

example of a *kinetic template reaction*. The general subjects of template reactions and complexes containing macrocyclic ligands have been reviewed elsewhere.²¹

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(21) D. H. Busch, *Record Chem. Progr.*, **35**, 107 (1964).

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Stereochemistry of Complex Inorganic Compounds. XXVIII.¹ The Walden Inversion in the Base Hydrolysis of Optically Active Cobalt(III) Complexes

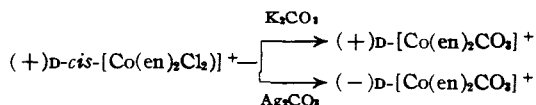
BY L. J. BOUCHER, E SHIN KYUNO, AND JOHN C. BAILAR, JR.

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The base hydrolysis of optically active *cis*-dichlorobis(ethylenediamine)cobalt(III) cation in concentrated aqueous solution leads to an inversion of configuration in the formation of the product. It is shown that the inversion takes place in the first step of the hydrolysis. Additional information about the same process in dilute solutions in the presence of silver ion is also given. Mechanisms are proposed for the reactions which take place in the presence and in the absence of silver ion.

Introduction

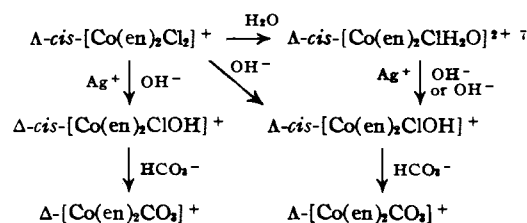
In comparison to the large number of substitution reactions in octahedral complexes which are known, examples of those that proceed with inversion of configuration are rare. The first example which was thoroughly studied involved the transformation of the optically active *cis*-dichlorobis(ethylenediamine)cobalt(III) ion into the optically active carbonatobis(ethylenediamine)cobalt(III) ion.²



It has been deduced from rotatory dispersion studies that the *cis*-[Co(en)₂Cl₂]⁺, *cis*-[Co(en)₂ClH₂O]²⁺, and [Co(en)₂CO₃]⁺ that are dextrorotatory at the Na D-line, (+)_D, have the same configuration.³ It is then apparent that inversion takes place in the reaction involving silver ion. The reactions were carried out by grinding the metal carbonate with the complex ion in a small amount of water to form a paste, followed by the extraction of the soluble products with water. Similar reactions with mercury(I) carbonate and silver oxalate did not give inverted products. However, when a large excess of potassium carbonate was used, an inverted product was formed.⁴

It has been suggested recently that in the reaction involving silver carbonate, the hydroxide and bicarbonate ions which are present play an important role. Further, when the base hydrolysis of (+)_D-*cis*-[Co(en)₂Cl₂]⁺ was carried out in the presence of silver ion, an inverted product was formed. Stable materials were formed by acidification of the reaction mixture and addition of bicarbonate ion.⁵ The following

reaction sequence summarizes the reported data on the formation of optically active [Co(en)₂CO₃]⁺.⁶



Under the conditions used, the presence of silver ion is necessary for an inversion process to occur in the base hydrolysis of $\Lambda\text{-}cis\text{-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$. Efforts to substitute other ions for silver, *i.e.*, Hg²⁺, Pb²⁺, or Tl⁺, were unsuccessful.⁵

An example of an inversion reaction that does not require the presence of silver ion is the ammoniation of $\Lambda\text{-}cis\text{-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ to form $\Delta\text{-}cis\text{-}[\text{Co}(\text{en})_2\text{NH}_3\text{Cl}]^{2+}$ in liquid ammonia at -77°.⁸ No analogous reaction has been reported to take place in aqueous solution.

We wish to report here additional information on the inversion reaction observed in the base hydrolysis of $\Lambda\text{-}cis\text{-}[\text{Co}(\text{en})_2\text{Cl}_2]^+$ in aqueous solution in the presence of silver ion, and the discovery of the conditions necessary for the same inversion reaction in the absence of silver ion.

Results

The base hydrolysis of *cis*-[Co(en)₂Cl₂]⁺ by addition of one equivalent of hydroxide into a solution of the complex gives, in addition to the expected *cis*- and *trans*-[Co(en)₂ClOH]⁺, both *cis*-[Co(en)₂(OH)₂]⁺ and unchanged *cis*-[Co(en)₂Cl₂]⁺.⁹ However, when a 2:1

(6) The (+)_D-[Co(en)₂Cl₂]⁺ ion has been assigned a lambda, Λ , absolute configuration. Λ and Δ refer to an isomer with a natural screw form which is left-handed and right-handed, respectively. For the original assignment see T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961). Further, the configuration of the (+)_D-[Co(en)₂Cl₂]⁺ ion has been related to that of the (+)_D-[Co(en)₂]³⁺ ion by rotatory dispersion studies: T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).

(7) J. P. Mathieu, *Bull. soc. chim. France*, **4**, 687 (1937).

(1) Paper XXVII: *Inorg. Chem.*, **3**, 1085 (1964).
(2) J. C. Bailar, Jr., and R. W. Auten, *J. Am. Chem. Soc.*, **56**, 774 (1934); J. C. Bailar, Jr., F. G. Jonelis, and E. H. Huffman, *ibid.*, **58**, 2224 (1936); J. C. Bailar, Jr., and D. F. Peppard, *ibid.*, **62**, 820 (1940).

(3) J. P. Mathieu, *Bull. Soc. Chim. France*, **3**, 476 (1936).
(4) J. C. Bailar, Jr., and J. P. McReynolds, *J. Am. Chem. Soc.*, **61**, 3199 (1939).

(5) F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *ibid.*, **85**, 1215 (1963).

(8) J. C. Bailar, Jr., J. H. Haslam, and E. M. Jones, *J. Am. Chem. Soc.*, **56**, 2226 (1936); R. D. Archer and J. C. Bailar, Jr., *ibid.*, **83**, 812 (1961).

(9) R. G. Pearson, R. E. Meeker, and F. Basolo, *ibid.*, **78**, 2673 (1956).

ratio of hydroxide ion to complex is used, only *cis*- and *trans*-[Co(en)₂(OH)₂]⁺ are formed. Further, addition of one mole of base to *cis*-[Co(en)₂ClH₂O]²⁺ leads only to the formation of *cis*-[Co(en)₂ClOH]⁺. The relative configurations of all of the optically active products formed in the base hydrolysis of optically active *cis*-[Co(en)₂Cl₂]⁺ can be established in a straightforward manner. The various materials are prepared by the reactions

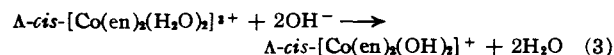
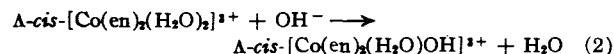
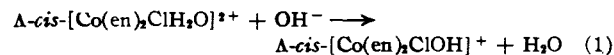


Table I gives the specific rotations of the compounds of interest. Addition of acid to the products of reactions 1, 2, and 3 immediately after their formation gave Λ -*cis*-[Co(en)₂ClH₂O]²⁺ and Λ -*cis*-[Co(en)₂(H₂O)₂]²⁺ with little racemization. Attempts to isolate the optically active hydroxo species as solids were unsuccessful. Compounds I, II, and III have been assigned the same absolute configuration on the basis of rotatory dispersion studies.^{3,7} It is also possible to assign the same configuration to the hydroxo species that are dextrorotatory at the D-line of sodium, on the basis of their interconversion with the aquo species and on the shapes of their rotatory dispersion curves. Therefore, any levorotatory reading (Na D-line) on a solution formed by the base hydrolysis of Λ -*cis*-[Co(en)₂Cl₂]⁺ indicates that an inversion has taken place during the reaction.

TABLE I
SPECIFIC ROTATIONS OF COMPLEXES^c

No.	Complex	α_{D} , deg.
I	Λ - <i>cis</i> -[Co(en) ₂ Cl ₂](NO ₃)	+715
II	Λ - <i>cis</i> -[Co(en) ₂ ClH ₂ O](NO ₃) ₂	+252
III	Λ - <i>cis</i> -[Co(en) ₂ (H ₂ O) ₂](NO ₃) ₂	+25 ^a
IV	Λ - <i>cis</i> -[Co(en) ₂ OHCl](NO ₃)	+327 ^b
V	Λ - <i>cis</i> -[Co(en) ₂ OH(H ₂ O)](NO ₃) ₂	+195
VI	Λ - <i>cis</i> -[Co(en) ₂ (OH) ₂](NO ₃)	+355

^a $[\alpha]_{\text{D}}^{25} = +266^\circ$. ^b A higher value, +695^o, has been reported: H. Fischlin, Dissertation, Zurich, 1919. ^c Experiments have shown that these rotations are almost unaffected by the presence of soluble salts in the solution, up to concentrations of 2 *N*.

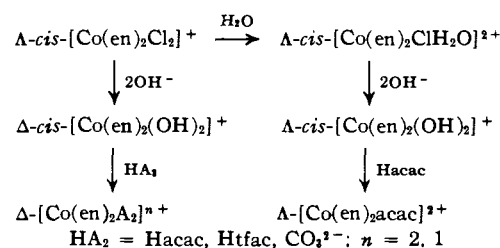
Under certain conditions (concentration of base and complex less than 0.50 *M*), the presence of silver ion is necessary for an inversion process to occur in the base hydrolysis of Λ -*cis*-[Co(en)₂Cl₂]⁺. However, when higher concentrations of base and complex were used, it was found that inversion occurred in the absence of silver ion. Two series of experiments were carried out to gather information on these processes.

The dependence of the degree of inversion on the concentration of silver ion in a solution of fixed concentration of complex and base is shown in Table II. As the concentration of silver ion is increased, the degree of inversion increases. It may be significant that the degree of inversion levels off at a 1:1 ratio of silver to hydroxide ion. The amount of inverted product formed is also dependent on the concentration of the complex, decreasing as the concentration of complex decreases (Table III). In these experiments, a satu-

rated solution of silver hydroxide was used (in contact with solid silver oxide). It is surprising that inversion is observed even at such low concentrations of silver and hydroxide ions. The data suggest that an association step may be important in determining the stereochemical path of the reaction. A slight blue shift in the ultraviolet spectrum of *cis*-[Co(en)₂Cl₂]⁺ upon addition of silver ion lends some support to this proposal. An alternate explanation is that the complex is adsorbed on the surface of solid or colloidal silver oxide, where it undergoes base hydrolysis with inversion.¹⁰ Dilution of the solution would decrease the degree of inversion by decreasing the number of molecules adsorbed. However, in the presence of a large excess of a colloidal suspension of a material which has good adsorptive properties (e.g., ferric hydroxide), the product shows predominantly retention of configuration. Even metal ions that form slightly soluble hydroxides, i.e., Tl⁺, Hg²⁺, and Pb²⁺, give a product which shows retention of configuration. This, however, does not rule out the possibility that silver hydroxide is an important reactant in the inversion process.

The base hydrolysis of Λ -*cis*-[Co(en)₂ClH₂O]²⁺ is independent of silver ion concentration (Table II), leading always to a product which shows retention of configuration. This confirms the previous conclusions that the inversion of configuration observed in the base hydrolysis of Λ -*cis*-[Co(en)₂Cl₂]⁺ must occur in the first step, i.e., in the formation of *cis*-[Co(en)₂ClOH]⁺.

It was noted above that when high concentrations of complex and hydroxide ion (1.0 to 2.0 *M*) were used, it was found that inversion occurred in the absence of silver ion.¹¹ Since the products of base hydrolysis rapidly racemize in strongly basic solution, a complexing agent that reacts with a hydroxo complex to form an optically stable material must be added if optical activity is to be maintained. Acetylacetonate (Hacac), trifluoroacetylacetonate (Htfac), carbonate, and bicarbonate ion are such complexing agents. The following reaction scheme summarizes the results of experiments with these reagents.



The configurations of the products were assigned on the basis of the rotatory dispersion curves (Fig. 1). The great similarity in the curves indicates that the products have the same configuration. Since the levorotatory [Co(en)₂CO₃]⁺ (Na D-line) has been assigned a Δ configuration, the levorotatory (Na D-line) [Co(en)₂acac]²⁺ and [Co(en)₂tfac]²⁺ are also assigned this configuration. From this, it follows that the inversion occurs in the first base hydrolysis of Λ -*cis*-[Co(en)₂Cl₂]⁺.

(10) This is similar to the suggestion that the reaction is largely "solid state" in character: F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958, p. 237.

(11) It was noted earlier that a large excess of potassium carbonate also gave the same result. This is probably due to the high concentration of hydroxide ion in the carbonate solution.

TABLE II
THE BASE HYDROLYSIS OF COMPLEX TO FORM OPTICALLY ACTIVE cis -[Co(en)₂(OH)₂]⁺ IN THE PRESENCE AND ABSENCE OF SILVER ION

Complex	Complex concn., <i>M</i>	OH ⁻ concn., <i>M</i>	Ag ⁺ concn., <i>M</i>	Product	
				α ²⁰ , deg.	[α] ²⁰ , deg.
Λ- <i>cis</i> -[Co(en) ₂ Cl ₂]NO ₂	0.25	0.50	0	+0.042 ± 0.001	+30 ± 1
Λ- <i>cis</i> -[Co(en) ₂ Cl ₂]NO ₂	0.25	0.50	0.25	-0.030	-22 ± 1
Λ- <i>cis</i> -[Co(en) ₂ Cl ₂]NO ₂	0.25	0.50	0.50	-0.104	-75 ± 1
Λ- <i>cis</i> -[Co(en) ₂ Cl ₂]NO ₂	0.25	0.50	0.75	-0.108	-78 ± 1
Λ- <i>cis</i> -[Co(en) ₂ ClH ₂ O](NO ₂) ₂	0.25	0.50	0	+0.196	+276 ± 2
Λ- <i>cis</i> -[Co(en) ₂ ClH ₂ O](NO ₂) ₂	0.25	0.50	0.25	+0.106	+149 ± 2

TABLE III
THE BASE HYDROLYSIS OF Λ-*cis*-[Co(en)₂Cl₂]⁺ TO FORM OPTICALLY ACTIVE cis -[Co(en)₂(OH)₂]⁺ IN THE PRESENCE OF SILVER HYDROXIDE^a

Concn. of complex, <i>M</i>	α ²⁰ (deg.) of product	[α] ²⁰ (deg.) of product
0.50	-0.054 ± 0.001	-92 ± 2
0.25	-0.046	-78
0.125	-0.034	-57
0.062	-0.004	-5

^a Saturated solution, about 0.002 *M*, in contact with solid silver oxide (amount equal that of complex).

Table IV shows the dependence of inversion on hydroxide ion concentration. At high hydroxide concentration, inversion is noted, but as the concentra-

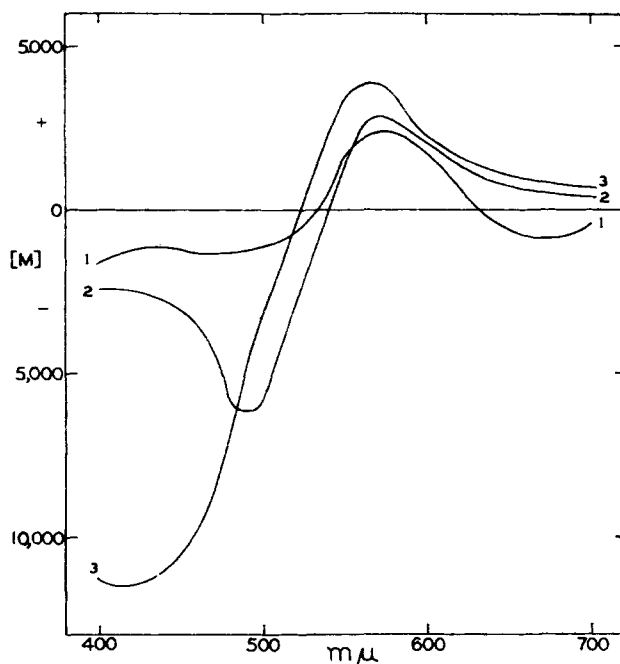
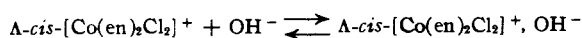


Fig. 1.—Rotatory dispersion curves: 1, Λ-*cis*[Co(en)₂Cl₂]NO₂; 2, Λ-[Co(en)₂CO₃]I; 3, Λ-[Co(en)₂fac]I₂.

tion decreases, the degree of inversion decreases and at very low concentrations most of the product has the configuration of the starting material. It may also be seen that increase in the ratio of base to complex increases the degree of inversion. The same effect was noted when acetylacetone was used in place of bicarbonate. The data show that the degree of inversion is dependent on the concentration of both complex and base, indicating that an association may be important in the inversion process.



The concentration dependence observed above is not due to a simple salt effect as is shown by the results of experiments carried out in various concentrations of sodium perchlorate. These experiments were carried out in 0.50, 1.00, and 2.0 *M* sodium perchlorate solutions with concentrations of complex and base as given in entry 6 of Table IV. Although the specific rotations were smaller than those in experiments without sodium perchlorate, in each case the isolated product was predominantly the Λ-[Co(en)₂CO₃]⁺ ion.

TABLE IV
THE BASE HYDROLYSIS OF Λ-*cis*-[Co(en)₂Cl₂]⁺ TO FORM OPTICALLY ACTIVE [Co(en)₂CO₃]⁺ AS A FUNCTION OF REACTANT CONCENTRATION

Concn. of complex, <i>M</i>	OH ⁻ concn., <i>M</i>	HCO ₃ ⁻ concn., <i>M</i>	Product α ²⁰ , deg.	[α] ²⁰ , deg.
1.00	2.00	1.00	-0.0416 ± 0.0004	-190 ± 2
0.50	1.50	0.50	-0.0196	-131 ± 3
0.50	1.00	0.50	-0.0216	-135 ± 2
0.50	0.50	0.50	+0.0016	+7 ± 2
0.125	0.375	0.125	-0.0036	-20 ± 2
0.125	0.25	0.125	+0.0056	+13 ± 1
0.125	0.125	0.125	+0.0070	+44 ± 4
0.05	0.10	0.05	+0.0176	+70 ± 1

Discussion

It has been shown that the base hydrolysis of Λ-*cis*-[Co(en)₂Cl₂]⁺ in very dilute solutions (<0.01 *M*) yields chiefly Λ-*cis*-[Co(en)₂ClOH]⁺, with retention of configuration. Some isomerization and racemization take place also.¹² The second base hydrolysis was found to lead, under all conditions studied, to the formation of optically active cis -[Co(en)₂(OH)₂]⁺ without inversion of configuration. The strong nucleophilic behavior of the hydroxide ion toward cobalt-amine complexes has been attributed to its high mobility in aqueous solution.¹³ It is suggested that the hydroxide ion moves through the solvent shells by means of a Grotthuss proton-transfer mechanism and appears in a position in the primary solvent shell of the complex suitable for substitution (*via* an S_N2 process).¹² It is also likely that the amine hydrogens are part of the Grotthuss chain and hence they may be abstracted to form amide groups. In the case of cis -[Co(en)₂Cl₂]⁺, the reactive complex then proceeds *via* a normal S_N1CB mechanism¹⁴ to form [Co(en)₂ClOH]⁺. In this process there is no apparent orientation of the complex with respect to the hydroxide ion.

In more strongly concentrated solutions (>0.25 *M*), the predominant mode of attack by the hydroxide ion must be different, since the reaction gives an inverted

(12) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962).

(13) M. L. Tobe, *Sci. Progr. (London)*, **48**, 485 (1960).

(14) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 129-132.

product. The data reported here show that the inversion takes place in the first base hydrolysis and suggest that an association process may be an important step in the inversion reaction. In these concentrated solutions there is undoubtedly a large amount of ion-pair formation. In fact, there is evidence for the ion pair, $[\text{Co}(\text{NH}_3)_6]^{3+}$, OH^- in solutions of comparable concentration. The hydroxide ion is thought to be hydrogen bonded to the amine groups in the complex.¹⁵ It is reasonable to assume that the same situation would arise in the case of *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ and that the hydroxide ion would form an ion pair preferentially on the side of the complex which is most positive. Figure 2 gives a possible structure for the ion pair. The hydroxide ion is located close to the 1,2 edge of the octahedron and is hydrogen bonded to amine groups N_1 and N_2 . An equivalent structure can be drawn involving amine groups N_3 and N_4 . The ion pair can undergo reaction *via* an $\text{S}_{\text{N}}2$ displacement or an $\text{S}_{\text{N}}1\text{CB}$ mechanism. The latter involves the abstraction (at least, partial) of a proton from amine group N_1 by the hydroxide ion to form an amide group. The cobalt-chlorine bond is lengthened and the complex rearranges to a trigonal bipyramid by movement of the amide group along the edge halfway toward the vacant chlorine position. The "hydroxide ion," still hydrogen bonded to N_1 and N_2 atoms, then attacks the 1,2 edge of the trigonal bipyramid to form an inverted product, *i.e.*, Δ -*cis*- $[\text{Co}(\text{en})_2\text{ClOH}]^+$. The attack must occur before the "hydroxide ion" can be incorporated into the solvent shell. Otherwise, a racemic product would be formed. Likewise, if the ion pair originally formed involves the N_3 and N_4 atoms, a *trans* product would result. The suggested mechanism is analogous to that proposed for the ammoniation of the complex in liquid ammonia at -77° .¹⁶

It has been suggested that when silver ion is added to a solution of the complex, a weak polar association of the silver ion with the negative chlorine atoms is formed.⁵ However, the evidence for such association is at best inconclusive. The slight shift in the ultraviolet spectrum of the complex is indicative of a very weak association of the silver ion with the complex, perhaps involving one or more water molecules. At any rate, there is no apparent reason why this interaction should enhance the $\text{S}_{\text{N}}2$ *trans* displacement process.¹⁷ This is exemplified by the reported failure of the strong nucleophiles NO_2^- and N_3^- to give inverted products when the reactions are carried out in the presence of silver ion.⁵ It is also noteworthy that the amount of *trans* product formed in the base hydrolysis of Δ -*cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ is less in the presence of silver ion than in its absence. This seems contrary to the behavior expected for a *trans* displacement mechanism.

The data reported here indicate that, in dilute solution, the presence of silver ion is necessary for inversion, as well as that the inversion takes place in the first base hydrolysis. A unimolecular process which leads to an inversion may now be proposed. The first step in the process is the electrophilic attack of the silver ion on

(15) J. F. Duncan and D. L. Kepert in "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 380-400.

(16) R. D. Archer and D. A. Chung, Paper Presented at the 141st National Meeting of the American Chemical Society, Washington, D. C., 1962.

(17) R. G. Pearson, D. N. Edgington, and F. Basolo, *J. Am. Chem. Soc.*, **84**, 3233 (1962).

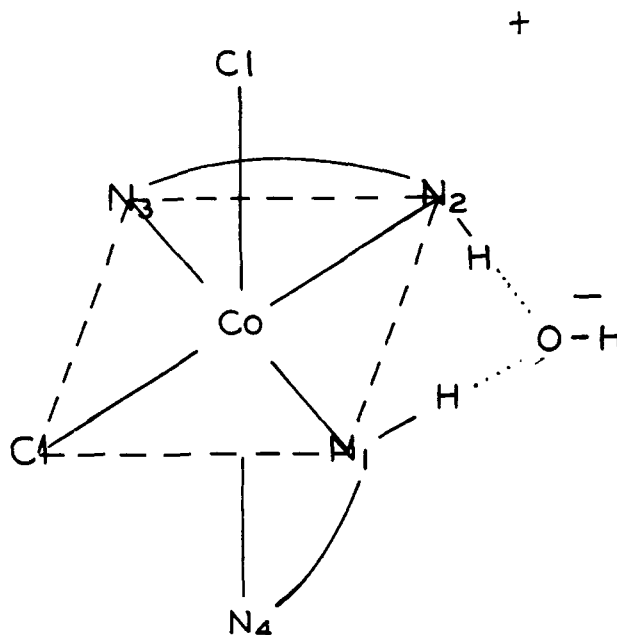


Fig. 2.—Proposed structure of an ion-pair intermediate.

the chlorine atom of the complex, forming a tenuous association. The next step is the removal of a proton from an amine group by a hydroxide ion *via* the Grotthuss chain to form an amide intermediate. These two steps may occur at the same time. In the complex, there are two different types of amine groups; those of one kind are *cis* to both chlorine atoms; those of the second kind are *cis* to one chlorine atom and *trans* to the other. Deprotonation of the latter would lead to an active intermediate not very different from that involved in the $\text{S}_{\text{N}}1\text{CB}$ mechanism, with the silver ion assisting in the release of the chlorine atom from the complex. This process is known to lead to over-all retention of configuration. Deprotonation at the nitrogen atom *cis* to both chlorine atoms would lead to a different situation. If it is assumed that the silver ion is almost always near the chlorine atoms, it would not be difficult for an electrophilic attack by the silver ion on a *cis* amide group to occur since it is already close to that position. This is consistent with the known affinity of heavy metals for amide groups.¹⁸ The cobalt-amide bond lengthens and at the same time the amide group is pulled toward the chlorine atom by the silver ion with a solvent molecule replacing it in the coordination sphere. The free amide group then replaces the chlorine atom with the elimination of silver chloride to form an inverted product. The insolubility of silver chloride may be an important factor in the reaction.

An important step in the inversion mechanism is the formation of the $\text{S}_{\text{N}}1\text{CB}$ intermediate. Inversion occurs if a molecule of the reagent is positioned with respect to the intermediate in such a way as to allow a "stereospecific" reaction to occur. In strongly basic aqueous solutions, as well as in liquid ammonia, the ion-pair formation accomplishes this. In the reactions with silver ion, the silver-chlorine association or silver-amide interaction accomplishes the same result. In

(18) J. C. Bailar, Jr., and D. H. Busch in "Chemistry of Coordination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Corp., New York, N. Y., 1956, pp. 59, 60.

TABLE V
 ELEMENTAL ANALYSIS AND OPTICAL ACTIVITY OF COMPLEXES^a

Compound	Calcd., %			Found, %			α_D^{20} , deg., =0.0004	$[\alpha]_D^{20}$, deg.
	C	H	N	C	H	N		
[Co(en) ₂ CO ₃]I·H ₂ O	15.62	4.71	14.58	15.41	4.42	14.34	-0.0340	-40 ± 1
[Co(en) ₂ acac]I ₂ ·H ₂ O	19.71	4.66	10.17	19.65	4.58	10.19	-0.0136	-14 ± 1
[Co(en) ₂ tfac]I ₂ ·H ₂ O	18.48	3.80	9.59	18.37	3.54	9.43	-0.0088	-9 ± 1
[Co(en) ₂ acac]I ₂							+0.2300	+460 ± 4

^a Microanalysis by J. Nemeth, University of Illinois.

principle, the silver ion should not be unique; other metal ions that form strong bonds with amide groups and yield insoluble chlorides should give the same result. Unfortunately, such metal ions are either coordinately saturated with ligands other than water or, even more important, they form sparingly soluble hydroxides. The necessity for an SnICB intermediate can be tested by using materials that do not contain acidic amine hydrogens. Experiments of this sort are now in progress.

Experimental

Preparation of Complexes.—The preparation and resolution of the following materials was carried out according to standard procedures: Λ -*cis*-[Co(en)₂Cl₂]Cl,¹⁹ Λ -*cis*-[Co(en)₂ClH₂O]Br,²⁰ Λ -*cis*-[Co(en)₂(H₂O)₂](NO₃)₂,⁵ Λ -[Co(en)₂acac]I₂,²¹ Λ -[Co(en)₂tfac]I₂.²² The nitrate, Λ -*cis*-[Co(en)₂Cl₂]NO₃, was prepared in a manner similar to that used for Λ -*cis*-[Co(en)₂Cl₂]Cl¹⁹ except nitric acid was used in place of hydrochloric acid to decompose the diastereoisomer. The chloroaquo nitrate, Λ -*cis*-[Co(en)₂ClH₂O](NO₃)₂, was prepared by metathesis between Λ -*cis*-[Co(en)₂ClH₂O]Br₂ and silver nitrate. Both Λ -*cis*-[Co(en)₂OH₂O](NO₃)₂ and Λ -*cis*-[Co(en)₂(OH)₂]NO₃ were prepared in solution by treating a 0.04 *M* solution of Λ -*cis*-[Co(en)₂(H₂O)₂](NO₃)₂ with an equal volume of 0.04 and 0.08 *M* sodium hydroxide solution, respectively. A solution of Λ -*cis*-[Co(en)₂OHCl]NO₃ was prepared by treating a 0.04 *M* solution of Λ -*cis*-[Co(en)₂ClH₂O](NO₃)₂ with an equal volume of 0.04 *M* sodium hydroxide solution.

Inversion Reactions.—The transformation of Λ -*cis*-[Co(en)₂Cl₂]Cl into Δ -[Co(en)₂CO₃]⁺, Δ -[Co(en)₂acac]⁺, and Δ -[Co(en)₂tfac]⁺ was accomplished by dissolving the starting material (0.002 mole) in 4 ml. of ice-cold 1.00 *N* potassium hydroxide solution. After 30 sec., an equimolar amount of potassium carbonate, acetylacetone, or trifluoroacetylacetone was added and

the solution was allowed to stand for 30 min. Powdered potassium iodide was added, and the complex iodide was fractionally precipitated by addition of several portions of ethanol. The transformation of Λ -*cis*-[Co(en)₂ClH₂O]²⁺ into Λ -*cis*-[Co(en)₂acac]²⁺ was carried out in a similar manner except that Λ -*cis*-[Co(en)₂ClH₂O]Br₂ was the starting material. The product was identified spectrophotometrically.²² Data are listed in Table V.

The data reported in Table II were gathered in the following way: An appropriate amount of silver nitrate and either Λ -*cis*-[Co(en)₂Cl₂]NO₃ or Λ -*cis*-[Co(en)₂ClH₂O](NO₃)₂ was dissolved in ice-cold water to give a 0.25 *M* solution, and potassium hydroxide was added. The mixture was stirred for 30 sec. and filtered. The filtrate was diluted and its optical activity determined at room temperature.

The data reported in Table III were gathered as follows. Saturated solutions of silver hydroxide (in contact with solid silver oxide, 0.01 mole) were prepared by dissolving equimolar amounts of silver nitrate and potassium hydroxide in cold water. An appropriate amount (0.005 mole) of Λ -*cis*-[Co(en)₂Cl₂]NO₃ was then added and the cold mixture was stirred for 1 min. After filtration, the solution was diluted and the optical activity of the solution determined.

The data reported in Table IV were gathered in the following way: Λ -*cis*-[Co(en)₂Cl₂]Cl ($[\alpha]_D +752^\circ$), 0.001 mole, was rapidly dissolved in the appropriately diluted cold aqueous 2.00 *M* potassium hydroxide and an equimolar amount of potassium carbonate was added. After standing for 30 min., the solution was filtered, ethanol was added, and the fractions were collected. The optical activity of an aqueous solution of the solid was measured, and the concentration of the solution was determined spectrophotometrically.

Apparatus.—The optical activity of the solutions was measured with a ETL-NPL Bendix Type 143A automatic polarimeter in 1-cm. cells. Rotatory dispersion curves were drawn by a Rudolph Model 260/655/850 recording spectropolarimeter. Spectrophotometric measurements were made with a Cary Model 14 *M* recording spectrophotometer using aqueous solutions in 1-cm. cells.

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