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Structural and Mechanistic Studies of Co-ordination Compounds. Part VIII.[1] Preparation, Aquation, and Base Hydrolysis of Some *trans*-Mono-substituted Tetra-aminecobalt(III) Cations

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The preparation and characterization of *trans*-[Co(NH$_3$)$_4$CNBr]$^+$, *trans*-[Co(cyclam)CNBr]$^+$, and *trans*-[Co(NH$_3$)$_4$N$_3$Cl]$^+$ cations and an improved preparation of *trans*-[Co(cyclam)N$_3$Cl]$^+$ cation are described. The aquation and base hydrolysis of these complex cations have been studied over a range of temperature. The thermodynamic and kinetic data are discussed, as before, in terms of the nephelauxetic effect of the amine ligands on the central cobalt(III) ion. Kinetic evidence is produced to support a dissociative mechanism for the base hydrolysis of octahedral cobalt(III)–amine complexes.

For a given pair of unidentate ligands A and X of complexes of the type *trans*-[Co(am)$_4$AX]$^{n+}$, the difference in the thermodynamic and kinetic properties for (am)$_4$ = cyclam, (en)$_2$, and (NH$_3$)$_4$, where cyclam represents 1,4,8,11-tetra-azacyclotetradecane and en represents ethylenediamine, is governed primarily by the nephelauxetic effect of the amine ligands on the central cobalt(III) ion.[2-4] Thermodynamically, the relative stability of a lower-charged complex to a higher-charged complex is expected to decrease along the above series of (am)$_4$. Kinetically, the aquation rate constants of these analogous complexes would increase but the base hydrolysis rate constants decrease along the same series. These suggestions were found true for an extensive series of chloro-complexes [4] with A = Cl$^-$, NCS$^-$, NO$_2$$^-$, CN$^-$, and NH$_3$. For complexes containing a different leaving group X, only the *trans*-[Co(am)$_4$NO$_2$Br]$^+$ system has been studied,[5-7] and it was found that this system also obeyed the above suggestions. It is, however, desirable to investigate another bromo-system to see if the suggestions are of general validity. We also intend to extend the study of the chloro-series to include azide as orienting ligand. This paper describes the preparation and kinetic studies of *trans*-[CoLCNBr]$^+$ and *trans*-[CoLN$_3$Cl]$^+$, where L = (NH$_3$)$_4$ and cyclam. The corresponding rate data of bisethylenediamine analogues are known.[8-10]

EXPERIMENTAL

trans-*Azidoaquo*(1,4,8,11-*tetra-azacyclotetradecane*)*cobalt*(III) *Perchlorate*.—Perchloric acid (5 ml; 70%) was added to a suspension of μ-peroxo-bis{*trans*-azido(1,4,8,11-tetra-azacyclotetradecane)cobalt(III)}perchlorate [11] in water (2 g in 10 ml). The solution was heated on a steam-bath for 10 min until a clear blue solution was formed. Excess of alcohol and ether were added successively to precipitate the *product* [Co(C$_{10}$H$_{24}$N$_4$)N$_3$H$_2$O](ClO$_4$)$_2$ which was filtered off, washed with absolute alcohol and ether, and dried (P$_2$O$_5$) (yield 1·2 g) (Found: C, 23·4; H, 4·95; N, 19·2; Cl, 14·0. Calc. for C$_{10}$H$_{26}$Cl$_2$CoN$_7$O$_9$: C, 23·0; H, 5·05; N, 19·1; Cl, 13·7%).

trans-*Chloroazido*(1,4,8,11-*tetra-azacyclotetradecane*)*cobalt*(III) *Perchlorate*.—Bosnich, Poon, and Tobe prepared this in poor yield.[12] An improved method involved the preparation of the intermediate *trans*-[Co(cyclam)N$_3$OH$_2$](ClO$_4$)$_2$, to a saturated solution (2 g in 10 ml) of which was added concentrated hydrochloric acid (2 ml) dropwise with stirring. The solution was allowed to stand in a salt–ice bath for $\frac{1}{2}$ h. Bluish green crystals of *trans*-[Co(cyclam)N$_3$Cl]ClO$_4$ began to separate, which were filtered off and recrystallized from

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[1] Part VII, W. K. Lee and C. K. Poon, *Inorg. Chem.*, 1973, **12**, 2016.

[2] C. K. Poon, *J. Amer. Chem. Soc.*, 1970, **92**, 4467.

[3] C. K. Poon, *Inorg. Chim. Acta Rev.*, 1970, **4**, 123.

[4] C. K. Poon, *Co-ordination Chem. Rev.*, 1973, **10**, 1.

[5] C. K. Poon and H. W. Tong, *J. Chem. Soc.* (*A*), 1971, 2151.

[6] C. K. Lui and C. K. Poon, *J.C.S. Dalton*, 1972, 216.

[7] C. H. Langford and M. L. Tobe, *J. Chem. Soc.*, 1963, 506.

[8] S. C. Chan, *J. Chem. Soc.*, 1964, 2716.

[9] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 1960, 4803.

[10] V. Ricevuto and M. L. Tobe, *Inorg. Chem.*, 1970, **9**, 1785.

[11] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 1966, **5**, 1514.

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

boiling dilute perchloric acid (*ca.* 10^{-3}M). The *product* was collected, washed with alcohol and ether, and air-dried (yield 0·8 g) (Found: C, 23·5; H, 4·9; N, 19·2; Cl, 14·0. Calc. for $C_{10}H_{24}Cl_2CoN_7O_4$: C, 23·2; H, 5·1; N, 19·1; Cl, 13·7%).

trans-*Chloroazidotetra-amminecobalt*(III) *Perchlorate*.—*trans*-$[Co(NH_3)_4Cl_2]N_3$ (10 g), prepared by the rapid addition of a cold saturated aqueous solution of *trans*-$[Co(NH_3)_4Cl_2]Cl$[13] to an ice-cold concentrated solution of sodium azide, was suspended in a boiling aqueous solution, saturated with NH_4Cl, until most of the solid had gone into the solution which gradually turned purple. The solution was filtered hot and the filtrate was cooled in an ice-bath. Excess of methanol was added to the filtrate to precipitate most of the undesired products which could be shown to contain NH_4Cl, the unchanged dichloro-complex, and *cis*-chloroazido- and other diazido-complexes. The desired *trans*-chloroazido-complex was most soluble and remained in solution. Ether was then cautiously added to the filtrate until the solution appeared cloudy and *trans*-$[Co(NH_3)_4N_3Cl]Cl$ slowly precipitated, contaminated by NH_4Cl. It was recrystallized three times by cautious addition of ether to a saturated methanolic solution. The purified compound was then dissolved in a minimum of methanol and concentrated perchloric acid (2 ml; 70%) was added. Addition of ether precipitated the desired *trans*-$[Co(NH_3)_4N_3Cl]ClO_4$ (yield, 0·5 g) (Found: H, 3·80; N, 32·7; Cl, 23·8. Calc. for $H_{12}Cl_2CoN_7O_4$: H, 3·98; N, 32·3; Cl, 23·3%). The poor yield is the consequence of the need to obtain an analytically pure sample. Much higher yields can be obtained with 5—10% contamination by NH_4Cl.

trans-*Bromocyanotetra-amminecobalt*(III) *Bromide*.—*trans*-$[Co(NH_3)_4CNOH_2]Cl_2$[14] (2 g) was suspended in boiling bromine-free hydrobromic acid (50 ml; 48%; redistilled from red phosphorus). The solid gradually dissolved. The solution, after being concentrated to *ca.* 20 ml, was filtered hot. On cooling, yellowish orange *crystals* of *trans*-$[Co(NH_3)_4CNBr]Br$ slowly separated. These were filtered off, washed with ethanol and ether, and dried in a vacuum desiccator (yield: 1 g) (Found: C, 3·70; H, 3·90; N, 22·2; Br, 50·4. Calc. for $CH_{12}Br_2CoN_5$: C, 3·84; H, 3·87; N, 22·4; Br, 51·0%). Attempts to recrystallize the compound from aqueous solution resulted in the formation of the cyanoaquo-compound. This compound was not sufficiently soluble in most organic solvents to make recrystallization possible. For the same reasons, attempts to prepare a different salt of this complex cation have not been successful.

trans-*Bromocyano*(1,4,8,11-*tetra-azacyclotetradecane*)-*cobalt*(III) *Nitrate*.—The method of preparation of this *compound* $[Co(C_{10}H_{24}N_4)CNBr]NO_3$, followed closely that of the chloro-analogue,[15,16] from bromine-free hydrobromic acid instead of hydrochloric acid (yield: 40%) (Found: C, 31·2; H, 5·60; N, 19·8; Br, 19·0. Calc. for $C_{11}H_{24}BrCoN_6O_3$: C, 30·9; H, 5·66; N, 19·7; Br, 18·7%). The yield can be improved by addition of alcohol and ether to the filtrate to precipitate a second crop.

Kinetics.—All these reactions, aquation and base hydrolysis, were followed spectrophotometrically *in situ* with use of either a Unicam SP 700 or SP 8000 recording spectrophotometer in a conventional manner as described previously.[5,16]

RESULTS

The behaviour of *trans*-$[Co(cyclam)N_3Cl]^+$ and *trans*-$[Co(cyclam)CNBr]^+$ in dilute nitric acid (0·01—0·1M) was very similar to that of other cyclam complexes of the same type, *trans*-$[Co(cyclam)AX]^+$.[6,15,16] The changing visible spectrum maintained isosbestic points throughout the entire reaction (at 584 nm for the azido-complex and at 400 and 467 nm for the cyano-complex). These isosbestic points were crossed by the spectrum of the corresponding *trans*-$[Co(cyclam)A(OH_2)]^{2+}$, where A = N_3^- and CN^- respectively. The initial spectrum was identical with that of the starting complex. Volhard's titration confirmed that the co-ordinated halide was released to *ca.* 60 and 90% respectively. Addition of an excess of the corresponding halide to the final solution forced the reaction to re-trace its own path. These observations clearly demonstrated that these cyclam complexes only partially aquated with complete retention of configuration. The reaction was followed spectrophotometrically at 550 and 350 nm respectively. The concentration X of the aquo-complex generated at any time t was determined from the observed absorbance at that time by use of the appropriate known molar absorptivities (ε for N_3Cl = 118 and for N_3OH_2 = 250 l mol^{-1} cm^{-1} at 550 nm and for CNBr = 149 and $CNOH_2$ = 78·9 l mol^{-1} cm^{-1} at 350 nm). The forward aquation rate constant, k_1, was obtained from the slope of the linear plot of the left-hand part of expression (1)[17] against time, where a = [starting complex] at $t = 0$, X_e = [aquo-complex] = [halide] at equilibrium.

$$2{\cdot}303\log\frac{aX_e + X(a - X_e)}{a(X_e - X)} = k_1\frac{2a - X_e}{X_e}t \qquad (1)$$

These plots were straight to two half-lives. The behaviour of *trans*-$[Co(NH_3)_4CNBr]Br$ in 0·1M-nitric acid was similar to that described above except that here the release of bromide was complete. The changing spectrum maintained isosbestic points at 399 and 457 nm with the final spectrum identical with that of *trans*-$[Co(NH_3)_4CNOH_2]^{2+}$. The reaction was followed at 500 nm and the first-order rate constant was obtained from the standard semilogarithmic plot of log $(D_t - D_\infty)$ against time, where D_t and D_∞ are respectively the absorbances at time t and after 10 half-lives. These plots were linear to 3 half-lives.

The spectrophotometric change associated with the aquation of *trans*-$[Co(NH_3)_4N_3Cl]ClO_4$ in 0·01M-nitric acid initially maintained isosbestic points at 448 and 562 nm. The initial spectrum was identical with that of the starting *trans*-chloroazido-complex. Volhard's titration confirmed that chloride was gradually released from co-ordination. At a later stage of the reaction, the changing spectra began to deviate from these isosbestic points while a new isosbestic point was gradually developed at 546 nm which was maintained until the end of the reaction. Colorimetric azide determination[18] confirmed that azide was partially released from co-ordination during the second stage of the reaction to *ca.* 60% at equilibrium. Since no attempt to prepare pure *cis*- and *trans*-$[Co(NH_3)_4N_3OH_2]^{2+}$ cations or to obtain their absorption spectra by any indirect method has been successful, the steric course of the aquation of *trans*-$[Co(NH_3)_4N_3Cl]^+$ was deduced by an indirect method. The Hg^{2+}-induced reaction of this complex cation was followed at a relatively

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[13] S. M. Jörgensen, *Z. anorg. Chem.*, 1897, **14**, 404; ' Handbook of Preparative Inorganic Chemistry,' vol. 2, 2nd edn., ed. G. Brauer, Academic Press, New York, 1965, p. 1537.

[14] . B. Baranovskii and A. V. Babaeva, *Russian J. Inorg. Chem.*, 1964, **9**, 1168.

[15] K. S. Mok and C. K. Poon, *Inorg. Chem.*, 1971, **10**, 225.

[16] C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1973, 1301.

[17] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanisms,' 2nd edn., Wiley, New York, 1961, p. 187.

[18] P. J. Staples, *Chem. and Industry*, 1960, 1210.

low Hg^{2+} concentration and it was found that the associated spectral change was virtually identical with that of the spontaneous aquation. In the presence of a large excess of Hg^{2+}, the induced reaction was virtually complete as soon as the complex was dissolved in the reagent solution. The visible spectrum then immediately measured had an absorption peak at 540 nm and the manner of the subsequent spectral change was the same as that of the second step in the spontaneous aquation. These observations seemed to suggest that the steric courses for both spontaneous and Hg^{2+}-induced aquation of *trans*-$[Co(NH_3)_4N_3Cl]^+$ were identical. With reference to the well known stereoretentive aquation of *trans*-$[Co(en)_2N_3Cl]^+$ [10] and Hg^{2+}-induced aquation of most halogenocobalt(III)–amine complexes [3] and to the known spectra of *cis*- and *trans*-$[Co(en)_2N_3OH_2]^{2+}$ ($\lambda_{max.}$ at 505 and 550 nm respectively [19]), it seems highly likely that the aquation of *trans*-$[Co(NH_3)_4N_3Cl]^+$ is stereoretentive. This deduction becomes invalid if the geometrical isomerization of the azidoaquo-complexes is too fast, even much faster than the Hg^{2+}-induced reaction, to be detected. This, $[Co(NH_3)_4N_3Cl]^+$ was not affected by the subsequent reaction. The first-order rate constant was obtained from the slope of the standard semi-logarithmic plot. These plots were linear to three half-lives. All these aquation data are in Tables 1 and 2.

TABLE 1

First-order rate constants for the aquation of *trans*-$[Co(am)_4N_3Cl]ClO_4$

$(am)_4$	t/°C	10^3k_1/s^{-1} [a]
$(NH_3)_4$	16·7	1·33
$(NH_3)_4$	18·4	1·66
$(NH_3)_4$	18·9	1·75
$(NH_3)_4$	20·0	2·06
$(NH_3)_4$	21·8	2·52
$(NH_3)_4$	22·1	2·63
$(NH_3)_4$	24·5	3·49
$(NH_3)_4$	25·1	3·88
$(NH_3)_4$	25·2	3·77

TABLE 2

First-order aquation rate constants of complexes of the type *trans*-$[Co(am)_4CNBr]^+$

$(am)_4$	t/°C	k_1/s^{-1} [a]
$(NH_3)_4$	23·2	$(3·30 \pm 0·02) \times 10^{-3}$
$(NH_3)_4$	34·5	$(1·21 \pm 0·03) \times 10^{-2}$
$(NH_3)_4$	47·6	$(4·60 \pm 0·15) \times 10^{-2}$
(cyclam)	41·9	$(2·39 \pm 0·05) \times 10^{-5}$
(cyclam)	49·5	$(5·83 \pm 0·10) \times 10^{-5}$
(cyclam)	58·2	$(1·58 \pm 0·03) \times 10^{-4}$
$(NH_3)_4$	25·0	$4·2 \times 10^{-3}$ [b]
$(en)_2$	25·0	$4·7 \times 10^{-4}$ [c]
(cyclam)	25·0	$2·8 \times 10^{-6}$ [d]

[a] This work except as indicated; each entry represents an average of three independent determinations in 0·1M-nitric acid and over a starting complex concentration between 1·2 and 2·8 mM. [b] Obtained by extrapolation; also $\Delta H^\ddagger = 19·7 \pm 0·3$ kcal mol^{-1}, $\Delta S^\ddagger = -3 \pm 1$ cal mol^{-1} K^{-1}. [c] In neutral aqueous solution; S. C. Chan, *J. Chem. Soc.*, 1964, 2716. [d] Obtained by extrapolation; also $\Delta H^\ddagger = 23·3 \pm 0·3$ kcal mol^{-1}, $\Delta S^\ddagger = -6 \pm 2$ cal mol^{-1} K^{-1}.

The base hydrolysis of these complexes was most conveniently followed in buffer solutions (for conditions, see Table 3). It has been shown [20] that the buffers used were non-interfering. In most cases, the changing visible spectrum maintained a set of isosbestic points (at 472 and 561 nm for *trans*-$[Co(cyclam)N_3Cl]^+$; at 376 and 496 nm for

TABLE 3

Second-order base hydrolysis rate constants of complexes of the type *trans*-$[Co(am)_4AX]^+$ [a]

$(am)_4$	A	X	t/°C	k_2/l mol^{-1} s^{-1}	10^3k_0/ s^{-1}	10^3k_1/ s^{-1}
$(NH_3)_4$ [b]	N_3	Cl	13·0	(5·23 ± 0·05) × 10^{-2}	0·85	0·84
$(NH_3)_4$ [b]	N_3	Cl	18·1	(1·10 ± 0·02) × 10^{-1}	1·6	1·6
$(NH_3)_4$ [b]	N_3	Cl	24·0	(2·63 ± 0·03) × 10^{-1}	3·3	3·3
$(NH_3)_4$ [b]	N_3	Cl	28·1	(4·55 ± 0·04) × 10^{-1}	5·4	5·4
$(NH_3)_4$	CN	Br	13·6	(7·33 ± 0·10)		
$(NH_3)_4$	CN	Br	21·9	(2·20 ± 0·10) × 10		
$(NH_3)_4$	CN	Br	27·2	(4·56 ± 0·06) × 10		
(cyclam)	N_3	Cl	25·4	(2·88 ± 0·05) × 10^{3}		
(cyclam)	N_3	Cl	30·2	(5·54 ± 0·10) × 10^{3}		
(cyclam)	N_3	Cl	34·5	(9·47 ± 0·15) × 10^{3}		
(cyclam)	N_3	Cl	40·2	(1·96 ± 0·03) × 10^{4}		
(cyclam)	CN	Br	17·5	(2·12 ± 0·05) × 10^{2}		
(cyclam)	CN	Br	25·4	(4·96 ± 0·10) × 10^{2}		
(cyclam)	CN	Br	34·1	(1·45 ± 0·02) × 10^{3}		
(cyclam)	CN	Br	43·4	(4·05 ± 0·08) × 10^{3}		
$(NH_3)_4$	N_3	Cl	0·0	6·6 × 10^{-3} [c]		
$(en)_2$	N_3	Cl	0·0	4·1 × 10^{-1} [d,e]		
(cyclam)	N_3	Cl	0·0	6·8 × 10 [f]		
$(NH_3)_4$	CN	Br	0·0	9·9 × 10^{-1} [g]		
$(en)_2$	CN	Br	0·0	1·8 [d,h]		
(cyclam)	CN	Br	0·0	2·0 × 10 [i]		

[a] This work except as indicated; reactions of cyclam complexes were studied in γ-collidine–nitric acid buffer solutions (pH = 7·0—8·6) and those of tetra-ammine complexes in 2,6-dimethylpiperidine–nitric acid buffer solutions (pH = 10·3—12·0); I = 0·1M ($NaNO_3$); [complex] between 0·9 and 2·8 mM; each entry was obtained from 5 to 7 different runs over a span of 0·9—1·0 pH unit. [b] $k_{obs} = k_0 + k_2[OH^-]$; k_1 was obtained by extrapolation of data in Table 1. [c] Obtained by extrapolation; also $\Delta H^‡$ = 24·0 ± 0·2 kcal mol^{-1}, $\Delta S^‡$ = 20 ± 3 cal mol^{-1} K^{-1}. [d] Reactions were studied in dilute NaOH solution; ionic strength was not maintained constant with any supporting electrolyte. [e] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 1960, 4803. [f] Obtained by extrapolation; also $\Delta H^‡$ = 23·5 ± 0·2 kcal mol^{-1}, $\Delta S^‡$ = 36 ± 5 cal mol^{-1} K^{-1}. [g] Obtained by extrapolation; also $\Delta H^‡$ = 22·3 ± 0·3 kcal mol^{-1}, $\Delta S^‡$ = 24 ± 4 cal mol^{-1} K^{-1}. [h] S. C. Chan, *J. Chem. Soc.*, 1964, 2716. [i] Obtained by extrapolation; also $\Delta H^‡$ = 20·1 ± 0·4 kcal mol^{-1}, $\Delta S^‡$ = 21 ± 5 cal mol^{-1} K^{-1}.

confirmed that the most consistent variation between the i.r. spectra of *cis*- and *trans*-isomers of cobalt(III)–cyclam complexes was in the 800—900 cm^{-1} region.[21] Here, the presence of two bands (at 888 and 900 cm^{-1}) near 900 cm^{-1} and only one band (at 824 cm^{-1}) near 800 cm^{-1} in this region of the i.r. spectrum of the new [Co(cyclam)CNBr]NO_3 complex was taken to indicate a *trans*-configuration. The assignment of a *trans*-configuration to $[Co(NH_3)_4N_3Cl]ClO_4$ prepared was made by comparing its absorption spectrum ($\lambda_{max.}$ = 584 nm) with those of the known *cis*- and *trans*-$[Co(en)_2N_3Cl]^+$ ($\lambda_{max.}$ = 530 and 584 nm respectively [22]) and *trans*-$[Co(cyclam)N_3Cl]^+$ ($\lambda_{max.}$ = 586 nm [12]). $[Co(NH_3)_4CNBr]Br$ was assigned a *trans*-configuration by chemical means in essentially the same way as that for the corresponding *trans*-$[Co(NH_3)_4CNCl]Cl$.[16]

The aquation and base hydrolysis rate constants of these complexes, extrapolated to 25 and 0 °C respectively, are in Tables 1—3. The variation of the aquation and base hydrolysis rate constants with the nature of the amine ligands fully supports the earlier suggestion [2] concerning the influence of kinetic nephelauxetic effect on the lability of octahedral cobalt(III)–amine complexes. Thermodynamically, the relative stability of a lower-charged complex to a higher-charged complex also decreases, as predicted, along the series of $(am)_4$: cyclam > $(en)_2$ > $(NH_3)_4$. Here, *trans*-$[Co(cyclam)N_3Cl]ClO_4$ aquates to *ca.* 60% at equilibrium at 25 °C; the aquation of the bisethylenediamine complex is virtually complete but further displacement of the azido-group is not noticeable; [10] for the tetra-ammine complex, not only is the release of the chloride complete, but the release of the co-ordinated azide also occurs to about 60% giving a mixture of *cis*- and *trans*-$[Co(NH_3)_4(OH_2)_2]^{3+}$. Similarly for the bromocyano-system, the extent of aquation of *trans*-$[Co(en)_2CNBr]Br$ is *ca.* 97% complete.[8] This is greater than that of *trans*-[Co(cyclam)CNBr]Br (*ca.* 80%) but smaller than that of *trans*-$[Co(NH_3)_4CNBr]Br$. The aquation of the tetra-ammine complex is complete even in the presence of 0·1M-bromide ion. The observed negative entropies of activation for the aquation of these complexes suggest that Tobe's correlation [23] of square pyramidal intermediate and retention of configuration with lower entropies of activation is also applicable for these bromo-complexes.

A search of existing kinetic data shows that changing the nature of the leaving group from chloride to bromide increases the rates of both acid and base hydrolysis of anionocobalt(III)–amine complexes. These data, extrapolated to the same temperature, for an extensive class of complexes containing orienting ligands of different electronic displacement property, are in Tables 4 and 5. With the exception of isothiocyanato-complexes, this leaving-group effect, as measured by the k_i^{Br}/k_i^{Cl} (i = 1 or 2) in both Tables, is significantly greater on base hydrolysis than on acid hydrolysis. These ratios are not greatly dependent on temperature since the activation energy of a given reaction does not vary much from chloro- to the corresponding bromo-complex.[24,25] This leaving-group effect is fully consistent with the proposed S_N1cb mechanism for the base hydrolysis and a dissociative interchange mechanism (I_d) for the aquation of these complexes.[3,4,26,27] On the basis of an S_N1cb mechanism, the second-order rate constant is directly proportional to $K_a \times k_{cb}$ where K_a is the acid ionization constant (amine proton) of the conjugate acid and k_{cb} is the aquation rate constant of the amido-conjugate base. It is expected [26] that a change of the leaving group from chloride to bromide would not significantly alter the value of K_a and, therefore, the kinetic ratio for base hydrolysis essentially

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[21] C. K. Poon, *Inorg. Chim. Acta*, 1971, **5**, 322.

[22] Estimated from the published spectra of *cis*- and *trans*-$[Co(en)_2N_3Cl]^+$; P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 1960, 4812.

[23] M. L. Tobe, *Inorg. Chem.*, 1968, **7**, 1260.

[24] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1962, 4531.

[25] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 5700.

[26] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967.

[27] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes,' Benjamin, New York, 1966.

gives the ratio of the k_{cb} for the bromo- and the corresponding chloro-complex. The presence of a good labilizing amido-group may promote a limiting S_N1 acid hydrolysis of the conjugate base which would probably be more sensitive to the nature of the leaving group than a dissociative interchange mechanism of spontaneous aquation in which solvent participation occurs to a certain extent in the transition state. For bimolecular reactions, on the other hand, the breakage of the cobalt–halogen bond does not proceed far in the transition state and so the effect of leaving group on a bimolecular reaction should be much smaller than that on a unimolecular reaction. Clearly, the above observation (Tables 4 and 5) denies a bimolecular mechanism for the base hydrolyis of these cobalt(III)–amine complexes. The reason behind the reversed behaviour of the isothiocyanato-complexes is not clear. Langford and Gray [27] have pointed out that the role played by the isothiocyanato-ligand in acid hydrolysis was rather extraordinary but the reason behind this remained a mystery.

TABLE 4

Effect of leaving group on the acid and base hydrolysis of complexes of the type *cis*- and *trans*-CoLAX$^+$ (X = Cl and Br) at 0·0 °C [a]

L	A	k_1^{Br}/s^{-1} [b]	k_1^{Cl}/s^{-1} [b]	k_1^{Br}/k_1^{Cl}	$\frac{k_2^{Br}}{\mathrm{l\ mol^{-1}\ s^{-1}}}$ [b]	$\frac{k_2^{Cl}}{\mathrm{l\ mol^{-1}\ s^{-1}}}$ [b]	k_2^{Br}/k_2^{Cl}
$(NH_3)_4$	*trans*-NO_2	4·1 × 10^{-3} [c,d]	1·4 × 10^{-3} [c,d]	2·9	1·5 × 10^{-2} [d,e]	3·0 × 10^{-3} [d,e]	5·0
$(en)_2$	*trans*-NO_2	1·4 × 10^{-4} [f]	3·6 × 10^{-5} [g]	3·9	6·8 × 10^{-1} [h,i]	8·0 × 10^{-2} [g,h]	8·5
(cyclam)	*trans*-NO_2	2·0 × 10^{-5} [c,j]	1·6 × 10^{-6} [c,k]	13	8·8 × 10^{2} [e,j]	2·8 × 10 [e,j]	31
$(NH_3)_4$	*trans*-CN	1·9 × 10^{-4} [c,l]	3·7 × 10^{-5} [c,m]	5·1	9·9 × 10^{-1} [l,n]	3·5 × 10^{-2} [m,n]	28
$(en)_2$	*trans*-CN	1·2 × 10^{-5} [i]	2·3 × 10^{-6} [o]	5·2	1·8 [h,i]	1·3 × 10^{-1} [h,o]	14
(cyclam)	*trans*-CN	7·1 × 10^{-8} [c,l]	1·1 × 10^{-8} [c,k]	6·5	2·0 × 10 [l,n]	8·1 × 10^{-1} [m,n]	25
$(en)_2$	*trans*-Cl	1·8 × 10^{-6} [p]	5·6 × 10^{-7} [q]	3·2	2·7 × 10^{2} [h,r]	8·5 × 10 [h,r]	3·2
$(en)_2$	*cis*-Cl	1·4 × 10^{-5} [p]	7·8 × 10^{-6} [c,p]	1·8	7·1 × 10 [h,r]	1·5 × 10 [h,r]	4·7
$(en)_2$	*trans*-OH	2·2 × 10^{-4} [p]	3·2 × 10^{-5} [s]	6·9	1·7 × 10^{-1} [h,r]	1·7 × 10^{-2} [h,r]	10
$(en)_2$	*cis*-OH	1·6 × 10^{-3} [p]	3·1 × 10^{-4} [s]	5·2	2·7 [h,r]	3·7 × 10^{-1} [h,r]	7·3
$(en)_2$	*trans*-NCS	4·8 × 10^{-9} [c,t]	4·6 × 10^{-10} [c,t]	10	2·0 [h,t]	3·4 × 10^{-1} [h,t]	5·9
$(pn)_2$	*trans*-NCS	2·1 × 10^{-7} [c,u]	2·1 × 10^{-8} [c,u]	10	9·6 × 10^{-1} [h,u]	1·8 × 10^{-1} [h,u]	5·3

[a] pn = Propylenediamine. [b] k_1^{Br} and k_2^{Br} Represent the first-order acid hydrolysis rate constant and the second-order base hydrolysis rate constant respectively of the bromo-complex; similarly, k_1^{Cl} and k_2^{Cl} represent those of the chloro-complex. [c] Extrapolated from published data at other temperatures. [d] C. K. Poon and H. W. Tong, *J. Chem. Soc.* (*A*), 1971, 2151. [e] At I = 0·3M. [f] C. H. Langford and M. L. Tobe, *J. Chem. Soc.*, 1963, 506. [g] S. Ašperger and C. K. Ingold, *J. Chem. Soc.*, 1956, 2862. [h] Ionic strength was not maintained constant with any supporting electrolyte; the solution was, however, rather dilute. [i] S. C. Chan, *J. Chem. Soc.*, 1964, 2716. [j] C. K. Lui and C. K. Poon, *J.C.S. Dalton*, 1972, 216. [k] K. S. Mok and C. K. Poon, *Inorg. Chem.*, 1971, **10**, 225. [l] This work. [m] C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1973,1301. [n] At I = 0·1M. [o] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 514. [p] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1963, 5700. [q] S. C. Chan, *Austral. J. Chem.*, 1967, **20**, 595. [r] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 1962, 4531. [s] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 1961, 4637. [t] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1956, 1691. [u] S. C. Chan, C. L. Chik, and B. Hui, *J. Chem. Soc.*, 1967, 607.

TABLE 5

Effect of leaving group on the acid and base hydrolysis of cobalt(III) complexes of the penta-amine type, *cis*-CoLAX^{2+} (X = Cl and Br), at 25 °C [a]

L	A	k_1^{Br}/s^{-1} [c]	k_1^{Cl}/s^{-1} [c]	k_1^{Br}/k_1^{Cl}	$\frac{k_2^{Br}}{\mathrm{l\ mol^{-1}\ s^{-1}}}$	$\frac{k_2^{Cl}}{\mathrm{l\ mol^{-1}\ s^{-1}}}$	k_2^{Br}/k_2^{Cl}
$(NH_3)_4$	NH_3	6·5 × 10^{-6} [b]	1·7 × 10^{-6}	3·8	1·4 [d]	2·5 × 10^{-1} [d]	5·6
$(en)_2$	$OH{\cdot}NH_2$	2·2 × 10^{-5}	5·1 × 10^{-6}	4·3	4·8 × 10	7·0	6·9
$(en)_2$	$MeNH_2$	3·6 × 10^{-7}	2·3 × 10^{-7}	1·6	5·0 × 10	1·3 × 10 [e]	3·9
$(en)_2$	$EtNH_2$	3·0 × 10^{-7}	1·5 × 10^{-7}	2·0	4·7 × 10	1·3 × 10 [e]	3·6
$(en)_2$	Pr^nNH_2	1·8 × 10^{-6}	3·2 × 10^{-7}	5·6	2·7 × 10^{2}	1·3 × 10 [e]	21
$(en)_2$	Pr^iNH_2	7·4 × 10^{-6}	1·2 × 10^{-6}	6·2	4·2 × 10^{2}	5·2 × 10 [e]	8·1
$(en)_2$	$CH_2{=}CH{\cdot}CH_2{\cdot}NH_2$	5·7 × 10^{-7}	1·9 × 10^{-7}	3·0	1·2 × 10^{2}	6·4	19
$(en)_2$	$CH{\equiv}C{\cdot}CH_2{\cdot}NH_2$	3·2 × 10^{-7}	1·3 × 10^{-7}	2·5	5·7 × 10	3·3	17

[a] Data from S. C. Chan, C. Y. Cheng, and F. Leh, *J. Chem. Soc.* (*A*), 1967, 1586, except as indicated; acid hydrolysis rate constants were obtained by extrapolation; base hydrolysis was studied at I = 0·1M. [b] A. B. Lamb and J. W. Marden, *J. Amer. Chem. Soc.*, 1911, **33**, 1873. [c] F. J. Garrick, *Trans. Faraday Soc.*, 1937, **33**, 486; S. C. Chan, *J. Chem. Soc.* (*A*), 1967, 291. [d] At I = 1·0M; D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, 1968, **7**, 174. [e] R. W. Hay and P. L. Cropp, *J. Chem. Soc.* (*A*), 1969, 42.

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