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Structural and Mechanistic Studies of Coordination Compounds. I. The Preparation and Aquation of *trans*-Chloronitro- and *trans*-Chlorocyano(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Cations

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The preparation and characterization of *trans*-Co(cyclam)NO_2Cl^+ and *trans*-Co(cyclam)$CNCl^+$ cations are described. The assignment of geometric configuration is based on infrared spectroscopy. In dilute nitric acid solution, pH 2, these complexes, supplied as the nitrates, aquate with complete retention of configuration with the loss of about 60% (at 33.0°) and 90% (at 67.0°), respectively, of the coordinated chloride at equilibrium. The aquation kinetics of these two complex cations have been studied over a range of temperature, giving the following activation parameters: *trans*-Co(cyclam)NO_2Cl^+, $\Delta H^{\ddagger} = 20.6 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -9 \pm 0.5$ cal deg^{-1} mol^{-1}; *trans*-Co(cyclam)$CNCl^+$, $\Delta H^{\ddagger} = 23.5 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -9 \pm 1.5$ cal deg^{-1} mol^{-1}. The thermodynamic and kinetic stability of octahedral cobalt(III)–amine complexes have been discussed in terms of the nephelauxetic effect of various ligands on the central metal ion. A dissociative mechanism is assigned to the aquation of these complexes. An "internal SN1CB" mechanism has been proposed for the aquation of *trans*-Co(cyclam)$OHCl^+$.

Introduction

The interpretation of acid hydrolysis rate data of cobalt(III)–amine complexes in terms of the duality of reaction mechanism has been seriously questioned in recent years.[1,2] Lately, Langford suggested that all these reactions were essentially unimolecular and that the steric course arose from a duality of geometry of the five-coordinate intermediate.[3] In order to put this proposition into test, Poon and Tobe have started a program to examine the substitution reactions of complexes of the type *cis*- and *trans*-Co(cyclam)ACl^+ (where cyclam is 1,4,8,11-tetraazacyclotetradecane and A is a nonlabile ligand) and have reported the aquation of *cis*- and *trans*-Co(cyclam)Cl_2^+ and *trans*-Co(cyclam)-$OHCl^+$.[4–7] Their results supported Langford's proposition. Tobe further pointed out that for these reactions a square-pyramidal intermediate was invariably associated with a lower entropy of activation whereas a trigonal-bipyramidal intermediate was associated with a higher entropy of activation.[8]

trans-Co(cyclam)NO_2Cl^+ and *trans*-Co(cyclam)CN-Cl^+, on one hand, resemble the pair *trans*-Co-(cyclam)$OHCl^+$ and *trans*-Co(cyclam)Cl_2^+ in having a stereoretentive ligand, cyclam, while, on the other hand, they resemble the controversial pair *trans*-Co(en)$_2$-NO_2Cl^+ and *trans*-Co(en)$_2CNCl^+$ in having π-accepting ligands NO_2^- and CN^-. It would, therefore, be desirable to study the reactions of these two complexes in order to examine the general validity of Langford's and Tobe's propositions.

Experimental Section

Preparation of the Compounds. 1,4,8,11-Tetraazacyclotetradecane.—This compound was prepared by the method of Bosnich, Poon, and Tobe.[4]

***trans*-Chloronitro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Chloride.**—The perchlorate salt of this cation described by Bosnich, Poon, and Tobe is insoluble in water.[9] The soluble chloride salt was prepared by a modification of their method. A concentrated aqueous solution (20 ml) of cobalt(II) chloride hexahydrate (5.0 mM) was added with stirring to an aqueous solution (50 ml) of cyclam (5.0 mM) and sodium nitrite (30 mM) and was bubbled through the solution for 0.5 hr. A strong aqueous solution (20 ml) of sodium tetraphenylboron (5.0 mM) was slowly added to the filtered solution to precipitate the light brown crystals of *trans*-$[NO_2Co(cyclam)O_2Co(cyclam)NO_2](B(C_6H_5)_4)_2$, which were filtered off, washed with water, and air dried. The peroxo-bridged compound was converted into the chloride salt by dissolving the solid in a minimum amount of dry acetone. Addition of an excess of a strong solution of lithium chloride in acetone immediately precipitated the peroxo-bridged compound as a dark brown viscous liquid. The supernatant acetone solution was poured off and the residue was washed twice with fresh acetone and ether. Concentrated hydrochloric acid (2 ml) was added to dissolve the viscous mass. To the filtered reddish solution, excess alcohol and ether were added to precipitate the pinkish red *trans*-$[Co(cyclam)NO_2Cl]Cl$ which was recrystallized

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(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967.

(2) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965.

(3) C. H. Langford, *Inorg. Chem.*, **3**, 228 (1964).

(4) B. Bosnich, C. K. Poon, and M. L. Tobe, *ibid.*, **4**, 1102 (1965).

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

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

(7) C. K. Poon and M. L. Tobe, *ibid.*, *A*, 1549 (1968).

(8) M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).

(9) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **5**, 1514 (1966).

from 6 *M* hydrochloric acid. The crystals were filtered off, washed with alcohol and ether, and air dried; yield 40%. *Anal.* Calcd for $[Co(C_{10}H_{24}N_4)NO_2Cl]Cl$: C, 31.9; H, 6.4; N, 18.6; total Cl, 18.9; ionic Cl, 9.43. Found: C, 32.3; H, 6.6; N, 18.6; total Cl, 18.9; ionic Cl, 9.45.

The **nitrate** was prepared by adding dropwise concentrated nitric acid to a saturated solution of the chloride (2.0 m*M*) in 6 *M* hydrochloric acid. The crystals were filtered off, washed with alcohol and ether, and air dried; yield 55%. *Anal.* Calcd for $[Co(C_{10}H_{24}N_4)NO_2Cl]NO_3$: Cl, 8.82. Found: Cl, 8.85.

***trans*-Chlorocyano(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Chloride.**—This compound was prepared from *trans*-[Co(cyclam)Cl_2]Cl through several intermediates. These intermediates were only partially characterized by comparing their infrared and visible spectra with those of the established bis-ethylenediamine analogs.

***trans*-[Co(cyclam)Cl_2]Cl.**—This compound was prepared by the method of Bosnich, Poon, and Tobe.[4]

***trans*-Co(cyclam)SO_3Cl.**—An aqueous solution (10 ml) of an equivalent amount of sodium sulfite heptahydrate (2.6 m*M*) was added with stirring to an aqueous solution (30 ml) of *trans*-[Co(cyclam)Cl_2]Cl (2.6 m*M*). Pale red crystals were obtained by adding an excess of alcohol and ether to the filtered red solution; yield 60%.

***trans*-Co(cyclam)SO_3CN.**—An aqueous solution (5 ml) of an equivalent amount of sodium cyanide (2.6 m*M*) was added with stirring to an aqueous solution (15 ml) of *trans*-Co(cyclam)SO_3Cl (2.6 m*M*). Excess acetone was added to the filtered yellow solution to precipitate *trans*-Co(cyclam)SO_3CN; yield 43%.

***trans*-[Co(cyclam)CNCl]Cl.**—*trans*-Co(cyclam)SO_3CN (2.7 m*M*) was added little by little to a stirred solution of concentrated hydrochloric acid (4 ml). After the addition had been completed, the solution was slightly warmed for 0.5 hr. Excess alcohol and ether were then added to the filtered solution to precipitate the yellow *trans*-[Co(cyclam)CNCl]Cl, which could be recrystallized by the addition of alcohol and ether to a saturated aqueous solution. The crystals were filtered off, washed with alcohol and ether, and air dried; yield 73%. *Anal.* Calcd for $[Co(C_{10}H_{24}N_4)CNCl]Cl$: C, 37.1; H, 6.7; N, 19.7; total Cl, 19.9; ionic Cl, 9.96. Found: C, 35.8; H, 6.7; N, 19.3; total Cl, 19.7; ionic Cl, 9.87.

The **nitrate** was prepared by adding concentrated nitric acid to a saturated solution of the chloride. *Anal.* Calcd for $[Co(C_{10}H_{24}N_4)CNCl]NO_3$: Cl, 9.33. Found: Cl, 9.22.

Equilibrium Measurements.—A solution of known concentration of the compound (in 0.01 *M* nitric acid) was heated in a thermostat for about 10 aquation half-lives. The visible absorption spectrum of a sample of this final solution was recorded. Another sample of known volume was removed, cooled, and immediately passed down a cooled column of Amberlite IR-100 cation-exchange resin in the acid form. The effluent and the washings, which contained all the ionic chloride, was titrated against standard silver nitrate solution by Volhard's method.

Kinetics.—The aquation of *trans*-[Co(cyclam)NO_2Cl]NO_3 was followed by adding a known volume of the appropriate solvent (0.01 *M* HNO_3), previously brought to the reaction temperature, to a known weight of the complex. The solution was immediately transferred to a silica cell at the temperature-controlled cell holder of a Unicam SP 700C spectrophotometer and the reaction was followed *in situ* by locking the spectrophotometer at a fixed wavelength (529 mμ) and allowing the recorder pen to move at a known rate. For the slower aquation of *trans*-[Co(cyclam)CNCl]NO_3, the reaction solution, made up at room temperature, was sampled into different Pyrex tubes which were sealed and placed "simultaneously" in a thermostat. After thermal equilibrium had been attained, tubes were withdrawn at suitable intervals of time and quickly cooled in an ice bath. The solutions were then warmed up to room temperature and the absorbances at 350 mμ were measured using a Unicam SP 500 spectrophotometer.

Physical Measurements.—The visible and ultraviolet electronic absorption spectra of freshly prepared solutions were measured on either a Unicam SP 700C or SP 800 spectrophotometer as convenient. Infrared spectra of Nujol mulls between KBr windows were measured with a Perkin-Elmer 337 spectrophotometer.

Results

(1) Aquation Equilibria.—When *trans*-[Co(cyclam)NO_2Cl]NO_3 was dissolved in 0.01 *M* HNO_3, the visible absorption spectrum slowly changed with time, with the maintenance of two well-defined isosbestic points at 490 and 424 mμ. The initial spectrum was identical with that of the starting *trans*-chloronitro complex. This indicated that the reaction was either of a single step or of multisteps with subsequent reactions proceeding very rapidly compared with the first. This also required that either a single light-absorbing species was formed or a mixture of species was formed at a constant ratio. When excess chloride was added to the final solution, the spectral change was just the reverse, retaining the same two isosbestic points. This strongly suggested that only a single product was formed in both the forward and backward reactions. That the longest wavelength absorption peak moved toward a shorter wavelength in the forward reaction is consistent with the replacement of the coordinated chloride by water in the reaction, since water is higher than chloride in the spectrochemical series. Release of the nitro group would have shifted the peak to the longer wavelength, however. With reference to the stereoretentive aquation of other *cis*- and *trans*-Co(cyclam)ACl^+($A^- = OH^-$, Cl^-) complexes,[6,7] one is forced to conclude that *trans*-Co(cyclam)NO_2Cl^+ in 0.01 *M* HNO_3 aquates reversibly with complete retention of configuration to an equilibrium mixture of *trans*-Co(cyclam)NO_2Cl^+ and *trans*-Co(cyclam)$NO_2H_2O^{2+}$. Similarly, *trans*-Co(cyclam)$CNCl^+$ in 0.01 *M* HNO_3 also aquates with retention of configuration to an equilibrium mixture. The changing visible absorption spectrum shows three isosbestic points at 460, 393, and 339 mμ. The equilibria may be illustrated by

$$\textit{trans}\text{-Co(cyclam)ACl}^+ + H_2O \overset{K}{\rightleftharpoons} \textit{trans}\text{-Co(cyclam)AH}_2O^{2+} + Cl^- \quad (A^- = NO_2^-, CN^-)$$

The equilibrium constants, determined by titrating the amount of ionic chloride in the equilibrium solutions, are collected in Table I.

Table I

Equilibrium Constants for the Following Reaction in 0.01 *M* HNO_3

$$\textit{trans}\text{-Co(cyclam)ACl}^+ + H_2O \overset{K}{\rightleftharpoons} \textit{trans}\text{-Co(cyclam)AH}_2O^{2+} + Cl^-$$

A	Temp, °C	$[RCl^+]$ initial,[a] m*M*	$[RH_2O^{2+}]$ equil,[a] m*M*	% aquated	10^4K, *M*
NO_2	33.2	3.45	2.00	58	2.76
NO_2	33.2	3.20	1.90	59	2.78
NO_2	33.2	3.10	1.80	58	2.49
CN	67.0	3.08	2.77	89.9	24.80
CN	67.0	3.84	3.35	87.2	22.90

[a] R stands for Co(cyclam)A.

(2) **Aquation.**—The studies of the aquation of *trans*-Co(cyclam)NO_2Cl^+ and *trans*-Co(cyclam)CN-Cl^+ were complicated by the reversibility of the respective reactions. Preliminary studies showed that the reverse processes, in the region of chloride concentration studied, followed a second-order kinetics, first order in each of the aquo complex and chloride concentrations. When the starting chloro complexes were supplied as the nitrate salts so as to satisfy the following conditions at time $t = 0$, [chloro complex] = a, [aquo complex] = $[Cl^-] = 0$; at time $t = t$, [aquo complex] = $[Cl^-] = x$; at time $t = \infty$ (equilibrium), [aquo complex] = $[Cl^-] = x_e$, the simplified expression for the opposed first- and second-order reactions could be used; *i.e.*

$$2.303 \log \frac{a x_e + x(a - x_e)}{a(x_e - x)} = k\frac{2a - x_e}{x_e}t$$

where k represents the aquation rate constant.[10]

In order to follow the reactions spectrophotometrically, a knowledge of the absorption spectra of the corresponding aquo complexes was necessary. Attempts to isolate these aquo complexes in pure crystalline form were unsuccessful. An indirect approach was used. A solution of the starting chloro complex in 0.01 M HNO_3 was allowed to reach equilibrium at the temperature at which the equilibrium constant had accurately been determined. It was then cooled to room temperature and the absorption spectrum was rapidly measured. From the knowledge of the equilibrium constant and the absorption spectrum of an authentic sample of the starting chloro complex, the spectrum of the corresponding aquo complex was determined.

The reaction was followed spectrophotometrically by measuring the absorbance as a function of time at the wavelength where the difference in the spectra of the chloro and aquo complexes was greatest. The quantities a, x, and x_e were calculated from the changing absorbance and the following molar absorptivities: ϵ_{NO_2Cl} 67.7 and $\epsilon_{NO_2H_2O}$ 37.0 M^{-1} cm^{-1} at 529 mμ; ϵ_{CNCl} 101.6 and ϵ_{CNH_2O} 78.9 M^{-1} cm^{-1} at 350 mμ. From the slope of the plot of log $[(ax_e + x(a - x_e))/a(x_e - x)]$ against time, the aquation rate constant, k, could be calculated. These data are collected in Tables II and III. Activation parameters were obtained from the plot of log (k/T) against $1/T$.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR THE AQUATION OF *trans*-[Co(cyclam)NO_2Cl]NO_3 IN 0.01 M HNO_3

Temp, °C	[Complex], mM	10^4k, sec^{-1}	Temp, °C	[Complex], mM	10^4k, sec^{-1}
30.0	2.03	0.79	37.8	2.51	1.85
30.0	3.00	0.74	37.8	3.17	1.91
30.0	3.58	0.82	37.8	3.52	1.88
33.2	1.55	1.06	42.3	2.29	3.34
33.2	3.22	1.21	42.3	2.69	2.79
33.2	3.48	1.05	42.3	3.03	3.05
			45.0	2.48	4.10

TABLE III

FIRST-ORDER RATE CONSTANTS FOR THE AQUATION OF *trans*-[Co(cyclam)CNCl]NO_3 IN 0.01 M HNO_3

Temp, °C	[Complex], mM	10^4k, sec^{-1}	Temp, °C	[Complex], mM	10^4k, sec^{-1}
67.0	0.960	0.74	71.0	1.15	1.10
67.0	0.972	0.74	76.5	1.65	1.89
71.0	0.842	1.23	76.5	1.65	2.04
71.0	0.879	1.22			

Discussion

Configurations of the Complexes.—The assignment of geometric configuration is based on the comparison of the infrared spectra of the two new monochloro complexes with those of some well-defined and related complexes. It was pointed out elsewhere[11] that the most consistent variations between the infrared spectra of cis and trans isomers of cyclam complexes had been found in the region 800–910 cm^{-1}. Here, 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}. Some relevant results are collected in Table IV. The close similarity in the infrared spectra in the region 800–910 cm^{-1} between the two new complexes and other related trans cyclam complexes has been taken to indicate a trans configuration. The above assignment must still be taken as tentative until complexes of the corresponding cis isomers are prepared and their infrared spectra are compared. The assignment is, on the other hand, consistent with other observations that trans cobalt(III)–cyclam complexes react with complete retention of configuration.[5,6] Thus starting with *trans*-[Co(cyclam)-Cl_2]Cl, it would be expected that the trans isomer of chlorocyano complex would be formed. In fact, Bosnich, Poon, and Tobe have already pointed out that the breakage of a suitable binuclear peroxo-bridged cobalt(III)–cyclam complex would produce a trans mononuclear complex as the final product.[9]

Thermodynamic and Kinetic Behavior of the Complexes.—The replacement of two ethylenediamine molecules by one cyclam has two significant effects which are separately discussed below.

Thermodynamic Effect.—Thermodynamically, *trans*-Co(cyclam)ACl^+, where $A^- = Cl^-$, NO_2^-, and CN^-, are much more stable with respect to *trans*-Co(cyclam)AH_2O^{2+} than the corresponding bis-ethylenediamine analogs. The latter complexes, supplied as the nitrates, aquate with complete loss of the coordinated chloride[12,13] whereas under similar conditions, the cyclam complexes only partially release the chloride at equilibrium.[6] This difference in the relative stability of the chloro complexes has been explained elsewhere in terms of the different ability of various amine ligands to reduce the Racah interelectronic parameter B of the central Co(III) ion.[14] cyclam, being placed higher

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[10] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 187.

[11] C. K. Poon, Ph.D. Thesis, University of London, 1967, pp 102–105; C. K. Poon, *Inorg. Chim. Acta*, in press.

[12] S. Asperger and C. K. Ingold, *J. Chem. Soc.*, 2862 (1956).

[13] S. C. Chan and M. L. Tobe, *ibid.*, 514 (1963).

[14] C. K. Poon, *J. Amer. Chem. Soc.*, **92**, 4467 (1970).

TABLE IV

INFRARED ABSORPTION SPECTRA (NUJOL MULLS) IN THE REGION 800–910 CM^{-1} OF SOME CIS AND TRANS cyclam COMPLEXES[a]

Complexes	Freq of absorption bands,[b] cm^{-1}							
cis-$[Co(cyclam)Cl_2]Cl$		890 w	872 s	869 s	841 w	824 w		808 s
cis-$[Co(cyclam)(NO_2)_2](PtCl_6)_{1/2}$			877 m	860 m	842 m	832 m	822 s[c]	805 m
trans-$[Co(cyclam)Cl_2]Cl$	906 s	888 s						818 s
trans-$[Co(cyclam)(NO_2)_2](PtCl_6)_{1/2}$	892 m, sh	887 m					830 s[c]	820 m, sh
trans-$[Co(cyclam)(CN)_2]Cl$	903 m	893 m						822 m
trans-$[Co(cyclam)NO_2Cl]NO_3$	898 m	885 m					829 s[c]	820 m, sh
trans-$[Co(cyclam)CNCl]NO_3$	903 m	891 m						825 m

[a] Data were taken from ref 11. [b] Abbreviations: s, strong; m, medium; w, weak; sh, shoulder. [c] This band arises from $\delta(NO_2)$.

than ethylenediamine in the nephelauxetic series[14] as defined by Jørgensen,[15] gives rise to a greater delocalization of the 3d electrons away from the metal ion. Consequently, the metal ion tends to attract the donor lone-pair electrons closer to itself. This occurs more easily for negatively charged ligands, such as Cl^- and NO_2^-, than for neutral molecules, such as H_2O. This results in a greater stability of chloro–cyclam complexes with respect to their aquo complexes than the corresponding bis-ethylenediamine analogs.

Kinetic Effect.—Some of the rate constants extrapolated to 25°, the steric course, and the activation parameters relevant to the subsequent discussion are collected in Table V. From Table V, it is clear that the aquation rates of trans cyclam complexes, with the exception of *trans*-$Co(cyclam)OHCl^+$, are slower than those of the corresponding bis-ethylenediamine analogs. A special mechanism for the aquation of *trans*-$Co(cyclam)OHCl^+$ will be discussed later in the text. That the reduction in rate is greater for *trans*-$Co(cyclam)CNCl^+$ (170 times at 25°) than for *trans*-$Co(cyclam)Cl_2^+$ (32 times at 25°) strongly supports Langford's proposition that all these reactions were unimolecular. When the duality of reaction mechanism was formulated, it was assumed that the π-conjugative effect of the orienting ligand was of the most important factor to decide the reaction mechanism. If this assumption had been true, the steric restrictions on the formation of the trigonal-bipyramidal intermediate would have seriously affected the reactivity of only the chloro (a π donor) but not the cyano (a π acceptor) cyclam complexes. The reduction in rate for *trans*-$Co(cyclam)Cl_2^+$ should have been greater than that for *trans*-$Co(cyclam)CNCl^+$. The complete retention of configuration in the aquation of cyclam complexes is, therefore, consistent with a tetragonal-pyramidal intermediate. Tobe's idea of using entropies of activation to differentiate between the two types of reaction intermediates is supported by the present investigation. It is interesting, however, to note from Table V that there is a whole range of $\Delta S^\ddagger$ from −9 to +20 cal deg^{-1} mol^{-1}. This seems to run parallel with the tendency of the complexes to change the nature of the intermediate gradually from "good" tetragonal pyramidal to "good" trigonal bipyramidal. An extensive investigation of the relationship between $\Delta S^\ddagger$ and the nature of reaction intermediates has been started and we wish to postpone further discussion to a later paper.

TABLE V

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE AQUATION OF *trans*-$CoLACl^+$

L	A	$k_{25°}$, sec^{-1}	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, cal deg^{-1} mol^{-1}	% steric change	Ref
cyclam	OH	1.2×10^{-2}	18.1	−7	0	*a*
cyclam	Cl	1.1×10^{-6}	24.6	−3	0	*a*
cyclam	CN	4.8×10^{-7}	23.5	−9	0	*b*
cyclam	NO_2	4.3×10^{-5}	20.6	−9	0	*b*
$(en)_2$	OH	1.6×10^{-3}	25.9	+20	75	*c*
$(en)_2$	Cl	3.5×10^{-5}	26.2	+14	35	*c*
$(en)_2$	CN	8.2×10^{-5}	22.5	−2	0	*d*
$(en)_2$	NO_2	1.0×10^{-3}	20.9	−2	0	*e*

[a] Reference 6. [b] This work. [c] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961). [d] Reference 13. [e] Reference 12.

The slower aquation rates of *trans*-$Co(cyclam)ACl^+$ than those of the corresponding *trans*-$Co(en)_2ACl^+$ has been explained elsewhere in terms of the greater ability of cyclam to expand the 3d shell of the central metal ion.[14] Therefore, cyclam complexes would not have as great a demand as bis-ethylenediamine analogs to expel the leaving group in order to gain a greater delocalization of the 3d electrons into the vacated orbital so that the ground-state electronic repulsion could be reduced in the transition state. In both series, the labilizing power of nonlabile ligands follows the same pattern[14]: $OH^- > NO_2^- > Cl^- \sim CN^- > NCS^-$. It is interesting to note that Cl^- and CN^- are grouped together and yet their π-conjugative abilities, being operative in opposite directions, and their ligand field strengths are so vastly different. However, they are very similar in their nephelauxetic effect on Co(III) and it is, therefore, through a greater importance of this effect on reaction rate that the above observation could be explained.

The increased reactivity of *trans*-$Co(cyclam)OHCl^+$ compared to that of *trans*-$Co(en)_2OHCl^+$ cannot fit into the above discussion of nephelauxetic effect. An alternative mechanism was suggested by Poon to explain this exceptional labilizing power of a trans hydroxo group.[16]

It was demonstrated elsewhere that a coordinated hydroxo group could facilitate the amine proton exchange in Co(III)–cyclam complexes.[17] Thus, in the

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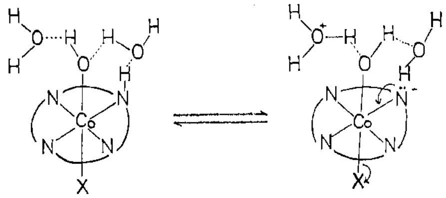
(15) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p 136.

(16) C. K. Poon, Ph.D. Thesis, University of London, 1967, p 163.

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

course of exchange, an "internal amido conjugative base" is momentarily generated. The amido group, NH_2^-, which is cis to the leaving group can now facilitate a dissociative reaction and profitably stabilize a tetragonal-pyramidal intermediate. This mechanism may, therefore, put the aquation rate of trans hydroxo complexes qualitatively midway between the rates of the base hydrolysis and aquation of other Co(III)-amine complexes. It is interesting to note that the 7.5 times increase in the aquation rate at 25° of *trans*-Co(cyclam)OHCl$^+$ compared to that of *trans*-Co(en)$_2$OHCl$^+$ agrees very well with the 8.0 times increase in the rate of base hydrolysis.[6,16] This high degree of consistency suggests that both types of reactions may very well proceed by the same mechanism. In the above comparison, the acid dissociation constants (of the amino proton) of the complexes would have been canceled out, thus making their difference unimportant in the above discussion.



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Substitution Reactions of Metallic Complexes of β,β′,β′′-Triaminotriethylamine. V. Kinetics of Acid Hydrolysis of Difluoro(triaminotriethylamine)cobalt(III)Ion[1]

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The kinetics of the primary acid hydrolysis reaction of $[Co(tren)F_2]^+$ ion [tren = β,β′,β′′-triaminotriethylamine, $N(CH_2CH_2NH_2)_3$] were studied in both neutral and acidic aqueous solutions. In acidic solutions, the reaction proceeded *via* an acid-independent pathway and also *via* an acid-catalyzed pathway involving an equilibrium between $Co(tren)F_2^+$ and $Co(tren)FFH^{2+}$ ions. The rate of the reaction is described by the rate law $-dC_t/dt = \{(k_0 + k_HK_{eq}[H^+])/(1 + K_{eq}[H^+])\}C_t$, where C_t is the total concentration of the complex in both protonated and nonprotonated forms, k_0 and k_H are the first-order rate constants for the acid hydrolysis reaction of the nonprotonated complex and protonated complex, respectively, and K_{eq} is the equilibrium constant for the protonation reaction. At 25.0°, the value of k_0 is 9.0×10^{-6} sec^{-1}, and the product k_HK_{eq} at ionic strength 0.5 *M* is 3.5×10^{-3} sec^{-1} M^{-1}. The activation parameters were calculated: $\Delta H^\ddagger = 22.3 \pm 0.6$ kcal mol^{-1} and $\Delta S^\ddagger = -6.5 \pm 2.0$ cal deg^{-1} mol^{-1} for the acid-independent path (k_0); $\Delta H^\ddagger = 21.0 \pm 0.3$ kcal mol^{-1} and $\Delta S^\ddagger = 2.3 \pm 1$ cal deg^{-1} mol^{-1} for the acid-catalyzed path (k_HK_{eq}) at ionic strength 0.5 *M*.

Introduction

Extensive investigations have been carried out on the kinetics of substitution reactions of cobalt(III) complexes of the type $Co(A)_4X_2^+$ where A represents a nonreplaceable monodentate or polydentate amine ligand and X represents the replaceable group, such as F^-, Cl^-, Br^-, and NO_2^-.[2]

In this laboratory we have been interested in the synthesis and kinetics of substitution reactions of octahedral cobalt(III) complexes of β,β′,β′′-triaminotriethylamine (tren).[3] As part of our study of the kinetics of acid hydrolysis reactions of dihalotriaminotriethylaminecobalt(III) complexes, we have investigated in this work the primary acid hydrolysis reaction of the difluoro(triaminotriethylamine)cobalt(III) ion. The results are presented and compared with similar data for the dichloro- and dibromo(triaminotriethylamine)cobalt(III) complexes and with those of the other fluoro-amine complexes.

Experimental Section

Materials.—Deionized water and reagent grade chemicals were used in all procedures. Sodium perchlorate used to adjust the ionic strength was anhydrous reagent grade quality. The deuterium oxide was obtained from Columbia Chemicals Co., Inc., and had an assay of 99.77%.

Preparation of Compounds. (1) **β,β′,β′′-Triaminotriethylamine Trihydrochloride.**—This compound was prepared by the method of Paoletti, Ciampolini, and Sacconi.[4]

(2) **Carbonato(triaminotriethylamine)cobalt(III) Perchlorate Monohydrate.**—The method of Scheidegger[5] was used for the preparation of this compound. *Anal.* Calcd for $[Co(tren)CO_3]ClO_4 \cdot H_2O$: C, 21.95; H, 5.23; N, 14.62; ClO_4, 26.00. Found: C, 22.53; H, 5.45; N, 14.40; ClO_4, 26.10.

(3) **Difluoro(triaminotriethylamine)cobalt(III) Perchlorate**

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(1) Presented at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 15, 1970.

(2) For review see F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967.

(3) (a) Part I: S. K. Madan, W. M. Reiff, and J. C. Bailar, Jr., *Inorg. Chem.*, **4**, 1366 (1965); (b) Part II: S. K. Madan and J. Peone, Jr., *ibid.*, **6**, 463 (1967); (c) Part III: S. K. Madan and J. Peone, Jr., *ibid.*, **7**, 824 (1968); (d) Part IV: W. V. Miller and S. K Madan, *ibid.*, **9**, 2362 (1970).

(4) P. Paoletti, M. Ciampolini, and L. Sacconi, *J. Chem. Soc.*, 3589 (1963).

(5) H. A. Scheidegger, Doctoral Thesis, E.T.H., Zurich, 1966.