Registry No. Acetatopentaamminecobalt(III), 16632-78-3; propionatopentaamminecobalt(III), 19173-62-7; Cr(II), 22541-79-3; V(II), 15121-26-3; Eu(II), 16910-54-6; trimethylacetatopentaamminecobalt(III), 33887-25-1.

References and Notes

(1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(2) H. Taube, *J. Am. Chem. Soc.*, **77**, 4481 (1955).

(3) (a) M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971). (b) For an earlier indication of an acid dependency for this reaction, see E. A. Deutsch, Ph.D. Thesis, Stanford University, 1967.

(4) See, for example: (a) H. Taube and E. S. Gould, *Acc. Chem. Res.*, **2**, 321 (1969); (b) A. Liang and E. S. Gould, *J. Am. Chem. Soc.*, **92**, 6791 (1970).

(5) Evidence that inner-sphere reduction of carboxylatocobalt(III) derivatives involves attack at the carbonyl oxygen has been summarized by K. L. Scott and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1832 (1972).

(6) (a) A. Liang and E. S. Gould, *Inorg. Chem.*, **12** 12 (1973); (b) J. C. Chen and E. S. Gould, *J. Am. Chem. Soc.*, **95**, 5539 (1973).

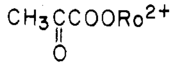
(7) (a) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964); (b) E. S. Gould, *ibid.*, **87**, 4370 (1965); **92**, 6797 (1970).

(8) (a) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**; 2639, 2647 (1974); (b) E. R. Dockal and E. S. Gould, *J. Am. Chem. Soc.*, **94**, 6673 (1972).

(9) (a) P. R. Guenther and R. G. Linck, *J. Am. Chem. Soc.*, **91** 3769 (1969); (b) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970).

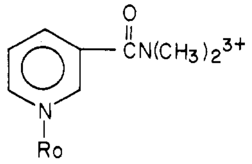
(10) E. R. Dockal, E. T. Everhart, and E. S. Gould, *J. Am. Chem. Soc.*, **93**, 5661 (1971).

(11) In addition to the measurements in aqueous media at high ionic strengths, a series of preliminary experiments was carried out in methanol–water and ethanol–water mixtures at ionicities in the range 0.1–0.2 *M* ($LiClO_4$). In all cases, specific rates were, as expected, lower than those in water, but differences in acidity patterns were evident. The V(II) and Cr(II) reductions of the formatopentaammine complex, the V(II) reduction of the pyruvato complex, I, and the Cr(II) and Eu(II) reductions of the *N*,*N*-dimethylnicotinamide complex, II, are each very nearly independent of added acid in the range (H^+) = 0.005–0.10 *M*, both in 80% methanol and 80% ethanol (v/v). On the other hand, the V(II) reductions of the aquopentaammine complex, the pyridine complex, III, and the dimethylnicotinamide complex, as well as the Eu(II) reduction of the pyridine complex, each in 80% methanol, proceed more rapidly at low acidity than at high, but the acid dependence is less sensitive to (H^+) than inverse first order. At present, we see no direct correlation of these patterns, either with reaction mechanism or with the structures of the reactants.

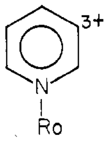


$CH_3\underset{\substack{\| \\ O}}{C}COORo^{2+}$

I



II



III

(Ro = "roseo" = $(NH_3)_5Co^{III}$)

(12) C. Lavallee and E. Deutsch, *Inorg. Chem.*, **11**, 3133 (1972).

(13) Such medium effects have been shown to be significant, however, in the reduction, by Cr(II), of $(NH_3)_5H_2OCo^{3+}$ [14a] and in the reductions of α,β-unsaturated carboxylato complexes of Co(III).[14b]

(14) (a) D. L. Toppen and R. G. Linck, *Inorg. Chem.*, **10**, 2635 (1971); (b) P. K. Thamburaj and E. S. Gould, *ibid.*, **14**, 15 (1975).

(15) For cases in which the protonated path is negligible,[3a] eq 2 simplifies to (1). This approximation is not admissible for the reductions by V(II) and Eu(II) in this study.

(16) See, for example: (a) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd ed, Reinhold, New York, N.Y., 1950, p 452; (b) J. Braunstein in "Ionic Interactions", Vol. I, S. Petrucci, Ed., Academic Press, New York, N.Y., 1971, p 179.

(17) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).

(18) (a) R. G. Linck, *Inorg. Chem., Ser. One*, **9**, 303 (1972); (b) F. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965); (c) R. C. Patel and J. F. Endicott, *ibid.*, **90**, 6364 (1968), have presented evidence that protonation of $Co(NH_3)_5F^{2+}$ increases its rate of (necessarily outer-sphere) reduction with $Ru(NH_3)_6^{2+}$ but have not included sufficient data to allow evaluation of a protonated specific rate.

(19) Related acid dependencies in the reductions of dicarboxylatocobalt(III) complexes have been described by J. R. Ward and A. Haim, *J. Am. Chem. Soc.*, **92**, 475 (1970), and by T. J. Przystas and A. Haim, *Inorg. Chem.*, **11**, 1016 (1972).

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Kinetics and Stereochemistry of the Spontaneous and Mercury(II)-Catalyzed Acid Hydrolysis for the Symmetrical Cis Isomer of the Dichloro(1,8-diamino-3,6-dithiaoctane)cobalt(III) Cation

JAY H. WORRELL

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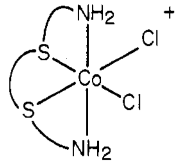
The spontaneous aquation of *s-cis*-$Co(eee)Cl_2^+$ and *s-cis*-$Co(eee)ClH_2O^{2+}$·, where eee is NH_2–CH_2CH_2–S–CH_2CH_2–S–$CH_2CH_2NH_2$, has been studied under various conditions of temperature and acid concentration. The rate and mechanism of mercury(II)-assisted hydrolysis is also reported for both ions. All reactions proceeded with retention of absolute configuration. Spontaneous aquation of both complex ions obeys the rate law $d[Co(III)]/dt = k[Co(III)]$ where $k = 1.77 \times 10^{-4}$ sec^{-1} and 1.10×10^{-6} sec^{-1} for the dichloro and aquochloro complexes, respectively, at 50° in 0.10 *M* $HClO_4$. Activation parameters for the dichloro compound are $\Delta H^{\ddagger} = +20.4$ kcal/mol and $\Delta S^{\ddagger} = -12.6$ eu. Mercury(II) forms a binuclear complex with *s-cis*-$Co(eee)Cl_2^+$ which aquates according to the rate law $-d[Co(eee)Cl_2^+]/dt = k_1K[Hg^{2+}][Co(III)]/1 + K[Hg^{2+}]$ where $k_1 = 2.72 \times 10^{-2}$ sec^{-1} and $K = 34.4$ M^{-1} at 15° in 0.10 *M* $HClO_4$. The Hg(II)-catalyzed aquation of *s-cis*-$Co(eee)ClH_2O^{2+}$ follows second-order kinetics, the rate law being $-d[Co(eee)ClH_2O^{2+}]/dt = k_t[Co(eee)ClH_2O^{2+}][Hg^{2+}]$ where $k_t = 8.41 \times 10^{-2}$ M^{-1} sec^{-1} at 50° in 0.10 *M* $HClO_4$ with $\Delta H^{\ddagger} = 22.7$ kcal/mol and $\Delta S^{\ddagger} = +6.75$ eu. These data are discussed and compared to nitrogen donor systems and trans sulfito systems with a view toward contrasting the unique deactivation role thioether donor atoms play when positioned trans to reactive sites within the complex.

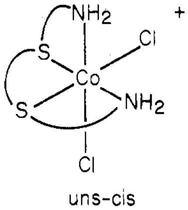
Introduction

The recent synthesis of various new quadridentate ligands has resulted in the preparation and isolation of interesting new complexes which because of their multiple sterochemistries,[1–16] donor atom arrangements,[2,8,9] and varied solvation spheres[3,7,10,12,15,16] are ideally suited for meaningful kinetic and mechanistic investigations. To date, such investigations have been limited to the acid and base hydrolysis for a number of cobalt(III) complexes derived from flexible open-chain tetramine ligands[13,17,18] and cyclic tetramines.[19,20]

Initially, Sargeson and Searle elegantly characterized and reported the aquation kinetics and stereochemistry for the D-*s-cis*-, D-*uns-cis*-, and *trans*-Co(*S*,*S*-trien)Cl_2^+ ions.[18] A macrocyclic ligand which is directly related to triethylene-



s-cis



uns-cis

teramine is 1,4,8,11-tetraazacyclotetradecane (cyclam). The kinetics of the substitution and isomerization reactions of *cis*- and *trans*-Co(cyclam)Cl_2^+ have been examined by Poon and Tobe.[19] In addition, two nonbranched tetraamine ligands have received enthusiastic attention. Dichlorocobalt(III) complexes of 3,7-diaza-1,9-nonanediamine, $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$, (2,3,2-tet), and 4,7-diaza-1,10-decanediamine, $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ (3,2,3-tet), serve as a link between the trien and cyclam derivatives by providing a series in which the secondary amines can assume a variety of configurations.[13,19]

It appears that geometric stability (cis and trans) is a prime function of chelate ring size;[10] however germane to substitutions and isomerization reaction mechanisms are the roles played by chelated secondary amine groups in such processes. A new approach to evaluating the functions of secondary nitrogen donor atoms in isomerization and substitution reactions would be to design a ligand moiety which is generally similar to those presently under intensive investigation yet which does not possess the secondary nitrogen group. One such ligand is 1,8-diamino-3,6-dithiaoctane.

In previous communications the preparation, reactions,[9] optical resolution, geometry, and absolute configurations[21] have been presented and discussed for a number of cobalt(III) complexes derived from the flexible linear quadridentate $NH_2CH_2CH_2–S–CH_2CH_2–S–CH_2CH_2NH_2$ (eee). We now report the results of a kinetic investigation for the acid hydrolysis of the stereospecific molecular ion *s-cis*-Co(eee)Cl_2^+.

Experimental Section

Materials. *s-cis*-Dichloro(1,8-diamino-3,6-dithiaoctane)cobalt(III) chloride was prepared by the method of Worrell and Busch.[3] The chloride salt was dissolved in water and $NaClO_4$ was added. The purple-blue [Co(eee)Cl_2]ClO_4 which precipitated was collected by filtration, washed with cold water, acetone, and ether, and air-dried. Anal. Calcd for [Co($C_6H_{16}N_2S_2$)Cl_2]ClO_4: C, 17.6; H, 3.92; N, 6.85. Found: C, 17.5; H, 3.90; N, 6.74. The visible–ultraviolet electronic spectrum has maximum absorptions at 610 nm (ϵ 308), 550 nm (sh), 285 nm (ϵ 12,200), and 223 nm (ϵ 13,450).

Acid solutions were prepared from standardized 10.0 *M* $HClO_4$ (Baker Analyzed reagent) and titrated against primary standard Na_2CO_3. Ionic strength of solutions was adjusted by adding an appropriate volume of 5.0 *M* standardized $NaClO_4$ solution to the reaction flask and then diluting to the mark with a precalculated volume of standard acid and/or distilled water.

Mercury(II) perchlorate stock solution (0.30 *M*) in 0.10 *M* $HClO_4$ was prepared by dissolving yellow mercury(II) oxide (Baker Reagent) in the appropriate volume of standardized perchloric acid and diluting the resulting solution to 1.0 l. The solution was standardized by titrating potentiometrically with sodium hydroxide solution to determine the total hydrogen ion plus mercury(II) ion concentration. The hydrogen ion concentration was determined by titrating with standard sodium hydroxide in the presence of sodium bromide to complex the mercury(II) ion. The mercury(II) ion concentration was determined by difference.

Kinetics. Rate data were collected spectrophotometrically using a Cary 14 recording spectrophotometer equipped with matched silica cells (1.0, 2.5, and 5.0 cm) and a thermostable cell holder and compartment. Temperature control was maintained to ±0.05° using a Forma Temp Jr. heating–refrigeration bath equipped with a precision temperature regulator. Aquation reactions were followed as a decrease in absorbance at several wavelengths and selected isosbestic points. First-order rate constants, k_{obsd}, were determined from the slopes of plots of log ($D_t - D_\infty$) vs. time, where D_t and D_∞ are the optical densities at time *t* and after 8–10 half-lives of the reaction, respectively. In all cases linear plots were obtained for at least 65% of reaction and in the majority of runs for 80–90% reaction. D_∞ values were also calculated from the known electronic absorption spectra for the *s-cis*-Co(eee)ClH_2O^{2+} and *s-cis*-Co(eee)$(H_2O)_2^{3+}$ ions for reactions having very long half-lives at elevated temperature. For the faster reactions, excellent agreement was observed between D_∞(calcd) and D_∞(exptl).

Sample Handling. For the spontaneous aquations, a weighed sample of recrystallized *s-cis*-[Co(eee)Cl_2]ClO_4 was dissolved in the appropriate volume of standard $HClO_4$ and $NaClO_4$ so that, when diluted in a volumetric flask to 100 ml or 200 ml with distilled water, the solution would give the predetermined concentrations of complex and acid and ionic strength. Flask volumes were calibrated at the temperature of the kinetic runs. Prethermostated samples were periodically withdrawn and placed in a preheated cell and the absorption spectrum recorded, or at a fixed wavelength, the change in absorbance was followed continuously at a chart speed of 0.25–1 in./min depending on the rate of the reaction. Extreme care was exercised in maintaining temperature control when transferring samples to the spectrophotometer cell. This was expecially important for the mercury(II) ion catalyzed reactions.

For these latter reactions given volumes of prethermostated complex, $HClO_4$, and $NaClO_4$ were added to a 5.0-cm cell and allowed to reach temperature equilibrium (2 min). A known volume of mercury(II) perchlorate with the appropriate acid concentration was then syringed into the cell from a calibrated thermostated syringe. The cell was quickly inverted for mixing and the change in absorbance at a fixed wavelength was recorded as described above.

Table I. Kinetic Data for the Aquation of *s-cis*-Co(eee)Cl_2^+

10^4[complex], *M*	[$HClO_4$], *M*	Temp, °C	10^4k_{obsd}, sec^{-1}
6.0	0.10	25	0.120
6.0	0.10	40	0.668
6.3	0.10	50	1.77
6.0	0.10	60	5.11
3.0	0.10	50	1.79
6.3	0.10	50	1.77
12.0	0.10	50	1.75
6.3	0.10	50	1.77
6.0	0.01	50	1.85
6.0	0.001	50	1.85

Results

Spontaneous Aquation of *s-cis*-Co(eee)Cl_2^+. An acidified aqueous solution of this complex exhibits an electronic absorption band maximum at 610 nm (ϵ 308) and a less intense shoulder positioned at about 550 nm (ϵ 246). The spectral transformation from *s-cis*-Co(eee)Cl_2^+ to *s-cis*-Co(eee)ClH_2O^{2+} proceeds with very well-defined isosbestic points at 586 and 466 nm, demonstrating the absence of labile intermediates participating in a simultaneous decomposition or isomerization reaction. At 25° and in 0.10 *M* perchloric acid the aquation of *s-cis*-Co(eee)Cl_2^+ is very slow, having a first-order rate constant of 0.12×10^{-4} sec^{-1} (half-life ~16 hr).

The rate of spontaneous chloride ion release from the *s-cis*-Co(eee)Cl_2^+ ion was followed spectrophotometrically at constant ionic strength (0.101 *M*) in the acid range 1×10^{-3} $M \leq [H_3O^+] \leq 0.10$ *M*. Table I presents the experimental data relevant to reaction 1 at 25, 40, 50, and 60°. Examination of column 4 indicates the reaction is first order in substrate concentration and independent of acid concentration in the ranges studied. A simple first-order rate expression describes the reaction kinetically as

$$H_2O + s\text{-}cis\text{-}Co(eee)Cl_2^+ \xrightarrow{k_{obsd}} s\text{-}cis\text{-}Co(eee)ClH_2O^{2+} + Cl^- \qquad (1)$$

$$-d[Co(eee)Cl_2^+]/dt = k_{obsd}[Co(eee)Cl_2^+]$$

Activation parameters were determined from the slope of a plot having ln k_{obsd}/T *vs.* $1/T$ giving the enthalpy of activation, $\Delta H^\ddagger$, as +20.4 ± 1.2 kcal/mol. We calculate the entropy of activation, $\Delta S^\ddagger$, from transition state theory to be −12.6 ± 3 eu.

Spontaneous Aquation of *s-cis*-Co(eee)ClH_2O^{2+}. The visible electronic absorption spectrum of *s-cis*-Co(eee)ClH_2O^{2+} has a single maximum positioned at 578 nm (ϵ 286) and upon spontaneous aquation this band shifts to higher energy with a simultaneous decrease in intensity. The product, *s-cis*-

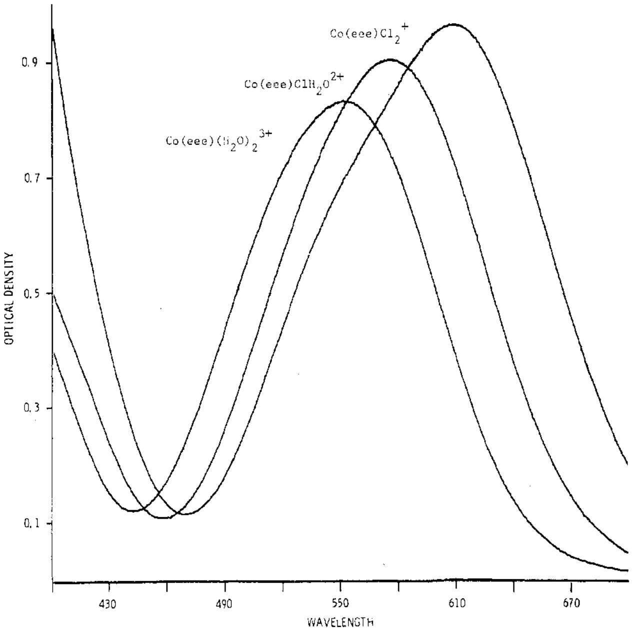


Figure 1. Spectral displays for 6.00×10^{-4} M solutions of *s-cis*-$Co(eee)Cl_2^+$, *s-cis*-$Co(eee)ClH_2O^{2+}$, and *s-cis*-$Co(eee)(H_2O)_2^{3+}$ ions, respectively, right to left.

Table II. Kinetic Data for the Aquation of *s-cis*-$Co(eee)H_2OCl^{2+}$ ([Complex] = 6.0×10^{-4})

$[HClO_4]$, M	Temp, °C	10^6k_{obsd}, sec^{-1}	$t_{1/2}$, hr
1.000	50	1.095	176
0.100	50	1.103	174
0.010	50	Thermal decompn after 40 hr	
0.001	50	Thermal decompn after 25 hr	
0.100	25	Reaction far from completion even after 6 months	

$Co(eee)(H_2O)_2^{3+}$, exhibits a maximum at 554 nm (ϵ 266). Both compounds have common isosbestic points at 555 and 448 nm.

The absorption spectrum of the *s-cis*-$Co(eee)ClH_2O^{2+}$ ion was determined in two ways: (1) the reactant was allowed to aquate until the recorded spectrum from 430 to 650 nm remained constant and (2) mercuric ion was added to the reactant and the spectrum recorded by scanning as a function of time. Both techniques gave identical results. The final product *s-cis*-$Co(eee)(H_2O)_2^{3+}$ was generated by allowing an acidic aqueous solution of *s-cis*-$Co(eee)ClH_2O^{2+}$ to aquate in the presence of mercuric ions. Also, acidification of an aqueous solution of *s-cis*-$[Co(eee)CO_3]ClO_4$ gave a recorded spectrum that was identical with that of the diaquo product obtained by Hg(II) ion displacement of bound chloride. Figure 1 presents the individual spectra for the dichloro, aquochloro, and diaquo ions from right to left, respectively.

Spontaneous aquation of the *s-cis*-$Co(eee)H_2OCl^{2+}$ ion is very slow. Table II presents the effect of temperature and acid concentration for the reaction illustrated in (2). The extreme

$$s\text{-}cis\text{-}Co(eee)H_2OCl^{2+} + H_2O \xrightarrow{k_{obsd}} s\text{-}cis\text{-}Co(eee)(H_2O)_2^{3+} + Cl^- \qquad (2)$$

reluctance of this complex ion to undergo spontaneous aquation even at elevated temperatures is further complicated by a thermal decomposition which is a function of the acid concentration as shown below. Within the acid range 0.10 M < $[H_3O^+]$ < 1.0 M the rate constant for aquation is 1.10×10^{-6} sec^{-1} at 50°. The rate constants for aquation were determined from optical density changes recorded over the first 100 hr at 50°, with D_∞ being calculated from the complex concentration and the known molar extinction coefficient at 568 nm, the isosbestic point of *s-cis*-$Co(eee)Cl_2^+$ and *s-cis*-$Co(eee)ClH_2O^{2+}$. Figure 2 presents a spectral display showing the *s-cis*-$Co(eee)Cl_2^+$ ion aquating to *s-cis*-$Co(eee)ClH_2O^{2+}$ with maintenance of isosbestic points. This is followed by the second stage of aquation to *s-cis*-$Co(eee)(H_2O)_2^{3+}$ which proceeds with well-defined isosbestic points for about 100 hr at 50° in 0.1–1.0 M $HClO_4$. Suddenly after approximately 40% reaction, the *s-cis*-$Co(eee)(H_2O)_2^{3+}$ or remaining unreacted *s-cis*-$Co(eee)ClH_2O^{2+}$ disproportionates as evidenced by a decrease in absorption with loss of isosbestic points. The solution darkens to a light brown coloration and ligand or ligand by-products appear on the liquid surface. Similar experiments at 10^{-3} and 10^{-2} M $HClO_4$ follow identical spectral changes, the only difference being that the rate of decomposition increases at lower acid concentration.

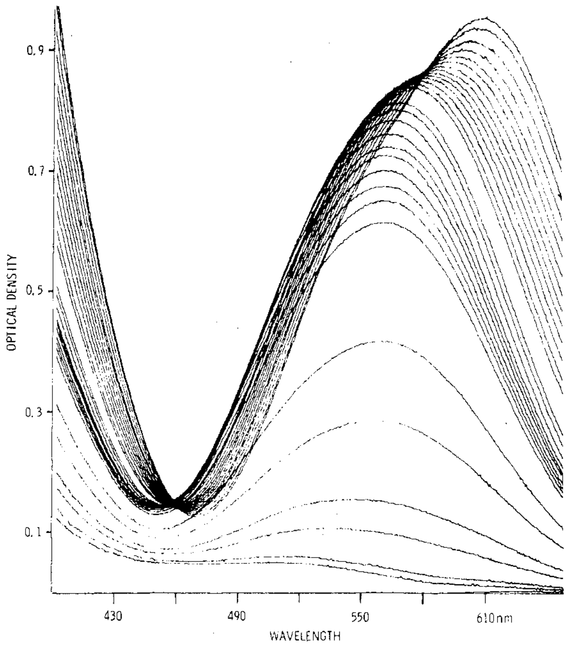


Figure 2. Spectral changes accompanying the spontaneous aquation and decomposition of a 6.00×10^{-4} M solution of $Co(eee)H_2OCl^{2+}$ at 50° in 1.00 M $HClO_4$.

The collection of additional data to determine activation parameters for reaction 2 was not pursued due to the slowness of the reaction and the lack of thermal stability of the Co(eee)ClH_2O^{2+} complex. It is assumed that within the accessible experimental range studied, the reaction obeys pseudo-first-order kinetics and is acid independent above 0.1 M H_3O^+.

Mercury(II)-Induced Aquations. Mercury(II)-catalyzed aquations of both *s-cis*-$Co(eee)Cl_2^+$ and *s-cis*-$Co(eee)ClH_2O^{2+}$ proceed at rates which are very rapid compared to the above spontaneous aquation reactions. Reaction 3 was followed kinetically using standard syringe and spectrophotometric techniques.

$$s\text{-}cis\text{-}Co(eee)Cl_2^+ + Hg_{aq}^{2+} \rightarrow s\text{-}cis\text{-}Co(eee)ClH_2O^{2+} + HgCl^+ \qquad (3)$$

Examination of the data presented in columns 2 and 3 of Table III shows that as the concentration of Hg_{aq}^{2+} increases, the apparent second-order rate constant defined by $k_t = k_{obsd}/[Hg^{2+}]$, assuming a mixed second-order rate law $d[Co(eee)Cl_2^+]/dt = k_t[Co(III)][Hg(II)]$, decreases in an unusual manner.

This behavior can be explained if there exists a prior complexation equilibrium between the $Co(eee)Cl_2^+$ and Hg_{aq}^{2+}

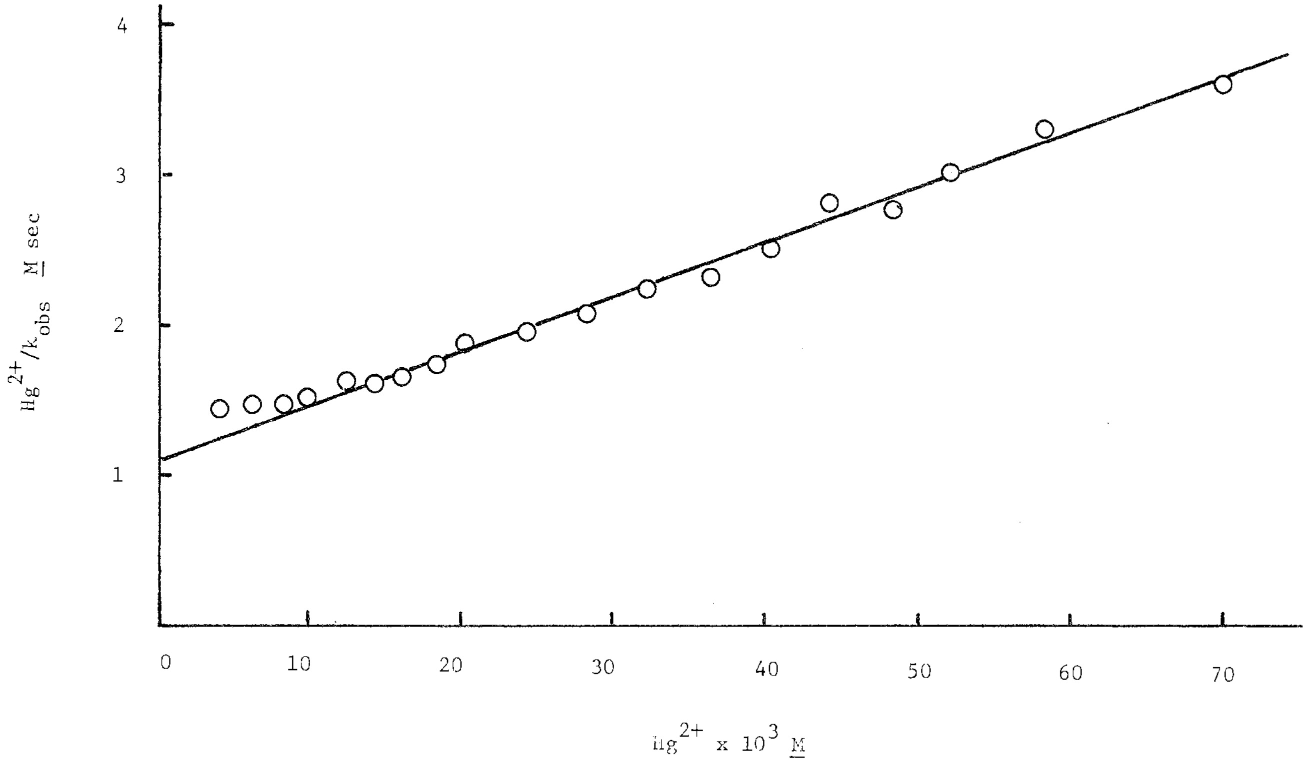


Figure 3. Determination of rate parameters related to mechanisms I and II.

Table III. Effect of Hg(II) on the Aquation Rate[a] of *s-cis*-$Co(eee)Cl_2^+$

$10^4[Hg_{aq}^{2+}]$, *M*	10^3k_{obsd},[c] sec^{-1}	k_t, M^{-1} sec^{-1}
40.0	2.72 ± 0.03	0.680
60.0	4.10 ± 0.07	0.684
80.0	5.31 ± 0.05	0.665
100.0	6.50 ± 0.08	0.650
120.0	7.31 ± 0.18	0.610
140.0	8.58 ± 0.03	0.611
160.0	9.35 ± 0.10	0.595
180.0	10.2 ± 0.05	0.566
200.0	10.5 ± 0.05	0.525
240.0	12.2 ± 0.14	0.509
280.0	13.4 ± 0.08	0.479
320.0	14.3 ± 0.30	0.446
360.0	15.4 ± 0.21	0.428
400.0	15.8 ± 0.42	0.395
480.0[b]	17.4 ± 0.33	0.363
520.0[b]	17.2 ± 0.18	0.329
560.0[b]	17.2 ± 0.56	0.306
600.0[b]	17.0 ± 0.67	0.284
700.0[b]	19.2 ± 0.88	0.274

[a] At 15.0°, [Co(III)] = 6.0×10^{-4} *M*, $[H^+] = 0.100$ *M*, and $\mu = 0.22$ adjusted with $NaClO_4$–$HClO_4$. [b] $NaClO_4$ not added; $\mu = 0.22$–0.31 as a function of Hg_{aq}^{2+} and $HClO_4$. [c] All data based on three to five determinations.

ions such that saturation occurs as the concentration of Hg_{aq}^{2+} is increased (eq 4). Subsequent aquation is then either the

$$s\text{-}cis\text{-}Co(eee)Cl_2^+ + Hg_{aq}^{2+} \overset{K}{\rightleftharpoons} s\text{-}cis\text{-}Co(eee)Cl_2Hg^{3+} \qquad (4)$$

result of a first-order decomposition of the Co^{III}–Cl_2–Hg^{II} bridged complex (eq 5) or the second-order reaction of Hg_{aq}^{2+}

$$s\text{-}cis\text{-}Co(eee)Cl_2Hg^{3+} \xrightarrow{k_1} s\text{-}cis\text{-}Co(eee)ClH_2O^{2+} + HgCl^+ \qquad (5)$$

with the remaining uncomplexed *s-cis*-$Co(eee)Cl_2^+$ (eq 6).

$$s\text{-}cis\text{-}Co(eee)Cl_2^+ + Hg_{aq}^{2+} \xrightarrow{k_2} s\text{-}cis\text{-}Co(eee)ClH_2O^{2+} + HgCl^+ \qquad (6)$$

Table IV.[a] Effect of Hg(II) on the Aquation Rate of *s-cis*-$Co(eee)ClH_2O^{2+}$

10^4[Hg(II)], *M*	Temp, °C	10^4k_{obsd}, sec^{-1}
23.9	50	2.01
47.9		4.24
71.9		5.96
95.8		8.09
143.8		11.8
191.7		16.2
320.8		26.8
143.8	40	3.59
143.8	30	1.03
143.8	25	0.536

[a] [Co(III)] = 6×10^{-4} *M*; $[H^+] = 0.10$ *M*; all runs in triplicate; ionic strength varies between 0.10 and 0.13 *M* as a function of $[Hg^{2+}]$.

The observed pseudo-first-order rate constant is related to the mechanistically derived rate constants by the relationship

$$k_{obsd} = \frac{k_1K[Hg_{aq}^{2+}]}{1 + K[Hg_{aq}^{2+}]} \quad \text{mechanism I (eq 4 and 5)}$$

or

$$k_{obsd} = \frac{k_2[Hg_{aq}^{2+}]}{1 + K[Hg_{aq}^{2+}]} \quad \text{mechanism II (eq 4 and 6)}$$

Both mechanisms predict that a plot of $k_{obsd}/[Hg^{2+}]$ vs. Hg^{2+} concentration should yield a straight line as shown in Figure 3. The intercept and slope give the parameters k_1 and K for mechanism I or k_2 and K for mechanism II. Constants extracted from this analysis are intercept = $1/k_1K = 1.07$ *M* sec and slope = $1/k_1 = 36.8$ sec, whereupon we calculate $k_1 = 2.72 \times 10^{-2}$ sec^{-1}, $K = 34.4$ M^{-1}, and $k_2 = 0.93$ M^{-1} sec^{-1}.

The aquation of $Co(eee)ClH_2O^{2+}$ catalyzed by Hg_{aq}^{2+} was examined at 30, 40, and 50° over a wide range of $[Hg_{aq}^{2+}]$ as shown in Table IV. At 0.10 *M* $HClO_4$, the mercuric ion dependence for the aquochloro complex followed simple mixed

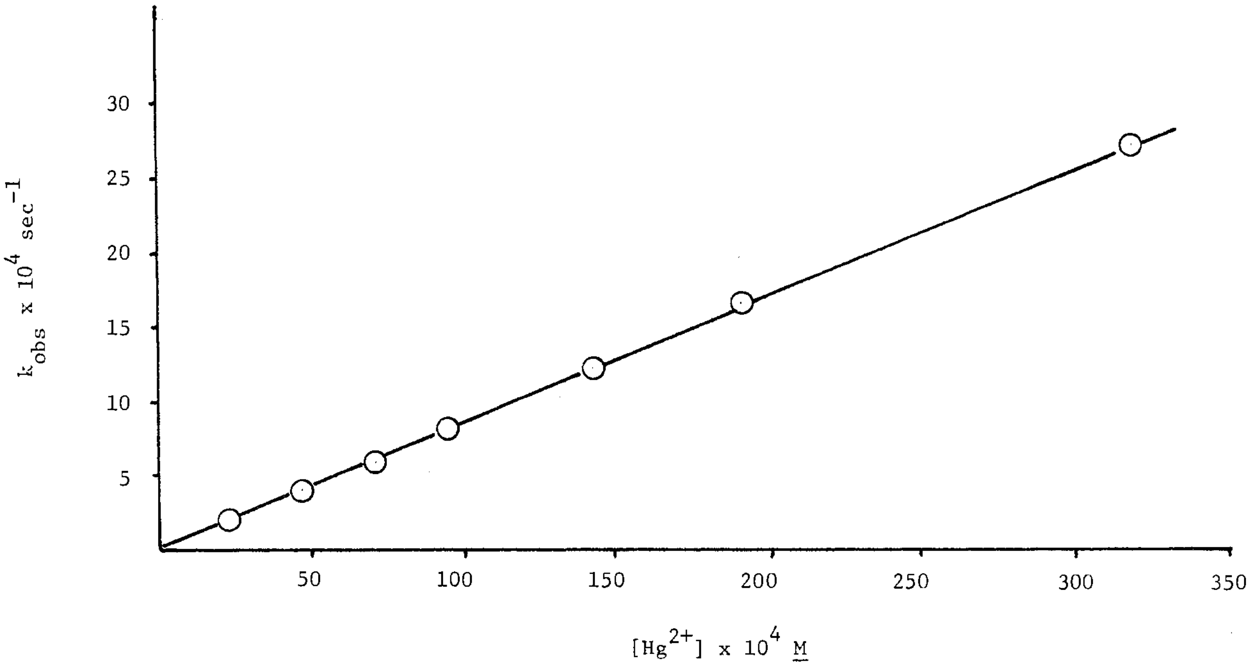


Figure 4. Effect of Hg(II) concentration on the aquation rate of Co(eee)ClH_2O^{2+} ion at 50°.

Table V. Rate Constants, Activation Parameters, and Steric Course for the Reaction *cis*-$CoACl_2{}^+ + H_2O \rightarrow CoAClH_2O^{2+} + Cl^-$ at 25°

A	10^4k, sec^{-1}	$\Delta H^‡$, kcal/mol	$\Delta S^‡$, eu	% steric change	Ref
Cyclam	160 (1333)[a]	18.3	−6	0	24
β-*S*,*S*-trien	14.5 (121)	21.1	−2.7 ± 1.4	0	18
$(en)_2$	2.5 (21)	22.0	−5	0	23
(+)-α-trien	1.58 (13)	21.5	−5.8 ± 1.4	0	18
eee	0.12 (1)	20.4	−12.6	0	This work

[a] Rates in parentheses are relative to eee as 1.

second-order kinetics consistent with the rate law

$$-\frac{d[\text{Co(eee)ClH}_2\text{O}^{2+}]}{dt} = k_t[\text{Co(eee)ClH}_2\text{O}^{2+}][\text{Hg}_{aq}{}^{2+}]$$

corresponding to the process given in eq 7. From Figure 4,

$$s\text{-}cis\text{-Co(eee)ClH}_2\text{O}^{2+} + \text{Hg}_{aq}{}^{2+} \xrightarrow{k_t} s\text{-}cis\text{-Co(eee)(H}_2\text{O)}_2{}^{3+} + \text{HgCl}^+ \quad (7)$$

the slope of the line defined by plotting k_{obsd} vs. $[Hg_{aq}{}^{2+}]$ gives $k_t = 8.41 \times 10^{-2}$ M^{-1} sec^{-1} at 50°. A plot of $1/T$ vs. ln k_t/T is given in Figure 5, where $\Delta H^‡$ is determined to be +22.7 kcal/mol. We calculate $\Delta S^‡$ from transition-state theory to be +6.75 eu.

Unlike the Hg(II)-catalyzed aquation of the *s*-*cis*-Co(eee)$Cl_2{}^+$ ion, evidence supporting an intermediate Hg^{II}–Cl–Co^{III} complexation equilibrium was not observed for the Hg(II)-catalyzed aquation of *s*-*cis*-Co(eee)ClH_2O^{2+}.

Discussion

Spontaneous Aquations. The dichloro complex of cobalt(III) containing the quadridentate ligand 1,8-diamino-3,6-dithiaoctane undergoes spontaneous hydrolysis as depicted in the reaction sequence (8)–(10). The deep blue $(+)_{546}$-*s*-*cis*-Co(eee)$Cl_2{}^+$ ion retains the *s*-*cis* geometry and its absolute configuration upon aquation. Examination of circular dichroism spectra of optically pure reactant in 0.10 *M* $HClO_4$ as a function of time clearly demonstrated the absence of isomerization[22] and yielded rate constants for eq 8 that are

$$\text{Co(eee)Cl}_2{}^+ + \text{H}_2\text{O} \xrightarrow{k_1} \text{Co(eee)ClH}_2\text{O}^{2+} + \text{Cl}^- \quad (8)$$

blue purple

$$\begin{tikzcd}[column sep=large] \text{Co(eee)ClH}_2\text{O}^{2+} + \text{H}_2\text{O} \arrow[r, shift left, "k_2"] \arrow[d, shift right, "-\text{H}^+"'] & \text{Co(eee)(H}_2\text{O)}_2{}^{3+} + \text{Cl}^- \arrow[l, shift left, "k_{-2}"] \arrow[d, shift right, "-\text{H}^+"'] \\ \text{Co(eee)ClOH}^{2+} + \text{H}_2\text{O} \arrow[u, shift right, "\text{H}^+"'] \arrow[r, "K", rightleftharpoons] & \text{Co(eee)(OH)H}_2\text{O}^{2+} + \text{Cl}^- \arrow[u, shift right, "\text{H}^+"'] \end{tikzcd} \quad \begin{matrix}(9)\\ \\(10)\end{matrix}$$

purple pink

red-pink pink

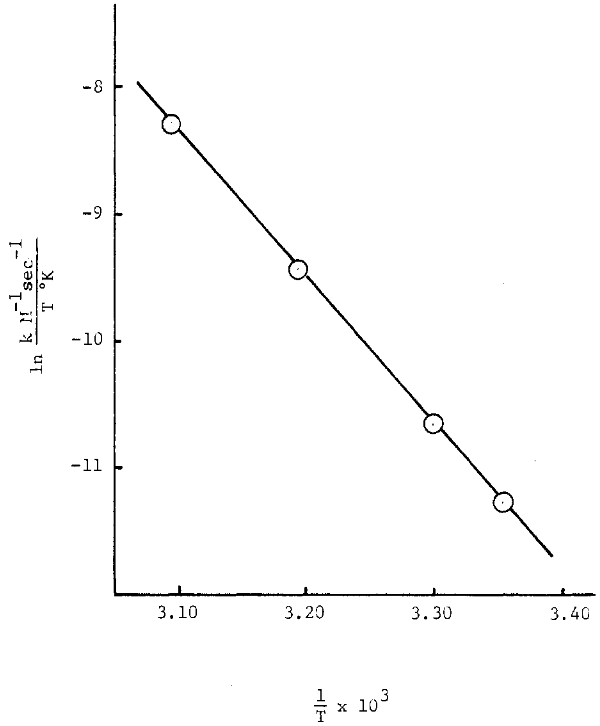


Figure 5. Temperature dependence of k_t for the Hg(II)-induced aquation of Co(eee)ClH_2O^{2+}.

in complete agreement with those determined spectrophotometrically.

Table V compares the rate constant, activation parameters, and steric course of aquation for *s-cis*-Co(eee)Cl_2^+ with those of closely related complexes. Replacement of two ethylenediamine ligands by cyclic and linear flexible quadridentate ligands lead to markedly different effects on the aquation lability of the complex. It can be seen that *s-cis*-Co(eee)Cl_2^+ exhibits the slowest aquation rate ($k_{obsd} = 0.12 \times 10^{-4}$ sec^{-1}) and most negative activation entropy (−12.6 eu) of the series, being 13 times less reactive than its most similar analog (+)-*α-cis*-Co(trien)Cl_2^+. The major physical difference between these two compounds is that the secondary nitrogen (>N–H) groups of trien have been replaced by two thioether (C–S–C) donors. This substitution imparts major contraints on the complex's ability to isomerize geometrically. Perhaps the larger sulfur donors impose a steric requirement which locks the configuration of adjacent chelate rings. This limited flexing of chelate rings in turn considerably reduces the exchange or movement of solvent molecules contained in the primary solvent shell surrounding the complex. In such a mechanism one would expect a reduced probability of water-assisted removal of the chloride ion.

Folding of the quadridentate as in *β-cis*-Co(*S*,*S*-trien)Cl_2^+ or folding and cyclizing as in Co(cyclam)Cl_2^+ very dramatically increases both the disorder in the primary solvent shell and the rate of aquation.

Tobe has suggested[23] that in a series of complexes of the type *cis*- or *trans*-CoACl_2^+ where A is a quadridentate ligand or two bidentate ligands having nitrogen donors, higher (usually positive) entropies of activation are diagnostic of an incipient trigonal-bipyramidal intermediate which generates varying degrees of isomeric change accompanying spontaneous aquation. Lower, usually negative values of $\Delta S^‡$, such as in the present example, are diagnostic of an incipient square-pyramidal transition state in which aquation occurs with retention of configuration.

The possibility that the entering water displaces chloride ion along an edge and eliminates the distant chloride ion from the coordination sphere also resulting in retention of configuration cannot be excluded. In these respects *s-cis*-Co(eee)Cl_2^+ is similar to *cis*-Co(en)$_2Cl_2^+$ and *s-cis*-Co(trien)Cl_2^+.

Because the rate of decomposition of Co(eee)ClH$_2$O^{2+} increases with decreasing acidity, the possibility of rapid geometrical isomerization followed by decomposition was considered. It should be noted that the structurally similar *α-cis*-Co(trien)Cl_2^+ system has but a single synthetic route to *α-cis* (uns-cis) isomers, namely, base hydrolysis. In the hope that a similar pathway to the yet undiscovered *uns-cis*-Co(eee)X_2^{n+} complexes may exist, a number of experiments were performed in basic medium.[21] Attempts to isolate and quantify the products illustrated in eq 10 were not successful due to the same general decomposition behavior as reported for the high-temperature spontaneous acid hydrolysis of Co(eee)ClH$_2$O^{2+}.

Limited kinetic and circular dichroism data concerning the absolute configuration of *s-cis*-Co(eee)(H$_2$O)$_2^{3+}$ as produced directly from the spontaneous aquation of (+)$_{546}$-*s-cis*-Co(eee)ClH$_2$O^{2+} suggest that configurational integrity is maintained.

Using the observed rate constant of 1.1 × 10^{-6} sec^{-1} at 50° for the aquation of Co(eee)ClH$_2$O^{2+} and assuming that the rate of aquation approximately doubles for each 10° interval, one can estimate the rate constant at 25° to be in the range (1.3–2.7) × 10^{-7} sec^{-1}. This is consistent with known trends which support the fact that the second stage of aquation occurs at a rate about 100 times slower than that of removal of the first chloride ion.

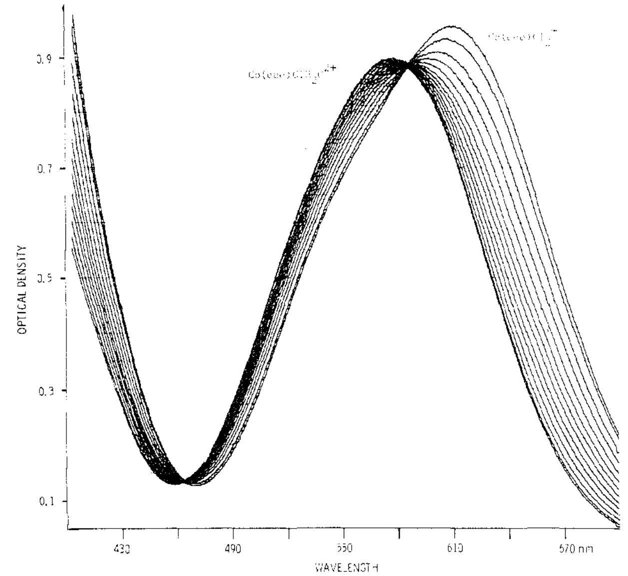


Figure 6. Spectral changes accompanying the mercury(II)-induced aquation of 6.00 × 10^{-4} *M s-cis*-Co(eee)Cl_2^+ in 0.10 *M* HClO$_4$.

Mercury(II)-Assisted Aquations. Very few quantitative data are available concerning the Hg(II)-assisted aquations of *cis*-CoACl_2^+ and *cis*-CoAH$_2$OCl^{2+} ions where A has the designations given in Table V. Sargeson has qualitatively reported that (+)-*α-cis*-Co(trien)Cl_2^+ and (+)-*α-cis*-Co(trien)ClH$_2$O^{2+} aquate very rapidly in the presence of Hg(II) and do so with complete retention of configuration.[25] For the dichloro complex Sargeson reported that reaction is complete within 30 sec at 0.005 *M* Hg(II) at 20°. If it is assumed that the half-life for the first stage of aquation is 3 sec, then the second-order rate constant can be estimated at about 46 M^{-1} sec^{-1}. This is a lower limit at best.

By way of comparison the (+)-*s-cis*-Co(eee)Cl_2^+ and (+)-*s-cis*-Co(eee)ClH$_2$O^{2+} ions also aquate under the influence of Hg(II) with complete retention of absolute configuration and with fixed isosbestic points at 586 and 466 nm as presented in Figure 6. Furthermore, in the present system, deactivation of sites trans to thioether donor atoms is even more striking than the spontaneous aquations. It is interesting to note that sulfur-bonded sulfito groups have a very pronounced trans-labilizing effect[26] and that by tying up one lone pair of electrons in a carbon chain, such as in the present ligand eee, labilization is drastically impaired.

In the reaction of Hg(II) with *s-cis*-Co(eee)Cl_2^+, it is not surprising that a preequilibrium complexation obtains. Other detailed studies which give evidence for such an association include the Hg(II)-catalyzed aquation of the *cis*-Co(en)$_2$(N$_3$)$_2^+$ ion[27] and more recently the work of Linck[28] with *cis*-Co(en)$_2Cl_2^+$. The researches of Birk[29,30] on the Hg(II)-induced aquation of *cis*-Cr(H$_2$O)$_4Cl_2^+$ is yet another outstanding example. Based on the limited data available, it is not unreasonable to expect that the presence of two halogen or pseudohalogen ions positioned cis to one another is a fundamental requirement for the complexation mechanism to be operative.

Although the reactive form of Co(eee)Cl_2^+ complexed or uncomplexed with Hg(II) could not be distinguished kinetically, indirect evidence and arguments can be advanced in favor of the non-double-bridged form being the kinetically reactive species.[30] This implies that a configuration involving complexation (double-bridging) is particularly stable and to accomplish aquation, a single bridged configuration must be attained.

Examination of Figure 1 clearly shows a deviation from linearity at low Hg(II) concentrations. The nature of this deviation suggests a more complex rate equation that would be consistent with the formation of a second binuclear complex, i.e.

$$cis\text{-}Co(eee)Cl_2Hg^{3+} + Hg^{2+} \overset{K_2}{\rightleftharpoons} cis\text{-}Co(eee)Cl_2Hg_2{}^{5+} \qquad (11)$$

$$-d \ln [Co(eee)Cl_2^+]/dt = k_c[Hg(II)]^2/1 + KK_2[Hg(II)]^2 \qquad (12)$$

That the present data fit mechanism I so well can be attributed to the limiting form of eq 12 which obtains if most of the $Co(eee)Cl_2^+$ is in the double-bridged complexed form $Co(eee)Cl_2Hg^{3+}$ as dictated when $K[Hg(II)] >> 1$. Similar conclusions exist for the reaction of Hg(II) with *cis*-$Co(en)_2Cl_2^+$ and *cis*-$Cr(H_2O)_4Cl_2^+$ ions: simply that the double-bridged configuration must be destroyed to accomplish the aquation reaction.[30]

Considering the affinity of mercury for sulfur, one must logically inquire as to the possible complexation or interaction of Hg(II) at the backside ligand thioether donor atoms, as opposed to positions adjacent to the leaving chloride groups. Evidence for such an interaction was expected to manifest itself in electronic absorption spectral changes for the free and complexed species. Using the technique of Armor and Haim,[31] the spectra of $Co(eee)C_2O_4^+$, $Co(eee)(acac)^{2+}$, and $Co(eee)(H_2O)_2^{3+}$ were examined as a function of Hg(II) concentration. No spectral evidence was found to support backside attack of Hg(II) on these complexes.

The Hg(II)-induced aquation of *s-cis*-$Co(eee)ClH_2O^{2+}$ gave a second-order rate constant which did not exhibit a trend toward increased values at higher mercury(II) concentration. In addition, this second state of aquation was amenable to a temperature-dependence study. At 25° the observed second-order rate constant, 5.36×10^{-5} M^{-1} sec^{-1}, indicates that this ion aquates 783 times slower than the corresponding *cis*-$Co(en)_2ClH_2O^{2+}$ ion under similar conditions. As in the first stage of aquation, spontaneous or induced, the presence of trans thioether donor atoms dramatically retards Co–Cl bond cleavage.

Registry No. *s-cis*-$Co(eee)Cl_2^+$, 32594-33-5; *s-cis*-$Co(eee)ClH_2O^{2+}$, 54983-97-0; *s-cis*-$Co(eee)(H_2O)_2^{3+}$, 54983-98-1; Hg(II), 14302-87-5.

References and Notes

(1) T. K. Huan, J. N. Mulvihill, A. R. Gainsford, and D. A. House, *Inorg. Chem.*, **12**, 1517 (1973).
(2) R. G. Asperger, *Inorg. Chem.*, **8**, 2127 (1969).
(3) R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1395 (1965).
(4) R. G. Asperger and C. F. Liu, *J. Am. Chem. Soc.*, **89**, 708 (1967).
(5) R. G. Asperger and C. F. Liu, *J. Am. Chem. Soc.*, **89**, 1533 (1967).
(6) S. Yoshikawa, T. Sekihara, and M. Goto, *Inorg. Chem.*, **6**, 169 (1967).
(7) M. Goto, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, **8**, 358 (1969).
(8) P. J. Garnett, D. W. Watts, and J. I. Legg, *Inorg. Chem.*, **8**, 2534 (1969).
(9) J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1563 (1969).
(10) J. H. Worrell, T. E. MacDermott, and D. H. Busch, *Chem. Commun.*, 661 (1969).
(11) B. Bosnich, W. R. Kneen, and A. T. Phillip, *Inorg. Chem.*, **8**, 2567 (1969).
(12) B. Bosnich and A. T. Phillip, *J. Am. Chem. Soc.*, **90**, 6352 (1968).
(13) M. D. Alexander and H. G. Hamilton, *Inorg. Chem.*, **8**, 2131 (1969).
(14) H. G. Hamilton and M. D. Alexander, *Inorg. Chem.*, **5**, 2060 (1966).
(15) H. G. Hamilton and M. D. Alexander, *J. Am. Chem. Soc.*, **89**, 5065 (1967).
(16) B. Bosnich, C. K. Poon, and M. C. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).
(17) R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, **8**, 1589 (1969).
(18) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 2172 (1967).
(19) (a) C. K. Poon and M. L. Tobe, *Inorg. Chem.*, **7**, 2398 (1968), and references therein; (b) M. L. Tobe and M. L. Tucker, *ibid.*, **12**, 2994 (1973).
(20) J. A. Kernohan and J. F. Endicott, *J. Am. Chem. Soc.*, **91**, 6977 (1969).
(21) J. H. Worrell and D. H. Busch, *Inorg. Chem.*, **8**, 1572 (1969).
(22) Isomerization to the uns-cis form must also change the absolute configuration of the complex from λ to Δ. See ref 9.
(23) M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).
(24) L. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 1549 (1968).
(25) A. M. Sargeson, *Aust. J. Chem.*, **17**, 385 (1964).
(26) D. R. Stranks and J. K. Yandell, *Inorg. Chem.*, **9**, 751 (1970).
(27) D. A. Loeliger and H. Taube, *Inorg. Chem.*, **5**, 1376 (1966).
(28) C. Bifano and R. G. Linck, *Inorg. Chem.*, **7**, 908 (1968).
(29) J. H. Espenson and J. P. Birk, *Inorg. Chem.*, **9**, 251 (1970).
(30) J. P. Birk, *Inorg. Chem.*, **9**, 735 (1970).
(31) J. N. Armor and A. Haim, *J. Am. Chem. Soc.*, **93**, 867 (1971).

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Chemistry and Optical Properties of 4d and 5d Transition Metal Compounds. IV. Magnetic Circular Dichroism Characterization of the Low-Energy Charge-Transfer Bands of $[Ru^{III}(NH_3)_5L]^{2+}$

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The low-energy, intense electronic excitations of $[Ru^{III}(NH_3)_5L]^{2+}$ are assigned to the charge-transfer process $e(\sim\pi L) \rightarrow t_2(\sim 4d\ Ru)$, and the relevant spin–orbit states are $\Gamma_7[{}^2B + {}^2E; {}^2T_{2g}(t_{2g}{}^5)] \rightarrow (\Gamma_6'[{}^2E'(\pi^3; \sim L)] + \Gamma_7'[{}^2E'(\pi^3; \sim L)])$. It is found that the order is $\Gamma_7' < \Gamma_6'$ for these two spin–orbit components of the excited state, ${}^2E'(\pi^3; \sim L)$, with the hole localized on ligand L. The conclusions are based on (i) measurements of the temperature dependence of the electronic absorption and magnetic circular dichroism (MCD) intensities of the low-energy region of $[Ru(NH_3)_5Br]Br_2$, (ii) the sign of the net intensity of Faraday *C* parameters, (iii) the relative energies of bands for complexes with $L^- = NCO^-$, Cl^-, and Br^-; and (iv) the agreement of results of reliable computational models with the experimental data. Γ_6' of $\Gamma_7 \rightarrow (\Gamma_6' + \Gamma_7')$ is experimentally found to have the dominating positive MCD activity as is predicted computationally with great reliance.

Introduction

We have had occasion recently to report[2] the synthesis and optical spectra of several ruthenium(III) d^5 molecule ions of C_{4v} symmetry having the formula $[Ru(NH_3)_5L]^{2+}$, where L^- is NCO^-, OAc^-, SCN^-, $SeCN^-$, or Cl^-. Optical spectra of the complex ions with L^- being Cl^-, Br^-, and I^- were also given by Hartmann and Buschbeck.[3] The interesting common feature about all of these spectra is the intense ($\epsilon_{max} \gtrsim 2000$; $\gtrsim 2$ D^2) optical band, the lowest energy band in each case as shown in Figure 1 for $[Ru(NH_3)_5L]^{2+}$, where L^- is NCO^-, Cl^-, or Br^-, for example. It then seemed reasonable to suggest that these intense bands originate from the configuration change $\sim\pi L \rightarrow t_2(\sim 4d\ Ru)$, and in C_{4v} notation it was suggested[2] that it may be the ligand-to-metal transition $e^4(\sim\pi L) \rightarrow e^3[(xz, yz)^3; \sim 4d\ Ru]$ or $\Gamma_7({}^2E) \rightarrow (\Gamma_6' + \Gamma_7')({}^2E')$ (Figure 2). We have now discovered that MCD confirms the suggestion that the excitation originates from Γ_7, and this Kramers ground state now has been found to be composed