$[Co(NH_3)_6][CuCl_5]$ down to ~16°K is in agreement with this analysis.

The antiferromagnetic transition at 8°K must arise from coupling of the magnetic wave functions transmitted by chloride ligands of adjacent molecules. This mechanism has been designated the cation–anion–anion–cation interaction,[14] and for half-filled σ orbitals, moderately weak spin coupling is expected. The low Néel point of 8°K reflects weak spin coupling in $[Co(NH_3)_6][CuCl_5]$.

The crystal structure for $[Cr(NH_3)_6][CuCl_5]$ shows that the shortest intermolecular chloride–chloride contacts occur for the axial chloride of one $CuCl_5^{3-}$ ion and axial chloride ligands of three adjacent $CuCl_5^{3-}$ units. The internuclear separations are 4.11 Å, and the copper–chloride(1)–chloride(2) angles are 144.74°. This separation is only 0.80 Å greater than the axial chloride–equatorial chloride intramolecular distance within a $CuCl_5^{3-}$ ion. The unpaired electron in the ground state is in a $3d_{z^2}$ orbital, which has a greater amplitude along the z axis than in the xy plane; thus, in the absence of angular dependencies, ligand axial–axial contacts are expected to be more important than ligand equatorial–equatorial contacts for the conduction of antiferromagnetic interactions.

The closest intermolecular equatorial chloride–other chloride separation, 4.14 Å, occurs between equatorial ligands of adjacent $CuCl_5^{3-}$ ions. In addition, there are four other equatorial chlorides at 4.75 Å. A detailed description of the cooperative magnetic interaction would be extremely difficult, although in principle a treatment similar to the classical work on the hexachloroiridate(IV) salts should be possible.[15] Another explanation would involve particle size or surface effects. We conclude that although the magnetism of the pentachlorocuprate(II) ion may be described by crystal field theory, below 16°K the susceptibility does not exhibit Curie–Weiss behavior but shows a complex behavior suggestive of antiferromagnetism.

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[14] J. B. Goodenough, "Magnetism and the Chemical Bond," Interscience Publishers, New York, N. Y., 1963, p 184.

[15] M. E. Lines, *Proc. Roy. Soc.* (London), **A271**, 105 (1963), and references therein.

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The Chemistry of Macrocyclic Complexes of Cobalt(III). Hydrolysis Rates and Equilibria in *trans*-$Co^{III}LX_2$ Systems[1]

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The specific rates and equilibria have been investigated for the hydrolytic reactions of some *trans*-$CoLX_2^+$ complexes where L is a macrocyclic ligand (of the Curtis type) and $X^- = Cl^-, Br^-$, or NCS^-. The relative lability of these complexes can be ascribed partly to nonbonded steric interactions between ligand methyl groups and the axial ligands X and partly to the formation of relatively long-lived intermediates where L is the Schiff-base amine 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. The kinetic and thermodynamic data for these systems can be related by linear free energy relations; however, the coefficients in the LFER's appear to be different for each system. The relatively positive values of $\Delta S^{\ddagger}$ found for many of the systems studied shows that $\Delta S^{\ddagger}$ is not generally correlated with stereochemical change and may not provide any simple information about the geometry of the activated complex.

Introduction

Despite extensive research and discussion, there remain many controversial issues pertaining to the mechanism of ligand substitution reactions in octahedral complexes.[3] Much of the recent discussion has centered around the stereochemical changes which occur during the exchange of ligands. It has been argued that such changes reflect the geometry of the activated

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[1] (a) Presented in part before the Division of Inorganic Chemistry, 156th National Meeting of American Chemical Society, Atlantic City, N. J., Sept 1968. (b) Preliminary aspects of this work were also presented at the XIth International Conference on Coordination Chemistry, Haifa, Israel, Sept 1968; see R. E. Ball, J. A. Kernohan, and J. F. Endicott, "Coordination Chemistry," M. Cais, Ed., Elsevier Publishing Co., Amsterdam, 1968. (c) Taken in part from the Dissertation submitted by J. A. K. to Boston University in partial fulfillment of the requirements of the Ph.D. degree, 1969. (d) Supported in part by the Public Health Service (Grant AM 08737) and in part by a Grant in Aid from the Graduate School, Boston University.

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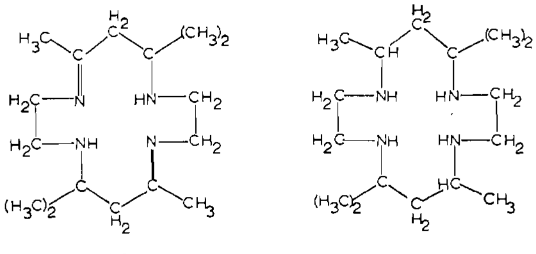
[3] For recent reviews see: (a) C. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1966; (b) N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966); (c) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967; (d) C. H. Langford and T. R. Stengle, *Ann. Rev. Phys. Chem.*, **19**, 193 (1968); (e) R. D. Archer, *Coord. Chem. Rev.*, **4**, 243 (1969).

complex.[3c] More recently it has been proposed[4] that stereochemical changes are accompanied by positive values of $\Delta S^{\ddagger}$ and that such observations are consistent with the formation of a trigonal-bipyramidal transition state.[4,5] The coordination of the central metal by a tetracoordinate macrocyclic ligand imposes important constraints on the geometry of the activated complex for both ligand-exchange reactions and steric changes around the metal center. Systematic studies have been reported for only a few such series of macrocyclic complexes, *e.g.*, for $Co^{III}LX_2$ complexes where L = 1,4,8,11-tetraazacyclotetradecane (cyclam),[6] for complexes where L = hematoporphyrin,[7] and for the pseudomacrocyclic bis(dimethylglyoxime).[8,9] It was partly on the basis of the tetragonality associated with the activated complex for ligand exchange in the cyclam complexes[6] that Tobe proposed[4] correlation between $\Delta S^{\ddagger}$ and the geometry of the dissociative activated complex.

In the present study we report our studies of the substitution chemistry of two series of cobalt(III) complexes containing macrocyclic ligands: Co(*trans*-[14]diene)X_2^+[10,11] and Co(teta or tet*b*)X_2^+.[12,13] (See Figure 1.) On the basis of the preparative chemistry[13,14] and the results of our studies[15] of the acid hydrolysis of bidentate carbonate in Co(*trans*[14]-diene)CO_3^+ and Co(tet*b*)CO_3^+, it is clear that both the saturated and unsaturated macroring systems have a very strong tendency to have their coordinating nitrogen atoms nearly planar. The tendency toward tetragonality may even be greater in these systems than in the analogous cyclam complexes. For example, although *cis*-Co^{III}(cyclam)X_2[6a,16] and *cis*-Co(tet*b*)-$(OH_2)_2^{3+}$[13,15] complexes are easily prepared and isomerize to the *trans* complexes only slowly,[6a,15,16] attempts to prepare *cis*-Co^{III}(teta)X_2 complexes have failed even when chelating ligands (X_2) were used.[13] Furthermore, the pair of geminal methyl groups in Curtis ligand systems crowds the fifth and sixth coordination positions[11,17] (see Figure 2) and should enhance the likelihood of a dissociative activated complex. Kinetic parameters for these systems should therefore provide a useful test of Tobe's correlation.[4]



TRANS[14]DIENE TETA OR TETB

Figure 1. Macrocyclic ligands.

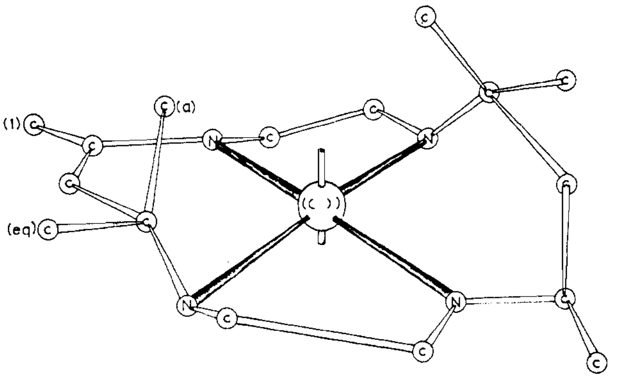


Figure 2.—Stereochemistry of the N-*dl-trans*[14]diene complexes. Based on ref 17a.

A somewhat more general interest in the substitution chemistry of Co(*trans*[14]diene)X_2^+ and Co(teta or tet*b*)X_2^+ complexes arises because there are two Co^{III}–N(imine) bonds in the former and none in the latter. Many of the unusual features of the chemistry of vitamin B_{12} and the porphyrin and dimethylglyoximate complexes of cobalt(III) have been attributed to the presence of Co^{III}–N(imine) groups.[7–9,18–20] A frequently occurring feature of the discussion of the chemistry of such complexes is the contention that electronic interaction between the cobalt center and the highly unsaturated ligand systems is sufficiently extensive to render the cobalt(III) oxidation state formalism inappropriate.[7,20] It is not altogether clear whether such interactions are to be regarded as a feature of the ground-state behavior of such complexes, the stabilization of a reactive intermediate, or the stabilization of the activated complex for ligand exchange. In any case systematic changes in some features of the substitution chemistry of cobalt(III) complexes would be anticipated with successively more unsaturated ligands. In this connection, we[15] have recently suggested that the extraordinarily rapid *cis* → *trans* isomerization of Co(*trans*[14]diene)$(OH_2)_2^{3+}$ may be due to a relatively long-lived[21] five-coordinate intermediate. A relatively long-lived five-coordinate inter-

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[4] M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).

[5] R. G. Linck, *ibid.*, **8**, 1016 (1969).

[6] (a) C. K. Poon and M. L. Tobe, *J. Chem. Soc.*, *A*, 1549 (1968); (b) *ibid.*, *A*, 2069 (1967).

[7] E. B. Fleischer, J. Jacobs, and L. Mestichelli, *J. Am. Chem. Soc.*, **90**, 2528 (1968).

[8] D. N. Hague and J. Halpern, *Inorg. Chem.*, **6**, 2059 (1967).

[9] H. G. Tsiang and W. K. Wilmarth, *ibid.*, **7**, 2535 (1968).

[10] *trans*[14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.[11]

[11] N. F. Curtis, *Coord. Chem. Rev.*, **3**, 3 (1968).

[12] teta = C-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.[13] The C-*dl* isomer is designated tet*b*.[13]

[13] (a) P. O. Whimp and N. F. Curtis, *J. Chem. Soc.*, *A*, 867 (1966); (b) *ibid.*, *A*, 1827 (1967).

[14] N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, **6**, 770 (1967).

[15] J. A. Kernohan and J. F. Endicott, *J. Am. Chem. Soc.*, **91**, 6977 (1969).

[16] C. K. Poon and M. L. Tobe, *Inorg. Chem.*, **7**, 2398 (1968).

[17] (a) M. F. Bailey and I. E. Maxwell, *Chem. Commun.*, 908 (1966); (b) R. R. Ryan, B. T. Kilbourn, and J. D. Dunitz, *ibid.*, 910 (1966); (c) B. T. Kilbourn, R. R. Ryan, and J. D. Dunitz, *J. Chem. Soc.*, 2407 (1969).

[18] E. Bennett, *Chem. Rev.*, **63**, 573 (1963).

[19] (a) G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968); (b) G. N. Schrauzer and R. J. Windgassen, *J. Am. Chem. Soc.*, **88**, 3738 (1966);

[20] (a) H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Chem. Brit.*, **5**, 156 (1969); (b) R. A. Firth, H. A. O. Hill, J. M. Pratt, R. J. P. Williams, and W. R. Jackson, *Biochemistry*, **6**, 2178 (1967); (c) L. Vallee and R. J. P. Williams, *Proc. Natl. Acad. Sci. U. S.*, **59**, 498 (1968).

[21] We will arbitrarily consider a species long lived if its lifetime is greater than about 10^{-10} sec, *i.e.*, species whose lifetimes are longer than or equal to diffusion-controlled lifetimes of solvent cage trapped species.[3b]

mediate should result in some unusual features in the substitution chemistry of Co(*trans*[14]diene)X_2^+ complexes which seem compatible with this model.

Experimental Section

Preparation of Complexes.—The preparation and characterization of Co^{III}(*trans*[14]diene)X_2 complexes are described in detail elsewhere.[14,22,23] Owing to the relatively high lability of these complexes, the aqueous solution spectra reported previously[14] are in error. The correct absorption spectra of the complexes employed in this study are summarized in Table I. These spectra are in good agreement with those reported by Curtis.[11,24,26]

TABLE I

ABSORPTION SPECTRA OF *trans*-$Co^{III}LX_2$ COMPLEXES (25° IN METHANOL EXCEPT AS INDICATED)

X	Metal ion bands, $cm^{-1} \times 10^{-3}$ [a] IA	IB	II	Uv bands λ_{max}, $cm^{-1} \times 10^{-3}$ [a]
		L = *trans*[14]diene		
OH_2[b]	17.3 (23.5)	24.2 sh	Masked	43.61 (1.49×10^4)
OH^- [b]	19.2 (40)[d]		26.6 (52)	*e*
Cl^- [f]	16.0 (46.0)	22.4 sh	Masked	36.6 (1.46×10^4)[c] 43.0 (1.57×10^4)
Cl^- [g]	16.0 (46.3)	22.4 sh	Masked	36.6 (1.5×10^4)[c] 43.6 (1.5×10^4)
Br^-	15.0 (64.5)	23.0 sh	31.6 sh	36.4 (1.9×10^4)[c]
NCS^-	18.7 (472)[c]		Masked	*e*
		L = teta		
OH_2[b,h]	17.7 (33.8)	21.4 (61.8)	Masked	38.9 (4.0×10^3)
OH_2[b,i]	17.3 (23.5)	24.2 sh	Masked	39.7 ($\sim 4 \times 10^3$)
	19.9 (47.5)[d]		25.1 (71.8)	40 sh
Cl^-	15.6 (31.4)[c]	20.8 (35.2)	24.6 sh	38.9 (1.38×10^4)
Br^- [h]	14.65 (44.7)	20.0 sh	Masked	33.2 (1.81×10^4)[c]
Br^- [j]	14.55 (44.8)	20.0 sh	Masked	33.8 (1.5×10^4)[c]
NCS^-	18.1 (293)[c]		Masked	*e*
		L = tetb		
OH_2	17.0 (35)	20.0 sh	31.2 sh	41.5 (4×10^3)
Cl^-	15.6 (34)[c]	20.7 (36)	24.4 sh	39.0 (1.4×10^4)

[a] Molar absorptivity in parentheses; sh = shoulder. All Co(III) complexes have intense ($\epsilon > 10^4$) far-uv absorbancies ($\lambda_{max} > 50 \times 10^{-3}$ cm^{-1}). [b] In H_2O. [c] Wavelength used in kinetic determinations. [d] Maximum of the broad asymmetric band. This band has a shoulder at $\sim 17 \times 10^{-3}$ cm^{-1}. [e] Not determined. [f] Isomer *a* (C-*meso*). [g] Isomer *b* (C-*dl*). [h] For the predominant (and probably most stable) isomer. [i] For the isomer designated teta'. [j] For the isomer designated teta''.

The Co(teta)X_2^+ complexes were prepared from [Co(teta)$(OH_2)_2$]$(ClO_4)_3$.[13a,14] Aqueous solutions of the diaquo complex were passed through a column of Dowex 1-X8 (50–100 mesh) anion-exchange resin (chloride form). The chloride solution washed from the resin was treated with concentrated HCl or HBr to obtain [Co(teta)Cl_2]Cl and [Co(teta)Br_2]Br, respectively. To obtain [Co(teta)$(SCN)_2$]SCN, the solution recovered from the resin was treated with an excess of NaSCN. We were unable to use the [Co(teta)X_2]ClO_4 salts in this study owing to their lack of noticeable solubility in water. The [Co(teta)X_2]X salts were recrystallized slowly from aqueous solutions containing an excess of the anion X'.

The preparation of the perchlorate salts of the Co(tetb)X_2^+ complexes is described in the literature.[13b] In many of our kinetic studies we have used [Co(tetb)Cl_2]Cl and [Co(tetb)Br_2]Br and we have found that these salts are most easily purified in the absence of perchlorate. Therefore we have prepared them by adding an excess of HX to the solutions which result from passing [Co(tetb)Cl_2]ClO_4 (prepared by adding HCl to [Co(tetb)CO_3]ClO_4[13b]) dissolved in 0.1 *M* NaOH over an anion-exchange resin as described above.

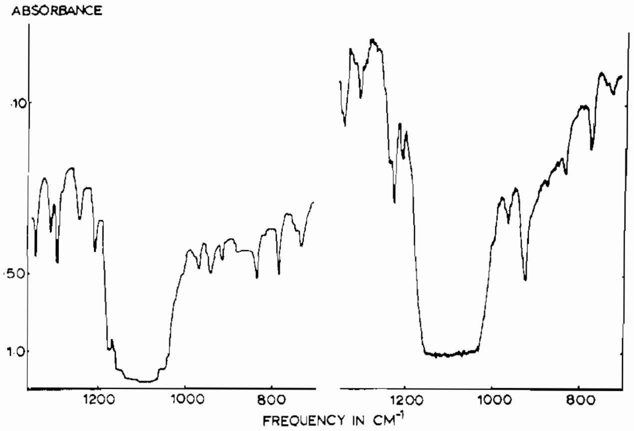

Figure 3.—Comparison of the fingerprint region in the infrared spectra of (a) [*trans*-Co(teta)$(OH_2)_2$]$(ClO_4)_3$ and (b) [*trans*-Co(teta')$(OH_2)_2$]$(ClO_4)_3$ (Nujol mulls).

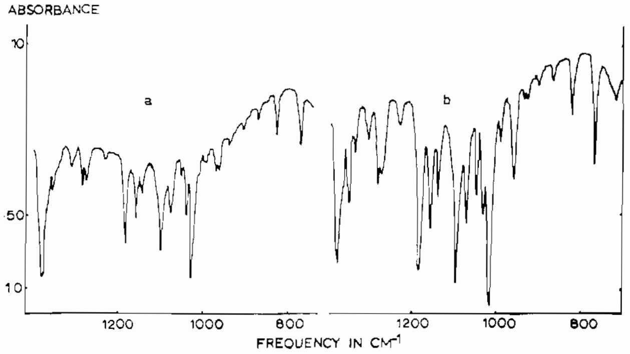

Figure 4.—Comparison of the fingerprint region in the infrared spectra of (a) [*trans*-Co(teta)Br_2]Br and (b) [*trans*-Co-teta'')Br_2]Br (Nujol mulls).

During the slow crystallization of [Co(teta)Br_2]Br two crystal fractions appeared which exhibited different physical properties. The first fraction consisted of yellow-brown, square, platelike crystals which formed about 10% of the total yield. After these were removed, the larger, second fraction could be isolated after about 48 hr. The first fraction (*i.e.*, the minor constituent) is designated [Co(teta'')Br_2]Br. These forms are interconvertible in that addition of concentrated HBr to a solution of [Co(teta'')Br_2]Br dissolved in 0.1 *M* NaOH resulted only in the formation of [Co(teta)Br_2]Br. For this reason we conclude that Co(teta)Br_2^+ and Co(teta'')Br_2^+ are isomeric, differing only in the configuration of atoms around the secondary amine nitrogen atoms. An analogous pair of isomers of [Co(teta)$(OH_2)_2$]$(ClO_4)_3$ can be isolated from the previously described[14] preparation of this complex. A small fraction of [Co(teta')$(OH_2)_2$]$(ClO_4)_3$ appeared about 1 week after the initial product fraction had been removed. The isomer pairs in both cases showed significant differences in their ultraviolet, infrared, and ^1H nmr spectra (see Tables I and II and Figures 3 and 4).

Procedure for Kinetic Runs.—Absorbance changes were followed using a 5-cm glass-jacketed (through which thermostated water was pumped) cell and a Cary Model 14 recording spectrophotometer. Reactions were followed at the near-uv maxima except for the cases of Co(teta)Cl_3, Co(teta)$(NCS)_3$, and [Co(*trans*[14]diene)$(NCS)_2$]ClO_4, which were followed at their visible maxima (see Table I).

Most of the complex salts used dissolved relatively slowly in water. In order to facilitate the mixing of solutions for kinetic runs, the complexes were dissolved in reagent grade methanol.

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[22] N. Sadasivan and J. F. Endicott, *J. Am. Chem. Soc.*, **88**, 5468 (1966).

[23] J. A. Kernohan, Dissertation, Boston University, 1969.

[24] Some of these spectra, particularly for the cyclic tetramine complexes, exhibit a significant solvent dependence.[25] This point will be developed in greater detail elsewhere.[25]

[25] R. E. Ball, J. A. Kernohan, and J. F. Endicott, in preparation.

TABLE II

COMPARISON OF IR AND NMR SPECTRA OF *trans*-$Co^{III}(teta)X_2$ ISOMER PAIRS

Prominent ir bands[a]			Chem shifts,[b] ppm, ^1H nmr methyl bands		
ν_{OH}	ν_{NH}	δ_{OH_2}	eq	a	i
		trans-$Co(teta)(OH_2)_2^{3+}$			
3.59 s, b	3.24 s	1.63 m, b	1.06	1.53	1.59, 1.69
		trans-$Co(teta')(OH_2)_2^{3+}$			
3.49 s, b	3.21 s	1.65 m, b	1.06	1.55 (u)	1.45, 1.55 (u)
		trans-$Co(teta)Br_2^+$			
. . .	3.19 s, sp		1.11[d]	1.33 (u)[d]	1.33 (u),[d] 1.42
		trans-$Co(teta'')Br_2^+$			
3.60 m[c]	3.39 m 3.27 m 3.21 m, sp 3.18 m, sp	1.61 m, b[c]	0.89[d]	1.04 (u)[d]	1.04 (u), 1.15[d]

[a] Determined in hexachlorobutadiene or Nujol mulls. Values in $cm^{-1} \times 10^{-3}$. Abbreviations: s, strong; m, medium; sp, sharp; b, broad. [b] With respect to external TMS—no corrections applied. The geminal methyl groups are designated eq ("equatorial" geminal methyl; assigned as the high-field singlet), a ("axial" geminal methyl; assigned as the low-field singlet), and i (assigned as the doublet). Spectra determined in D_2O except as indicated. Bands which were superimposed are listed with a common chemical shift and designated "u" (unresolved). [c] Crystals of [*trans*-$Co(teta'')Br_2$]Br generally seemed to contain about 0.5 mol of water. [d] Determined in DMSO-d_6.

Aliquots of the methanolic solutions were mixed in the spectrophotometric cell with an aqueous solution of $HClO_4$ and $NaClO_4$, ionic strength 0.11, at the reaction temperature. The aqueous solution was injected into the cell through a syringe fitted with a Teflon needle. Concentrations of complex and acid were such that on dilution in the cell, the absorbance was between 1.0 and 2.0, the ionic strength was 0.1 *M*, and the solutions were generally about 10% in methanol (except for Co(teta)Cl_3 and Co(tet*b*)Cl_3 in which $[CH_3OH] = 20\%$). The rate constants obtained in solutions of varying methanol concentrations up to 25% were the same within experimental error (±5%). Temperature control was within ±0.1°.

Kinetic runs were carried out at five temperatures over a range of 20°. Enthalpies and entropies of activation were calculated from the rate constants using the Eyring equation.[26]

Rates of base hydrolysis were determined spectrophotometrically by observing the appearance of the hydroxochloro species near their energy maxima in the visible spectrum. These are 5500 Å for Co(teta)$OHCl^+$ and 5250 Å for Co(*trans*[14]diene)-$OHCl^+$. Reactions were carried out under pseudo-first-order conditions by mixing in a 5-cm water-jacketed spectrophotometric cell a small amount of complex dissolved in methanol with a buffer solution at the reaction temperature of 19.8°. The ionic strength was 0.2. The buffers used were mixtures of 0.1 *M* HNO_3 and 2,6-lutidine. The reactions were too fast to measure by this technique when $[OH^-]$ exceeded the complex (2.6×10^{-3} *M*) but were conveniently slow in buffered solutions up to pH 7.2.

Treatment of Kinetic Data.—First-order rate constants were determined for all complexes, except Co(teta)Cl_2^+ and Co(tet*b*)-Cl_2^+, from the slope of plots of log $(A_t - A_\infty)$ *vs.* time (where A_t is the measured absorbance at time *t*). Under the conditions of our experiments (especially since it was necessary to use the chloride salts) the aquations of Co(teta)Cl_2^+ and Co(tet*b*)Cl_2^+ were complicated by the reverse reactions. For these two systems, observed absorbances were converted to concentrations and the differential rate equations appropriate to the reversible equilibrium (1) were integrated to give (2).[27,28] Values of k_1/K

$$CoLCl_2^+ + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoLOH_2Cl^{2+} + Cl^- \qquad (1)$$

$$\frac{1}{2\sqrt{\frac{K+A_0^2}{2} + KA_0}} \ln \left\{ \frac{\sqrt{\frac{K+A_0^2}{2} + KA_0} - \frac{K+A_0}{2} - X}{\sqrt{\frac{K+A_0^2}{2} + KA_0} + \frac{K+A_0}{2} + X} \right\} = \frac{k_1 t}{K} \qquad (2)$$

were obtained from the slopes of the left-hand function in (2) *vs. t*. An example of such a plot is shown in Figure 5. Values of the equilibrium constant *K* were determined independently from the equilibrium studies described below.

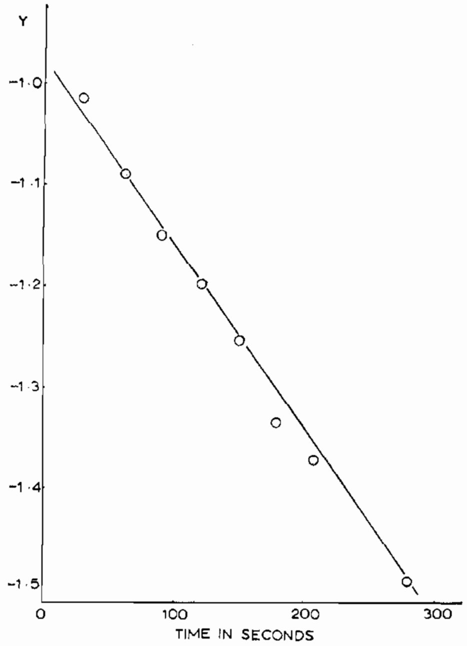

Figure 5.—Plot of

$$\gamma = \log \left\{ \frac{\sqrt{\frac{K+A_0^2}{2} + KA_0} - \frac{K+A_0}{2} - X}{\sqrt{\frac{K+A_0^2}{2} + KA_0} + \frac{K+A_0}{2} + X} \right\}$$

vs. time. Parameters used in the calculation of γ are $X = A_0 - A_t$ and $K = 2.7 \times 10^{-3}\ M^{-1}$. $[Co(III)]_{t=0} = 7.2 \times 10^{-3}\ M$ at 35.6° in 0.10 *M* HNO_3.

Procedures for the Equilibrium Studies.—Acid dissociation constants were determined (at room temperature) from the midpoints of the buffer regions determined in the titration of acidic solutions of the $CoL(OH_2)_2^{3+}$ complexes with standard NaOH. The pH values of solutions were determined using an Instrumentation Laboratories Model 145 pH meter.

Complex equilibria are discussed below in terms of the stability constants K_2 and K_3. The Co(teta)Cl_2^+ and Co(tet*b*)Cl_2^+ complexes were sufficiently inert that it was possible to separate the complex cations from the equilibrium mixture using Dowex 50W-X4 cation-exchange resin (acid form). The $[Cl^-]$ in the resulting solution was determined using Volhard's method.[29] Equilib-

$$\left.\begin{array}{ll} CoL(OH_2)_2^{3+} + X^- \rightleftharpoons CoLOH_2X^{2+} + H_2O & (K_2) \\ CoLOH_2X^{2+} + X^- \rightleftharpoons CoLX_2^+ + H_2O & (K_3) \end{array}\right\} \quad (3)$$

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[26] S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

[27] For $A_0 = [CoLCl_2^+]$ at $t = 0$ and $X = [CoLCl_2^+]$ at time *t*; $K = k_1/k_{-1}$. Note that in most of our studies the initial conditions are $[CoLCl_2^+]_{t=0} = [Cl^-]_{t=0}$.

[28] Hütte, "Mathematische Formeln and Tafeln," I. Szabo, Ed., Wilhelm Ernst and Sohn, Berlin, 1959, p 107.

[29] A. I. Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1961, p 265.

rium constants determined this way were in good agreement (within 10%) with values determined using the spectroscopic technique described below.

For the more labile complexes separation of the complex cations could not be accomplished without changing the distribution of species in solution. Therefore we have determined the values of K_1 and K_2 for these complexes by deducing the distribution of complex ions from the visible absorption spectra of equilibrated solutions. Although the visible energy absorption bands of *trans*-$Co^{III}LX_2$ complexes are not very intense, the positions of the band maxima are easily interpretable[30] and there are generally large predictable differences among $CoLX_2^+$, $CoLOH_2X^{2+}$, and $CoL(OH_2)_2^{3+}$. The association constants K_2 and K_3 were determined by dissolving either the dihalo or diaquo complexes in 0.1 *M* perchloric or nitric acid (containing 10% methanol) and determining the visible spectrum at various halide concentrations (from 10^{-3} to 0.1 *M*). Since the extinction coefficients of the aquohalo species are unknown, estimates were obtained for the association constants from the position of the visible maxima, and hence an estimate of the extinction coefficient at the expected maximum of the aquohalo complex was obtained.[31] Using this initial estimate of ϵ_{max} an approximate value of K_3 (or sometimes K_2) was obtained. This approximate value of K_3 was then used to calculate an estimated distribution of $CoLX_2^+$ and $CoLOH_2X^{2+}$ species; from this estimated distribution of complexes a new estimate of the molar absorptivity of the $CoLOH_2X^{2+}$ species was obtained. This iterative technique was cycled three times or until successive estimates of ϵ and K_3 agreed to within 5%. From a series of at least three determinations in differing halide concentrations values of association constants were generally found which differed by ±5%. An exception is the case of Co(tet*a*)Br_2^+ where the preparations of the bromide salt appear to have contained varying amounts of HBr. The value of the stability constant for this complex therefore should be regarded as relatively uncertain.

Values of K_2 were determined at five different temperatures over a temperature range of 20°. The temperature variation of K_2 for Co(tet*a*)$(OH_2)_2^{3+}$ with chloride was determined from the extent of reaction (as described above) at each different temperature.

Results

A. Kinetic Studies.—Our kinetic studies of the acid and base hydrolyses of macrocyclic complexes are summarized in Tables III and IV, respectively. We have previously reported the separation and characterization of two isomers of *trans*-Co(*trans*[14]-diene)Cl_2^+.[14] It has since been shown that the isomer which we identified as "isomer *a*" is the stable isomer.[25] On this basis and by comparison with the analogous Ni(*trans*[14]diene)$^{2+}$ and Cu(*trans*[14]diene)$^{2+}$ complexes[11] we have identified the most stable isomer with the most symmetrical complex (*i.e.*, "isomer *a*" is probably N-*meso*-*trans*[14]diene). Hydrolysis rates are quoted in Tables III and IV for this complex. We have also measured the rate of the first step of acid hydrolysis of *trans*-Co(N-*dl*-*trans*[14]diene)Cl_2^+.[32] The rate of hydrolysis for the latter complex (25°, 0.1 *M* $HClO_4$) is 2.3 × 10^{-2} sec^{-1}. So far we have not prepared both of the isomers for the other *trans*-Co(*trans*[14]diene)X_2^+ complexes.

TABLE III

RATE CONSTANTS FOR THE ACID HYDROLYSES OF *trans*-$CoLX_2^+$ COMPLEXES[a]

X	Temp, °C	[H⁺], *M*	10^2k,[b] sec^{-1}
		L = *trans*[14]diene[c]	
Cl	28.4 ± 0.2	0.1	4.28 ± 0.11 (3)
	25.0 ± 0.2	0.0014	3.25 ± 0.14 (3)
		0.01	3.81 ± 0.08 (3)
		0.05	3.19 ± 0.03 (3)
		0.1	3.73 ± 0.15 (7)
		0.1[d]	3.50 ± 0.02 (2)
		Av at 25°	3.56 ± 0.19 (16)
	24.6 ± 0.2	0.1	2.47 ± 0.16 (7)[e]
	20.3 ± 0.2	0.1	1.58 ± 0.04 (4)
	14.4 ± 0.2	0.1	0.56 ± 0.02 (4)
	10.4 ± 0.2	0.1	0.45 ± 0.08 (3)
Br	27.8 ± 0.2	0.1	4.7 ± 0.2 (4)
	24.6 ± 0.2	0.1	5.1 ± 0.2 (3)
	23.7 ± 0.2	0.1	3.47 ± 0.04 (5)
	19.2 ± 0.2	0.1	1.48 ± 0.06 (4)
	15.3 ± 0.2	0.1	0.90 ± 0.03 (3)
	9.8 ± 0.2	0.1	0.42 ± 0.02 (3)
SCN	24.8 ± 0.2	0.1[d]	17.5 ± 0.8 (4)
		L = tet*a*	
Cl	45.1 ± 0.2	0.1[d]	0.385 ± 0.007 (3)
	40.4 ± 0.2	0.1[d]	0.265 ± 0.002 (2)
	35.6 ± 0.2	0.1[d]	0.089 ± 0.006 (2)
	29.5 ± 0.2	0.1[d]	0.062 ± 0.002 (2)
	25.0 ± 0.2	0.1[d]	0.024 ± 0.002 (2)
Br	29.9 ± 0.2	0.1	4.4 ± 0.1 (3)
	24.7 ± 0.2	0.1	3.3 ± 0.3 (5)
	20.6 ± 0.2	0.1	1.9 ± 0.1 (3)
	15.4 ± 0.2	0.1	0.83 ± 0.04 (4)
	9.8 ± 0.2	0.1	0.25 ± 0.01 (2)
SCN	8.6 ± 0.2	0.1[d]	25 ± 5 (2)
	9.8 ± 0.2	0.1[d]	41 ± 3 (2)
		L = tet*a''*	
Br	25.0 ± 0.2	0.1	3.74 ± 0.07 (3)
		L = tet*b*	
Cl	25.0 ± 0.2	0.1[d]	0.021 ± 0.002 (2)

[a] All kinetic studies were performed in solutions of ionic strength 0.1 ($NaClO_4$–$HClO_4$) except as indicated. [b] Error limits are average deviations. Number of determinations in parentheses. [c] Isomer *a*. [d] In 0.1 *M* HNO_3. [e] In 50% methanol.

TABLE IV

BASE HYDROLYSIS OF $CoLCl_2^+$ COMPLEXES IN 2,6-LUTIDINE–HNO_3 BUFFERS

Co(*trans*[14]diene)Cl_2^+		Co(tet*a*)Cl_2^+	
pH	10^2k,[a] sec^{-1}	pH	10^2k,[a] sec^{-1}
6.79	2.85 ± 0.02 (2)	6.80	3.64 ± 0.01 (2)
6.50	2.17 ± 0.01 (2)	5.91	0.44 ± 0.01 (2)
5.98	1.77 ± 0.01 (2)	5.65	0.078

[a] At 19.8° and ionic strength 0.25. Number of determinations in parentheses. Error limits are average deviations.

B. Equilibrium Studies.—Acid dissociation constants determined for the macrocyclic complexes in this study are compared to the corresponding constants for several *trans*-diaquocobalt(III) complexes in Table V. Stability constants K_2 and K_3 determined for the various $CoLH_2X^{2+}$ and $CoLX_2^+$ complexes are reported in Table VI.

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[30] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

[31] Note that the energies and intensities at the long-wavelength absorption maxima of the $Co^{III}LX_2$ (L = *trans*[14]diene, tet*a*, tet*b*, cyclam, $(en)_2$, $(NH_3)_4$, etc.) complexes are very similar.

[32] That is, "isomer *b*."

TABLE V

ACID DISSOCIATION CONSTANTS OF SOME *trans*-DIAQUO TETRAMINE COMPLEXES OF COBALT(III) (25°, VARIABLE IONIC STRENGTH)

Complex	Ref	pK_1	pK_2
Co(*trans*[14]diene)$(OH_2)_2^{3+}$	*a*	4.02 ± 0.01	8.2 ± 0.1
Co(teta)$(OH_2)_2^{3+}$	*a*	2.7 ± 0.05	6.4 ± 0.05
Co(teta')$(OH_2)_2^{3+}$	*a*	2.9 ± 0.05	6.6 ± 0.05
Co(cyclam)$(OH_2)_2^{3+}$	*b*	2.9 ± 0.1	7.2 ± 0.1
Co(trien)$(OH_2)_2^{3+}$	*c*	5.4	7.3
Co(en)$_2(OH_2)_2^{3+}$	*d*	4.4	7.9

[a] This work. [b] Reference 6. [c] A. M. Sageson and G. H. Searle, *Inorg. Chem.*, **6,** 787 (1967). [d] J. Bjerrum and S. E. Rasmussen, *Acta Chem. Scand.*, **6,** 1265 (1952).

TABLE VI

STABILITY CONSTANTS FOR VARIOUS *trans*-$CoLX_2^+$ (K_3) AND *trans*-$CoLOH_2X^{2+}$ (K_2) COMPLEXES

X	Temp, °C	10^2K_2,[a] M^{-1}	K_3,[a] M^{-1}
		L = *trans*[14]diene	
Cl	25[b]	25 ± 2 (3)	95 ± 5 (3)
Br	25[b]	8.0 ± 0.4 (3)	43 ± 2 (3)
NCS	25[b]	. . .	0.27 ± 0.03 (3)[d]
		L = teta	
Cl	25	13 ± 1 (3)	333 ± 25 (3)[d]
	30		312 ± 27 (2)[d]
	36		392 ± 25 (3)[d]
	40		372 ± 19 (4)[d]
	45		333 ± 28 (2)[d]
	49		339 ± 19 (2)[d]
Br	9.5		43 ± 15 (3)[c]
	16.4		23 ± 10 (3)[c]
	22		45 ± 16 (3)[c]
	25	1.8 ± 0.6 (3)[c]	
	27		29 ± 10 (3)[c]
NCS	25		0.25 ± 0.02 (3)[d]

[a] Mean value and average deviation. Number of determinations in parentheses. Determined in 0.10 *M* $HClO_4$ except as indicated. [b] There was no observable change in the visible spectrum of the equilibrium mixture when the temperature was varied from 20 to 45°. [c] Preparations of [Co(teta)Br_2]Br often contained some HBr. This resulted in considerable indeterminacy in [Br^-] in solutions dilute in added bromide. In solutions of high [Br^-] (up to 0.1 *M*) this error was negligible. The average deviations of values of K_2 and K_3 determined for solutions containing between 0 and 0.1 *M* added bromide were about one-third of the deviations listed. Listed deviations take account of the maximum indeterminacy in [Br^-] in the more dilute solutions. [d] Determined in 0.1 *M* HNO_3.

TABLE VII

RATE CONSTANTS FOR BASE HYDROLYSIS AT 25°

Complex	k_{OH^-}, M^{-1} sec^{-1}	k_{OH^-}/k_{H_2O}
trans-Co(teta)Cl_2^+	5.7 × 10^5	3.1 × 10^9 [a]
trans-Co(trans[14]diene)Cl_2^+	2.17 × 10^5	1.4 × 10^7 [a]
trans-Co(cyclam)Cl_2^+	6.70 × 10^4	6.0 × 10^{10} [b]
trans-Co(en)$_2Cl_2^+$	2.30 × 10^3	3.7 × 10^7 [c]
trans-Co(en)$_2Cl_2^+$	3.00 × 10^3	9.0 × 10^7 [c]
cis-Co(en)$_2Cl_2^+$	1.00 × 10^3	4.0 × 10^6 [c]
cis-Co(trien)Cl_2^+	2.00 × 10^5	1.3 × 10^9 [c]

[a] This work was done at 19.8°. Known E_a values for base hydrolysis all lie between 22.5 and 24.9 kcal/mol: S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962); 564 (1963). The same kind of range has been found for activation energies of the acid hydrolysis of the macrocyclic complexes. Thus the ratio k_{OH^-}/k_{H_2O} is unlikely to have been greatly affected by temperature. [b] Reference 6. Work done at 25°. [c] R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, **78,** 709 (1956). Work done at 25°.

Discussion

A. Base Hydrolysis.—It appears that the cyclic tetramine complexes are among the most sensitive to base hydrolysis of all cobalt(III) complexes (Table VII). This is consistent with the hypothesis that the SN1CB mechanism for base hydrolysis involves loss of a proton from an amine *cis* to the leaving group.[33]

As noted in Table V the hydroxyaquocobalt(III) complexes are exceptionally stable. If a similar high stability obtains for the corresponding chlorohydroxy complexes and in view of the apparently general correlation between the free energy of activation and the free energy of reaction, then similar mechanistic considerations should be important for both acid and base hydrolysis (or at least with respect to variations of k_{OH^-}/k_{H_2O}). Therefore the unique mechanistic problems of ligand exchange in cobalt(III) complexes with cyclic ligands are discussed in detail only for the acid hydrolysis. Many of the considerations below should also be applicable to base hydrolysis.

B. Acid Hydrolysis.—There are two striking features of the aquation kinetics of the *trans*-Co(*trans*-[14]diene)X_2^+ complexes: the complexes are relatively labile and the rates of aquation are not very sensitive to changing the ligand X. Several related systems are compared in Table VIII. The two orders of magnitude faster rate for *trans*-Co(teta)Cl_2^+ than for *trans*-Co(cyclam)Cl_2^+ may well arise from steric crowding due at the least to the geminal methyl groups in the former. The similarity in rates for complexes with the isomerically related ligands teta, teta'', and tetb

TABLE VIII

COMPARISON OF SPECIFIC RATE CONSTANTS FOR THE FIRST AQUATION (25°)

$$trans\text{-}CoLX_2^+ + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoLXOH_2^{2+} + X^-$$

L	X	$k_{-1} = K_3k_1$, M^{-1} sec^{-1}[a]	k_1, sec^{-1}	Ref
teta	Cl	0.087 ± 0.02	2.6 × 10^{-4}	*b*
	Br	1.2 ± 0.5	3.8 × 10^{-2}	*b*
	NCS	1.5 ± 0.8	6 ± 3[c]	*b*
teta''	Br		3.8 × 10^{-2}	*b*
tetb	Cl		2.1 × 10^{-4}	*b*
N-*meso*-*trans*[14]diene	Cl	3.4 ± 0.5	3.6 × 10^{-2}	*b*
	Br	2.2 ± 0.4	5.1 × 10^{-2}	*b*
	NCS	0.05 ± 0.02	0.18	*b*
N-*dl*-*trans*[14]diene	Cl		2.3 × 10^{-2}	*b*
cyclam	Cl		1.1 × 10^{-6}	*d*
	NCS		"Very fast"	*d*
(en)$_2$	Cl		3.5 × 10^{-5}	*e*
trans-(*SS*)-trien	Cl		7.5 × 10^{-4}	*f*

[a] Error limits estimated from errors in K_3 and k_1 (Tables VII and III). [b] This work. Estimated errors in values of k_1 are ≤10% (see Table III), except as noted. [c] Extrapolated from data in Table III assuming 25 kcal ≤ E_a ≤ 30 kcal. [d] Reference 6. [e] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Am. Chem. Soc.*, **75,** 3089 (1953). [f] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *ibid.*, **89,** 825 (1967).

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(33) F. R. Nordmeyer, *Inorg. Chem.*, **8,** 2780 (1969).

suggests that the differences in stereochemistry[34] in these systems are not large enough to change the magnitude of the interaction between ligand methyl groups and the fifth and sixth coordination positions. In the absence of specific structural information (but based on examination of molecular models) we would guess that the azomethyne groups of the *trans*[14]diene ligand would hold the six-membered chelate rings of this macroligand relatively flatter than the six-membered rings of the related tetramines; *i.e.*, steric interactions (in six-coordinate complexes) might be expected to be somewhat less for the former (see also discussion below). This argument is certainly consistent with the observed insensitivity of the aquation rates to the ligands X for the *trans*-Co(*trans*[14]diene)X_2^+ complexes (*e.g.*, see Figure 6) compared to the much larger variation of aquation rates of the Co(teta)X_2^+ complexes. Thus it seems unlikely that the relatively high lability of *trans*-Co(*trans*[14]diene)Cl_2^+ arises from anomalously large steric interactions in this complex. In fact, *trans*-Co(teta)Cl_2^+ is only about 3 times as stable as *trans*-Co(*trans*[14]diene)Cl_2^+ while the latter is about 10^2 times more labile than the former. These observations are certainly consistent with the hypothesis that the Co^{III}–N(imine) groups tend to labilize the complex; however, this comparison is not so straightforward for other systems suggesting that several factors may contribute significantly. In order to more critically assess the chemical manifestations of Co–N(imine) bonding, a detailed mechanistic analysis follows below.

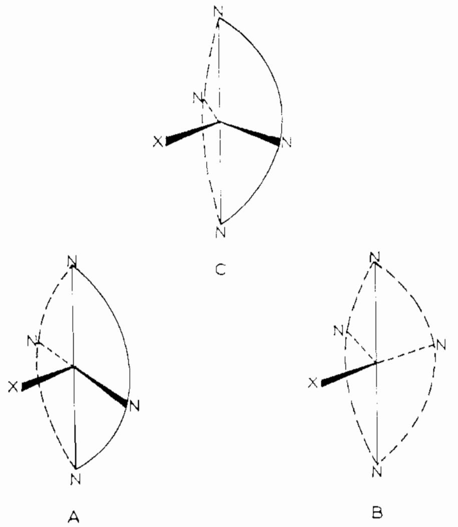

Figure 6.—Five-coordinate geometries. A is derived from *trans*-$CoLX_2^+$, B is derived from *cis*-$CoLX_2^+$, and C is the trigonal-bipyramidal intermediate.

1. Generality of the Relationship between Hydrolysis Rates and Equilibria.—For the complexes investigated in this study the rate of acid hydrolysis or more correctly values of $\Delta G^{\ddagger}$ seem to parallel variations in the standard free energies of reaction (Figure 7). However, no single free energy correlation of the type (4)

$$\Delta G^{\ddagger}{}_{C_i,X_k} = \alpha_{C_i,X_k}\Delta G^{\circ}{}_{C_i,X_k} + \beta_{C_i,X_k} \qquad (4)$$

(where α and β are empirical parameters and the subscripts C_i and X_k refer to the *i*th cationic residue and the *k*th anionic leaving group, respectively) can relate hydrolyses of all cobalt(III) complexes, even for complexes of the same charge type. Since the systems compared here differ in many ways this point must be considered with some care. The simple correlation proposed by Langford[35,36] for the special case of hydrolyses of cobalt(III) complexes in which the metal ion residue is the same (*i.e.*, $Co(NH_3)_5{}^{3+}$) is equivalent to the statement that $\alpha_{C,X_k} = \alpha_{C,X_l} = 1.0$ and $\beta_{C,X_k} = \beta_{C,X_l}$, for any *k* and *l*. The present information about the first hydrolysis of *trans*-$CoLCl_2^+$ complexes (in which case the leaving group is the same but the metal ion residue differs in each case) indicates that for the specific case of Cl^- the α parameters are relatively small[37] (*i.e.*, $\alpha_{C_i,X} \approx 0 \approx \alpha_{C_j,X}$) and that $\beta_{C_i,X} \neq \beta_{C_j,X}$, yet our observation that for hydrolysis of *trans*-$CoLX_2^+$ complexes a relation such as (4) is at least approximately true *provided* L is not varied suggests that in these systems $\alpha_{C_i,X_k} \simeq \alpha_{C_j,X_l}$ (constant L) and that the difference $(\beta_{C_i,X_k} - \beta_{C_j,X_l})$ depends only

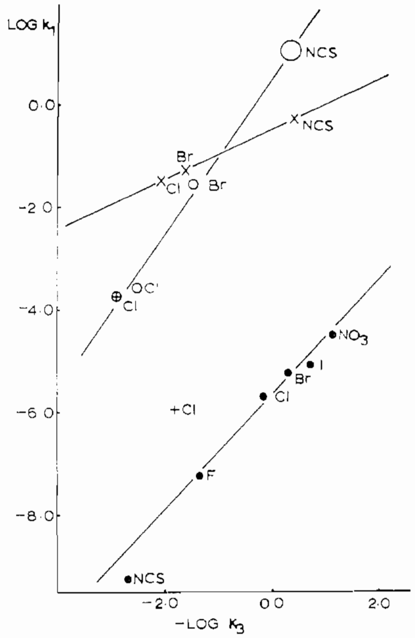

Figure 7.—Variations of hydrolysis rate with complex instability (after Langford[35]). The upper lines represent data from this study: ×, *trans*-Co(*trans*[14]diene)X_2^+; ○, *trans*-Co(teta)X_2^+; ⊕, *trans*-Co(tetb)Cl_2^+. Data for *trans*-Co(cyclam)Cl_2^+, +, and for $Co(NH_3)_5X^{2+}$, ●, are included for comparison. The leaving group, X, is indicated in the figure.

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[34] It should be recalled that the stereochemistry of the teta and tetb ligands is sufficiently different that *cis*-Co^{III}(tetb)X_2 complexes form easily if X_2 is a bidentate chelate while the analogous *cis*-Co^{III}(teta)X_2 complexes do not seem to form.

[35] C. H. Langford, *Inorg. Chem.*, **4**, 265 (1965).

[36] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965.

[37] Note that the values of the stability constants of *trans*-$CoLCl_2^+$ complexes vary over about a 20-fold range (Table IX) in the order Co(teta)Cl_2^+ > Co(*trans*[14]diene)Cl_2^+ > Co(cyclam)Cl_2^+, while the first hydrolysis specific rates vary over a range of 3 × 10^4 (Table VIII) in the order Co(*trans*[14]diene)Cl_2^+ > Co(teta)Cl_2^+ > Co(cyclam)Cl_2^+. Note that subscripts on C_i and X_k have been dropped when the species designated are identical.

on the ligand L. These several observations are consistent with (4) if $\beta_{\mathrm{C}_i,\mathrm{X}_k}$ depends largely on the ligands L (which are "*cis*" to the leaving group in all of the cases considered here) and if $\alpha_{\mathrm{C}_i,\mathrm{X}_k}$ is also a function of the cationic residue, varying with the ligands L. It is to be noted α has been shown to vary as the metal ion in the cationic residue is changed[38,39] so these conclusions are not too surprising. Furthermore, $\Delta H^{\neq}$ is generally much greater (by more than 20 kcal) than ΔH°, so values of α and β are either temperature dependent or $\alpha \simeq \Delta S^{\neq}/\Delta S^\circ$ and $\beta \simeq \Delta H$ (for a given family of complexes). An entropy correlation such as this has been found in other systems.[39]

It may be concluded then that the available information supports a linear free energy correlation such as (4) in the hydrolysis of metal complexes. However, both the parameters α and β appear to depend on the ligands in the cationic residue and there are striking differences in these parameters for the aquations of complexes of the *trans*-Co(teta)X_2^+ series and the *trans*-Co(*trans*[14]diene)X_2^+ series. It is a major concern of this study to gain insight into the reasons for such differences in behavior.

2. Intermediate Stereochemistry and $\Delta S^{\neq}$.—An interesting feature of Table IX is that $\Delta S^{\neq}$ for the acid hydrolysis of a *trans*-$\mathrm{CoLX_2}^+$ complex can be very positive even when L is a cyclic ligand. It is of particular interest that $\Delta S^{\neq}$ should be so positive for the studies reported here since steric considerations would predict enhancement of a dissociative mechanism for complexes containing the Curtis ligands and since there are no stereochemical changes associated with these reactions.[40]

TABLE IX

KINETIC AND THERMODYNAMIC PARAMETERS FOR *trans*-$\mathrm{CoLX_2}^+ + \mathrm{H_2O} \rightleftharpoons \mathrm{CoLOH_2X}^{2+} + \mathrm{X}^-$

L	X	10^4k,[a] sec^{-1}	$\Delta H^{\neq}$, kcal	$\Delta S^{\neq}$, eu	K_3,[a] M^{-1}	ΔH°, kcal
teta	Cl	2.65	27.4 ± 0.5	16.9	333	−0.8 ± 1
	Br	385	22 ± 1	7.7 ± 2	~30	~0[b]
trans[14]diene	Cl	362	23.2 ± 0.5	12.3 ± 1	95	0 ± 2[c]
	Br	510	23.5 ± 1	13.7 ± 2	43	0 ± 2[c]
cyclam	Cl	0.011	24.6	−3	59	
en	Cl	0.35	26.2	14		

[a] Values determined at 25°. [b] Indeterminacy of K_3 prohibits accurate estimate. [c] Estimate based on lack of temperature variations of the visible spectra of equilibrated solution. See Table VII.

In a recent study Alexander and Hamilton[41] have reported systems in which hydrolytic reactions accompanied by stereochemical change exhibit negative values of $\Delta S^{\neq}$. It must be concluded that the entropy correlation proposed by Tobe[4] has only limited validity.

A more careful consideration of mechanistic details taking account of the constraints imposed by the cyclic ligand systems leads us to conclude that net stereochemical changes observed in ligand substitution reactions are not necessarily useful criteria for the stereochemistry of any reaction intermediates. In the limit of a dissociative mechanism, generating a five-coordinate intermediate, there seem to be three reasonable intermediate geometries: two based on a square pyramid (A and B in Figure 6) and one based on a trigonal bipyramid.[42] These structures are drawn in Figure 6 to emphasize their similarity and the fact that C is intermediate between A and B. It has been pointed out that these five-coordinate geometries are so closely related that they may be interconverted by means of a normal vibrational mode[43] and their interconversion may be facile.[44] In the complexes containing the Curtis ligands much of the instability of the *cis* geometry appears to arise from steric repulsions between the ligand methyl groups when the macro rings are folded; a similar instability of B with respect to A is to be expected. Furthermore, there is no obvious reason that C cannot be more stable than B for these cyclic complexes since some of the ligand (X)–methyl and methyl–methyl steric repulsion could be relieved in such a geometry.

If one postulates a dissociative mechanism for ligand exchange in these macrocyclic complexes and if this mechanism is to be consistent with any stereochemical changes which accompany the exchange of ligands, then the portion of the reaction accompanied by stereochemical change must follow the sequence:[45] *trans*-$\mathrm{CoLX_2}^+ \rightarrow \mathrm{A} \rightarrow \mathrm{C} \rightarrow \mathrm{B} \rightarrow$ *cis*-$\mathrm{CoLXOH_2}^{2+}$. Even if the trigonal-bipyramidal geometry were the most stable for the complexes being considered here, no stereochemical change would be expected on ligand exchange due to the relative instability of B and of the *cis*-$\mathrm{CoLX_2}^+$ complexes.

The above considerations should have some general relevance to mechanistic arguments about simpler

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[38] Values of α less than 1.0 in such correlations have previously been found for Cr(III).

[39] T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, **7**, 1915 (1968).

[40] It is to be noted that *cis*-$\mathrm{Co^{III}}$(teta)$\mathrm{L_2}$ complexes do not form even when $\mathrm{L_2}$ is a particularly good chelating ligand (*e.g.*, $\mathrm{CO_3}^{2-}$, en, $\mathrm{C_2O_4}^{2-}$, etc.) while *cis*-$\mathrm{Co^{III}}$(tet*b*)$\mathrm{L_2}$ complexes form readily. This is a clear manifestation of a very large steric barrier to the folding of the coordinated teta ligand. It should further be observed that the hydrolysis rates are comparable in the *trans*-$\mathrm{Co^{III}}$(teta)$\mathrm{X_2}$ and *trans*-$\mathrm{Co^{III}}$(tet*b*)$\mathrm{X_2}$ complexes. Finally it should be recalled that while *cis*-Co(*trans*[14]diene)$(\mathrm{OH_2})_2^{3+}$ is known only as a very short-lived transient, *cis*-Co(tet*b*)$(\mathrm{OH_2})_2^{3+}$ is kinetically stable to isomerization.[15] Thus the referee's suggestion that the large positive values of $\Delta S^{\neq}$ which we observed imply the formation of *cis*-$\mathrm{CoLOH_2X}^{2+}$ complexes which isomerize rapidly to the final products is unnecessarily complicated and inconsistent with the known chemistry of the complexes and parameters in Tables VIII and IX (especially with the similar $\Delta H^{\neq}$ values).

[41] M. D. Alexander and H. G. Hamilton, Jr., *Inorg. Chem.*, **8**, 2131 (1969).

[42] The cyclic ligands used in this study each have two different kinds of nitrogen atoms and therefore structure B can be realized in two geometrically different isomers. It is not obvious that these isomers would necessarily differ in their stabilities nor that their existence would in any way affect the present discussion. Structure B should be subject to steric constraints similar to those of the corresponding *cis* complexes and there are probably significant differences in stability for different conformations around the nitrogen atoms.[11] At this point these differences in energy are not completely obvious and the following discussion is not dependent upon such differences since the most stable *cis* isomers appear to be much less stable than any of the *trans* isomers. It does appear that there is only one trigonal bipyramid (apart from the diastereoisomers arising due to the asymmetric nitrogen atoms). The cyclic ligands cannot have a single chelate ring lying in the trigonal plane. The trigonal geometry with two of the chelate rings in the trigonal plane is highly strained. The trigonal angle of 120° seems to stress a five-membered chelate ring even without the additional constraints of cyclic ligands or the problems of packing in six methyl groups.

[43] R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1970).

[44] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

[45] This assumes that the mechanism for ligand exchange proceeds through the same sequence of intermediates for *cis*-$\mathrm{CoLXOH_2X}^{2+} + \mathrm{X}^- \rightarrow$ *trans*-$\mathrm{CoLX_2}^+ + \mathrm{OH_2}$ as for its reverse.

systems. Values of $\Delta S^{\ddagger}$ may be useful in comparisons of very closely related families of complexes, as in the limited comparisons of Niththyananthan and Tobe,[46] and the relatively positive values of $\Delta S^{\ddagger}$ found in the present study may imply a relaxation of steric constraints in a dissociative activated complex for these cyclic ligand systems, with the overall energetics of the substitution reactions dictating the stereochemistry of the product. The correlation of the rate of hydrolysis with the free energy of reaction (see above discussion) for cobalt(III) complexes tends to support the hypothesis that the amount of stereochemical change should be strongly correlated to the relative stabilities of *cis* and *trans* products.[47] Unfortunately the available information is not sufficient to determine whether stereochemical changes accompany ligand exchange only in systems where such change is thermodynamically favorable.

3. Possible Effects of Intermediate Lifetimes.— In order to account for the very rapid isomerization of *cis*-Co(*trans*[14]diene)$(OH_2)_2^{3+}$ we have previously postulated that the Co^{III}–N(imine) groups help increase the lifetime of a five-coordinate intermediate species.[15] There have been several qualitative discussions of the expected effects of intermediate lifetimes.[3c,46,48,49] As noted above there are several possible five-coordinate intermediates in a limiting dissociative mechanism. These might be expected to vary in their lifetimes as well as in their relative stabilities. Furthermore, the observations (1) that with some highly unsaturated ligand systems five-coordinate complexes of cobalt(III) appear to exist in equilibrium with six-coordinate complexes,[20] (2) that scavanging efficiencies and the per cent of stereochemical change vary for different induced and spontaneous aquations,[3] and (3) that limiting dissociative intermediates are implied by the ligand-exchange reactions in many systems[3,7–9,48,49] have led us to examine whether some of the usual patterns of substitution reactions which have been observed in this study might arise from the generation of intermediates with different lifetimes. A five-coordinate species with long enough lifetime for the displaced ligand X to diffuse into the bulk solvent should have kinetic characteristics different from shorter lived species for which X remains in the second coordination sphere. Treatment of a model involving more than one intermediate is too complex for this discussion. However, the model discussed below does exhibit several features which are instructive and should also be characteristic of more complex models.

Consider the case of a purely dissociative mechanism for a complex $CoLX_2^+$, with the formation of first an intermediate $CoLX^{2+},X^-$ with X^- in the second coordination sphere, followed by the loss of X^- to the bulk solvent leaving the five-coordinate intermediate $CoLX^{2+}$ which finally reacts with solvent to form the product $CoLXOH_2^{2+}$ (eq 5–7). Furthermore

$$CoLX_2^+ \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} CoLX^{2+},X^- \tag{5}$$

$$CoLX^{2+},X^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} CoLX^{2+} + X^- \tag{6}$$

$$CoLX^{2+} + H_2O \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} CoLXOH_2^{2+} \tag{7}$$

if we assume that the concentration conditions are such that reverse of (6) is negligible, then these reactions can be treated as consecutive first-order reactions.[50] For $k_5 \ll k_{-5}$, k_6 the characteristic set of rate constants for these reactions is $\lambda_1 = k_{-6} + k_7$, $\lambda_2 \simeq k_{-5} + k_6$, and $\lambda_3 \simeq k_5k_6/(k_{-5} + k_6)$. Since λ_3 is the smallest of these, this will correspond to the measured "hydrolysis" rate constant. The limiting cases are then $\lambda_3 \simeq k_5k_6/k_{-5} = K_5k_6$ for relatively short-lived species ($k_6 \ll k_{-5}$) and $\lambda_3' \simeq k_5$ for relatively long-lived intermediates ($k_6 \gg k_{-5}$). For the *trans*-$CoLX_2^+$ complexes which are the subject of this study,[51] it is to be expected that reactions 5 and 7 depend on X^-. Thus any relationship between λ_3 and K_{eq} is expected to depend on X^- differently for long-lived than for short-lived intermediates. Both λ_3 and K_3 are expected to be more dependent on X^- for short-lived five-coordinate intermediates than for very long-lived intermediates. This would be consistent with our observations and the hypothesis that lifetimes of the Co(teta)X^{2+} species are generally much shorter than the lifetimes of Co(*trans*[14]diene)X^{2+} species.

Finally our observation that the hydrolysis of *trans*-Co(*trans*[14]diene)Cl_2^+ is much more rapid than the hydrolysis of *trans*-Co(tet*a*)Cl_2^+ is consistent with a relatively shorter lived intermediate in the latter reaction since this simplified model predicts that λ_3 (with $k_6 \ll k_{-5}$) should generally be less than λ_3' (with $k_6 \gg k_{-5}$), other factors (*i.e.*, k_5) being approximately equal.

Concluding Remarks

There are probably several mechanistic models which could adequately account for the data presented in this paper. However, the dissociative model, in which the five-coordinate intermediates have varying stabilities and lifetimes, does permit us to relate these data to observations on different cobalt(III) systems. In particular it appears that the observed hydrolysis rates for several systems are compatible with such a model if Co^{III}–N(imine) groups increase the lifetime of a five-coordinate intermediate. Within the context of this model the *trans*-Co(*trans*[14]diene)X_2^+ complexes do exhibit chemical behavior between that expected for simple amine complexes and that expected for cobalt(III) complexes with highly unsaturated ligands.[7–9,20]

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[46] R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, **8**, 1598 (1969).

[47] This argument does not imply that the same products should be observed in the hydrolysis of *cis*-$CoLX_2^+$ and *trans*-$CoLX_2^+$ complexes since there can be an activation barrier for the conversion of one five-coordinate intermediate into another. The distribution of intermediates cannot be statistical unless these activation barriers are negligible.

[48] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, **1**, 573 (1962).

[49] J. Halpern, R. A. Palmer, and L. M. Blalzly, *J. Am. Chem. Soc.*, **88**, 2877 (1966).

[50] S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

[51] Note that for pentaammine complexes (7) is independent of X^- and (6) is probably not very dependent on X^- (provided charge types are similar).