Structural and Mechanistic Studies of Co-ordination Compounds. Part IV.[1] The Preparation, Aquation, and Base Hydrolysis of *trans*-Chloronitro- and *trans*-Bromonitro-(1,4,8,11-tetra-azacyclotetradecane)cobalt-(III) Cations

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The preparation and characterization of *trans*-[Co(cyclam)NO$_2$Br]$^+$ cation is described. The kinetics of the aquation and base hydrolysis of this complex cation and those of the base hydrolysis of *trans*-[Co(cyclam)NO$_2$Cl]$^+$ have been studied over a range of temperature. The first-order aquation rate constants are slower than those of the corresponding bis(ethylenediamine) and tetra-ammine analogues, whereas the second-order base hydrolysis rate constants are faster. These results support the earlier prediction made on the basis of the kinetic nephelauxetic effect of these amine ligands on the central cobalt(III) ion. Unimolecular mechanisms are assigned to these reactions.

THE influence of nephelauxetic effect on thermodynamic and kinetic stability of octahedral cobalt(III)–amine complexes has been discussed and successfully tested in a few different systems.[2-4] Much work has been done on complexes containing the π-accepting NO$_2^-$ group as an orienting ligand. It was predicted that unimolecular aquation rate constants of complexes of the type *trans*-[Co(Am)$_4$NO$_2$X]$^+$, where X represents a monodentate leaving group, would decrease along the following series of (Am)$_4$: (NH$_3$)$_4$ > (en)$_2$ > cyclam, where en represents ethylenediamine and cyclam represents 1,4,8,11-tetra-azacyclotetradecane, and that the base hydrolysis rate constants would vary in the opposite direction.[3] This prediction was found true for the chloro- and bromo-tetra-ammine and bis(ethylenediamine) systems.[3] For the cyclam series, only the aquation rate data of *trans*-[Co(cyclam)NO$_2$Cl]$^+$ are available for comparison and they are found to be consistent with the above proposition.[4] In order to test the applicability of the kinetic nephelauxetic effect more fully, it is desirable to obtain more suitable rate data of the cyclam system for comparison. This paper describes the preparation, aquation, and base hydrolysis of *trans*-[Co(cyclam)NO$_2$Br]$^+$ and the base hydrolysis of *trans*-[Co(cyclam)NO$_2$Cl]$^+$.

EXPERIMENTAL

1,4,8,11-Tetra-azacyclotetradecane (cyclam) was prepared by the method of Bosnich, Poon, and Tobe.[5]

trans-Bromonitro(1,4,8,11-tetra-azacyclotetradecane)-*cobalt*(III) *Bromide*.—The perchlorate salt of this cation described by Bosnich, Poon, and Tobe is insoluble in water.[6] The soluble bromide salt was prepared by a modification of their method. A methanolic solution (20 ml) of cobalt bromide (1·2 g, 5·0 mmol) was added with stirring to a clear methanolic solution (20 ml) of cyclam (1 g, 5·0 mmol) and sodium nitrite (0·35 g, 5·0 mmol). The solution turned deep brown and *trans*-[NO$_2$Co(cyclam)-O$_2$Co(cyclam)NO$_2$]Br$_2$ began to crystallize out. The crystals were filtered off, washed with acetone and ether, and were air dried. More of the compound could be obtained by adding acetone to the mother liquor. Addition of bromine-free hydrobromic acid (48%, 20 ml) to the

peroxo-bridged compound decomposed it into *trans*-[Co(cyclam)NO$_2$Br]$^+$, which gradually separated out from the solution as the pinkish red bromide. The compound was recrystallized from 48% hydrobromic acid. The crystals were filtered off, washed with alcohol and ether, and were air dried (yield: 0·5 g, 22%) [Found: C, 25·7; H, 4·7; Br, 34·3; N, 15·0. Co(C$_{10}$H$_{24}$N$_4$)(NO$_2$)(Br$_2$) requires C, 25·8; H, 5·2; Br, 34·4; N, 15·1%]. Attempts to prepare the nitrate salt were unsuccessful.

trans-Chloronitro(1,4,8,11-tetra-azacyclotetradecane)cobalt-(III) *Nitrate*.—The preparation of this compound followed closely the method described in a previous paper by decomposing *trans*-[O$_2$NCo(cyclam)O$_2$Co(cyclam)NO$_2$]Cl$_2$ with concentrated hydrochloric acid,[4] except that the peroxo-bridged intermediate was isolated by a different method. Here the peroxo-bridged compound was prepared in methanolic solution rather than in water in the same manner by adding a cobalt chloride solution to a solution containing the stoicheiometric amount of cyclam and sodium nitrite. Addition of an excess of ether precipitated the desired product. The yield was about three quarters of that of the previous method. This method, however, was more direct and the use of the expensive sodium tetraphenylborate could be avoided.

Kinetics.—The aquation of *trans*-[Co(cyclam)NO$_2$Br]Br was followed spectrophotometrically *in situ* at 552 nm using a Unicam SP 700 recording spectrophotometer in a conventional manner, which has been described.[4] The base hydrolysis of both complex cations was studied spectrophotometrically in a similar manner except that here the appropriate buffer was added to the complex previously dissolved in distilled water in order to start the reaction.

Physical Measurements.—The visible and u.v. electronic absorption spectra of freshly prepared solutions were measured on either a Unicam SP 700 or SP 800 spectrophotometer as convenient. I.r. 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

The behaviour of *trans*-[Co(cyclam)NO$_2$Br]$^+$ in 0·01M-nitric acid was very similar to that of *trans*-[Co(cyclam)-

[1] Part III, W. K. Chau and C. K. Poon, *J. Chem. Soc. (A)*, 1971, 3087.
[2] C. K. Poon, *J. Amer. Chem. Soc.*, 1970, **92**, 4467.
[3] C. K. Poon and H. W. Tong, *J. Chem. Soc. (A)*, 1971, 2151.
[4] K. S. Mok and C. K. Poon, *Inorg. Chem.*, 1971, **10**, 225.
[5] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.
[6] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1966, **5**, 1514.

$NO_2Cl]^+$.[4] Here, the changing visible spectrum, which shifted the absorption peak towards a shorter wavelength, maintained isosbestic points at 441 and 498 nm throughout the entire reaction. These isosbestic points were crossed by the calculated spectrum of trans-$[Co(cyclam)NO_2OH_2]^{2+}$. The initial spectrum was identical with that of the starting bromonitro-complex. Addition of an excess of bromide forced the reaction to retrace its own path. It can, therefore, be concluded that trans-$[Co(cyclam)NO_2Br]^+$ aquates reversibly with complete retention of configuration to an equilibrium mixture according to the following equation:

$$\text{trans-}[Co(cyclam)NO_2Br]^+ + H_2O \overset{K}{\rightleftharpoons}$$
$$\text{trans-}[Co(cyclam)NO_2OH_2]^{2+} + Br^-$$
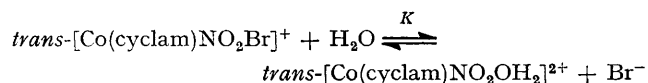
where K represents the equilibrium constant of the reaction.

The reaction was followed spectrophotometrically at 552 nm where the difference in absorbance between the initial and final visible spectra was greatest. Although attempts to isolate trans-$[Co(cyclam)NO_2OH_2]^{2+}$ in any pure crystalline salt have been unsuccessful, this complex cation has, however, been adequately characterized in solution and its visible absorption spectrum has been accurately determined.[4] From the knowledge of the molar absorptivities of trans-$[Co(cyclam)NO_2Br]^+$ and trans-$[Co(cyclam)NO_2OH_2]^{2+}$ at 552 nm (86.1 and $18.8 M^{-1} cm^{-1}$ respectively) and from the observed changing absorbance at the same wavelength, the concentration X of the aquo-complex generated at time t could be determined. The forward aquation rate constant, k_1, is given by the expression:

$$\ln\left[\frac{X_e(a^2 + aX_e + aX - X_eX)}{a(a + X_e)(X_e - X)}\right] = k_1\left[\frac{a^2 + 2aX_e - X_e^2}{X_e(a + X_e)}\right]t$$

where a represents the initial concentration of the starting bromo-complex and X_e the equilibrium concentration of the aquo-complex. The experimental values of k_1 were obtained from the linear plots of the left-hand expression against time. Good linear plots were obtained over 3 half-lives. From the values of a and X_e, the equilibrium constant, K, of the reaction could be calculated. The equilibrium constant so determined agreed well with the value determined independently by titrating the amount of

TABLE 1

First-order aquation rate constants and equilibrium constants for the reaction

$$\text{trans-}[Co(cyclam)NO_2Br]^+ + H_2O \rightleftharpoons$$
$$\text{trans-}[Co(cyclam)NO_2OH_2]^{2+} + Br^-$$
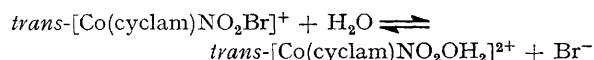
$[HNO_3] = 0.01M$; [Complex] between 2.41 and 3.93 mM

Temp. (°C)	10^4k_1 (s⁻¹)	10^2K (M)
18·35	2.39 ± 0.06 [a]	5.2 ± 0.1 [a]
23·7	4.67 ± 0.06 [b]	6.6 ± 0.3 [b]
28·9	8.50 ± 0.03 [a]	8.2 ± 0.2 [a]
32·4	13.20 ± 0.10 [a]	9.5 ± 0.3 [a]

[a] An average of 3 different runs. [b] An average of 4 different runs.

ionic bromide against standard silver nitrate solution in the equilibrated solution. These data are collected in Table 1. Activation parameters were obtained from the plot of

log (k_1/T) against $(1/T)$ where T represents the reaction temperature in absolute scale.

Preliminary studies of the base hydrolysis of trans-$[Co(cyclam)NO_2Cl]^+$ showed that the reaction was most conveniently studied in the pH 8.4—9.4 range (Borax, boric acid buffer). Studies of the changing visible spectrum showed that isosbestic points at 431 and 503 nm, the positions of which were independent of the pH of the solution, were maintained. When the final solutions were acidified with an excess of nitric acid and the visible absorption spectra were measured, it was found that these spectra were virtually the same as that of trans-$[Co(cyclam)NO_2OH_2]^{2+}$. It can be concluded that the base hydrolysis of trans-$[Co(cyclam)NO_2Cl]^+$ is complete and stereoretentive. The reaction was studied spectrophotometrically at 474 nm and the observed pseudo-first-order rate constants, k_{obs}, were obtained from the standard semilogarithmic plots of log $(D_t - D_\infty)$ vs. time, where D_t and D_∞ are respectively the absorbances at time t and after 10 half-lives. These plots were linear to three half-lives. 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, Kw, at the same temperature was obtained from the appropriate curve of Kw vs. temperature.[7] The second-order rate constants were obtained from the slope of the linear plots of k_{obs} vs. hydroxide-ion concentrations. The base hydrolysis of trans-$[Co(cyclam)-NO_2Br]^+$ was similarly studied at 418 nm in γ-collidine–nitric acid buffer solutions (pH 7.2—8.0 range). Here, isosbestic points were maintained at 444 and 505 nm. These data are collected in Table 2.

TABLE 2

Second-order rate constants for the reactions

$$\text{trans-}[Co(cyclam)NO_2X]^+ + OH^- \longrightarrow$$
$$\text{trans-}[Co(cyclam)NO_2OH]^+ + X^-$$
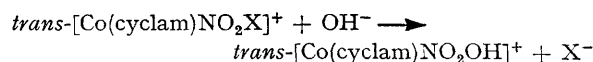
$\mu = 0.3M$ for $X = Cl^-$ and $0.05M$ for $X = Br^-$ with $NaNO_3$; [Complex] between 1.40 and 2.40 mM

X	Temp. (°C)	k_2 * (M⁻¹ s⁻¹)
Cl^-	21·0	$3.77 \pm 0.08 \times 10^2$
Cl^-	26·9	$7.55 \pm 0.20 \times 10^2$
Cl^-	34·0	$16.1 \pm 0.40 \times 10^2$
Br^-	22·3	$1.01 \pm 0.05 \times 10^4$
Br^-	27·7	$1.97 \pm 0.05 \times 10^4$
Br^-	32·8	$3.15 \pm 0.10 \times 10^4$

* From 6 different runs over a span of 0.8 pH unit.

DISCUSSION

The assignment of a trans-configuration to the new bromonitro-complex was made on the basis of i.r. spectroscopy. It has been found true for all known cobalt(III)–cyclam complexes that the most consistent variation between the i.r. spectra of cis- and trans-isomers had been found in the 800—910 cm⁻¹ region. 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.[8] The appearance of bands at 898, 888, 825 $[\delta(NO_2)]$, and 810 cm⁻¹ in

[7] 'Handbook of Chemistry and Physics,' 48th edn., ed. R. C. Weast, Chemical Rubber Co., Ohio, 1968, D-92.
[8] C. K. Poon, Inorg. Chim. Acta, 1971, 5, 322.

this region of the i.r. spectrum of the new bromonitro-complex has been taken to indicate a *trans*-configuration.

TABLE 3

Aquation and base hydrolysis rate constants of complexes of the type *trans*-$[Co(Am)_4NO_2X]^+$

$(Am)_4$	X	$k_1{}^a$ (at 25°, s^{-1})	$\Delta S_1^{\ddagger\,a}$ (cal deg^{-1} mol^{-1})	$k_2{}^a$ (at 0°, M^{-1} s^{-1})
$(NH_3)_4$	Cl$^-$	$2\cdot7 \times 10^{-2\,b}$	$-4 \pm 1{}^b$	$3\cdot0 \times 10^{-3\,b}$
$(en)_2$	Cl$^-$	$9\cdot8 \times 10^{-4\,c}$	$-2{}^c$	$8\cdot0 \times 10^{-2\,c}$
$(cyclam)$	Cl$^-$	$4\cdot3 \times 10^{-5\,d}$	$-9 \pm 0\cdot5{}^d$	$2\cdot8 \times 10{}^e$
$(NH_3)_4$	Br$^-$	$7\cdot2 \times 10^{-2\,b}$	$1 \pm 1{}^b$	$1\cdot5 \times 10^{-2\,b}$
$(en)_2$	Br$^-$	$4\cdot2 \times 10^{-3\,f}$		$6\cdot8 \times 10^{-1\,g}$
$(cyclam)$	Br$^-$	$5\cdot5 \times 10^{-4\,e}$	$-3 \pm 1{}^e$	$8\cdot8 \times 10^{2\,e}$

^{a} k_1 Represents the first-order aquation rate constant and k_2 represents the second-order base hydrolysis rate constant. They were obtained by extrapolation. $\Delta S_1^{\ddagger}$ represents the entropy of activation for the aquation reaction. ^{b} Ref. 3. ^{c} S. Ašperger and C. K. Ingold, *J. Chem. Soc.*, 1956, 2862. ^{d} Ref. 4. ^{e} This work. ^{f} C. H. Langford and M. L. Tobe, *J. Chem. Soc.*, 1963, 506. ^{g} S. C. Chan, *J. Chem. Soc.*, 1964, 2716.

Some of the rate constants and activation parameters relevant to the subsequent discussion are collected in Table 3. It is clear that the present investigation supports the earlier proposition concerning the influence of nephelauxetic effects on the lability of octahedral cobalt(III)–amine complexes.[2,3] Furthermore, the present results could be taken as another strong support for the revised assignment of unimolecular reaction mechanism to the aquation of cobalt(III)–amine complexes containing π-accepting orienting ligands.[9,10] Although Tobe's idea [11] of correlating square pyramidal intermediate and retention of configuration with lower entropies of activation has been questioned recently,[1,12] it would seem worthwhile to note that it was those sterically crowded systems that deviated most from the criteria. However, for the present simple strain- and sterically-free systems, Tobe's criteria is supported.

[9] C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228.
[10] C. K. Poon, *Inorg. Chim. Acta Rev.*, 1970, **4**, 123.
[11] M. L. Tobe, *Inorg. Chem.*, 1968, **7**, 1260.

[12] J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, 1970, **9**, 1504.