(C_2O_4)_2(H_2O)_2]^-$, which would be optically inactive if it had a *trans* structure but might retain some of its activity if it were the *cis* isomer. (Werner (250) has actually isolated both *cis*- and *trans*-$[Cr(C_2O_4)_2(H_2O)_2]^-$ salts.) In support of his mechanism Thomas cited the observations that (*1*) silver oxalate is precipitated from these solutions (202), (*2*) the conductivity of the solutions increases upon dilution (205), and (*3*) the rate of racemization in acetone–water is less than that in water (182). He correlated the rapid rate of racemization of $[Fe(C_2O_4)_3]^{-3}$ as compared to that of $[Cr(C_2O_4)_3]^{-3}$ with the immediate precipitation of silver oxalate from a solution of the former, but a slow precipitation from a solution of $[Cr(C_2O_4)_3]^{-3}$. Other investigators have shown that this precipitate is not silver oxalate but is either $Ag_3[M(C_2O_4)_3]\cdot 6H_2O$ (119) or $K_nAg_m[M(C_2O_4)_3]\cdot xH_2O$ (117) where $n + m = 3$. Furthermore, the conductivity measurements of Thomas and Fraser (205) could not be checked by Johnson (108). Rideal and Thomas (182) verified Werner's observation (247) that racemizations are slower in acetone–water than in water alone, and they performed one of the first kinetic studies on the racemization of a complex ion to show that $[Cr(C_2O_4)_3]^{-3}$ undergoes racemization in water at 22°C. with a half-life of 1.28×10^3 min.; in 40 per cent acetone–water the value is 2.10×10^3 min., and in 60 per cent acetone–water it is 2.64×10^3 min. They interpret this to support a dissociation mechanism, for in the less polar solvent the complex is expected to have a smaller tendency to dissociate. However, one may argue that a change in solvent may also effect an intramolecular process, although it is not possible to state *a priori* what the precise nature of this effect might be. Recent work of Schweitzer and Lee (186), employing numerous solvent mixtures at various concentrations, indicates, on the basis of analogous activation energies, that the mechanism of racemization is the same in all of these solvent systems.

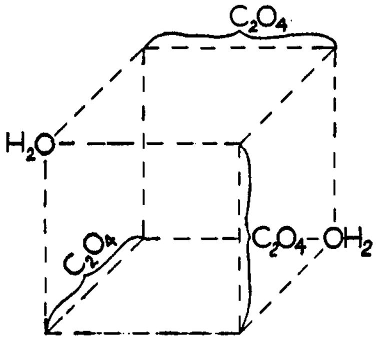
Johnson (108) has written an excellent review on the resolution and racemization of tris(oxalato) complex ions. He expressed the opinion that only complexes with essentially covalent bonds should be capable of resolution, and therefore questioned the resolvability of $[Al(C_2O_4)_3]^{-3}$. His attempts to repeat the work of previous investigators who claimed to have resolved these ions were not successful (187). Delepine (51) has likewise been unable to obtain any evidence for the resolution of these complexes by his method of active racemates. On the basis of rapid exchange of oxalate ion, Long (132) has concluded that the possibility of resolution of $[Fe(C_2O_4)_3]^{-3}$ and $[Al(C_2O_4)_3]^{-3}$ is slight. At any rate, it would be expected that any optical activity would be short-lived, rather than as reported with half-life ranging from ¼ to 22 hr. There is therefore some doubt as to whether or not these substances have ever been resolved.

Johnson has also challenged the statement that dissociation can account for the racemization of $[Co(C_2O_4)_3]^{-3}$ and $[Cr(C_2O_4)_3]^{-3}$ on the basis that (*1*) he was unable to obtain any direct evidence for the dissociation of these ions (108), (*2*) the compounds undergo racemization in the solid state (108a), and (*3*) the rate of racemization is not decreased by the presence of oxalate ion (21). That crystalline salt hydrates of strychnine or potassium with either $[Co(C_2O_4)_3]^{-3}$ or $[Cr(C_2O_4)_3]^{-3}$ undergo racemization is a direct indication that the process can occur without dissociation. The racemization of the solid is neither the result of nor accompanied by decomposition, as shown by the fact that a sample 80 per cent racemized has the same spectrum in chloroform as the pure dextro or levo starting material.

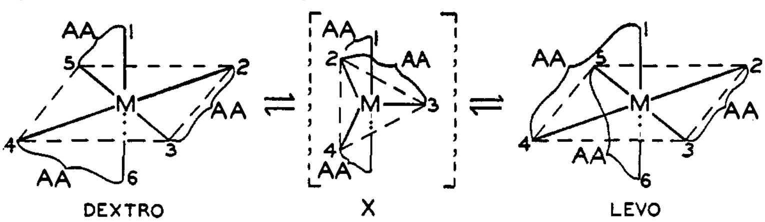
However, there is sufficient evidence to show that water plays an important role in the racemization of these crystals. For instance, when *d*- or *l*-$K_3[Cr(C_2O_4)_3]\cdot 2H_2O$ is heated at 120°C. in evacuated sealed tubes of sufficient capacity to discount any possibility of condensation of liquid water, the optical activity is essentially lost in several hours compared to several months with the dry solid. Another interesting observation was that from 10 to 20 per cent of the original activity always remained regardless of the temperature. Johnson and Mead (108a) suggest that water enters into the composition of the complex ions and when removed leaves them in an unstable "expanded" state. Because of certain constraints in the crystal, individual $[M(C_2O_4)_3]^{-3}$ ions may not "contract" immediately and when they do, the chance of inversion is conceivably less than 50 per cent. Therefore they represent the process of dehydration and racemization as follows:

$$d\text{-}[Cr(C_2O_4)_3]^{-3}\cdot 12H_2O \rightarrow d\text{-}[Cr(C_2O_4)_3]^{-3}\cdot yH_2O \rightarrow (p)l\text{-}\{Cr(C_2O_4)_3\}\cdot yH_2O + (1-p)d\text{-}\{Cr(C_2O_4)_3\}\cdot yH_2O$$

$p \mathrel{\overline{<}} 0.5$ is the probability of inversion; $y \mathrel{\overline{<}} 11$; [ ], original or "expanded" form; { }, final or "contracted" form. A more definite postulate as to the role played by water in the racemization of these compounds has been made previously by Charonnat (38). He visualized an expansion of the coördination number to eight and represented the complex as a cube with water at diagonal corners and suggested that as the water was expelled the complex could revert either to its original configuration or to that of its mirror image.

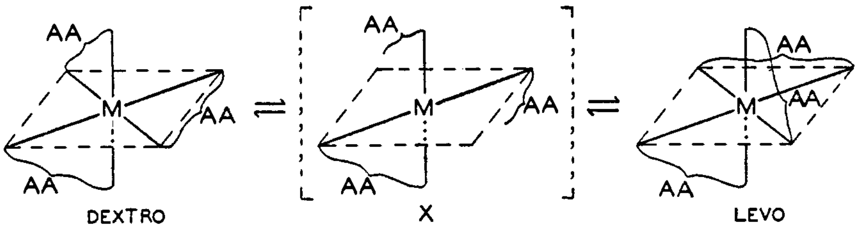


Beese and Johnson (21) have investigated the rate of racemization of $[Cr(C_2O_4)_3]^{-3}$ in the presence of foreign ions and observed that the rate is markedly accelerated by positive ions, the effect increasing with the charge of the cation. Anions, except for hydroxide ion, which increases the rate, have no effect on the rate of racemization. It was also observed that the presence of oxalate ion did not retard the rate of racemization but instead actually accelerated the reaction. Since 1 *M* calcium ion gives no precipitate with a solution of the complex, it was estimated that the concentration of oxalate ion is increased by at least a factor of 10^9 when the complex is dissolved in a fairly concentrated solution of potassium oxalate. Therefore, it would appear that either the time between dissociation and rearrangement is small compared to the interval between fruitful collisions with oxalate ions, even in the presence of an overwhelming quantity of potassium oxalate (in such a case the velocity of racemization is equal to the velocity of dissociation), or the racemization does not involve dissociation. Beese and Johnson are of the opinion that the latter is correct and thus the process must involve an intramolecular rearrangement. They mention that it should be possible to settle this question by the use of potassium oxalate enriched in the heavier isotopes of oxygen to establish if there is an exchange of oxalate ion. Long (131, 132) has conducted such an experiment, tagging the oxalate ion with radiocarbon. The results obtained showed that with $[Al(C_2O_4)_3]^{-3}$ and $(Fe(C_2O_4)_3]^{-3}$ there was rapid exchange, but there was essentially no exchange with $[Cr(C_2O_4)_3]^{-3}$ and $[Co(C_2O_4)_3]^{-3}$. Since, under these same conditions, the racemization of the chromium(III) and the cobalt(III) complexes is quite rapid, it would not appear to take place by a mechanism which involves a dissociation of the coördination complex. The results support an intramolecular rearrangement, which according to Werner (247) may take place as follows:

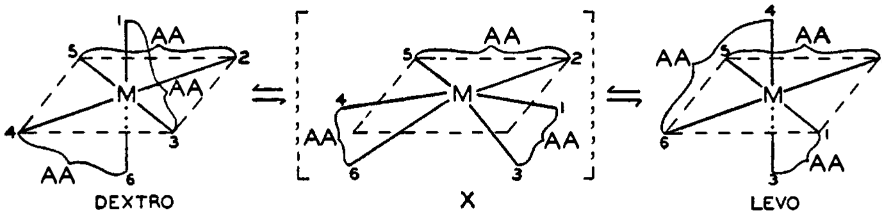


Werner was of the opinion that one chelate group could become detached at one position (position 5 in above diagram), the pentacovalent intermediate would rearrange (perhaps to a trigonal bipyramid structure, X), and then the group could reattach itself with equal ease between 2 and 4 to give the original isomer or between 4 and 3 to yield the mirror-image isomer. However, it should be made clear that this is only one of several possible mechanisms that would allow an intramolecular rearrangement.

According to Werner (243) $[\mathrm{Coen_3}]^{+3}$ does not racemize even in hot acid, and Bushra and Johnson (36) suggest that the ethylenediamine ring cannot be opened as readily as can the oxalate. Therefore if only one ring need be opened, it would appear that $[\mathrm{Coen_2C_2O_4}]^+$ should be capable of racemization; Werner (254) did find that this substance slowly lost its optical activity. However, Bushra and Johnson observed that the loss of activity was not due to racemization but was accompanied by decomposition of the complex. If it is assumed that in this complex the two ethylenediamine rings do not open (as appears to be the case with $[\mathrm{Coen_3}]^{+3}$) and that the oxalate group would behave as it does in $[\mathrm{M(C_2O_4)_3}]^{-3}$, it would seem that the failure of $[\mathrm{Coen_2C_2O_4}]^+$ to racemize may suggest the necessity that more than one ring open. Furthermore, the complex ion $[\mathrm{Cren(C_2O_4)_2}]^-$ racemizes with an activation energy of 15.8 kcal., which is the same as that for $[\mathrm{Cr(C_2O_4)_3}]^{-3}$ (36), thus indicating that two rings must open and in turn reattach at either the same positions or at exchanged positions.



More recently, Ray and Dutt (179) have reported the results of a detailed kinetic study on the racemization of the tris(biguanidinium)cobalt(III) ion. It was observed that cations catalytically retard the reaction while anions have no effect, except for hydroxide ion, which increases the velocity. Furthermore, from data collected at various temperatures the Arrhenius constant, *PZ*, was calculated and found to be extremely low for a unimolecular change. On the basis of these results it is argued that the rearrangement occurs without the rupture of any bonds. They also point out that since all six bonds in the complex are equivalent, there is no reason why two such bonds attached to one and the same chelate group should not occasionally be broken at the same time, thus giving rise to a dis-



sociation process; however, such a process has been shown to be untenable. Therefore it is their interpretation that the bonds need not be broken but that the chelate rings may merely shift around to give a distorted octahedron, which may then return to the original configuration or to its mirror image. This may be visualized from the above diagram if we consider that ring 5-2 remains fixed while ring 1-3 moves down 45° staying in its plane 1-3-M-5, while at the same time ring 4-6 moves up 45° in its plane 4-6-M-2 to yield X. It is apparent then that if this motion continues in the same direction through another 45° the enantimorph is formed, but if the path of motion is reversed, the starting material is regenerated. It is stated that the complex is not likely to lose its regular octahedral configuration until and unless the activation energy supplied is redistributed internally and transferred specifically to the rotational and vibrational degree of freedom of the bonds concerned. This amounts to an increase in the time interval between preactivation and critical activation with an increased chance of deactivation. The probability factor *P* and hence the *PZ* value will thereby be lowered, which is what Ray and Dutt report (179). Recent investigations on the rates of racemization of tris(dipyridyl) and tris(*o*-phenanthroline) complexes of nickel(II) and iron(II) have been interpreted to indicate support of this type of intramolecular rearrangement (57). Since the structures of these two diamines are such that they cannot behave as a monodentate, any intramolecular process may be expected to occur by way of some distorted octahedral intermediate.

TABLE 14

Racemization and dissociation rates of some nickel(II) and iron(II) complexes

COMPLEX	DISSOCIATION CONSTANTS $-\log K_3$	RACEMIZATION			DISSOCIATION		
		k (25°C.)	E_a	$\Delta S^‡$	h (25°C.)	E_a	$\Delta S^‡$
		min.$^{-1}$	*kcal.*	*E.U.*	*min.*$^{-1}$	*kcal.*	*E.U.*
$[Ni(ophen)_3]^{+2}$..	18 (44b)	6.0×10^{-4} (162)	25	2.3	6.0×10^{-4} (162)	25	2.3
$[Ni(dipy)_3]^{+2}$...	15 (44b)	1.4×10^{-1} (44b)	22	2.7	1.4×10^{-1} (162)	22	2.7
$[Fe(ophen)_3]^{+2}$..	21 (125a)	4.0×10^{2} (44b)	31	29	4.5×10^{-3} (28a)		
$[Fe(dipy)_3]^{+2}$...	16 (20a)	3.6×10^{-2} (44b)	20	19	7.3×10^{-3} (20b)	26	8.8

However, it should be mentioned that kinetics alone cannot be expected to settle the overall problem. Two plausible approaches of a more definitive nature suggest themselves. First, it would be desirable to investigate a system where an attached atom is itself rendered optically active by the bond to the central atom; if bonds are broken, the attached atom would undergo racemization at a rate comparable to that of the racemization of the entire complex. If no bonds are broken, there should be mutarotation to an activity due solely to that of the donor atom or atoms. Unfortunately, here one must be cognizant of the complication due to stereospecificity as described in Section D. The second approach would be to employ unsymmetrical bidentate groups of the type AB and to correlate the changes of geometrical isomerism during racemization with those expected on the basis of the various processes.

Schweitzer and Lee (186) observed no change in the rate of racemization of $[Ni(dipy)_3]^{+2}$ in the presence of dipyridyl and suggested that this result indicates that dissociation cannot account for the loss of optical activity. Similar results were obtained for solutions of $[Ni(ophen)_3]^{+2}$ containing excess *o*-phenanthroline, and Davis and Dwyer (44a) interpreted these observations in support of an intramolecular process. However, it should be reëmphasized (page 506) that the failure of the presence of excess chelating agent to alter the rate of racemization does not exclude the possibility of a dissociation mechanism. Certainly there would be no change in the rate of racemization if the dissociated product were either symmetrical and thus optically inactive or lost its optical activity very rapidly. Recent studies (162) on the rate of racemization[8] and rate of dissociation of $[Ni(ophen)_3]^{+2}$ suggest that the racemization does in fact proceed by a dissociation mechanism (table 14). Preliminary experiments with $[Ni(dipy)_3]^{+2}$ likewise indicate a dissociation process for its racemization (162). Davies and Dwyer (44b) have investigated the rates of racemization of analogous iron(II) complexes and have shown that these data differ from those for the nickel(II) complexes. It can be seen from the data summarized in table 14 that the iron(II) complexes racemize more rapidly than they dissociate, so that the racemization must involve an intramolecular process. It is not readily apparent why these very similar cations should racemize by different paths. One difference that has been observed between these complexes is in their magnetic susceptibility. The paramagnetism of $[Ni(dipy)_3]^{+2}$ suggests orbital hybridization of the type $s\ p^3\ d^2$ as compared to $d^2\ s\ p^3$ for the diamagnetic $[Fe(dipy)_3]^{+2}$. The more labile outer orbital (200) complex of nickel(II) may be considered as being consistent with a dissociation mechanism for racemization. Such an interpretation is, however, not compatible with the fact that $[Fe(ophen)_3]^{+2}$ dissociates approximately ten times faster than $[Ni(ophen)_3]^{+2}$.

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[8] The values referred to here and in table 14 for the rates of racemization are in the form allowing direct comparison with the rates of dissociation, and hence are twice the values stated by some workers. If the reaction is viewed as

$$\text{dextro} \overset{k}{\rightleftharpoons} \text{optically inactive products} \underset{k}{\rightleftharpoons} \text{levo}$$

then k for racemization is obtained from the slope, m, of the conventional $\log \alpha$ *vs.* t plot by the relationship $k = -2.30\ m$. Alternatively, if the reaction is considered a direct inversion

$$\text{dextro} \overset{k'}{\rightleftharpoons} \text{levo}$$

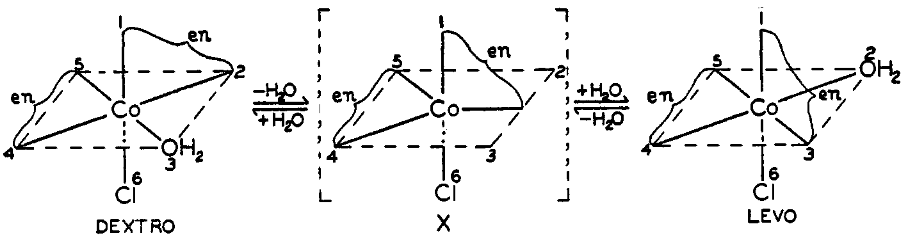
k' is found from the same plot to be given by $k' = -\frac{1}{2}(2.303\ m)$. For purposes of comparison with rates of dissociation use of the first method has apparent advantages; hence the values tabulated are for $k = 2k'$.

Holden and Harris (85) have made kinetic studies on the racemization of $[\mathrm{Coen_2CO_3}]^+$ and postulate the following mechanism:

$$\begin{tikzcd}
{[\mathrm{Coen_2CO_3}]^+} \arrow[r, "\mathrm{H_2O}"] & \underset{\mathrm{A}}{[\mathrm{Coen_2H_2O\,CO_3}]^+} \arrow[r, shift left, "-\mathrm{H}^+"] \arrow[d, shift left, "\mathrm{H}^+"] & \underset{\mathrm{B}}{[\mathrm{Coen_2OH(CO_3)}]} \arrow[l, shift left, "+\mathrm{H}^+"] \\
& \underset{\mathrm{C}}{[\mathrm{Coen_2H_2OHCO_3}]^{+2}} \arrow[u, shift left, "-\mathrm{H}^+"] \arrow[r, shift left, "+\mathrm{H_2O}"] & \underset{\mathrm{D}}{[\mathrm{Coen_2(H_2O)_2}]^{+3}} + \mathrm{HCO_3^-} \arrow[l, shift left, "-\mathrm{H_2O}"]
\end{tikzcd}$$

Species A, B, C, and D appear to be able to undergo racemization independently of one another. In the absence of free carbonate, D is present to some extent and undergoes racemization much more readily than the other forms. This leads to a racemization rate law with the rate proportional to $[\text{complex}]^{1/2}[\mathrm{H}^+]^{1/2}$, in agreement with experiment. However, when free carbonate is added, formation of D is suppressed and the racemization of A, B, and C must account for the observed process. This predicts a rate law with three terms, all proportional to [complex], one independent of $[\mathrm{H}^+]$. one proportional to $1/[\mathrm{H}^+]$, and one proportional to $[\mathrm{H}^+]$. The experimental results can be explained on this basis. Since the rate of racemization is slower by several-fold than the rate of exchange of complexed carbonate with free carbonate, it is presumed that the associative and dissociative equilibria do not effect racemization of themselves. The racemization appears to be an intramolecular process.

It is not to be expected that because the tris(oxalato) complexes undergo racemization by an intramolecular process, other systems cannot lose their optical activity by a dissociation mechanism. In fact, there is good evidence that complex ions of the types $[\mathrm{M(AA)_2a_2}]$ and $[\mathrm{M(AA)_2ab}]$ undergo inversion as a consequence of the dissociation of water from the corresponding aquo complexes. Mathieu (141) has done an excellent piece of work on the racemization of $[\mathrm{Coen_2Cl_2}]^{+1}$, $[\mathrm{Coen_2NO_2Cl}]^{+1}$, $[\mathrm{Coen_2NCSCl}]^{+1}$, and $[\mathrm{Coen_2NH_3Br}]^{+2}$ ions. He observed that aqueous solutions of these optically active complex ions undergo mutarotation to the corresponding monoaquo complexes without racemization and with retention of configuration. The ion $[\mathrm{Coen_2Cl_2}]^{+1}$ proved to be the most suitable for detailed study, and in this case it was observed that the rate of mutarotation (half-life = 1×10^4 min. at 30°C.) was the same as the rate of chloride formation. However, the resulting aquo complex, $[\mathrm{Coen_2H_2OCl}]^{+2}$, lost its optical activity at a rate independent of the rate of ionization of the second chloro group. This was demonstrated in three ways: (*1*) An acid (pH = 2) solution of the active complex was completely racemized when only 15 per cent of the coördinated chloro group had ionized; (*2*) the analogous reaction in a buffer solution (pH = 4.9) produced an optically active product even after 97 per cent of the complexed chloride had been released; and (*3*) the temperature dependence or activation energy of the two reactions is different. Therefore, it is clear that the replacement of a chloride ligand is not directly responsible for the racemization of $[Coen_2Cl_2]^+$ but rather the loss of activity occurs with the aquo complexes. Mathieu (141) states that the racemization of $[Coen_2H_2OCl]^{+2}$ must involve the dissociation of water from the complex,

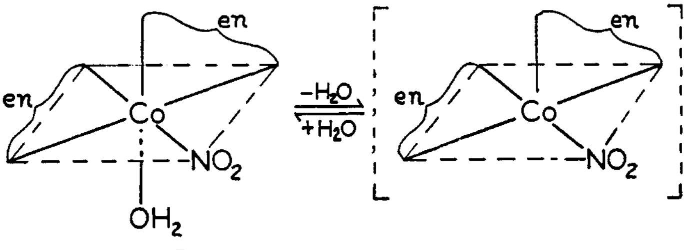


such that the pentacovalent intermediate (X) might rearrange so as to permit the recombination of water to yield either the original material or its enantiomorph. This is illustrated in the above diagram, ring 1-2 shifting so that the intermediate has a trigonal bipyramid structure and may accept water with equal ease at position 2 or 3. An experiment that should be performed on this system is a determination of the rate of exchange of water, using O^{18} to determine whether this is the same as the rate of racemization.

Preliminary experiments in our laboratories (195) have allowed an indirect estimate of the rate of dissociation of water in *cis*-$[Coen_2H_2ONO_2]^{+2}$. This was done by determining the rate of formation of $[Coen_2(NO_2)_2]^+$ with increasing concentration of nitrite ion. The results showed that the rate leveled off at concentrations of nitrite ion above 1 *M*. These results are compatible with the reaction process,

$$[Coen_2H_2ONO_2]^{+2} \underset{\underset{+H_2O}{k_2}}{\overset{\overset{-H_2O}{k_1}}{\rightleftharpoons}} [Coen_2NO_2]^{+2} \xrightarrow[k_3]{NO_2^-} [Coen_2(NO_2)_2]^+$$

or dissociation of the aquo-complex to the activated intermediate, followed by competitive reactions between water (k_2) and nitrite ion (k_3). The rate of formation of $[Coen_2(NO_2)_2]^+$ at which there is a zero-order dependence on nitrite-ion concentration would mean that essentially all of the $[Coen_2NO_2]^{+2}$ that is being formed is converted to the dinitro or, in other words, the rate constant is equal to k_1. In order to rule out complications due to specific ionic effects, work is now in progress to find other reagents that behave like the nitrite ion, and to study other solvent systems to see if under the same condition the same limiting rate constant (k_1) is attained with various reagents. On the basis of our present knowledge one may take this as a good approximation of the rate of dissociation. Mathieu (141) finds that $[Coen_2NO_2Cl]^+$ undergoes mutarotation at the same rate at which the chloro group ionizes but that the resulting $[Coen_2H_2ONO_2]^{+2}$ is still optically active even after standing for two months. On the basis of the fact that the dissociation of water from the complex appears to have a half-life of approximately 13 min. at 35°C., one is prompted to suggest that the dissociation occurs with essentially retention of configuration.

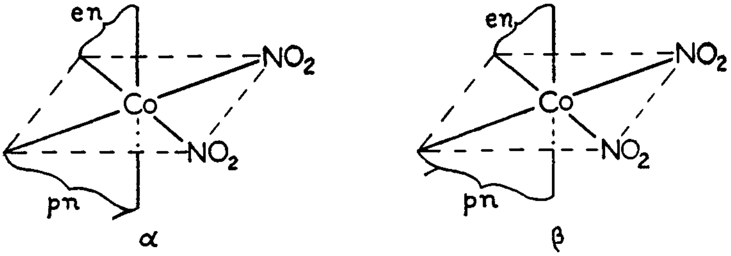


DEXTRO

Additional support is afforded a tetragonal pyramid structure for the intermediate, in that optically active $[Coen_2NO_2Cl]^+$ reacts with either nitrite ion or thiocyanate ion without racemization and with retention of configuration (140, 248), as has also been found to be true for *trans*-$[Coen_2NO_2Cl]^{+1}$. Mathieu (141) also observed that solutions of optically active $[Coen_2NH_3H_2O]^{+3}$ and $[Coen_2H_2ONCS]^{+2}$ remained active for several months, a result which would suggest a tetragonal pyramid intermediate, but here, too, it will be necessary to determine the rate of dissociation of water from the complex. The eventual racemization may be attributable to a finite but small probability of the tetragonal pyramid rearranging before reacting.

D. Optically active ligands in complexes

Considerable attention has been devoted to the coördination of optically active organic residues with metal ions, and some rather interesting stereospecific effects have been observed. Bailar (7) has recently written an excellent review of this subject. Researches in this connection have largely involved the use of either propylenediamine or *trans*-cyclopentanediamine. Since propylenediamine is unsymmetrical, it introduces additional complications as a result of the increase in the number of geometrical isomers resulting from the relative positions of the methyl groups; this does not occur with cyclopentanediamine. For instance, there are two possible *cis* isomers of $[Coenpn(NO_2)_2]^+$,



depending upon whether the methyl group is adjacent to both nitro groups (α) or opposite one nitro group (β). There can be only one geometrical form of the *trans* isomer, but since the propylenediamine can be either dextro or levo it turns out that ten isomers are theoretically possible: *trans-d*, *trans-l*, αD*d*, βD*d*, αD*l*, βD*l*, αL*d*, βL*d*, αL*l*, and βL*l*.[9] Werner (256) was able to isolate and characterize all ten isomers. Except for some recent work by Johnson (108b), this appears to be the only conclusive evidence for the realization of isomerism resulting from the position of the methyl group in propylenediamine. Hurlimann (93) and Watts (221) investigated the analogous compound containing two molecules of propylenediamine, $[\mathrm{Copn_2(NO_2)_2}]^+$, which theoretically allows the existence of twenty-six isomers. They were able to isolate only four compounds, which consisted of two pairs of mirror-image isomers. It was therefore concluded that the position of the methyl groups did not make a big enough difference in the solubility characteristics to permit their separation. Another possibility is that these are the most stable forms and consequently the only ones formed.

Tschugaeff and Sokoloff (213) prepared several platinum(II) complexes containing *l*-propylenediamine (table 15) and noticed that the molecular rotation caused by each molecule of *l*-propylenediamine is approximately +96°. Several years later, Smirnoff (194) prepared $[\mathrm{Pt}(l\text{-pn})_3]\mathrm{Cl_4}$ and found it to have a molecular rotation of +1025°. If each diamine had contributed only +96°, as was true with the planar platinum(II) complexes, the rotation should have been +288°. One is thus forced to conclude that the substance isolated is not merely a racemic mixture of D*lll* and L*lll* but that it is primarily one of these. This illustration was the first indication of the stereospecificity with which optically active ligands must enter a coördination sphere. Jaeger and Blumendal (104) made a detailed study of this phenomenon, using optically active *trans*-1,2-cyclopentanediamine.

TABLE 15

Optical activity of l-propylenediamine complexes of platinum

COMPOUND	$[M]_D$	COMPOUND	$[M]_D$
$[\mathrm{Pt}l\text{-pn}(\mathrm{NH_3})_2]\mathrm{Cl_2}$	+94	$[\mathrm{Pt}(l\text{-pn})_2]\mathrm{Cl_2}$	+192
$[\mathrm{Pt}(l\text{-pn})\mathrm{en}]\mathrm{Cl_2}$	+96	$[\mathrm{Pt}(l\text{-pn})_3]\mathrm{Cl_4}$	+1025
$[\mathrm{Pt}(l\text{-pn})\mathrm{tn}]\mathrm{Cl_2}$	+98		

The reaction between racemic $[\mathrm{Coen_2Cl_2}]^+$ and *l*-cyclopentanediamine was found to yield two isomers,

$$\mathrm{DL\text{-}[Coen_2Cl_2]Cl} + l\text{-cptdin} \rightarrow \mathrm{D\text{-}[Coen_2}l\text{-cptdin]Cl_3} + \mathrm{L\text{-}[Coen_2}l\text{-cptdin]Cl_3}$$

one (L*l*) of which was difficult to isolate. If the racemic base was used, only two of the four possible isomers could be conveniently isolated.

$$\mathrm{DL\text{-}[Coen_2Cl_2]Cl} + dl\text{-cptdin} \rightarrow \mathrm{D\text{-}[Coen_2}l\text{-cptdin]Cl_3} + \mathrm{L\text{-}[Coen_2}d\text{-cptdin]Cl_3}$$

Jaeger and Blumendal also prepared a complex containing two molecules of cyclopentanediamine; the *trans* isomer could be isolated only in the *ll* and *dd* forms, the *trans-dl* isomer never being obtained. Furthermore, it was found that

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[9] D and L are used to designate the configuration of the complex, and *d* and *l* to designate the rotations of the optically active coördinated groups.

upon heating, the *trans-ll* isomer yielded only the *cis*-D*ll* form, whereas *trans-dd* gave *cis*-L*dd*; the other two possible combinations of the *cis* isomer, L*ll* and D*dd*, were not isolated. Likewise an attempt to prepare $[Co(d\text{-cptdin})_2(l\text{-cptdin})]Cl_3$ yielded only the D*lll* and L*ddd* isomers.

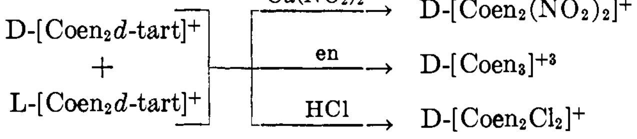
$$\begin{array}{l}\text{L-}[Co(d\text{-cptdin})_2Cl_2]Cl + l\text{-cptdin} \rightarrow \text{L-}[Co(d\text{-cptdin})_2 l\text{-cptdin}]Cl_3 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\downarrow \\ \qquad\qquad\qquad\qquad\qquad \text{L}[Co(d\text{-cptdin})_3]Cl_3 + \text{D}[Co(l\text{-cptdin})_3]Cl_3\end{array}$$

It appears that the desired intermediate undergoes disproportionation to yield the other more stable isomers. With complexes that contain three optically active bidentate groups, eight isomers can theoretically exist (D*lll*, D*lld*, D*ldd*, D*ddd*, L*lll*, L*lld*, L*ldd*, and L*ddd*), but in the case of the complex ions $(Co(cptdin)_3]^{+3}$ (104), $[Co(pn)_3]^{+3}$ (214), and $[Pt(pn)_3]^{+3}$ (194) only the D*lll* and L*ddd* isomers have been isolated. However, Lifschitz (130) has been able to isolate both the D*ddd* and the L*ddd* forms of α-$[Co(d\text{-alanine})_3]$, which exists in both α- and β-forms, since alanine is an unsymmetrical AB-type bidentate. The β-forms are so insoluble that he was unable to separate them. Bailar (7) suggests that the tendency to form only the L*ddd* isomers probably also exists with the alanine compounds, but the extreme stability of the cobalt–alanine rings may preclude rearrangement from a less stable to a more stable form.

Recent studies by Bailar and his students indicate that even in the more labile diammine systems, where generally only specific isomers had been isolated, the other forms may be present but the various isomers differ in reactivity. For example, it was reported by Bailar and McReynolds (12) that $[Co(l\text{-pn})_2CO_3]Cl$ can be prepared in two forms, which on the basis of their rotatory dispersion curves are believed to be the D*ll* and L*ll* diastereoisomers. These were referred to as "stable" and "unstable," because it was observed that upon heating in solution one form was converted into the other. However, the more recent work of Sister Mary Martinette and Bailar (138) shows that such terminology is not strictly correct. The L*ll* isomer is isolated by concentration of an aqueous solution of the complex on a steam bath, and the D*ll* isomer is obtained when the same solution is concentrated at room temperature. It appears that both the D*ll* and the L*ll* isomer slowly rearrange in solution to give the same equilibrium mixture. Another instance (109) in which the two isomers that should exist must indeed be produced is furnished by the reaction:

$$\text{DL-}[Coen_2CO_3]^+ \xrightarrow{d\text{-}H_2tart} \text{D-}[Coen_2 d\text{-tart}]^+ + \text{L-}[Coen_2 d\text{-tart}]^+$$

Although the diastereoisomers were too soluble and thus could not be effectively separated by fractional crystallization, the presence of both isomers in the original reaction mixture was readily established, as they differ greatly in reactivity. The reactions reported may be summarized as follows:



$$\left.\begin{array}{c}\text{D-}[Coen_2 d\text{-tart}]^+ \\ + \\ \text{L-}[Coen_2 d\text{-tart}]^+\end{array}\right] \begin{array}{l}\xrightarrow{Ca(NO_2)_2} \text{D-}[Coen_2(NO_2)_2]^+ \\ \xrightarrow{en} \text{D-}[Coen_3]^{+3} \\ \xrightarrow{HCl} \text{D-}[Coen_2Cl_2]^+\end{array}$$

In each case the reaction practically stops once the more reactive D*d* has been consumed. However, at elevated temperatures, approximately 70 per cent of D-$[\text{Coen}_3]^{+3}$ was produced, indicating that an asymmetric synthesis had taken place.

These rather surprising results have been successfully extended to the resolution of organic acids and have been suggested as a possible way to relate the generic configurations of these acids. For example, Bailar, Jonassen, and Gott (10) report that when a mixture of D-$[\text{Co}(l\text{-pn})_2d\text{-tart}]\text{Cl}$ and D-$[\text{Co}(l\text{-pn})_2l\text{-tart}]\text{Cl}$ is heated in aqueous solution at 70°C. with an excess of *l*-propylenediamine, the *l*-tartrate ion is preferentially displaced from the complex. Furthermore, it was observed that under these same conditions D-$[\text{Co}(l\text{-pn})_2l\text{-tart}]^+$ is completely converted to D-$[\text{Co}(l\text{-pn})_3]^{+3}$ in 40 min. as compared to 2 hr. required for the same reaction to occur with D-$[\text{Co}(l\text{-pn})_2d\text{-tart}]^+$. It should be of extreme interest to make a detailed study of the kinetics of these reactions as well as their thermodynamics in an attempt to answer the question as to whether this difference in property is caused by a difference in rate of reaction or in stability or perhaps both. Gott and Bailar (79) have been able to partially (30 per cent) resolve tartaric, lactic, chloropropionic, and bromopropionic acids by a slightly different reaction. When an aqueous solution of D-$[\text{Co}(l\text{-pn})_2\text{CO}_3]^+$ was treated with a 100 per cent excess of a racemic mixture of an organic acid and evaporated to dryness, the dextro enantiomorph always entered the coördination sphere, as either a monodentate or a bidentate group. If the molecule or anion readily entered the coördination sphere of the complex, it should have a dextro configuration regardless of the sign of rotation. Therefore it may be possible to relate the generic configurations of optical antipodes for analogous compounds on the basis of the ease with which they enter the coördination sphere of a given optically active complex.

The application of optically active complex ions for the resolution of certain amino acids had previously been reported by Shibata and his students (190, 191). They report an interesting asymmetric oxidation in which *l*-$[\text{Coen}_2\text{NH}_3\text{Cl}]^{+2}$ oxidizes the levo form of 3,4-dihydroxyphenylalanine more rapidly than it does the dextro form. The authors attribute this to an "enzyme-like action" of the inorganic complex. However, Bailar (6) suggests as an alternative explanation that the levo form of the amino acid becomes a part of the complex more readily than does its enantiomorph. Similar studies by Pugh (175) gave results that are not in complete agreement with those of Shibata. An extremely interesting observation has recently been made by Dwyer (57, 65a), which may perhaps be related to these stereospecific phenomena. He found that the injection of 0.15 mg. of *d*-$[\text{Ru(ophen)}_3](\text{ClO}_4)_2$ into the peritoneal cavity of a mouse kills it in about 90–120 sec. and that 0.15 mg. of the levo isomer acts as an antidote. The racemic mixture will kill also, but at higher concentrations.

E. Oxidation–reduction reactions of optical isomers

It is possible to achieve certain conditions with complex inorganic compounds that have no counterpart with compounds of carbon. For example, it has been of interest (6) to design an experiment which would involve the addition or removal of an electron from the central atom of an optically active complex. Hamblin and Johnson (84) attempted to prepare optically active $[\mathrm{Fe(dipy)_3}]^{+3}$ by the oxidation of l-$[\mathrm{Fe(dipy)_3}]^{+2}$ with chlorine but were unsuccessful. Recently Dwyer and Gyarfas (59, 60) have reported the first successful oxidation–reduction reaction of an optically active complex ion without racemization. However, as will be apparent in Section IV,F, the reactions of the peroxo complexes observed by Werner in 1910 were actually oxidation–reduction reactions and occurred without loss of optical activity. When d- or l-$[\mathrm{Ru(ophen)_3}](\mathrm{ClO_4})_2$ was oxidized with ceric nitrate the resulting blue solution containing $[\mathrm{Ru(ophen)_3}](\mathrm{ClO_4})_3$ was optically active but of opposite rotation. Although the activity of this solution was lost rapidly at 20°C., if the solution was immediately reduced with ferrous sulfate, d- or l-$[\mathrm{Ru(ophen)_3}](\mathrm{ClO_4})_2$ was regenerated with its rotation unchanged.

$$\underset{\text{(orange)}}{[\mathrm{Ru(ophen)_3}]^{+2}} \xrightleftharpoons[\mathrm{FeSO_4}]{\mathrm{Ce(SO_4)_2}} \underset{\text{(blue)}}{[\mathrm{Ru(ophen)_3}]^{+3}}$$

$$[M]_D = \left\{\begin{matrix} +1834^\circ & \leftrightarrow & -568^\circ \\ -1818^\circ & \leftrightarrow & +584^\circ \end{matrix}\right\}$$

The difference in the sign of rotation has been attributed to the abnormal rotatory dispersion of these compounds, and it is believed that the oxidation and reduction take place without any change in configuration. The authors say that complete rotatory dispersion curves of all these complexes will be taken in order to determine whether an inversion occurs during the reactions. They also report the potential of the reaction

$$d\text{- or } l\text{-}[\mathrm{Ru(ophen)_3}]^{+2} \rightleftharpoons l\text{- or } d\text{-}[\mathrm{Ru(ophen)_3}]^{+3} + e$$

in 6 N sulfuric acid at 0°C. to be -1.17 v. The same value was obtained for the racemate, and it appears that this is the first time that the oxidation potential of an enantiomorphous form has been compared with that of the racemic mixture.

Similar results have been reported (61) for the reaction:

$$d\text{- or } l\text{-}[\mathrm{Ru(dipy)_3}]^{+2} \rightleftharpoons l\text{- or } d\text{-}[\mathrm{Ru(dipy]_3}]^{+3} + e$$

These reactions have since been extended to include the other two members of this group of elements: namely, iron and osmium. The results obtained were in general those to be anticipated in that the iron complexes, being more labile, were found to undergo racemization very rapidly, while the osmium compounds were optically stable. Dwyer and Gyarfas (63) were able to resolve $[\mathrm{Fe(ophen)_3}]^{+2}$ by converting it to the antimonyl d-tartrate. In this connection, it is of interest to note that from a solution of racemic $[\mathrm{Fe(ophen)_3}]^{+2}$ containing excess antimonyl d-tartrate, the complex was slowly precipitated completely as l-$[\mathrm{Fe(ophen)_3}](d\text{-}\mathrm{SbOC_4H_4O_6})_2\cdot 4\mathrm{H_2O}$, leaving a colorless filtrate. This is due to the lability of the complex, so that the equilibrium between the dextro and levo complex ions is shifted toward the less soluble diastereoisomer until finally none of the dextro complex remains. A similar observation was made by Werner (247) on the resolution of $[\mathrm{Cr(C_2O_4)_3}]^{-3}$ with strychnine. It may also be pointed out here that one reason why Jaeger was able to isolate only certain specific diastereoisomers from his reaction mixtures may be that the complexes were sufficiently labile to allow rearrangement to give the less soluble salt. The oxidation of a solution of *d*- or *l*-$[Fe(ophen)_3]^{+2}$ with ceric sulfate at room temperature yielded an optically inactive reaction mixture. However, when the reaction was carried out at 6°C. the solution was active but the rate of racemization was too great to permit an accurate measurement of the specific rotation, which was estimated to be approximately 60 per cent of that of the ferrous complex at the sodium *D* line. A recent report (65) describes the isolation of *d*- and *l*-$[Fe(dipy)_3](ClO_4)_3 \cdot 3H_2O$, which were obtained by the oxidation of *d*- and *l*-$[Fe(dipy)_3]^{+2}$, respectively. It is now clear why the earlier experiments of Hamblin and Johnson on this system were not successful. Dwyer and Gyarfas (65) state that the oxidation with chlorine is so slow that appreciable racemization occurs even at optimum conditions, because the half-life of the active iron(III) complex ion in solution is only a few minutes. Therefore, they finally used ceric ammonium nitrate as the oxidant. It is interesting that the dipyridyl complexes of iron(II) undergo racemization approximately twice as fast as the analogous *o*-phenanthroline compounds (57) but that apparently the reverse is true for the iron(III) complexes.

The optically stable osmium(III) complexes were conveniently prepared by the oxidation of the osmium(II) compounds with chlorine (65). The optical rotation of *d*- and *l*-$[Os(ophen)_3]^{+3}$ ions at the sodium *D* line is zero, whereas at 5461 Å. the specific rotations are $[\alpha]^{20}_{5461} = +380°$ and $-360°$, respectively. Since the sodium *D* line is commonly used in polarimetric work, it is well to note that in this case had measurements been made only at that one wave length it would have been erroneously concluded that the solutions were optically inactive. Because of the large rotatory dispersion generally associated with optically active complexes, the activity should always be checked at more than one wave length.

Considerable attention is presently (28, 43, 129, 148) being devoted to the kinetics and probable mechanism of electron-transfer reactions. These studies have been made by the application of isotopic tracer techniques. However, Dwyer and Gyarfas (64) have demonstrated how these studies can be accomplished with optically active complexes of $[Os(dipy)_3]^{+2}$ and $[Os(dipy)_3]^{+3}$. Individual solutions of these ions do not undergo racemization but when *d*-$[Os(dipy)_3]^{+2}$ is mixed with an equivalent amount of *l*-$(Os(dipy)_3]^{+3}$, the optical activity of both ions is lost as a result of the following equilibria:

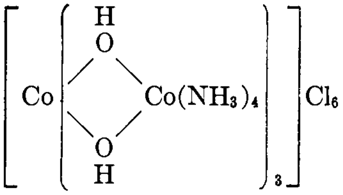
$$\text{D-}[Os(dipy)_3]^{+2} \rightleftharpoons \text{D-}[Os(dipy)_3]^{+3} + e$$

$$\text{L-}[Os(dipy)_3]^{+3} + e \rightleftharpoons \text{L-}[Os(dipy)_3]^{+2}$$

Therefore in this system the rate of loss of optical activity is a measure of the rate of electron exchange. The advantage of this method over the use of tracer techniques is that the kinetics of the electron transfer can be studied at various conditions without the necessity of altering these conditions by the separation of the oxidant and (or) the reductant. The obvious disadvantage is that optically active systems suitable for such a study are rare indeed, at present the only good ones being the osmium(II)–osmium(III) complexes of dipyridyl and *o*-phenanthroline. The authors report that the mixed solution 5×10^{-4} *M* with respect to both ions, was completely inactive in less than 15 sec. at 25°C.; at 10°C. this required approximately 65 sec., and at 5°C., 95 sec. The rate at 10°C. was very much greater in 2 *N* ammonium nitrate solution, but much slower in acetone than in water. This rapid loss of optical activity, plus the fact that the electron transfer is believed to take place with retention of configuration, lends support to the current theory of electron-exchange reactions in aqueous solution. On the basis of the Franck–Condon principle, Libby (129) postulates that the slow exchange between simple ions such as Fe(II)–Fe(III) (193), Ce(III)–Ce(IV) (82), and Eu(II)–Eu(III) (148) in aqueous solution is due to the hydration atmospheres being unable to move in the time required for the electron transfer. This results in the formation of ions in an incorrect environment, requiring the later movement of hydration energy from one site to another and thus constituting a barrier inhibiting the exchange. The hydration atmospheres of the simple ions probably involve considerable differences in energy and geometric arrangement. Exchange of coördinated ions such as MnO_4^{-2}–MnO_4^{-} (28, 90), $[Fe(CN)_6]^{-4}$–$[Fe(CN)_6]^{-3}$ (28, 43, 206), and $[Os(dipy)_3]^{+2}$–$[Os(dipy)_3]^{+3}$ (69) is very fast, because it is likely that no movement of these donor groups larger than the natural amplitude of the zero-point motion is required in the electron transfer. In addition, the energies of hydration of these larger ions are necessarily much smaller because of the size of such ions. For these reasons the barrier is reduced greatly in magnitude by the addition of the highly symmetrical and firmly coördinated groups.

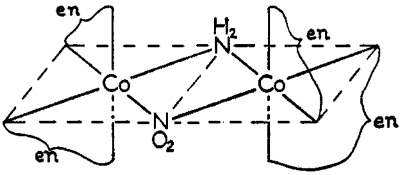
F. Polynuclear complexes

The intriguing problems in the stereochemistry of monomolecular hexacovalent complexes become even more complicated with the polynuclear complexes. This is no doubt one reason why only a relatively small amount of work has been done with these substances. One of the most important compounds of this type from a theoretical point of view is

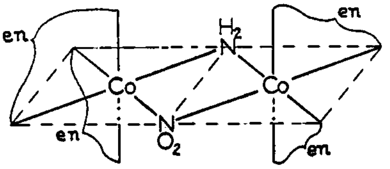


$$\left[Co\left[(OH)_2Co(NH_3)_4\right]_3\right]Cl_6$$

which Werner (225) prepared and resolved in 1914. Since the compound contains no carbon it demonstrated that the presence of carbon in such complexes is not a necessary condition for optical activity. Another interesting example reported by Werner (249) is the tetrakis (ethylenediamine)-μ-amido-μ-nitrodicobalt(III) ion, that may exist either as the *dl*-isomer

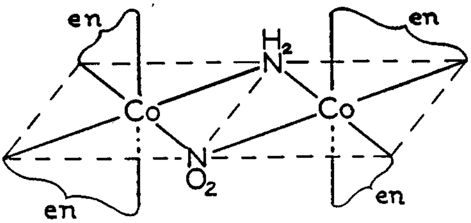


DEXTRO



LEVO

or as the optically inactive meso form.



MESO

Werner was able to separate the optical antipodes by fractional crystallization of the *d*-α-bromocamphor-π-sulfonate salts. Evaporation of aqueous solutions of either optically active complex yielded the unresolvable meso isomer.

Peroxo complex ions of cobalt have been known for a long time (71), but Werner (263, 264) was the first to make a detailed systematic study of these compounds. From an aerated ammoniacal cobalt(II) solution he isolated a green complex which was represented as

$$[(H_3N)_5Co^{III}—O_2—Co^{IV}(NH_3)_5](NO_3)_5$$

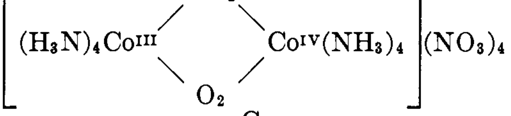
A

and a red-brown compound:

$$[(H_3N)_5Co^{III}—O_2—Co^{III}(NH_3)_5](NO_3)_4$$

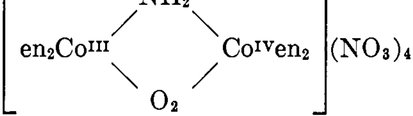
B

Compound A was designated as a binuclear peroxo complex of cobalt(III) and cobalt(IV) on the basis of analytical evidence. Analogous green complex ions of tri- and tetrapositive cobalt with two bridges (-μ-amido-μ-peroxo-) between the cobalt atoms were obtained,



$$\left[(H_3N)_4Co^{III}\begin{matrix}NH_2\\ \diagup\quad\diagdown\\ \diagdown\quad\diagup\\ O_2\end{matrix}Co^{IV}(NH_3)_4\right](NO_3)_4$$

C

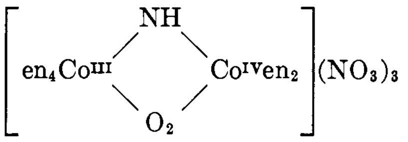


$$\left[en_2Co^{III}\begin{matrix}NH_2\\ \diagup\quad\diagdown\\ \diagdown\quad\diagup\\ O_2\end{matrix}Co^{IV}en_2\right](NO_3)_4$$

D

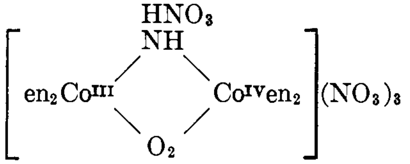
Magnetic susceptibility measurements (133, 142) give effective moments for compounds A, C, and D of 1.7 B.M., showing the presence of an unpaired electron; compound B is diamagnetic. The magnetic data, although in accord with structures A, C, and D, do not exclude other possible structures (207), such as one in which the compounds contain instead only cobalt(III) and the superoxide ion, $:\underset{\cdot\cdot}{O}\,\dot{:}\,\underset{\cdot\cdot}{O}:^-$ (29, 78). Except for the fact that three equivalents of oxygen are liberated per mole of C, all of the present available data can just as well be explained on the basis of a superoxide ion type of structure (118). The exact structure of these compounds is therefore not known, but some attempt is being made to clarify this problem (207).

Compound D is asymmetric and should therefore be optically active. Werner (264) was able to resolve this complex and found that it had an unusually high optical rotation ($[\alpha]_D = -815°$) compared to analogous cobalt(III) compounds. The optical activity decreased gradually and completely vanished after some weeks. Several reactions were carried out on the dark green *l*-D and in every case a red to brown dextrorotatory product was obtained. For example, if ammonia is allowed to react with *l*-D, the product has a specific rotation of $[\alpha]_D = +160$ and Werner designated its structure as



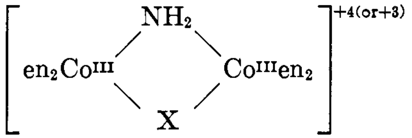
E

If acid is used, a value of $[\alpha]_D = +208°$ is obtained; the product is said to be



F

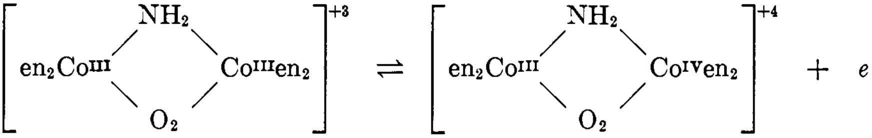
However, Werner claimed that *l*-C is reduced by sodium iodide, nitrous acid, or sulfur dioxide to



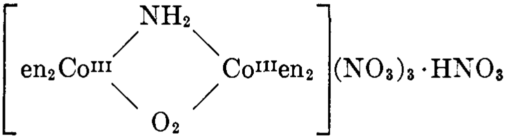
G

where X = OH^-, NO_2^-, or SO_4^{-2}. Since in all cases G is still optically active, ($[\alpha]_D = +110°$, $+158°$, and $+200°$ for G with X = OH^-, NO_2^-, and SO_4^{-2}, respectively) this would represent the first case of reduction of an optical antipode without loss of activity.

Thompson and Wilmarth (207) have recently made an excellent beginning toward a definite elucidation of the structure of these compounds. They were able to show that the change of the dark green complex D into the red compounds reported by Werner involved a one-electron reduction. In fact, the oxidation–reduction reaction



is reversible with an electrode potential of somewhat more than −1.0 v. Therefore compound E appears to be



H

Structure H is likewise supported by the fact that this compound is diamagnetic. Now that these structures appear to be clearly defined, and as oxidation–reduction reactions are involved, it would be of interest to perform some studies on these compounds analogous to the work of Dwyer and Gyarfas with the complexes of iron, ruthenium, and osmium. In particular, one would like to test the loss of optical activity in a solution containing equivalent amounts of D and H of different generic configuration. The results of this experiment may throw some light on the existence of cobalt(IV) in D, because in such a case one would expect a rapid electron exchange or, in other words, rapid racemization.

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