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Structural and Mechanistic Studies of Coordination Compounds. VII.[1] The Apparently Abnormal Behavior in the Acid Hydrolysis of *trans*-Chloroammine(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Cation

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The preparation and characterization of *trans*-Co(cyclam)NH_3Cl^{2+} cation is described. The apparently abnormal behavior in the preferential release of coordinated ammonia rather than chloride in the acid hydrolysis of *trans*-[Co(cyclam)NH_3Cl]Cl_2 has been unambiguously shown to arise from an unfavorable equilibrium constant for the more rapid chloride aquation of this cation. Kinetically, the first-order chloride aquation rate constant is slower than those of the corresponding bis(ethylenediamine) and tetraammine analogs, whereas the second-order chloride base hydrolysis rate constant is faster. These results are satisfactorily explained in terms of the thermodynamic and kinetic nephelauxetic effects of cyclam on the central cobalt(III) ion.

Introduction

It is well known that coordinated ammonia in octahedral cobalt(III)–amine complexes is very stable with respect to substitution by other ligands in solutions. Apart from photochemical reactions which deal essentially with reactions of complexes in electronic excited states,[2] all the well-studied thermal ligand substitution reactions of complexes of the type $Co(NH_3)_5X^{n+}$ ($X = F^-, Cl^-, Br^-, I^-, NCS^-, NO_2^-, H_2PO_4^-$, and HPO_4^{2-}) and of the type *cis*- and *trans*-$Co(en)_2NH_3X^{2+}$ (en = ethylenediamine; $X = Cl^-$ and Br^-) in aqueous solution only involve the release of the group X.[3] Release of NH_3 has never been observed under normal conditions.

In an earlier communication[4] we reported that an acidic solution of *trans*-[Co(cyclam)NH_3Cl]Cl_2, where cyclam represents 1,4,8,11-tetraazacyclotetradecane, underwent a distinct spectral change with isosbestic points maintained at 467 and 590 nm in the visible region. The final solution was green and its spectrum was consistent with the presence of a mixture of *trans*-Co(cyclam)OH_2Cl^{2+} and *trans*-Co(cyclam)Cl_2^+. It was inferred that coordinated ammonia rather than chloride was abnormally released in accordance with the following reactions. This paper was designed to investigate the origin of this abnormal behavior.

$$\textit{trans}\text{-Co(cyclam)}NH_3Cl^{2+} + H_2O \xrightarrow{\text{slow}} \textit{trans}\text{-Co(cyclam)}OH_2Cl^{2+} + NH_3 \qquad (1)$$

$$\textit{trans}\text{-Co(cyclam)}OH_2Cl^{2+} + Cl^- \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \textit{trans}\text{-Co(cyclam)}Cl_2^+ + H_2O \qquad (2)$$

Experimental Section

The compound *trans*-[Co(cyclam)NH_3Cl]$Cl_2\cdot H_2O$ was prepared by two different methods.

(1) A solution (5 ml) of liquid ammonia in dimethyl sulfoxide (1:10) was added with stirring to a suspension of *trans*-[Co(cyclam)Cl_2]Cl[5] (1.0 g, 2.7 mmol) in dimethyl sulfoxide (30 ml). Stirring was continued until all the solid had gone into solution which subsequently turned red. An excess of acetone was slowly added to the filtered solution to precipitate the crude product. The compound was recrystallized by dissolving the crude product in a minimum amount of dilute hydrochloric acid (1 *M*) and acetone was slowly added with stirring to the filtered solution until yellow crystals of *trans*-diammine impurity began to appear. These solids were filtered off and an excess of acetone was added to the mother solution to precipitate the remaining compounds. This procedure of fractional recrystallization was repeated (about three times) until the final compound was red and gave a constant absorption spectrum; yield 0.6 g, 60%. *Anal.* Calcd for [Co($C_{10}H_{24}N_4$)NH_3Cl]$Cl_2\cdot H_2O$: C, 30.0; H, 7.2; N, 17.4; total Cl, 26.6; ionic Cl, 17.7. Found: C, 29.3; H, 6.8; N, 17.4; total Cl, 25.8; ionic Cl, 17.6.

(2) Hydrogen peroxide (20 ml, 30%) was added to an ice-cold suspension of *trans*-[Co(cyclam)NCSCl]ClO_4 [5] (1.0 g, 2.2 mmol) in hydrochloric acid (20 ml, 6 *M*). After standing in the ice bath for 2 hr, the solution was warmed gently over a steam bath for 0.5 hr. Alcohol and ether were added to the cold filtered solution to precipitate the red crude product. The compound was recrystallized by adding alcohol and ether to a saturated solution of the crude product in 6 *M* hydrochloric acid. The red crystals were collected and washed with alcohol and ether. They were dried under vacuum at the boiling point of acetone; yield 0.45 g, 55%. *Anal.* Found: C, 30.1; H, 7.4; N, 17.8; total Cl, 26.9; ionic Cl, 17.6.

The **nitrate** was prepared by the addition of concentrated nitric acid (1 ml) to a saturated aqueous solution of the chloride (20 ml). Addition of alcohol and ether to the solution precipitated the desired product. *Anal.* Calcd for [Co($C_{10}H_{24}H_4$)NH_3Cl]$(NO_3)_2$: Cl, 8.2. Found: Cl, 8.2. The purity of the compound was further confirmed by the observation that the visible absorption spectrum of this compound was identical with that of the chloride.

Kinetics. The substitution reactions of *trans*-Co(cyclam)NH_3Cl^{2+} by chloride and thiocyanate in acid solutions were followed by sampling the appropriate reaction solution, made up at room temperature, into different Pyrex tubes which were sealed and placed "simultaneously" in a thermostat. The reaction temperature was maintained accurately to ±0.1°. After thermal equilibrium had been attained, tubes were withdrawn at intervals and quickly cooled in an ice bath. The solutions were then warmed to room temperature and the absorbance at the appropriate wavelength was measured with a Unicam SP700 spectrophotometer. The faster base hydrolysis of this complex cation was initiated by adding a thermostated buffer solution to the freshly prepared and well-thermostated aqueous solution of the complex. The reaction solution was immediately transferred to a silica cell at the temperature-controlled cell holder of a Unicam SP700 spectrophotometer and the changing absorbance at 500 nm was recorded as a function of time. The pH of the reaction solution was measured with a set of Radiometer micro electrodes, K4112 calomel electrode and G222C glass electrode, dipped into a separate test solution which was maintained under the same condition in the thermostated silica cell. The pH was found unchanged with the reaction.

Analysis. Elemental analysis of C, H, N, and Cl was done by the Australian Microanalytical Service, Division of Applied Chemistry, CSIRO, University of Melbourne. In the absence of ionic halide, thiocyanate was analyzed by the titrimetric method against standard silver nitrate solution using ferric alum indicator. Ammonia was analyzed spectrophotometrically as indophenol following the procedure of Bolleter, Bushman, and Tidwell.[6]

Physical Measurements. The visible and ultraviolet electronic

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[1] Part VI: C. K. Poon and H. W. Tong, *J. Chem. Soc., Dalton Trans.*, in press.

[2] V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, London, 1970, Chapter II.

[3] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

[4] K. S. Mok and C. K. Poon, *Chem. Commun.*, 1358 (1971).

[5] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 4, 1102 (1965).

[6] W. T. Bolleter, C. J. Bushman, and P. W. Tidwell, *Anal. Chem.*, 33, 592 (1961).

absorption spectra of complex solutions were measured on either a Unicam SP700 or SP8000 spectrophotometer. Infrared spectra of Nujol mulls between KBr windows were measured with a Perkin-Elmer 337 spectrophotometer. The pH of buffer solutions was measured with a Radiometer pH meter, Type PHM26.

Results

(1) Kinetics of Substitution Reactions by Chloride Ions. It was demonstrated previously[4] that the observable acid hydrolysis of *trans*-[Co(cyclam)NH_3Cl]Cl_2 in 0.01 *M* $HClO_4$ led abnormally to the formation of *trans*-Co(cyclam)OH_2Cl^{2+} which then rapidly picked up a chloride to establish an equilibrium between *trans*-Co(cyclam)Cl_2^+ and the chloroaquo cation (eq 1 and 2). Preliminary kinetic studies showed that the presence of chloride did not affect the rate of ammonia release. In order to follow the reaction as a function of acid concentration and at a constant ionic strength, the reaction solutions were kept at a constant chloride concentration (0.50 *M*) with varying amounts of hydrochloric acid and sodium chloride. The pseudo-first-order rate constant, k_{obsd}, was obtained from the plot of log $(D_\infty - D_t)$ against time, where D_∞ and D_t are the absorbance at 315 nm at the end of the reaction and at time *t*, respectively. The results are collected in Table I.

(2) Kinetics of Substitution Reactions by Thiocyanate Ions. When *trans*-Co(cyclam)NH_3Cl^{2+} was dissolved in 0.01 *M* nitric acid containing 0.2 *M* thiocyanate ions, the visible absorption spectrum slowly changed with time, with maintenance of an isosbestic point at 568 nm. The initial spectrum was identical with that of the starting *trans*-chloroammine complex. The final spectrum, with the absorption peak developed at 510 nm, was distinctly different from those[5] of *trans*-Co(cyclam)NCSCl$^+$ and *cis*- and *trans*-Co(cyclam)$(NCS)_2^+$; but it was very similar to that of $Co(NH_3)_5 \cdot NCS^{2+}$.[7] Addition of alcohol and ether to this final solution precipitated a red compound which could be converted to the perchlorate by the addition of sodium perchlorate to a saturated aqueous solution of the compound. The analytical results of the compound were consistent with the calculated values for [Co(cyclam)NH_3NCS]$(ClO_4)_2$. *Anal.* Calcd: coordinated Cl^-, 0; NCS^-, 10.9; NH_3, 3.1. Found: coordinated Cl^-, 0; NCS^-, 10.7; NH_3, 2.8. The presence of infrared bands at 2050 and 850 cm^{-1} confirmed the presence of thiocyanate in the complex. The appearance of a doublet at 889 and 901 cm^{-1} and a band at 812 cm^{-1} could be taken to assign a *trans*-configuration to this compound (see Discussion). Further reaction of this red compound with more thiocyanate ion in acidic solution very slowly gave a final product, the absorption spectrum of which was identical with that of *trans*-Co(cyclam)$(NCS)_2^+$. It can, therefore, be concluded that chloride is released from *trans*-Co(cyclam)NH_3Cl^{2+} to give *trans*-Co(cyclam)NH_3NCS^{2+} as the first reaction product. The reaction was followed spectrophotometrically by measuring the changing absorbance as a function of time at 510 nm and the first-order rate constant, obtained from the slope of the standard semilogarithmic plot, was found to be independent of the thiocyanate concentration. Reactions were, therefore, studied at a fixed thiocyanate concentration (0.02 *M*). Attempts to follow the reaction at some higher acid concentrations were complicated by some side redox reactions with thiocyanate. The rate data determined at pH 2 were collected in Table II.

Table I. Observed First-Order Rate Constants for the Reaction[a] *trans*-Co(cyclam)NH_3Cl^{2+} + H^+ + Cl^- → *trans*-Co(cyclam)Cl_2^+ + NH_4^+

Temp, °C	[H^+], *M*	$10^5 k_{\text{obsd}}$,[b] sec^{-1}	$10^6 k_1$,[b] sec^{-1}	$10^7 k_2$,[b] *M*$^{-1}$ sec^{-1}
78.3	0.01	0.510	0.08	0.43
78.3	0.02	0.294		
78.3	0.05	0.164		
78.3	0.10	0.115		
78.3	0.30	0.100		
78.3	0.50	0.092		
86.6	0.01	2.00	2.7	1.7
86.6	0.02	1.15		
86.6	0.05	0.576		
86.6	0.10	0.465		
86.6	0.30	0.306		
86.6	0.50	0.290		
94.3	0.01	6.50	8.7	5.6
94.3	0.02	3.66		
94.3	0.05	2.03		
94.3	0.10	1.29		
94.3	0.30	1.14		
94.3	0.50	0.95		

[a] Conditions: [Cl^-] = 0.50 *M*; [complex] between 1.20 and 2.80 m*M*; $\mu = 0.51 \pm 0.01$ *M*. [b] $k_{\text{obsd}} = k_1 + k_2/[H^+]$; k_1 and k_2 were obtained from the plots of k_{obsd} against $1/[H^+]$.

Table II. First-Order Rate Constants for the Reaction[a] *trans*-Co(cyclam)NH_3Cl^{2+} + NCS^- → *trans*-Co(cyclam)NH_3NCS^{2+} + Cl^-

Temp, °C	$10^4 k$,[b] sec^{-1}
72.4	0.66 ± 0.02
78.4	1.32 ± 0.02
83.8	2.56 ± 0.08

[a] [HNO_3] = 0.01 *M*; [NCS^-] = 0.20 *M*; [complex] between 1.20 and 2.80 mM; $\mu = 0.51 \pm 0.01$ *M*, maintained constant with 0.29 *M* $NaNO_3$. [b] An average of two separate determinations.

(3) Base Hydrolysis. The base hydrolysis of *trans*-Co(cyclam)NH_3Cl^{2+} was most conveniently followed in a 2:6 lutidine-nitric acid buffer system. The visible absorption spectrum slowly changed with time with an isosbestic point maintained at 555 nm. The initial spectrum was identical with that of the starting complex. Titration of the final acidified solution indicated that the coordinated chloride was released. Addition of an excess of chloride to the final acidified solution slowly shifted the absorption spectrum back to the starting *trans*-chloroammine complex. It can be, therefore, concluded that the base hydrolysis of this complex cation leads to the formation of *trans*-Co(cyclam)NH_3OH^{2+}. The reaction was studied spectrophotometrically at 500 nm where the absorption peak of the final spectrum occurs. The observed pseudo-first-order rate constants, k_{obsd}, were obtained from the standard semilogarithmic plots. The hydroxide ion concentration in each of the runs was obtained by measuring the pH of the reaction solution at the reaction temperature. The ionic product of water, K_w, at the same temperature was obtained from the appropriate curve of K_w *vs.* temperature.[8] The second-order rate constants were obtained from the slope of the linear plots of k_{obsd} *vs.* hydroxide ion concentrations. These data are collected in Table III.

(4) Mercury(II)-Induced Acid Hydrolysis. The spectrophotometric change of *trans*-[Co(cyclam)NH_3Cl]Cl_2 in 0.01 *M* perchloric acid containing an excess of mercuric perchlorate was distinctly different from that associated with spontaneous acid hydrolysis. Here, isosbestic points were maintained at 402 and 540 nm and the final solution was red. The final

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(7) D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, 9, 655 (1970).

(8) "Handbook of Chemistry and Physics," R. C. Weast, Ed., 48th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1968, p D-92.

Table III. Second-Order Rate Constants for the Reaction[a] *trans*-$Co(cyclam)NH_3Cl^{2+} + OH^- \rightarrow$ *trans*-$Co(cyclam)NH_3OH^{2+} + Cl^-$

Temp, °C	$10^{-4}k_{OH}$,[b] M^{-1} sec^{-1}
24.0	1.2 ± 0.1
33.2	3.8 ± 0.2
37.3	6.3 ± 0.2

[a] [Complex] between 1.20 and 2.80 mM; $\mu = 0.21 \pm 0.01$ M with $NaNO_3$. [b] From four different runs over a span of 0.8 pH unit.

spectrum was identical with that obtained by acidifying the final base hydrolyzed solution of the same complex. It is, therefore, clear that chloride is released in the mercury(II)-induced acid hydrolysis to give *trans*-$Co(cyclam)NH_3OH_2{}^{3+}$ as the final product.

(5) Determination of Aquation Equilibrium. When *trans*-$[Co(cyclam)NH_3Cl](NO_3)_2$ was dissolved in 0.01 M nitric acid and the visible absorption spectrum was measured, it was found that the spectral change at the initial stage of the reaction was distinctly different from that of *trans*-$[Co(cyclam)NH_3Cl]Cl_2$ in the same acidic solution. Here, isosbestic points at 404 and 540 nm were maintained for a short period of time with the absorbance in the 550–700-nm region gradually decreasing. The absorbance above 600 nm then began to rise with two new isosbestic points developed at 467 and 588 nm which were maintained to the end of the reaction. The resulting solution was green. In fact, the second stage of the reaction was virtually identical with that of the only observable reaction of *trans*-$[Co(cyclam)NH_3Cl]Cl_2$. Addition of silver nitrate at the beginning of the reaction immediately gave a white precipitate, suggesting that chloride was released from coordination. Assuming that the initial reaction of the nitrate salt obeyed the scheme

$$trans\text{-}[Co(cyclam)NH_3Cl]^{2+} + H_2O \overset{K}{\rightleftharpoons} trans\text{-}[Co(cyclam)NH_3OH_2]^{3+} + Cl^{-1}$$

the aquation equilibrium constant K was determined by allowing a known solution of the complex in 0.01 M nitric acid (1.0×10^{-2} M, 20 ml) to stand at 71.5° for 7 hr. During this time the chloride aquation was over 80% complete whereas the second-step reaction was not noticeable. The solution was then cooled and rapidly passed through a cation-exchange resin column of Amberlite IR-120 in the acid form. The effluent and washings which contained all the ionic chloride were titrated against standard silver nitrate solution. An average value of $(2.0 \pm 0.1) \times 10^{-4}$ M was obtained over two separate determinations.

Discussion

The assignment of a trans configuration to the new chloroammine complex was made on the basis of infrared spectroscopy. It was found true that the most consistent variation between the infrared spectra of cis and trans isomers of cobalt(III)-cyclam complexes had been found in the 800–900-cm^{-1} regions.[9] Complexes with a trans configuration show two bands near 900 cm^{-1} and one band near 810 cm^{-1} while those with a cis configuration have at least five bands spread fairly evenly between 800 and 910 cm^{-1}. The appearance of bands at 902, 890, 820 [$\rho_r(NH_3)$], and 814 cm^{-1} in this region of the infrared spectrum of the new $[Co(cyclam)NH_3Cl]Cl_2 \cdot H_2O$ has been taken to indicate a trans configuration.

A summary of the acid and base hydrolysis rate constants together with those of the corresponding bis(ethylenediamine) and tetraammine analogs are collected in Table IV.

Table IV. Rate Constants for the Acid and Base Hydrolysis of Complexes of the Type *trans*-$Co(am)_4NH_3Cl^{2+}$

$(am)_4$	$k_{1,Cl}$[a] (at 25°), sec^{-1}	k_{1,NH_3}[a] (at 25°), sec^{-1}	$k_{2,Cl}$[a] (at 0°), M^{-1} sec^{-1}	k_{2,NH_3}[a] (at 0°), M^{-1} sec^{-1}
cyclam	7.3×10^{-8} [b-d]	4.2×10^{-11} [b,d]	4.0×10^{2} [b,e]	1.7[b,d]
$(en)_2$	3.4×10^{-7} [f]		1.3[g]	
$(NH_3)_4$	1.7×10^{-6} [h]		1×10^{-2} [i]	

[a] $k_{1,Cl}$ and k_{1,NH_3} represent the first-order acid hydrolysis rate constants for the release of chloride and ammonia respectively; $k_{2,Cl}$ and k_{2,NH_3} represent the corresponding second-order base hydrolysis rate constants. [b] This work. [c] After substracting the base hydrolysis contribution at pH 2. [d] At $\mu = 0.51 \pm 0.01$ M. [e] At $\mu = 0.21 \pm 0.01$ M. [f] In 0.1–0.17 M $HClO_4$: M. L. Tobe, *J. Chem. Soc.*, 3776 (1959). [g] At $\mu = 0.005$ M: R. S. Nyholm and M. L. Tobe, *ibid.*, 1707 (1956). [h] In water; the rate constant was virtually independent of ionic strength (0.01–0.17 M): F. J. Garrick, *Trans. Faraday Soc.*, 33, 487 (1937). [i] Extrapolated from the published data at other temperatures; ionic strength was not reported, but it could be estimated from the published data to be about 0.04 M: A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, 9, 1261 (1955).

It is clear from Table IV that the coordinated chloride is some 1.7×10^3 times more labile at 25° than the coordinated ammonia. When the complex was started as the nitrate salt, ionic chloride was definitely detected at the beginning of the reaction, even though the final reaction product remains to be *trans*-$Co(cyclam)OH_2Cl^{2+}$. The apparently abnormal behavior in the acid hydrolysis of *trans*-$[Co(cyclam)NH_3Cl]Cl_2$[4] can now be explained in terms of an unfavorable equilibrium constant K (2.0×10^{-4} M at 71.5°) for the more rapid chloride aquation (eq 3) which shifts the equilibrium almost completely to the left and makes the hydrolysis of the coordinated chloride unnoticeable. This contrasts sharply with the corresponding equilibrium constant of 3.6×10^{-2} M at 62.6° for *trans*-$Co(en)_2NH_3Cl^{2+}$[10] and 2.4×10^{-1} M at 25.0° for $Co(NH_3)_5Cl^{2+}$.[11] Thus, for a concentration of 5×10^{-3} M of the starting *trans*-$[Co(cyclam)NH_3Cl]Cl_2$ complex only 2% of the chloroaquo species would be formed at equilibrium at 71.5°. To be consistent with the observed acid dependence of the rate of ammonia release, which could be represented by the general rate expression, $k_{obsd} = k_1 + k_{OH}[OH^-]$, the acid hydrolysis of *trans*-$Co(cyclam)NH_3Cl^{2+}$ can now be represented by the reaction scheme

$$trans\text{-}Co(cyclam)NH_3Cl^{2+} + OH_2 \overset{\text{fast}}{\rightleftharpoons} trans\text{-}Co(cyclam)NH_3OH_2{}^{3+} + Cl^- \qquad (3)$$

$$trans\text{-}Co(cyclam)NH_3Cl^{2+} + OH_2 \xrightarrow{k_1} trans\text{-}Co(cyclam)OH_2Cl^{2+} + NH_3 \qquad (4)$$

$$trans\text{-}Co(cyclam)NH_3Cl^{2+} + OH^- \xrightarrow{k_{OH}} trans\text{-}Co(cyclam)OHCl^{+} + NH_3 \qquad (5)$$

$$trans\text{-}Co(cyclam)OHCl^{+} + H^+ \overset{\text{very fast}}{\rightleftharpoons} trans\text{-}Co(cyclam)OH_2Cl^{2+} \qquad (6)$$

$$trans\text{-}Co(cyclam)OH_2Cl^{2+} + Cl^- \overset{\text{fast}}{\rightleftharpoons} trans\text{-}Co(cyclam)Cl_2{}^{+} + OH_2 \qquad (7)$$

$$NH_3 + H^+ \overset{\text{very fast}}{\rightleftharpoons} NH_4{}^{+} \qquad (8)$$

The much reduced thermodynamic stability of the coordinated ammonia and the increased stability of the coordinated chloride in *trans*-$Co(cyclam)NH_3Cl^{2+}$ with respect to acid hy-

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(9) C. K. Poon, *Inorg. Chim. Acta*, 5, 322 (1971).

(10) Calculated from the published data on the extent of aquation of *trans*-$[Co(en)_2NH_3Cl](Cl,ClO_4)$: R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956).

(11) Calculated from the published data: F. J. Garrick, *Trans. Faraday Soc.*, 33, 487 (1937).

drolysis as compared to those of bis(ethylenediamine) and tetraammine analogs can be understood in terms of the thermodynamic nephelauxetic effect of these various amine ligands on the central cobalt(III) ion. It has been discussed and successfully tested in a few systems[12-14] that the central cobalt(III) ion in cyclam complexes would very much prefer negatively charged ligands, such as Cl^- and OH^-, to neutral molecules, such as NH_3 and OH_2, than the corresponding bis(ethylenediamine) and tetraammine complexes. The relative stability of *trans*-$Co(am)_4NH_3OH_2{}^{3+}$ with respect to *trans*-$Co(am)_4OH_2Cl^{2+}$ and the latter with respect to *trans*-$Co(am)_4Cl_2{}^+$ would, therefore, be expected to decrease with $(am)_4$ as follows: $(NH_3)_4 > (en)_2 >$ cyclam. Thus, although the $Co\text{-}NH_3$ bond in bis(ethylenediamine) and tetraammine complexes is very stable that it is never broken under normal kinetic conditions, it is weakened enough in the cyclam complex that its dissociation is observed here. This also explains satisfactorily the much smaller chloride aquation equilibrium constant of this complex as compared to those of other lower charged Co^{III}-cyclam complexes, *e.g.*, $K = 7.0 \times 10^{-3}$ *M* at 70.4° for *trans*-$Co(cyclam)Cl_2{}^+$.[15]

When the rapid preequilibrium of eq 3 was disturbed and shifted completely to the right either by removing the chloride with Hg^{2+} or by converting the ammineaquo species into its conjugate base with hydroxide ion (base hydrolysis) or into the isothiocyanatoammine complex with thiocyanate, release of ammonia was not observed and the system appeared normal.

Assuming an SN1cb mechanism[3,13,16] for the base hydrolysis of cobalt(III)-amine complexes, the present investigation appears to give some indication on the nature of the amido conjugate base. It is controversial whether a *cis*- or a *trans*- conjugate base relative to the leaving group is responsible for the hydrolysis reaction whenever both types of amines are present in the complexes.[3,13,16-19] In the present investigation, the base hydrolysis of *trans*-$Co(cyclam)NH_3Cl^{2+}$ with ammonia release would probably occur *via* a cis conjugate base formed from one of the cyclam secondary nitrogens. Otherwise, the observed base-catalyzed path for the release of the coordinated ammonia would involve the breakage of $Co{=}NH_2$, which is rather unlikely.

The entropy of activation for the ammonia aquation ($\Delta S^\ddagger = 20$ eu) was very much higher than those of stereoretentive chloride and bromide aquation ($\Delta S^\ddagger \leqslant 0$) of other Co^{III}-cyclam complexes.[13] It is quite probable that the coordinated ammonia, by virtue of its acidic protons, is strongly solvated in the ground state. The lengthening of the $Co\text{-}NH_3$ bond in the transition state would seriously break down the structure of the solvating water molecules and would, therefore, be accompanied by a big increase in the entropy.

The facts, as shown in Table IV, that the chloride aquation rate constants of analogous *trans*-$Co(am)_4NH_3Cl^{2+}$ complexes decrease and that the base hydrolysis rate constants increase along the above series of $(am)_4$ further support the earlier proposal[12-14] concerning the influence of the kinetic nephelauxetic effect of these amine ligands on the central cobalt(III) ion.

Registry No. *trans*-$[Co(cyclam)NH_3Cl]Cl_2$, 34424-18-5; *trans*-$[Co(cyclam)Cl_2]Cl$, 15220-74-3; *trans*-$[Co(cyclam)NCSCl]ClO_4$, 34424-17-4; *trans*-$[Co(cyclam)NH_3Cl](NO_3)_2$, 40685-47-0; *trans*-$[Co(cyclam)Cl_2]^+$, 19973-61-6; *trans*-$[Co(cyclam)NH_3NCS](ClO_4)_2$, 40685-49-2; *trans*-$[Co(cyclam)NH_3OH]^{2+}$, 40685-50-5; *trans*-$[Co(cyclam)NH_3OH_2]^{3+}$, 40685-51-6; chlorine, 7782-50-5; thiocyanate, 302-04-5; hydroxide, 14280-30-9.

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(12) C. K. Poon, *J. Amer. Chem. Soc.*, 92, 4467 (1970).

(13) C. K. Poon, *Inorg. Chim. Acta Rev.*, 4, 123 (1970).

(14) C. K. Poon, *Coord. Chem. Rev.*, 10, 1 (1973).

(15) C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 2069 (1967).

(16) M. L. Tobe, *Accounts Chem. Res.*, 3, 377 (1970).

(17) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 89, 5129 (1967).

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

(19) D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 8, 1595 (1969).

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Stereospecificity in the $[Co(en)_2(N\text{-}Me\text{-}(S)\text{-}ala)]^{2+}$ and $[Co(en)_2((S)\text{-}pro)]^{2+}$ Ions

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Both $\Lambda\text{-}(+)_{589}$- (82%) and $\Delta\text{-}(-)_{589}$-$[Co(en)_2(N\text{-}Me\text{-}(S)\text{-}ala)]^{2+}$ (18 ± 2%) ions result on treating *trans*-$[Co(en)_2X_2]X$ (X = Cl, Br) with *N*-methyl-(*S*)-alanine in alkaline methanol solutions; a similar isomer distribution, 80 ± 2% $\Lambda\text{-}(+)_{589}$- and 20 ± 2% $\Delta\text{-}(-)_{589}$, is obtained by mutarotation on carbon and on cobalt. The analogous reaction with (*S*)-proline results in both $\Delta\text{-}(-)_{589}$- (74 ± 1%) and $\Lambda\text{-}(+)_{589}$- (26 ± 1%) $[Co(en)_2((S)\text{-}pro)]^{2+}$ being formed; equilibration on activated charcoal gives a 77 ± 1% $\Delta\text{-}(-)_{589}$-(*S*) and 23 ± 1% $\Lambda\text{-}(+)_{589}$-(*S*) isomer distribution.

Introduction

Investigations into the stereospecific coordination of N-substituted amino acids in asymmetric cobalt(III) complexes have provided some information on the kinetic and thermodynamic relationships between diastereoisomers containing adjacent asymmetric centers, one of which is a metal atom. The initial studies on the $[Co(en)_2(sar)]^{2+}$ [1] and β_2-$[Co(trien)(sar)]^{2+}$ [2] ions (sar = *N*-methylglycinate anion) established that the configuration about the N center of sarcosine was

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