trans-Chlorohydroxo-, D*-*cis*-Chlorohydroxo-, and D*-*cis*-Dichlorobis(ethylenediamine)cobalt(III) Base Hydrolysis Stereochemistry[1a]

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Abstract: The base hydrolysis of D*-*cis*-$[Co(en)_2Cl_2]^+$ in concentrations as low as 0.03 M in both complex and base leads to a predominance of L*-*cis*-$[Co(en)_2(OH)_2]^+$ over the corresponding D* species. The inversion of configuration occurs not in the first hydrolysis step as previously deduced, but as a result of the direct action of two hydroxide ions on the dichloro complex without going through a stable chlorohydroxo complex. A concerted two-pronged *trans*-attack mechanism explains these results. Alternatives are also discussed. An equilibrium between *trans*-$[Co(en)_2ClOH]^+$ and *trans*-$[Co(en)_2(OH)_2]^+$ is established in solutions at a rate estimated to lie close to that of the base hydrolysis of *cis*-$[Co(en)_2Cl_2]^+$ (orders of magnitude more rapid than previously reported), but in agreement with predictions based on other rates. The base hydrolysis of *cis*-$[Co(en)_2ClOH]^+$ occurs with almost complete ($\geq 95\%$) retention of configuration.

The present work was undertaken to determine the products of the base hydrolysis of D*-*cis*-$[Co(en)_2Cl_2]^+$ in concentrated aqueous solutions in the interest of a clearer understanding of the mechanism or mechanisms involved. Equation 1 is the generalized two-step base hydrolysis reaction omitting optical isomer notations.

$$\textit{cis}\text{-}[Co(en)_2Cl_2]^+ \xrightarrow{OH^-} \underset{\textit{cis, trans}}{[Co(en)_2ClOH]^+} \xrightarrow{OH^-} \underset{\textit{cis, trans}}{[Co(en)_2(OH)_2]^+} \qquad (1)$$

Boucher, Kyuno, and Bailar[2] showed that the base hydrolysis reactions of D*-*cis*-$[Co(en)_2Cl_2]^+$ lead to a predominance of L* product over the D* product at high concentrations and 0°. Relative amounts of the various complexes in solution at the conclusion of the base hydrolyses were not determined for either step of the reaction. In kinetic concentrations, Chan and Tobe[3] found that the major portion of the optically active isomers formed in each step of the reaction has the same configuration as the starting material. Inversion had been reported earlier by Bailar and his coworkers[4] for reactions with silver carbonate or a large excess of potassium carbonate. By performing an extensive series of reactions using various combinations of silver and hydroxide ions, Dwyer, Sargeson, and Reid[5] successfully tested their proposition that the silver carbonate reaction was, in fact, due to both the silver and hydroxide ions present in solution. Using the intermediates of the two-step base hydrolysis reaction, D*-*cis*- and *trans*-$[Co(en)_2ClOH]^+$, Dwyer and coworkers found that the second step of the reaction proceeds with major retention of configuration and deduced that the inversion reaction "must" take place during the first step of the base hydrolysis. Boucher, *et al.*,[2] applied the same deductive reasoning to their results. The results of this study indicate that such deductions are not valid.

Results

The hydroxo complexes resulting from the base hydrolysis of D*-*cis*-$[Co(en)_2Cl_2]^+$ are labile to the extent that direct analyses are not feasible. Acidification of the hydroxo complexes to the corresponding aquo complexes proceeds with total retention of configuration[3] and produces a more inert system, which can be analyzed at 0°.

A computer program based on a least-squares evaluation was used to analyze the spectra of acidified reaction solutions which contained as many as five components.[6] Spectral analysis of multicomponent systems is usually quite limited in precision and accuracy, especially when the spectra of the individual components are similar. Synthetically constructed samples show good agreement between percentages of components added experimentally and percentages calculated from 30 points on the sample spectra; see Table I.

Base Hydrolysis of *trans*-$[Co(en)_2ClOH]^+$. The solution composition for one set of variable time data for the *trans*-$[Co(en)_2ClOH]^+$ base hydrolysis reaction is listed in Table II. While the concentration of the *cis*-dihydroxo complex increases with time, the *trans* isomer decreases as the reactant *trans*-$[Co(en)_2ClOH]^+$ decreases. These results would be suggestive of isomerization between the dihydroxo products if a number of studies[7] had not shown that the isomerization is too

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[1] (a) Based on a dissertation submitted by E. A. Dittmar to the Graduate School of Tulane University, 1967. The absolute configurations of the dissymmetric *cis* ions are designated herein as D* and L*, *cf.* ref 2 and 25a. The D* is equivalent to $\Delta(C_2)$, the Δ recommended by a 1966 IUPAC subcommittee, but is equivalent to $\Lambda(C_3)$ and to the Λ currently under consideration by IUPAC. Considering the current confusion over Δ and Λ, D* and L* appear preferable. Abbreviations include en = ethylenediamine; cyclam = 1,4,8,11-tetraazacyclotetradecane; *cis*-ClCl = *cis*-$[Co(en)_2Cl_2]^-$; *cis*-ClH_2O = *cis*-$[Co(en)_2ClH_2O]^{2+}$; *cis*-H_2OH_2O = *cis*-$[Co(en)_2(H_2O)_2]^{3+}$; *cis*-ClOH = *cis*-$[Co(en)_2ClOH]^+$; *cis*-OHOH = *cis*-$[Co(en)_2(OH)_2]^-$; D*-ClCl = D*-*cis*-$[Co(en)_2Cl_2]^+$; D*-ClOH = D*-*cis*-$[Co(en)_2ClOH]^+$; D*-OHOH = D*-*cis*-$[Co(en)_2(OH)_2]^+$; *trans*-ClH_2O = *trans*-$[Co(en)_2ClH_2O]^{2+}$; *trans*-H_2OH_2O = *trans*-$[Co(en)_2(H_2O)_2]^{3+}$; *trans*-ClOH = *trans*-$[Co(en)_2ClOH]^+$; *trans*-OHOH = *trans*-$[Co(en)_2(OH)_2]^+$. (b) NASA Fellow, 1963–1966. (c) To whom correspondence should be addressed at the Department of Chemistry, University of Massachusetts, Amherst, Mass. 01002.

[2] L. J. Boucher, E. Kyuno, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **86**, 3656 (1964).

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

[4] (a) J. C. Bailar, Jr., and W. Auten, *J. Am. Chem. Soc.*, **56**, 774 (1934); (b) J. C. Bailar, Jr., F. G. Jonelis, and E. H. Huffman, *ibid.*, **58**, 2224 (1936); (c) J. C. Bailar, Jr., and J. P. McReynolds, *ibid.*, **61**, 3199 (1939); (d) J. C. Bailar, Jr., and J. C. Peppard, *ibid.*, **62**, 820 (1940).

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

[6] E. A. Dittmar, Ph.D. Dissertation, Tulane University, 1967.

Table I. Computer Program Spectral Analysis of Synthetic Mixtures of Complexes

Complex[a]	% Added	Found	Added	Found	Added	Found
cis-ClCl	6.9	6.7	9.0	11.4	8.6	8.9
cis-ClH$_2$O	7.7	8.0	13.1	11.4	9.9	10.0
trans-ClH$_2$O	41.3	39.6	44.9	43.0	47.5	47.2
cis-H$_2$OH$_2$O	23.3	23.7	15.2	17.0	22.3	21.5
trans-H$_2$OH$_2$O	20.8	22.0	17.8	17.2	11.7	12.4
cis-ClH$_2$O	40.3	41.4	32.4	33.7	10.7	11.1
cis-H$_2$OH$_2$O	50.1	49.9	58.8	59.8	76.1	77.3
trans-H$_2$OH$_2$O	9.6	8.7	8.8	6.5	13.2	11.6
trans-ClH$_2$O	56.3	54.4	37.7	35.7	72.9	70.3
cis-H$_2$OH$_2$O	30.5	31.2	47.3	49.2	16.1	16.2
trans-H$_2$OH$_2$O	13.2	14.4	15.0	15.1	11.0	13.5
cis-ClCl	16.1	15.3	7.9	8.1	9.0	8.6
cis-ClH$_2$O	17.5	18.3	19.3	19.2	13.2	13.8
trans-ClH$_2$O	66.4	66.4	72.8	72.7	77.8	77.7

[a] All complexes are bis(ethylenediamine)cobalt(III) derivatives.

Table II. Composition of Solutions after the Incomplete Reaction of 0.1 *M* *trans*-[Co(en)$_2$ClOH]$^+$ with 0.3 *M* Hydroxide Ion

Approx time, sec	% *trans*-ClOH[a]	*trans*-OHOH[a]	*cis*-OHOH[a]	*cis*-ClOH[a]
60	70.2	7.9	21.9	0.0
90	63.7	5.7	30.1	0.5
120	56.8	6.2	36.2	0.8
120	55.2	5.2	38.5	1.1
130	53.8	6.5	39.3	0.4
180	48.6	4.5	46.1	0.8
265	35.8	5.0	58.0	1.2
315	29.2	4.4	65.1	1.3

[a] All complexes are bis(ethylenediamine)cobalt(III) derivatives.

high concentrations of this study. The compositions of solutions after the incomplete base hydrolysis of *trans*-[Co(en)$_2$ClOH]$^+$ for various concentration ratios are listed in Table III together with the ratios of the *trans* complexes. Data from reactions with limited amounts of hydroxide ion were used to show that hydroxide ion is necessary for the establishment of the equilibrium. The ratios of *trans* products in the base hydrolysis of D*-*cis*-[Co(en)$_2$Cl$_2$]$^+$ are listed in Table IV.[8]

Neglecting aquation [$k_1 = 4.5 \times 10^{-4}$ sec^{-1} at 0°[9]], the apparent second-order rate constant for the data in Table II is 0.016 ± 0.003 sec^{-1} mole^{-1} based on the disappearance of the *trans*-chlorohydroxo complex initially added. But, the *trans* equilibrium is established before any *cis*-dihydroxo complex can be detected. The corrected second-order rate constant for the stereochemical conversion of *trans*-[Co(en)$_2$ClOH]$^+$ to *cis*-[Co(en)$_2$(OH)$_2$]$^+$ is 0.013 ± 0.002 sec^{-1} mole^{-1}. For the corrected value, the initial concentrations of the *trans*-chlorohydroxo and hydroxide ions are taken to be the differences between the concentrations added and the concentrations used immediately for establishment of the *trans* equilibrium.

Base Hydrolysis of D*-*cis*-[Co(en)$_2$ClOH]$^+$. The results of the base hydrolysis of D*-*cis*-[Co(en)$_2$ClOH]$^+$ in varying concentration ratios are listed in Table V. The reaction produces mainly *cis* product with essentially complete retention of configuration. Spectral analysis shows the presence of the *trans*-chlorohydroxo rather than the *trans*-dihydroxo complex because of the *trans* equilibrium noted above. Data resulting from reactions in 38% ethanol at 0 and −20°[6] show less slow [$k_1 = 3.6 \times 10^{-6}$ sec^{-1} at 25°[7c]] and, indeed, that the equilibrium lies in the direction of the *trans* ion [*cis*/*trans* = 0.85 at 25°[7c]]. Rather, the results point to an equilibrium between the *trans* complexes which is rapidly established and is approximately independent of both hydroxide and chloride ion molarity at the precision but, nevertheless, agree with the results in aqueous solutions.

Table III. Composition of Solutions after the Incomplete Base Hydrolysis of *trans*-[Co(en)$_2$ClOH]$^+$

Time, sec	Approximate Concn, *M* *trans*-ClOH	OH$^-$	% *trans*-ClOH	*trans*-OHOH	*cis*-OHOH	*cis*-ClOH	*trans*-ClOH/*trans*-OHOH
125[a]	0.1	0.5	40.4 ± 3.5	4.8 ± 0.5	53.8 ± 3.2	1.0 ± 0.2	7.3 ± 2.3
130	0.1	0.3	*d*	*d*	*d*	*d*	8.7 ± 2.0
300	0.1	0.2	43.5 ± 1.9	5.1 ± 0.3	50.0 ± 1.7	1.4 ± 0.2	8.6 ± 0.8
300[a]	0.2	0.2	56.8 ± 1.7	5.0 ± 0.4	37.0 ± 1.8	1.2 ± 0.4	10.2 ± 1.7
400	0.1	0.1	60.2 ± 0.5	5.8 ± 0.7	33.3 ± 0.8	0.7 ± 0.1	10.3 ± 1.0
1200[a]	0.03	0.03	56.2 ± 0.9	7.2 ± 0.2	36.2 ± 0.9	0.4 ± 0.3	7.4 ± 1.1
900	0.1	0.05	66.1 ± 2.2	6.3 ± 0.3	27.0 ± 2.0	0.6 ± 0.1	10.5 ± 0.8
1800	0.1	0.03	71.5 ± 1.1	8.0 ± 0.6	20.3 ± 0.8	0.2 ± 0.3	8.8 ± 0.8
40[b]	0.1	2×10^{-3}	95.6	4.4	*e*	*e*	21.9
30[b]	0.1	4×10^{-3}	93.8	6.2	*e*	*e*	15.2
30[c]	0.1	0.01	91.2	8.8	*e*	*e*	10.3
30[c]	1×10^{-3}	1×10^{-3}	90.3	9.1	*e*	0.6	9.9
40[c]	1×10^{-3}	1×10^{-3}	90.9	8.2	*e*	0.8	11.0
40[c]	1×10^{-3}	1×10^{-3}	90.7	9.3	*e*	*e*	9.7
120[c]	1×10^{-3}	1×10^{-3}	91.0	8.0	*e*	1.0	11.4
300[c]	1×10^{-3}	1×10^{-3}	90.1	7.7	0.9	1.3	11.7
600[c]	1×10^{-3}	1×10^{-3}	89.0	7.3	2.6	1.1	12.2

[a] % composition based on three runs; *trans* ratio based on five runs. [b] Analysis of duplicate runs. [c] Analysis of single runs. [d] See Table II. [e] Zero within experimental error.

Base Hydrolysis of D*-*cis*-[Co(en)$_2$Cl$_2$]$^+$. The results of the base hydrolysis of D*-*cis*-[Co(en)$_2$Cl$_2$]$^+$ for various concentration ratios are listed in Table VI. Of prime importance is the result that L*-*cis*-[Co(en)$_2$-

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[7] (a) J. Y. Tong and P. E. Yankwich, *J. Am. Chem Soc.*, **80**, 2664 (1958); (b) J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6**, 1265 (1952); (c) W. Kruse and H. Taube, *J. Am. Chem. Soc.*, **83**, 1280 (1961).

[8] The *trans* equilibrium appears only slightly affected by changes in solvent to 38% ethanol and in temperature to −20°; ref 6.

[9] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

Table IV. Ratios of *trans* Products in the Base Hydrolysis of D*-*cis*-$[Co(en)_2Cl_2]^+$

Approx time, sec	Approx concn, *M* D*-ClCl	OH⁻	*trans*-ClOH/*trans*-OHOH
30	0.1	0.3	6.4 ± 0.7
30	0.1	0.2	6.2 ± 0.4
20	0.1	0.1	6.7 ± 0.4
45	0.03	0.03	6.1 ± 0.4
50	0.1	0.03	5.9–∞[a]

[a] Results for less than stoichiometric amounts of hydroxide are erratic.

Table V. Products Formed in the Base Hydrolysis of D*-*cis*-$[Co(en)_2ClOH]^+$

Approx time, sec	Approx concn, *M* D*-ClOH	OH⁻	% *cis*-OHOH	*trans*-ClOH	D*-OHOH
25	0.1	0.3	96 ± 1	4 ± 1	94 ± 1
35	0.1	0.2	96 ± 1	4 ± 1	99 ± 1
45	0.1	0.1	95 ± 1	5 ± 1	104 ± 6
60	0.03	0.03	93 ± 1	7 ± 1	100 ± 3
50	0.1	0.03	92 ± 2	8 ± 2	96 ± 9

Table VI. Products Formed in the Base Hydrolysis of D*-*cis*-$[Co(en)_2Cl_2]^+$

Approx time, sec	Approx concn, *M* D*-ClCl	OH⁻	% *trans*-ClOH	*cis*-ClOH	*trans*-OHOH	*cis*-OHOH	Total *trans*
50	0.1[a]	0.03	*b*	23.1 ± 1.2	*b*	*c*	76.9 ± 1.2
45	0.03[a]	0.03	71.8 ± 0.7	12.8 ± 0.9	11.8 ± 0.6	3.6 ± 0.6	83.6 ± 0.3
20	0.1[a]	0.1	70.6 ± 0.3	11.6 ± 0.5	10.8 ± 0.6	7.0 ± 0.3	81.4 ± 0.3
35	0.1	0.2	61.9 ± 0.6	5.0 ± 0.8	9.9 ± 0.6	23.2 ± 1.5	71.8 ± 0.7
25	0.1	0.3	57.5 ± 1.6	6.2 ± 1.9	8.3 ± 0.6	28.0 ± 1.7	65.8 ± 1.4
50	0.1	0.3	54.3 ± 0.7	1.6 ± 0.2	8.7 ± 0.3	35.4 ± 0.8	63.0 ± 1.0

Approx time, sec	Approx concn, *M* D*-ClCl	OH⁻	% Total *trans*	D*-ClOH	L*-ClOH	D*-OHOH	L*-OHOH
50	0.1[a]	0.03	76.9 ± 1.2	22.4 ± 1.1	0.7 ± 0.3	*c*	*c*
45	0.03[a]	0.03	83.6 ± 0.3	11.8 ± 0.9	1.0 ± 0.2	0.9 ± 0.4	2.7 ± 0.5
20	0.1[a]	0.1	81.4 ± 0.3	9.8 ± 0.8	1.8 ± 0.4	1.9 ± 0.4	5.1 ± 0.2
35	0.1	0.2	71.8 ± 0.7	3.7 ± 0.8	1.3 ± 0.1	10.5 ± 1.0	12.7 ± 0.6
25	0.1	0.3	65.8 ± 1.4	3.7 ± 1.0	2.5 ± 1.0	11.6 ± 0.6	16.4 ± 1.2
50	0.1	0.3	63.0 ± 1.0	0.8 ± 0.1	0.8 ± 0.1	15.8 ± 0.4	19.6 ± 0.7

[a] Contains unreacted D*-ClCl. [b] Erratic, but total *trans* consistent. [c] Zero within experimental error.

ClOH]$^+$ is never produced in a greater amount than the corresponding D* enantiomer, while the reverse is true for the *cis*-$[Co(en)_2(OH)_2]^+$ optical isomers. The increase in inverted product with concentration is shown by comparing the reactions in which both complex and hydroxide ions are 0.1 and 0.03 *M*. The ratio of inverted to retained *cis*-dihydroxo product remains about 3:1, but the amount of inverted product increases at the higher concentration. The lower percentage of total *trans* product when less than 1 equiv of hydroxide ion (0.1 *M*:0.03 *M*) is present and the absence of the *cis*-dihydroxo complex indicate the importance of base concentration to rearrangement. A minimum ratio of base, lying between 0.3 and 1 equiv, is required for the observation of inversion to the L*-dihydroxo product.

The percentage of *trans*-$[Co(en)_2ClOH]^+$ in the product decreases with increasing equivalents of base consistent with reaction of this species with the excess hydroxide ion. Racemic *cis*-$[Co(en)_2(OH)_2]^+$ is produced, while the concentration of *trans*-$[Co(en)_2(OH)_2]^+$ is reduced in equilibrium proportions with the decreasing *trans*-$[Co(en)_2ClOH]^+$ concentration. The percentage of *cis*-$[Co(en)_2ClOH]^+$ also decreases with increasing equivalents of base due to its reaction with excess hydroxide ion. Furthermore, the increases in D*- and L*-dihydroxo products with time for the three hydroxide to one dichloro concentration ratio are consistent with the *trans* species forming racemic *cis*-dihydroxo complexes and the D*- and L*-chlorohydroxo complexes forming D*- and L*-dihydroxo complexes, respectively (last entry of Table VII).

An increase in inverted product (above that calculated assuming subsequent reaction; see Table VII) is supported by the differences observed in going from the 0.1 *M*:0.1 *M* to 0.1 *M*:0.2 *M* complex to hydroxide concentration ratios. The differences between calculated and observed changing from the 0.1 *M*:0.2 *M* series to the 0.1 *M*:0.3 *M* series lack significance because the deviations in the results are about as large as the differences in the results.

In the series using 3 equiv of base, the *cis*-$[Co(en)_2ClOH]^+$ still present after 50 sec appears to be racemic. The samples invariably contain significantly more of the D* enantiomer for shorter reaction periods.

Discussion

***trans*-$[Co(en)_2ClOH]^+$.** The results of the base hydrolysis for all three complexes reported herein support the establishment of a rapid equilibrium between *trans*-$[Co(en)_2ClOH]^+$ and *trans*-$[Co(en)_2(OH)_2]^+$ which is almost independent of chloride and hydroxide ions under most conditions studied. This equilibrium was not observed by Chan and Tobe[3] because they followed the reaction spectroscopically at a wavelength at which the molar extinction coefficients of the *trans* complexes are almost identical. Reaction paths which are consistent with the results obtained in the present study are shown in reaction sequence 2.

$$\begin{tikzcd} trans\text{-}[Co(en)_2ClOH]^+ \arrow[r, shift left, "OH^-"] \arrow[d, "OH^-", "(slow)"'] & trans\text{-}[Co(en)_2(OH)_2]^+ \text{ (fast)} \arrow[l, shift left, "Cl^-"] \\ cis\text{-}[Co(en)_2(OH)_2]^+ & \end{tikzcd} \qquad (2)$$

If the rapid interchange of ligands in the complex were due to an ion-pairing phenomenon in the concentrated solutions, a phenomenon which is not prominent among *trans* complexes,[10] a reduction or elimination of the effect should be observed in less con-

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(10) (a) R. G. Pearson, P. M. Henry, and F. Basolo, *J. Am. Chem. Soc.*, **79**, 5379 (1957); (b) M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 4614 (1962); (c) M. L. Tobe and D. W. Watts, *ibid.*, 2991 (1964); (d) M. N. Hughes and M. L. Tobe, *ibid.*, 1204 (1965).

Table VII. Comparison of Changes in Products with Concentration for the Base Hydrolysis of D*-*cis*-$[Co(en)_2Cl_2]^+$

Comparison concn, *M*		Changes in intermediates		Calcd changes in % products[a]		Obsd changes in % products	
D*-ClCl	OH^-	Complex	%	D*-OHOH	L*-OHOH	D*-OHOH	L*-OHOH
From							
0.03	0.03	Total *trans*	−2.2 ± 0.4	3.1 ± 1.3	0.3 ± 0.6	1.0 ± 0.6	2.4 ± 0.5
to		D*-ClOH	−2.0 ± 1.2				
0.1	0.1	L*-ClOH	+0.8 ± 0.4				
From							
0.1	0.1	Total *trans*	−9.6 ± 0.8	10.9 ± 1.4	5.3 ± 0.9	8.6 ± 1.1	7.6 ± 0.6
to		D*-ClOH	−6.1 ± 1.1				
0.1	0.2	L*-ClOH	−0.5 ± 0.4				
From							
0.1	0.2	Total *trans*	−6.0 ± 1.5	3.0 ± 2.0	1.8 ± 1.8	1.1 ± 1.2	3.7 ± 1.3
to		D*-ClOH	0.0 ± 1.3				
0.1	0.3	L*-ClOH	+1.2 ± 1.0				
From							
0.1	0.3[b]	Total *trans*	−2.8 ± 1.7	4.3 ± 2.0	3.1 ± 2.0	4.2 ± 0.7	3.2 ± 1.4
to		D*-ClOH	−2.9 ± 1.0				
0.1	0.3	L*-ClOH	−1.7 ± 1.0				

[a] Calculated changes in *cis*-OHOH species based on assuming the total *trans* is converted to racemic *cis*-OHOH, and the D*-ClOH and L*-ClOH are converted to D*-OHOH and L*-OHOH, respectively. [b] Comparison based on changes for double reaction time.

centrated solutions. However, the same equilibrium has been found to be established in 30 sec in concentration 10^{-3} *M* in both complex and hydroxide ion. If the establishment of the equilibrium were base catalyzed, concentrations of hydroxide ion which are below those necessary for equilibrium concentrations of the *trans*-dihydroxo complex would be effective. Such a base catalysis would necessitate the *trans*-hydroxoaquo complex being a participating species. It has been found that the minimum concentration of hydroxide ion corresponds to equilibrium proportions.

The low anion dependence and stereospecificity suggest a dissociative mechanism involving a five-coordinate tetragonal pyramid which is in accord with the belief that the *trans*-hydroxo ligand promotes a unimolecular reaction by labilizing the chloro ligand.[11] An inner–outer sphere equilibrium such as that proposed by Taube and Posey[12] could be operative in this case, even though a low charge exists on the complex, because the solvent molecules in the outer sphere have the unique properties of being the conjugate acid of the attacking ion and of having high proton mobility *via* Grotthus chain reactions. The low charge and small amount of ion pairing which has been observed in *trans* systems make it less likely that there is an intimate ion aggregate[10d,13] which rearranges to result in the observed equilibrium.

The role of the solvent is not known. Poon and Tobe[14] discovered an aquation equilibrium between *trans*-$[Co(cyclam)Cl_2]^+$ and *trans*-$[Co(cyclam)ClH_2O]^{2+}$. Anionic substitution reactions on the dichloro complex are first order, and a chloroaquo intermediate is supported by the rate data. However, base hydrolysis shows second-order kinetics.

A judgment about the rate of the base hydrolysis of the *trans*-chlorohydroxo complex can be made on the basis of the erratic results of the *cis*-dichloro complex with limited base, *i.e.*, the 0.1 *M*:0.03 *M* reactions. In this series the *trans*-chlorohydroxo complex being produced competes with considerable success with the *cis*-dichloro complex for the hydroxide ion. The absence of *cis*-dihydroxo product indicates that the *cis*-chlorohydroxo intermediate reacts more slowly. Therefore, the equilibrium between the *trans* complexes is established in solution at a rate lying close to that of the base hydrolysis of *cis*-$[Co(en)_2Cl_2]^+$ (k_2 = 15.1 mole^{-1} sec^{-1} at 0°[3]). The reported specific rate constant for the base hydrolysis reaction of the *trans*-chlorohydroxo complex at 0° (k_2 = 0.017 mole^{-1} sec^{-1})[3] is actually based on the rate of stereochemical conversion to the *cis*-dihydroxo product rather than on the rate of base hydrolysis. Apparently Chan and Tobe[3] should have paid heed to the earlier studies by Pearson, Meeker, and Basolo.[15,16] Unfortunately, the latter base hydrolysis results are for the mixed *cis*- and *trans*-$[Co(en)_2ClOH]^+$ products of the *trans*-$[Co(en)_2Cl_2]^+$ base hydrolysis reaction at 25°.[15a] Even so, considering the mixed base hydrolysis rate and the minor amount of *cis*-$[Co(en)_2ClOH]^+$ in the mixed first step products, a specific rate constant of greater than unity (mole^{-1} sec^{-1}) is predicted at 0° from the earlier study. The importance of the reverse reaction as noted in the present study means the actual rate is even greater.

The existence of an equilibrium between the *trans* complexes offers a possible explanation for some of the unexpected observations previously reported for the three complexes of this study. Pearson, Meeker, and Basolo[15b] found that the addition of 1 equiv of hydroxide ion to the *cis*-dichloro complex produces not only the hydroxochloro isomers, but the dihydroxo product as well, although the rates at which the chlorohydroxo isomers react were thought to be slow enough compared with that of the *cis*-dichloro complex that competition should not exist. Chan and Tobe[3] reported a large apparent difference in the reactivity of *trans*-$[Co(en)_2Cl_2]^+$ and *trans*-$[Co(en)_2ClOH]^+$ toward hydroxide ion when compared with the difference in the reactivity between the respective *cis* isomers. Ingold,

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(11) C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **194**, 344 (1962).

(12) H. Taube and F. A. Posey, *J. Am. Chem. Soc.*, **75**, 1463 (1953).

(13) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

(14) C. K. Poon and M. L. Tobe, *Coord. Chem. Rev.*, **1**, 81 (1966).

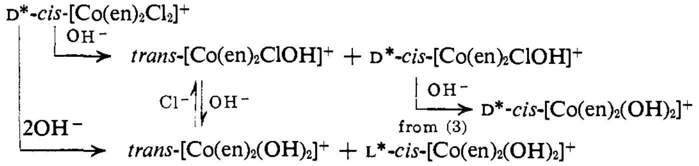
(15) (a) R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, **78**, 709 (1956); (b) R. G. Pearson, R. E. Meeker, and F. Basolo, *ibid.*, **78**, 2673 (1956).

(16) Recent investigations in D_2O [S. C. Chan, *J. Chem. Soc., Sect. A*, **1310** (1966)] and with the corresponding flucrohydroxo complexes [S. C. Chan and O. W. Lau, *ibid.*, 1800 (1966)] also have been studied by methods which do not distinguish between their cited mechanism and our observations; *i.e.*, they have followed the reactions by chloride titrations after removal of the cationic complexes and by spectrophotometric absorbance changes at wavelengths at which the two *trans* species have comparable absorbance.

Nyholm, and Tobe[11] pointed out that the apparent slow rate for base hydrolysis of *trans*-$[Co(en)_2ClOH]^+$ relative to the corresponding *cis* complex was the reverse of the order generally observed between *cis* and *trans* isomers.

The stereochemical conversion to the *cis*-dihydroxo complex is quite slow, which is in agreement with the high-energy barrier to rearrangement that strong field complexes must overcome.[17] If the rearrangement proceeds by means of an attack *trans* to the leaving group as the complex collapses toward a trigonal bipyramid, the rearrangement is facilitated if π bonding with a remaining ligand can occur with the empty orbitals in the trigonal plane.[18] The *trans*-dichloro complex undergoes base hydrolysis with little rearrangement.[3] The hydroxo ligand has a stronger field than the chloro and is a poorer π donor. Therefore, the *trans*-chlorohydroxo complex would be expected to undergo even less rearrangement as observed in the present study. Reaction takes place by the high-energy rearrangement path because the less energetic one is an equilibrium reaction which cannot consume the reactant. Whether or not *trans* product is formed in the process which gives rearrangement cannot be determined.

The importance of the conjugate-base concept[17a] for these reactions (sequence 2) should not be overlooked. The acidic protons on the amine ligands attract the hydroxide ion, and the developing conjugate base perturbs the electronic distribution of the complex, loosening the structure of the entire complex. Such loosening aids in the dissociation of the chloro ligand of the *trans*-$[Co(en)_2ClOH]^+$ for the rapid retention equilibrium and facilitates movement of the amines for the rearrangement process.

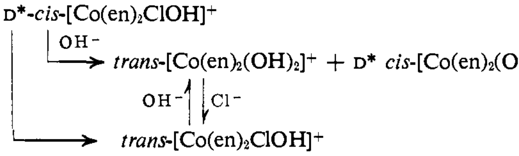


(4)

D*-*cis*-$[Co(en)_2ClOH]^+$. The almost exclusive production of D*-*cis*-$[Co(en)_2(OH)_2]^+$ in the base hydrolysis of D*-*cis*-$[Co(en)_2ClOH]^+$ supports an attack by the entering ligand *cis* to the leaving group.[17a,19] These results differ from those of Chan and Tobe,[3] who reported that 63% of the *cis*-dihydroxo product is the D* enantiomer. Apparently their products stood long enough for appreciable racemization to occur. The presence of only a small percentage of rearranged product is indicative of the high ligand field stabilization energy barrier to rearrangement.

That the *trans* product is observed as *trans*-$[Co(en)_2ClOH]^+$ is in agreement with the *trans* equilibrium in which the chlorohydroxo complex predominates. Less than 0.5% of the total concentration would have to be *trans*-$[Co(en)_2(OH)_2]^+$ to be consistent with the per cent *trans*-$[Co(en)_2ClOH]^+$ present. The method of analysis is not reliable at this level. Alternately, the *trans*-chlorohydroxo species may arise from the isomerization of the *cis*-chlorohydroxo isomer. Nothing has been reported in the literature concerning such an isomerization.

Reaction paths which are consistent with the observed results are shown in reaction sequence 3. The slight discrepancies between the percentages of *cis*- and D*-*cis*-$[Co(en)_2(OH)_2]^+$ can be accounted for by accumulative errors in rotational and concentration values.



(3)

D*-*cis*-$[Co(en)_2Cl_2]^+$. Since L*-*cis*-$[Co(en)_2(OH)_2]^+$ is produced in greater quantity than the corresponding D* enantiomer while the reverse is true for the *cis*-$[Co(en)_2ClOH]^+$ optical isomers, the L*-dihydroxo product is being produced not by a two-step process through the normal L*-chlorohydroxo complex, but rather by the reaction of two hydroxide ions with the D*-dichloro ion. When only one hydroxide ion reacts with the D*-dichloro complex to produce stable chlorohydroxo complexes, a large amount of *trans*-$[Co(en)_2ClOH]^+$ is formed and D* is the predominant *cis*-chlorohydroxo enantiomer. The predominant reaction paths which explain the results obtained for the dichloro base hydrolysis reaction are shown in sequence 4.

Both *trans* and inverted products may occur by means of a *trans* attack.[17a,18] The structure of the complex is electrostatically suited to such an attack. A negative ion will be repelled from the highly negative chloro ligands[11] and attracted toward the positive protons on the amine nitrogens. The two amine groups N_2 and N_3 (Figure 1) are *cis* to one chloro ligand and *trans* to the other, while the amine groups N_1 and N_4 are *cis* to both chloro ligands. If any electronic or electrostatic interaction exists between the protons on the amine nitrogens and the chloro ligands, molecular models indicate that one of the protons on each of the amines N_2 and N_3 should be more acidic than the other amine protons. These two sites are thus more susceptible to hydroxide ion attack.[20] If (as suggested earlier) coordination sphere mobility increases as the conjugate base develops, the movement of the amines should be facilitated by the electrostatic repulsion between hydroxide ions on the back (*trans* to the chloro ligands) of the complex. A concerted movement of three moieties from the back toward the front of the complex may be envisioned, the hydroxyl portion of the developing conjugate base moving into the void being created by the amine portion as this amine moves into the void being created by the chloro ligand leaving

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(17) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, 1967; (b) F. Basolo, Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1967, p 408; (c) R. D. Archer, *ibid.*, **62**, 452 (1967).

(18) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1966.

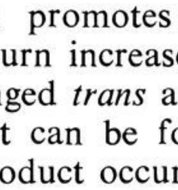
(19) D. D. Brown, C. K. Ingold, and R. S. Nyholm, *J. Chem. Soc.*, 2674 (1953).

(20) J. C. Bailar, Jr., *Rev. Pure Appl. Chem.*, **16**, 91 (1966), reviews the development of the octahedral (Bailar) inversion. Bailar makes the opposite acidity choice to explain the inversion. His choice, although logical for the carbonato results, is consistent with neither the predominance of *trans* product nor the retained *cis*-chlorohydroxo product.

the coordination sphere. If both possible sets of three moieties complete their movement of coordinating position exchange before one set has established complete bonding, the L*-dihydroxo product would be formed; otherwise, the *trans*-chlorohydroxo intermediate would be stabilized. The *trans* equilibrium prevents observations arguing for or against the formation of *trans*-dihydroxo complex directly from the dichloro complex. That *trans* attack occurs readily in the dichloro complex is explained by its weak ligand field strength which imposes only a low-energy barrier to rearrangement. The analogous Rh(III) dichloro complex undergoes base hydrolysis with retention of configuration[21] as is consistent with a stronger ligand field strength.

More inverted product is formed as both reacting complex and base concentrations are increased. Increased concentration promotes increased backside ion pairing which in turn increases the probability of completing a two-pronged *trans* attack before a stable chlorohydroxo product can be formed. Whether an increase in inverted product occurs when more than 2 equiv of base are used is not clear. One piece of evidence strongly favoring the insensitivity of the reaction to more than 2 equiv of base is the data of Boucher, Kyuno, and Bailar[2] for the reactions of 0.5 *M* complex with 2 and 3 equiv of hydroxide ion. Both concentrations give the same rotations for the total solutions. The concentrations are high enough that the only rotating species left in solution should be the *cis*-dihydroxo species. The apparent changes which Boucher, *et al.*,[2] observed with increasing base concentrations at lower complex concentrations (0.125 *M*) are not significant because other rotating species are present as shown by the present work. An increase in base concentration is expected to increase the relative number of ion pairs and ion triplets and thereby increase the amount of inversion.

The formation of an intermediate with one monodentate ethylenediamine, *i.e.*



in which N_1 or N_4 of Figure 1 is temporarily uncoordinated, could also produce an inverted product through subsequent chloride replacement by the free nitrogen and a water molecule or hydroxide ion. We might tend to reject this mechanism since cobalt(III) base hydrolyses *normally* displace chloride rather than amines. Furthermore, the replacement of just one chloride by the free nitrogen donor would give an inverted *cis*-ClOH ion, whereas we have observed predominant retention with no significant trend in the amount of inverted *cis*-ClOH under conditions which give appreciably more inverted *cis*-OHOH. However, consistent with this mechanism, the per cent of *cis*-ClOH which is inverted does appear to increase under these same conditions. Therefore, if the chloride *trans* to the monodentate ethylenediamine is replaced before the free nitrogen recoordinates, say three out of every four times, our data would be consistent with this mechanism.

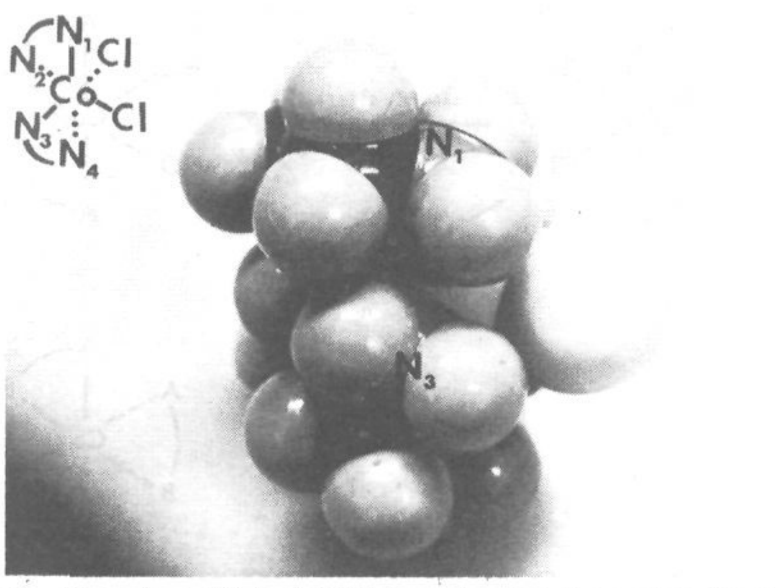


Figure 1. The D*-*cis*-$[Co(en)_2Cl_2]^+$ ion, showing the amine group orientations. The inset shows the coordinating atom orientations for the figure. The atoms N_1 and N_4 are geometrically equivalent as are atoms N_2 and N_3.

Inversion also can be explained by a front side ion pair (fsip) mechanism. For this mechanism the second step must occur prior to diffusion of the first chloride from the second coordination sphere. The stereochemistry of the two steps is *trans* > D* > L* for the first step and *trans* and L* (by *trans* attack) > D* for the *cis* species during the fsip second step. Any *cis*-dihydroxo formed from the *trans*-chlorohydroxo ion pair would be racemic. While this mechanism predicts the correct stereochemistry, the rate of diffusion of chloride from the second coordination sphere ($t_{1/2}$ estimated as about 10^{-7} sec[22]) is enough faster than the second base hydrolysis ($t_{1/2} > 1$ sec under our reaction conditions) that no detectable inversion product should be observed unless the ion pair promotes an extremely rapid *trans* attack.

The simultaneous attack of two hydroxides on the two chlorides in a trigonal twist manner[23] would also give inversion, but the hydroxide ion concentration dependence should be greater than has been observed.

The latter three possibilities could be distinguished from the two-prong *trans* attack mechanism if an unsymmetrical diamine were used in place of ethylenediamine for analogous studies. The monodentate, trigonal twist, and fsip mechanisms should give a different isomer than the favored mechanism, as indicated in Figure 2.

Furthermore, the asymmetric five-coordinate conjugate base intermediate, which might otherwise explain an inversion mechanism,[17a,b,24] is ruled out for the inversion by our results. A five-coordinate species would be applicable only if the two steps were independent, which is not true for the inversion. However, the majority of the products (*i.e.*, the *trans*- and *cis*-chlorohydroxo species) are probably a result of a five-coordinate conjugate base intermediate.[17a,18]

Finally, the deductive reasoning that the products of the first step of a two-step reaction can be obtained from the over-all reaction and the second step[2,5,25] is invalid. For this study, such reasoning implies a predominance of the L* enantiomer of the *cis*-chloro-

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[21] S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 1741 (1963).

[22] C. H. Langford, private communication.

[23] C. S. Springer, Jr., and R. E. Sievers, *Inorg. Chem.*, **6**, 852 (1967).

[24] R. G. Pearson and F. Basolo, *ibid.*, **4**, 1522 (1965).

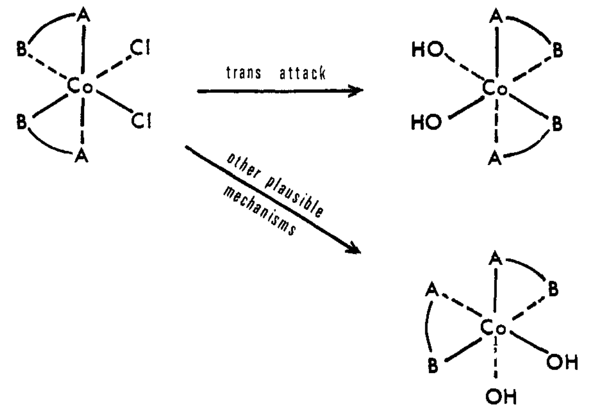

Figure 2. Predominant *cis* inversion products for unsymmetrical diamines.

hydroxo complex, which is not in agreement with the experimental results.

Experimental Section

Preparation of Complexes. The preparation and resolution of the following complexes were carried out according to published procedures: D*-*cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$,[7a,25a,26] D*-*cis*-$[Co(en)_2ClH_2O]Br_2\cdot H_2O$,[5,27] *trans*-$[Co(en)_2ClOH]Cl\cdot H_2O$,[3,9] *cis*- and *trans*-$[Co(en)_2(H_2O)_2](NO_3)_3$.[7b] D*-*cis*-$[Co(en)_2(H_2O)_2]^{3+}$ was prepared from D*-*cis*-$[Co(en)_2CO_3]I$ which had been prepared from D*-*cis*-$[Co(en)_2ClH_2O]Br_2\cdot H_2O$.[5] Purity was ascertained by spectral comparisons with published maxima and minima and by elemental analyses made by Alfred Bernhardt, Max-Planck Institute, West Germany.

Anal. Calcd for D*-*cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$: C, 15.83; H, 5.98; N, 18.46. Found: C, 16.03; H, 5.80; N, 18.69. Calcd for D*-*cis*-$[Co(en)_2ClH_2O]Br_2\cdot H_2O$: C, 11.71; H, 4.91; Cl (coord), 8.64; Br (ionic), 38.94. Found: C, 11.80; H, 5.04 Cl (coord), 8.51; Br (ionic), 39.00. Calcd for *trans*-$[Co(en)_2ClOH]Cl\cdot H_2O$: C, 16.85; H, 6.72; Cl, 24.87. Found: C, 16.69; H, 6.82; Cl, 25.13. Calcd for *cis*-$[Co(en)_2(H_2O)_2](NO_3)_3$: C, 11.98; H, 5.02; N, 24.44. Found: C, 12.13; H, 5.10; N, 24.32. Calcd for *trans*-$[Co(en)_2(H_2O)_2](NO_3)_3$: C, 11.98; H, 5.02; N, 24.44. Found: C, 12.11; H, 5.12; N, 24.48. Calcd for D*-*cis*-$[Co(en)_2CO_3]I$: C, 16.41; H, 4.41; N, 15.31. Found: C, 16.53; H, 4.41; N, 15.22.

Spectra. The spectra of the complexes have been previously reported: *cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$,[28] *cis*-$[Co(en)_2ClH_2O]^{2+}$,[3] *trans*-$[Co(en)_2ClH_2O]^{2+}$,[3] *cis*- and *trans*-$[Co(en)_2(H_2O)_2](NO_3)_3$.[7b] The spectra for this work were recorded in aqueous 0.16 *M* sodium perchlorate at about pH 1. This acidity is necessary to prevent the formation of *trans*-$[Co(en)_2OHH_2O]^{2+}$.[7c] The spectra show no salt or pH effects between 455 and 600 mμ. The cell compartment of the spectrophotometer was cooled by circulating ice water. The analyses were made using the molar extinction coefficients of the pure complexes and the absorbance readings at intervals of 5 mμ between and including 455 and 600 mμ.

Molar Rotations. The optical rotatory dispersion curves have been reported for the *cis* species studied[29] and the three *cis* species dextrorotatory at 541 mμ all have the same configuration. The molar rotations used in this study are listed in Table VIII.

Base Hydrolysis Reactions. All solutions, the solid complexes, and the syringes and graduated cylinders used for transferring and collecting solutions were cooled in ice baths for at least 1 hr. Carbonate-free water and sodium hydroxide were used. Five reactions were run at each concentration for approximately the same length of time. If changes with time were to be studied, eight to ten runs were made.

Table VIII. Molar Rotations of Complexes at 541 mμ

Complex	$[M]_{541}$
D*-*cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$	+1209
D*-*cis*-$[Co(en)_2ClH_2O]Br_2\cdot H_2O$	+1348
D*-*cis*-$[Co(en)_2(H_2O)_2]^{3+}$ [a]	+1196

[a] Product of the acidification of D*-*cis*-$[Co(en)_2CO_3]I$.

To illustrate, for the reaction of 0.1 *M* D*-*cis*-$[Co(en)_2Cl_2]^+$ with 0.1 *M* hydroxide ion, the complex (3.00×10^{-3} mole) was dissolved in water (1.50 ml). Sodium hydroxide (1.50 ml, 0.213 *M*) was added to the dissolved complex. (In the reactions of D*-*cis*-$[Co(en)_2ClH_2O]^{2+}$, sufficient hydroxide ion was added to produce the chlorohydroxo complex *in situ* prior to hydrolysis.) After about 20 sec the reaction was quenched with perchloric acid (0.2 *M*). The solution was diluted with water acidified to about pH 1 with perchloric acid and with sufficient 2 *M* sodium perchlorate to produce a concentration of 0.16 *M* sodium perchlorate in a total volume of 15.0 ml. A spectrum and a polarimeter reading were obtained for this solution (solution A).

Separation of Complexes According to Charge. The method of Carunchio, *et al.*,[30] was greatly modified to meet the needs of the dichloro system. Saturated sodium perchlorate (0.25 and 1.00 ml) was added to aliquots (5.00 ml) of solution A to produce solutions having concentrations of 0.5 and 2.0 *M* sodium perchlorate. These solutions were passed at a rate of approximately 1 ml/3 min through ion-exchange columns (Dowex 50-8X, Na^+ form, 20–50 mesh) which had been pretreated to about pH 1 and the appropriate sodium perchlorate concentration. The columns were jacketed with flowing ice water. The eluent (solution B) from the column through which the 0.5 *M* sodium perchlorate solution has passed contained *cis*-$[Co(en)_2Cl_2]^+$ and small amounts of *trans*-$[Co(en)_2ClH_2O]^{2+}$. The eluent (solution C) from the other column contained the ions in solution B plus *cis*-$[Co(en)_2ClH_2O]^{2+}$. No attempt was made to remove the ions completely from the columns. Sufficient eluent was collected to permit spectral and rotational analyses from which the rotational value of solution A was separated into the contribution from each rotating species. Preliminary experiments showed that passage through the ion-exchange column did not cause racemization of the optically active *cis* species and that little racemization or isomerization occurred in the time period between quenching the reaction and measurement of the solutions. The rotational measurements were made on solutions at about 20°.

Calculations. The effective [M] for the *cis*-dichloro complex was calculated from solution B using the equation $[M] = 10\alpha/lC$ (α = rotation in degrees, l = path length in decimeters, and C = concentration in moles per liter) and applied to the total rotation of solution C to determine the contribution of the *cis*-dichloro complex. From the resultant rotation attributable to the *cis*-chloroaquo complex, its effective [M] was calculated. Then application of these two effective molar rotations to the total rotation of solution A permitted the determination of the effective [M] of the *cis*-diaquo complex.

Apparatus. The spectrophotometric measurements were made with a Cary Model 14 recording spectrophotometer using 1- and 10-cm cells. The optical activity of the solutions was measured with a Bendix NPL automatic recording polarimeter using 1- and 2-cm cells and a filter of wavelength 541 ± 0.5 mμ, having a measured precision of 5×10^{-4}°.

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(25) (a) R. D. Archer and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **83**, 812 (1961); (b) E. Kyuno, L. J. Boucher, and J. C. Bailar, Jr., *ibid.*, 87, 4458 (1965).

(26) J. C. Bailar, Jr., and C. L. Rollinson, *Inorg. Syn.*, **2**, 222 (1946).

(27) A. Werner, *Helv. Chim. Acta*, **4**, 113 (1921); *Ann.*, **386**, 122 (1911).

(28) F. Basolo, *J. Am. Chem. Soc.*, 72, 4393 (1950).

(29) (a) J. P. Mathieu, *Bull. Soc. Chim. France*, [5] **3**, 476 (1936); (b) T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).

(30) V. Carunchio, G. Grassini-Strazza, G. Ortaggi, and C. Padiglione, *J. Inorg. Nucl. Chem.* 27, 841 (1965).