cobalt than does glycine, but a higher affinity for hydrogen ion. No obvious explanation exists for these observations.

Acknowledgment.—The authors wish to express their appreciation to Dr. F. H. Westheimer for helpful discussion of the calculations involving the Kirkwood–Westheimer theory.

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions in Complex Ions. II. Stereochemical Changes Accompanying Some Reactions of Cobalt(III) Complexes[1,2]

BY FRED BASOLO, BOB D. STONE[3,4] AND RALPH G. PEARSON

RECEIVED APRIL 23, 1952

The reactions of several geometric isomers of cobalt(III) complexes with various reagents have been studied. A semi-quantitative estimate of the relative amounts of *cis* and *trans* isomers produced *in situ* was made by means of a spectrophotometric determination. A discussion is given showing various structural changes to be expected on the basis of four different reaction mechanisms. However, the results of this study show clearly that no one of these mechanisms is operative in all substitution reactions.

The mechanisms whereby ligands attached covalently to the central metallic ion in hexacovalent complexes are removed and replaced by other groups is of considerable interest. Although this problem has received considerable attention,[5] little can be said as to how these substitution reactions actually proceed. One plausible approach toward obtaining useful data in this connection is that utilized as early as 1912 by Werner.[6] He investigated the reactions of the geometric isomers of several complexes of cobalt(III) with various reagents and qualitatively estimated the ratios of the isomeric products isolated from these reactions. Unfortunately, Werner was unable to correlate his findings with any reaction mechanism(s) and concluded that there was no relationship between the position occupied by the incoming group and that of the outgoing group.

Since rearrangements of cobalt(III) complexes could occur during isolation, it can be argued that Werner's observations need not be a true measure of the immediate products of reaction. Because of this, it was decided that some of these reactions should be reinvestigated using milder reaction conditions and some technique which will allow an estimate of the ratios of geometric isomers as they are produced. Since geometric isomers of cobalt (III) complex ions usually have different absorption spectra,[7] a spectrophotometric technique was applied to get a semi-quantitative estimate of the relative amounts of *cis* and *trans* isomers obtained as products of reaction. In addition, several reactions were investigated which had not been included in Werner's study.

Experimental

Spectral Measurements.—All measurements were made at room temperature with a Beckman model DU spectrophotometer in silica cells having a 1-cm. light path. Molecular extinction coefficients were calculated from the familiar equation

$$\epsilon = 1/cd \log_{10} (I_0/I)$$

Compounds.—The compounds used were prepared by the procedures described in the literature and purified either by recrystallization or reprecipitation by the addition of ethanol–ether to a concentrated aqueous solution of the salt.[8] Although the compounds showed the correct analysis, there was no assurance that any of them consisted of a single isomeric form. However, many of these isomers are separated by differences in solubility, and considerable care was taken to discard intermediate fractions, retaining only the least and most soluble fractions.

Procedure.—Solutions of the *cis* and *trans* isomers were prepared using as solvent a stock solution containing the desired reagent. After reaction took place, the absorption spectra of the reaction mixtures between 300 and 600 mμ were determined by comparison with blanks of the same stock solution. For example, to study the reaction of chloroamminebis-(ethylenediamine)-cobalt(III) ions with sodium hydroxide

$$[\mathrm{Coen_2NH_3Cl}]^{+}_{2} + \mathrm{OH^-} \longrightarrow [\mathrm{Coen_2NH_3OH}]^{+}_{2} + \mathrm{Cl^-}$$

the chloroammine complexes were dissolved in a 0.5 *M* solution of sodium hydroxide and the spectra of the reaction products were determined by comparison with the sodium hydroxide solution. In addition, the absorption spectra of the *cis*- and *trans*-hydroxoamminebis-(ethylenediamine)-cobalt(III) ions which were used as standards, were determined by the same procedure in the same stock solution. The standards used were actually the *cis*- and *trans*-aquamminebis-(ethylenediamine)-cobalt (III) ions which in alkali react to yield hydroxo complexes

$$[\mathrm{Coen_2NH_3H_2O}]^{+3} + \mathrm{OH^-} \longrightarrow [\mathrm{Coen_2NH_3OH}]^{+2} + \mathrm{H_2O}$$

and it is assumed that this proton transfer does not alter the configuration of these complexes.

The absorption spectra shown in Fig. 1 may serve to illustrate the method employed to estimate the relative amounts of *cis* and *trans* isomers present in a given reaction mixture.[9] For example, the maximum difference in the spectra of *cis*- and *trans*-hydroxoamminebis-(ethylenediamine)-cobalt(III) ions is at 370 mμ. At this wave length the molecular extinction coefficient of the *cis* standard is 77 as compared to 53 for the *trans* complex. Since the extinction coefficient of the reaction mixture of the *cis*-chloroammine complex is also 77, it is concluded that the product is 100% *cis*-$[\mathrm{Coen_2NH_3OH}]^{+2}$. The extinction coefficient of the reaction mixture of the *trans*-chloroammine

---

[1] Paper I of this series: F. Basolo, J. G. Bergmann and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952).

[2] Presented at the New York Meeting of the American Chemical Society, September, 1951.

[3] Atomic Energy Commission Pre-doctoral Fellow, 1950–1952.

[4] Taken in part from a thesis submitted by Bob D. Stone in partial fulfillment of the requirements for the Ph.D. degree, 1952.

[5] For a review see, J. C. Bailar, Jr., *Chem. Revs.*, **19**, 67 (1936).

[6] A. Werner, *Ann.*, **386**, 1 (1912).

[7] Y. Shibata, *J. Coll. Sci. Imp. Univ. Tokyo*, 37 (1915); F. Basolo, THIS JOURNAL, **72**, 4393 (1950); Y. Shimura, *ibid.*, **73**, 5079 (1951).

[8] Gmelin, "Handbuch der anorganischen Chemie," No. 58B (Kobaltammine) Berlin, 1930.

[9] The detailed absorption spectra which were used to determine the relative amounts of *cis* and *trans* isomers reported in Table I are available in the doctorate thesis of Bob D. Stone.

complex is 72 at 370 mμ. Substitution in the expression

$$\frac{\epsilon_{\text{reaction mixture}} - \epsilon_{trans\ \text{standard}}}{\epsilon_{cis\ \text{standard}} - \epsilon_{trans\ \text{standard}}} \times 100 = \%\ cis \text{ in the reaction mixture}$$

gives 79% *cis*- and consequently 21% *trans*-$[Coen_2NH_3OH]^{+1}$.

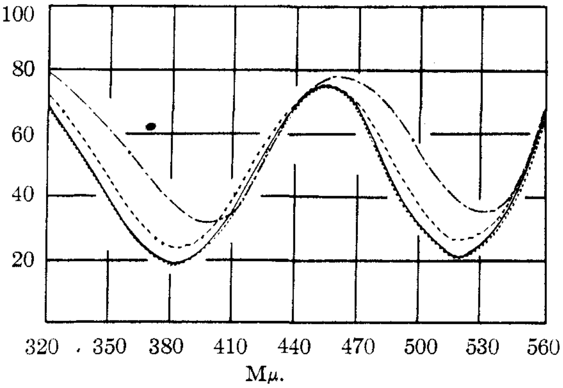


Fig. 1.—Absorption spectra of reaction products of *cis*- and *trans*-$[Coen_2NH_3Cl]^{+2}$ with hydroxide ion in 0.5 *M* NaOH: ——, *cis*-$[Coen_2NH_3Cl]^{+2}$ (0.0063 *M*); ----, *trans*-$[Coen_2NH_3Cl]^{+2}$ (0.0073 *M*). Absorption spectra of standards in 0.5 *M* NaOH: ....., *cis*-$[Coen_2NH_3H_2O]^{+3}$ (0.0053 *M*); — — —, *trans*-$[Coen_2NH_3H_2O]^{+3}$ (0.0047 *M*).

In every case the absorption of the reaction mixture was checked at various times to make certain that a steady state had been reached. The time required for the reactions to reach equilibrium varied considerably. The reactions with hydroxide ion were virtually instantaneous whereas aquation of the chloroammine and chlorothiocyanato complexes was not complete even after five days at 65°. Under these same conditions the *cis*- and *trans*-aquoammine and aquothiocyanatobis-(ethylenediamine)-cobalt(III) standards rearranged to mixtures which consist of primarily the *cis* isomers (Fig. 2). However, these aquo standards remained unchanged in alkali for at least five hours, which means that little or no rearrangement had taken place under the conditions of hydrolysis. Reaction mixtures of aquation in the presence of silver ion were allowed to stand overnight as were also the reaction mixtures with nitrite and thiocyanate ions.

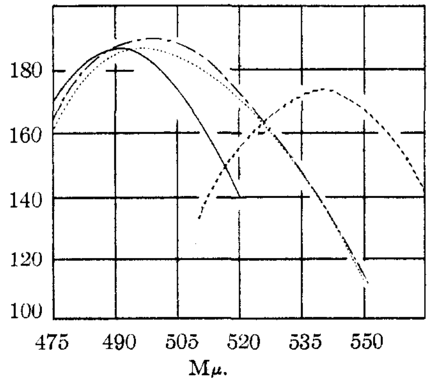


Fig. 2.—Absorption spectra of *cis*- and *trans*-$[Coen_2(H_2O)NCS]^{+2}$ in 0.5 *M* $HClO_4$: ——, *cis* (0.0019 *M* solution allowed to stand two days at 65° had the same spectrum); ----, *trans* (0.0027 *M* spectrum determined immediately); ...., *trans* (same solution after standing one day at 65°); — — —, *trans* (same solution after standing two days at 65°).

The molar concentrations of the solutions of the complexes were between 1×10^{-2} and 1×10^{-5}, depending upon the absorption characteristics of the compound and the wave length at which the measurement was taken.

The aquation reactions were carried out in 0.5 *M* aqueous perchloric acid while 0.5 *M* sodium hydroxide was used for the hydrolysis reactions. An aqueous solution which was 0.5 *M* in perchloric acid and 0.25 *M* in silver perchlorate was used for the aquation in presence of silver ion. The reactions with nitrite ion and thiocyanate ion were run in methanol–water mixtures (95% methanol by volume) with concentrations of 0.35 *M* sodium nitrite and 0.35 *M* potassium thiocyanate, respectively. The reaction of $[Coen_2NO_2Cl]^+$ with nitrite ion was also run in water and in water–dioxane solvent. The same results were found in all three solvent mixtures.

Since a salt of the *cis*-aquonitrobis-(ethylenediamine)-cobalt(III) complex has not been isolated, the spectrum used here as a standard was an aqueous solution of the aquation product of *cis* chloronitrobis-(ethylenediamine)-cobalt(III) chloride. That this product is largely the *cis*-aquonitro isomer, is shown by its optical activity.[10]

The accuracy of our measurements is reliable to only ±15% in some cases; the lack of greater accuracy is largely due to the slight differences in the absorption spectra of the

TABLE I

STEREOCHEMICAL CHANGES DURING SUBSTITUTION REACTIONS OF SOME COBALT(III) COMPLEX IONS

Reactant		Reagent	Product	Spectra	
cis	*trans*			% *cis*	% *trans*
			A. $[Coen_2NH_3Cl]^{+2}$		
+		NaOH	$[Coen_2NH_3OH]^{+2}$	100	...[a]
	+	NaOH	$[Coen_2NH_3OH]^{+2}$	80	20[b]
+		$AgClO_4 + HClO_4$	$[Coen_2NH_3H_2O]^{+3}$	75	25
	+	$AgClO_4 + HClO_4$	$[Coen_2NH_3H_2O]^{+3}$	20	80
+		$NaNO_2$	$[Coen_2NH_3NO_2]^{+2}$	80	20
	+	$NaNO_2$	$[Coen_2NH_3NO_2]^{+2}$	35	65
+		KCNS	$[Coen_2NH_3NCS]^{+2}$	30	70
	+	KCNS	$[Coen_2NH_3NCS]^{+2}$	90	10
			B. $[Coen_2NO_2Cl]^{+1}$		
+		NaOH	$[Coen_2NO_2OH]^{+1}$	100	...
	+	NaOH	$[Coen_2NO_2OH]^{+1}$	50	50
+		$H_2O + HClO_4$	$[Coen_2NO_2H_2O]^{+2}$	100	...[c]
	+	$H_2O + HClO_4$	$[Coen_2NO_2H_2O]^{+2}$	...	100
+		$AgClO_4 + HClO_4$	$[Coen_2NO_2N_2O]^{+2}$	100	...
	+	$AgClO_4 + HClO_4$	$[Coen_2NO_2H_2O]^{+2}$	...	100
+		$NaNO_2$	$[Coen_2(NO_2)_2]^{+1}$	100	...[d]
	+	$NaNO_2$	$[Coen_2(NO_2)_2]^{+1}$	...	100
+		KCNS	$[Coen_2NO_2NCS]^{+1}$	Largely	...[e]
	+	KCNS	$[Coen_2NO_2NCS]^{+1}$	...	Largely
			C. $[Coen_2NCSCl]^{+1}$		
+		NaOH	$[Coen_2(OH)_2]^{+1}$	85	15
	+	NaOH	$[Coen_2(OH)_2]^{+1}$	80	20
+		NaOH; $HClO_4$	$[Coen_2NCSH_2O]^{+2}$	90	10
	+	NaOH; $HClO_4$	$[Coen_2NCSH_2O]^{+2}$	90	10
+		$NaNO_2$	$[Coen_2(NO_2)_2]^{+1}$	...	100
	+	$NaNO_2$	$[Coen_2(NO_2)_2]^{+1}$	...	100
			D. $[Coen_2Cl_2]^{+1}$		
+		NaOH	$[Coen_2(OH)_2]^{+1}$	40	60[f]
	+	NaOH	$[Coen_2(OH)_2]^{+1}$	60	40[g]
+		$NaNO_2$	$[Coen_2(NO_2)_2]^{+1}$	50	50
	+	$NaNO_2$	$[Coen_2(NO_2)_2]^{+1}$	50	50
+		KCNS	$[Coen_2NCScl]^{+1}$	90	10
	+	KCNS	$[Coen_2NCScl]^{+1}$	15	85[h]
			E. $[Coen_2NH_3H_2O]^{+3}$		
+		$NaNO_2$	$[Coen_2NH_3NO_2]^{+2}$	80	20[i]
	+	$NaNO_2$	$[Coen_2NH_3NO_2]^{+2}$	35	65[j]
+		KCNS	$[Coen_2NH_3NCS]^{+2}$	40	60[k]
	+	KCNS	$[Coen_2NH_3NCS]^{+2}$	40	60[l]
			F. $[Coen_2NO_2H_2O]^{+2}$		
+		$NaNO_2$	$[Coen_2(NO_2)_2]^{+1}$	100	...[m]
	+	$NaNO_2$	$[Coen_2(NO_2)_2]^{+1}$	...	100[n]
+		KCNS	$[Coen_2NO_2NCS]^{+1}$	100	...[o]
	+	KCNS	$[Coen_2NO_2NCS]^{+1}$	...	100[p]

Werner's results[6,8,13] obtained primarily by the isolation of reaction products are: [a] 80% *cis* and 20% *trans*; [b] 50% *cis* and 50% *trans*; [c,d] and [e] largely *cis*; [f] largely *trans*; [g] largely *cis*; [h] 35% *cis* and 65% *trans*; [i–p] largely retention of configuration.

---

(10) A. Werner, *Ber.*, **44**, 3273, 3276 (1911).

cis and *trans* isomers of some of the compounds. In addition, the reaction of $[Coen_2NO_2Cl]^{+1}$ with thiocyanate ion did not proceed to completion and here only a qualitative estimate (Table I) could be made based on the wave lengths at which the absorption maxima occurred.

Results.—The data are summarized in Table I.

Discussion

The mechanisms of substitution reactions in carbon compounds are postulated to be primarily of two types, the familiar SN1 and SN2 reaction paths.[11] First-order kinetics and racemization are characteristic of reactions which proceed by the SN1 mechanism, while second-order kinetics and stereochemical specificity are associated with the SN2 process. The kinetics of a number of reactions of complex ions have been investigated.[12] Most of these have been found to be second order, but aquation reactions are said to be pseudo-first order. Unfortunately, in none of these cases can the second-order kinetics be taken as proof of a bimolecular process[13] so it is not known whether these reactions proceed by a displacement (SN2) or dissociation (SN1) mechanism. Likewise, although there are many examples of substitution reactions of complex ions in which there is no appreciable racemization,[14] this is not necessarily indicative of a displacement mechanism. It will become apparent from the discussion which follows that in dealing with the octahedral configuration one need not expect an SN1 mechanism to be accompanied by racemization as is the case with the tetrahedral configuration.

Dissociation (SN1) Mechanism.—The stereochemical changes which may be expected to accompany substitution reactions of certain complex ions have been considered with the aid of molecular models and the conclusions reached for a dissociation process are summarized in Table II. Two seemingly plausible assumptions have been made in this approach. One is that intermediate structures of the planar and pentagonal pyramid type[15] need not be considered as these structures cannot be achieved without excessive rearrangement. The second assumption is that the incoming group enters the activation complex at the most accessible position(s). For the tetragonal pyramid intermediate this position appears to be the one perpendicular to the tetragonal plane while for the trigonal bipyramid structure there are three open positions at the three angles of 120°. On the basis of these assumptions it appears that if the pentacovalent intermediate is a tetragonal pyramid, the configuration of the product should be the same as that of the reactant. However, if the intermediate is a trigonal bipyramid then the product is expected to be a mixture of *cis* and *trans* isomers. In this case the three positions of attack designated in Table II need not be equivalent, as these are certain to be influenced by inductive and steric effects of the groups attached to the central metal atom.

Displacement (SN2) Mechanism.—In a similar fashion the conclusions reached for a displacement reaction mechanism are shown in Table II. The assumption made here is that the activated complex has a pentagonal bipyramid structure as the formation of this requires a minimum of atomic motion. The approach of an incoming group from the front-side (position adjacent to the outgoing group) of the complex is not shown in Table II, as this should result in a retention of configuration. However, if the approach is from the back-side (position opposite to that of the outgoing) the anticipated configuration(s) of the product depends upon the particular isomer undergoing reaction as shown in Table II. If the reactant has a *trans* configuration, the product will be exclusively *cis*, whereas a *cis* starting material is expected to yield a mixture of *cis* and *trans* products. Here too it should be made clear that the actual statistical synthesis of geometric isomers need not be expected because of steric and inductive factors.

It is apparent that there are many limitations to the stereochemical approach to an elucidation of the mechanism(s) of substitution reactions in octahedral complexes. Much of the data collected here will be more readily interpreted if it can be determined whether these reactions are unimolecular or bimolecular. However, even in absence of this information, observations on *trans* isomers should be of interest since these *trans* isomers are expected to yield exclusively *cis* products only in case of a displacement reaction with a back-side approach of the incoming group. On that account most of the attention in the discussion which follows is directed toward the *trans* isomer, since it is expected to be somewhat more indicative of reaction mechanism.

A. Chloroamminebis-(ethylenediamine)-cobalt(III) Ion.—*trans*-$[Coen_2NH_3Cl]^{+2}$ reacts with hydroxide and thiocyanate ions to yield primarily *cis* products. These observations suggest either a displacement reaction with the incoming group approaching largely from the back-side or an ionization mechanism with a trigonal bipyramid intermediate structure. Aquation of the *trans* isomer in the presence of silver ion and the reaction with nitrite ion yield mostly *trans* products. This may be taken as an indication of either a front-side displacement or dissociation with a tetragonal pyramid structure for the intermediate. However, it should be pointed out that even in methanol–water solvent mixtures the reactions with nitrite ion and thiocyanate ion are probably complicated by reaction through the aquo complex. This supposition is supported by the fact that the product of the reaction with nitrite ion is the same regardless of whether the starting material is the chloroamminebis-(ethylenediamine)-cobalt(III) ion or the corresponding aquoammine.

B. Chloronitrobis-(ethylenediamine)-cobalt(III) Ion.—With the one exception of the reaction of *trans*-$[Coen_2NO_2Cl]^{+1}$ with hydroxide ion, both the *cis* and *trans* isomers of this complex reacted to

---

(11) See, for example, A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 113.

(12) A. B. Lamb and J. W. Marden, THIS JOURNAL, **33**, 1873 (1911); G. N. Brönsted and R. Livingston, *ibid.*, **49**, 435 (1927); B. Adell, *Z. anorg. allgem. Chem.*, **249**, 251 (1942).

(13) F. Basolo, *Chem. Revs.*, **51**, in press (1953).

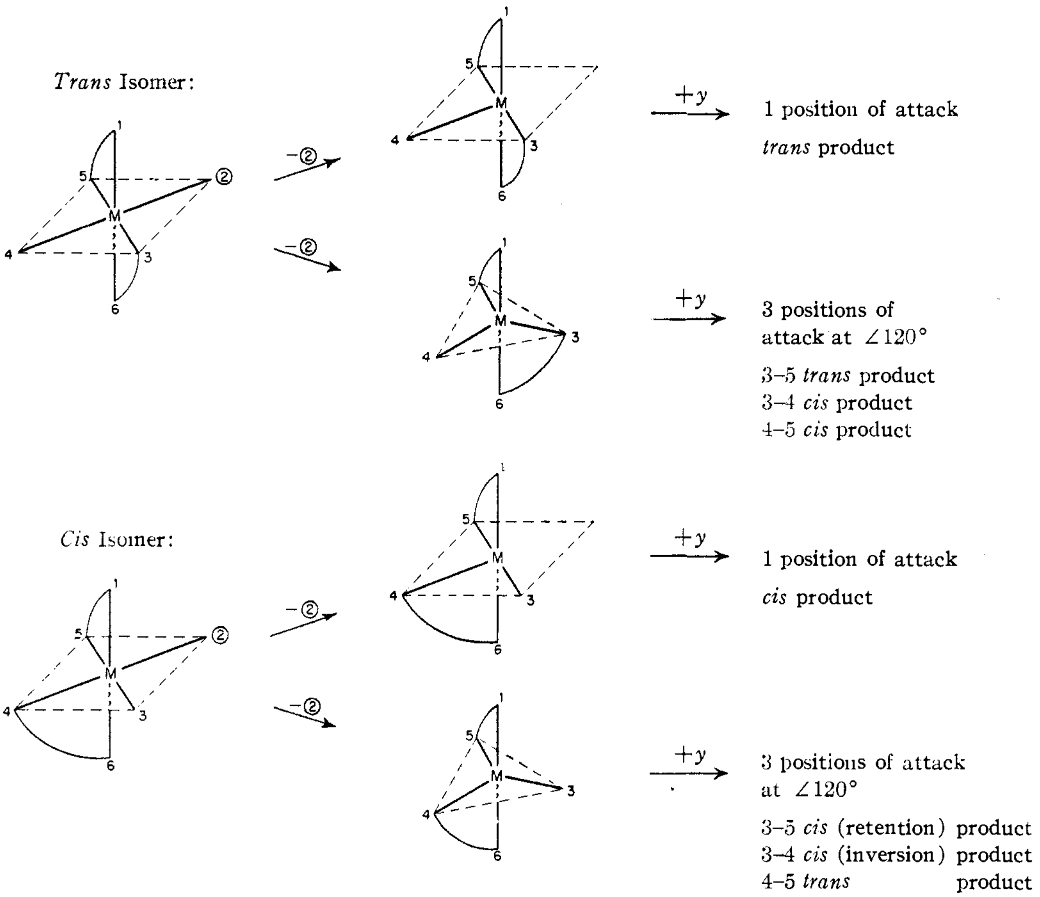
(14) A. Werner, *Ber.*, **45**, 1228 (1912); J. P. Mathieu, *Bull. soc. chim.*, **4**, 687 (1937); J. C. Bailar and R. Auten, THIS JOURNAL, **56**, 774 (1934).

(15) G. E. Kimball, *J. Chem. Phys.*, **8**, 198 (1940).

TABLE II

SOME STRUCTURAL CHANGES THAT MAY OCCUR DURING SUBSTITUTION REACTION OF [M(AA)$_2$ax] COMPLEXES

*S*N1-*Dissociation Mechanism*



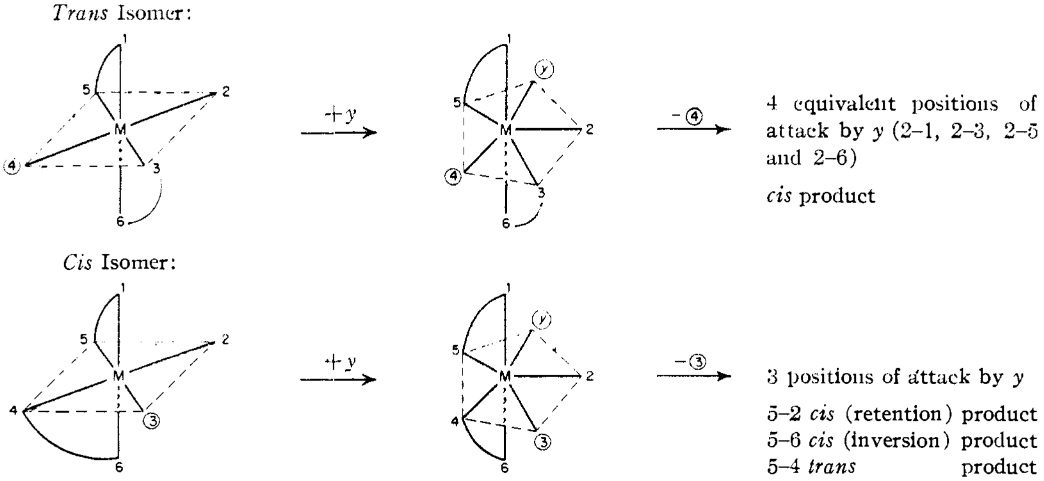
1 position of attack
trans product

3 positions of attack at ∠120°
3–5 *trans* product
3–4 *cis* product
4–5 *cis* product

1 position of attack
cis product

3 positions of attack at ∠120°
3–5 *cis* (retention) product
3–4 *cis* (inversion) product
4–5 *trans* product

*S*N2-*Displacement Mechanism* (back-side attack only as front-side attack always results in retention of configuration).



4 equivalent positions of attack by y (2–1, 2–3, 2–5 and 2–6)
cis product

3 positions of attack by y
5–2 *cis* (retention) product
5–6 *cis* (inversion) product
5–4 *trans* product

yield products of the same geometric configuration as the reacting isomer. These results support either a displacement mechanism with a front-side attack or dissociation with the activation complex having a tetragonal pyramid structure. It is noteworthy that aquonitrobis-(ethylenediamine)-cobalt(III) complexes also react with nitrite and thiocyanate ions with retention of configuration (Table I-F). Here again it is probable that the reactions of the chloronitro complexes proceed through an intermediate formation of the aquo complex.[16]

This is the only case in which aquation was sufficiently rapid to permit a determination of the configuration of the aquo complexes. The aquonitro-

---

[16] Kinetic studies on the reactions of [Coen$_2$NO$_2$Cl]$^{+1}$ with water and with nitrite ion to be published in THIS JOURNAL support this view.

bis-(ethylenediamine)-cobalt(III) isomers do rearrange in solution but even after 14 days at room temperature they had not come to equilibrium. It is of interest that the aquo products are identical whether or not the reaction was run in the presence of silver ion. The fact that *trans*-$[\mathrm{Coen_2NO_2Cl}]^{+1}$ reacts with hydroxide ion to yield a mixture of *cis* and *trans* products is in accord with a general tendency for the hydrolysis reactions of *trans* isomers to give primarily *cis*-hydroxo compounds.

C. Chlorothiocyanatobis-(ethylenediamine)-cobalt(III) Ion.—The reaction of $[\mathrm{Coen_2NCSCl}]^{+1}$ with excess alkali results in the formation of the dihydroxo compound. However, if an equivalent amount of alkali is used followed by treatment with excess acid, $[\mathrm{Coen_2NCS(H_2O)}]^{+2}$ can be obtained and here again the *trans* isomer yields largely a *cis* product. Aquation in the presence of silver ion could not be studied because of the formation of a silver addition compound.[17] Since the spectra of *cis*- and *trans*-$[\mathrm{Coen_2(NCS)_2}]^{+1}$ are virtually identical, the reaction with thiocyanate could not be studied. Likewise the reactions with nitrite yielded only the dinitrobis-(ethylenediamine)-cobalt(III) compounds and the structures of the intermediate nitrothiocyanato complexes could not be determined with any certainty.

D. Dichlorobis-(ethylenediamine)-cobalt(III) Ion.—The reaction of $[\mathrm{Coen_2Cl_2}]^{+1}$ with alkali cannot be used to produce the monosubstituted complex because the two chloro groups are replaced at comparable rates.[18] However, both groups are conveniently replaced in an excess of alkali and the relative amounts of *cis* and *trans* isomers obtained are in good agreement with the observations of Werner. Similarly, reaction with excess nitrite ion yields the dinitro compounds. However, since it is known that the chloronitrobis-(ethylenediamine)-cobalt(III) complexes produce the dinitro compounds with retention of configuration, it can be seen that the dichloro salts must be yielding a mixture of *cis* and *trans* isomers of the intermediate chloronitro compounds. Reaction of thiocyanate ion with *trans*-$[\mathrm{Coen_2Cl_2}]^{+1}$ yields primarily the *trans*-chlorothiocyanatobis-(ethylenediamine)-cobalt(III) ion; this reaction is therefore analogous to the behavior of the *trans*-chloronitro compound.

Conclusions.—The results of this study may be summarized as follows: (1) *trans* isomers react with hydroxide ion to yield primarily the *cis*-hydroxo complexes. (2) Except for the reaction of hydroxide ion with *trans*-$[\mathrm{Coen_2NO_2Cl}]^{+1}$, both the *cis* and *trans* isomers of $[\mathrm{Coen_2NO_2Cl}]^{+1}$ react in general with retention of geometric configuration. (3) Aquation of *cis*- and *trans*-$[\mathrm{Coen_2NO_2Cl}]^{+1}$, whether in the presence or absence of silver ion, yields the same aquo products. (4) All of the aquo complexes studied rearrange in solution to give an equilibrium mixture of geometric isomers which is primarily *cis*. (5) Reactions of aquo complexes with nitrite and thiocyanate ions generally take place with retention of geometric configuration. (6) These results are indicative of the fact that no single reaction mechanism is operative in all substitution reactions of complex ions. However, it does appear that the hydrolysis reactions proceed either by dissociation with a trigonal bipyramid intermediate or by displacement with the incoming groups approaching largely from the back-side. On the other hand, the retention of geometric configuration during the reactions of the chloronitro compounds and the aquo complexes suggest a different reaction mechanism. These reactions would appear to proceed either by dissociation with largely a tetragonal pyramid intermediate or by a displacement with primarily a front side attack.

The semi-quantitative nature of these data should be emphasized. The difficulties which of necessity arise are twofold; first, it is not possible to be absolutely certain of the purity of the geometric isomers employed and second, the absorption spectra of the isomers are in some instances very similar. It should also be mentioned that in cases studied by Werner and by us, the results of the spectrophotometric studies are found to be in reasonable accord with the results of Werner's earlier observations (see footnote to Table I). The only exceptions are the hydrolysis of *trans*-$[\mathrm{Coen_2NH_3Cl}]^{+2}$ and the reaction of *cis*-$[\mathrm{Coen_2NH_3H_2O}]^{+3}$ with potassium thiocyanate. Since the possibility of molecular rearrangement does exist with the isolation technique employed by Werner, discrepancies such as these are to be expected.

EVANSTON, ILLINOIS

---

[17] A. Werner, *Ann.*, **386**, 139 (1912); *Ber.*, **44**, 879 (1911).

[18] J. P. Mathieu, *Bull. soc. chim.*, [5] **3**, 2121 (1936).