Structural and Mechanistic Studies of Co-ordination Compounds. Part 18.[1] Preparation and Hydrolysis of *trans*-Bromo- and Chloro-cyano-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-7,14-diene)-cobalt(III) Cations

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Complexes *trans*-$[Co(CN)(L^1)X]^{n+}$ [L^1 = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-7,14-diene; X = Cl, Br, or OH_2] and *trans*-$[CoL^1(OH_2)(SO_3)]^+$ have been prepared, and the acid and base hydrolyses of the halogeno-complexes have been studied over a range of temperature. For the acid hydrolysis, a linear free-energy relation has been established between the kinetic data of cyanotetra-aminecobalt(III) complexes and those of the corresponding azido- and isothiocyanato-complexes. The base hydrolysis of these complexes is discussed in terms of a ' limiting ' S_N1(CB)mechanism in which the formation of a reactive amido-conjugate base is the rate-determining step.

PREVIOUSLY [1-5] we have shown that the specific rates of acid hydrolysis of analogous complexes of the type *trans*-$[CoA(L)X]^+$ (A = Cl, N_3, or NCS) increased with increasing extent of unsaturation in the macrocyclic quadridentate amine L, while the ratio $k_{Br} : k_{Cl}$ (X = Br or Cl respectively for a given L and A) decreased. However, the behaviour of nitro-complexes, *trans*-$[CoL(NO_2)X]^+$, is abnormal [6,7] in that the first-order aquation rate constants are virtually independent of the extent of unsaturation in the amine macrocycles. This behaviour was explained in terms of a co-operative π-conjugative effect.[7]

The present paper was designed to pursue this co-operative π-conjugative effect further by studying the reactions of complexes containing a different π-accepting cyano-orientating ligand. Attempts to prepare pure cyano-complexes of the type *trans*-$[Co(CN)(L)X]^+$ (X = Cl or Br) with macrocycles relatively free from steric effects, such as 2,3-dimethyl-1,4,8,11-tetra-azacyclotetradeca-1,3-diene (L^2) and 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene (L^3), and of *trans*-$[Co(CN)(L^4)Br]^+$ (L^4 = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane) have not been successful. This paper describes the preparation and acid hydrolysis of *trans*-$[Co(CN)(L^1)X]^+$ (L^1 = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-7,14-diene, X = Cl and Br). The kinetic behaviour of corresponding complexes [8,9] of 1,4,8,11-tetra-azacyclotetradecane (L^5, cyclam) and of *trans*-$[Co(CN)(L^4)Cl]^+$ (ref. 10) is known. On the other hand, these *trans*-$[Co(CN)(L^1)X]^+$ complexes also represent a suitable

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[1] Part 17, C. K. Poon, W. K. Wan, and S. S. T. Liao, *J.C.S. Dalton*, 1977, 1247.

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

[3] W. K. Lee and C. K. Poon, *J.C.S. Dalton*, 1974, 2423.

[4] C. K. Poon and C. L. Wong, *J.C.S. Dalton*, 1976, 966.

[5] C. K. Poon and C. L. Wong, *Inorg. Chem.*, 1976, **15**, 1573.

[6] R. W. Hay and G. A. Lawrance, *J.C.S. Dalton*, 1975, 1556.

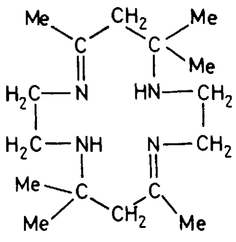
[7] C. K. Poon and C. L. Wong, *J.C.S. Dalton*, 1977, 523.

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

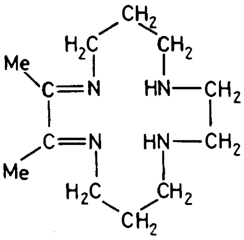
[9] C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1974, 1.

[10] W. K. Chau, W. K. Lee, and C. K. Poon, *J.C.S. Dalton*, 1974, 2419.

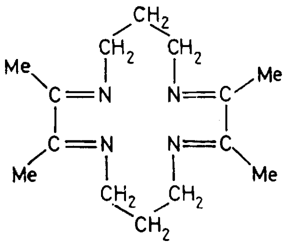
system to substantiate the S_N1(CB) mechanism [11] for the base hydrolysis of octahedral cobalt(III) amine complexes. It has been demonstrated [12] for these L^1 complexes that the second-order base hydrolysis rate constants are independent of the nature of both orientating (Cl^- and NCS^-) and leaving (Cl^- and Br^-) groups. This, together with the observation of general-base catalysis and the appropriate activation parameters, have been taken [12] to indicate a 'limiting' S_N1(CB) mechanism, in which deprotonation of an amine ligand becomes the rate-determining step, for the base hydrolysis of these L^1 chloro- and isothiocyanato-complexes. This paper also describes the study of the base hydrolysis of these L^1 cyano-complexes to test this limiting behaviour further.



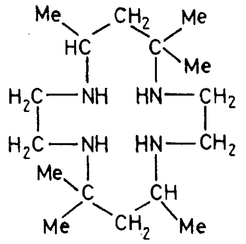
L^1



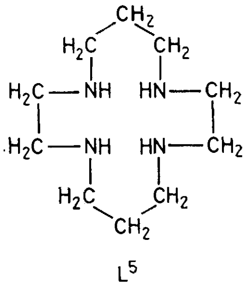
L^2



L^3



L^4



L^5

EXPERIMENTAL

Preparation of the Complexes.—trans-*Aqua*(5,5,7,12,12,14-*hexamethyl*-1,4,8,11-*tetra-azacyclotetradeca*-7,14-*diene*)*sulphitocobalt*(III) *perchlorate monohydrate*, *trans*-$[CoL^1(OH_2)(SO_3)][ClO_4]\cdot H_2O$. This complex was prepared by adding a stoicheiometric amount of sodium sulphite (1.07 g in 5 cm^3 of water) to a hot aqueous solution of *trans*-(*RS*)-$[CoCl(L^1)(OH_2)][ClO_4]_2$ [3] (5 g in 30 cm^3). To the resulting orange-red solution, a stoicheiometric amount of $Ag[ClO_4]$ (1.75 g in 5 cm^3 of water) was added. The solution was warmed to coagulate the AgCl precipitate which was then filtered off. Precipitation of the desired orange product was induced by adding ethanol–acetone (2 : 1, 300 cm^3) followed by an excess of diethyl ether. The solid was filtered off, washed with ethanol–diethyl ether (1 : 6) and then with diethyl ether, and dried *in vacuo* at 65 °C (yield 75%) (Found: C, 34.8; H, 6.2; Cl, 6.8; N, 9.9; S, 6.1. Calc. for $C_{16}H_{36}ClCoN_4O_9S$: C, 34.6; H, 6.5; Cl, 6.4; N, 10.1; S, 5.8%).

trans-*Aquacyano*(5,5,7,12,12,14-*hexamethyl*-1,4,8,11-*tetra-azacyclotetradeca*-7,14-*diene*)*cobalt*(III) *perchlorate dihydrate*, *trans*-$[Co(CN)L^1(OH_2)][ClO_4]_2\cdot 2H_2O$.* Sodium cyanide (0.44 g in 10 cm^3 of water) was added to a hot aqueous solution of *trans*-$[CoL^1(OH_2)(SO_3)][ClO_4]\cdot H_2O$ (5 g in 30 cm^3). The solution became orange-yellow almost instantaneously. Perchloric acid (70%, 5 cm^3) was added to the hot solution which immediately became yellow. On cooling and on the addition of excess of $Na[ClO_4]$, a yellow crystalline product precipitated out and was filtered off, washed with ethanol–diethyl ether (1 : 4) and then with diethyl ether, and dried in air (yield 90%) (Found: C, 33.0; H, 6.0; Cl, 11.5; N, 11.4. Calc. for $C_{17}H_{38}Cl_2CoN_5O_{11}$: C, 33.0; H, 6.2; Cl, 11.5; N, 11.3%), $\lambda_{max.}$ 438 (ε 151), $\lambda_{min.}$ 372 nm (ε 46 $dm^3\ mol^{-1}\ cm^{-1}$).

trans-*Chlorocyano*(5,5,7,12,12,14-*hexamethyl*-1,4,8,11-*tetra-azacyclotetradeca*-7,14-*diene*)*cobalt*(III) *perchlorate monohydrate*, *trans*-$[CoCl(CN)L^1][ClO_4]\cdot H_2O$. This complex was prepared by adding $[NH_4]Cl$ (0.09 g in 10 cm^3 of methanol) to a hot methanolic solution of *trans*-$[Co(CN)L^1(OH_2)][ClO_4]_2\cdot 2H_2O$ (1 g in 50 cm^3). Ethanol (100 cm^3) was added to the resulting hot solution, followed by an excess of diethyl ether to precipitate out the desired yellow solid which was filtered off and washed with diethyl ether (yield 80%) (Found: C, 39.0; H, 6.4; Cl, 13.6; N, 13.3. Calc. for $C_{17}H_{34}Cl_2CoN_5O_5$: C, 39.4; H, 6.6; Cl, 13.7; N, 13.5%), $\lambda_{max.}$ 450 (ε 148), $\lambda_{min.}$ 380 nm (ε 56 $dm^3\ mol^{-1}\ cm^{-1}$).

trans-*Bromocyano*(5,5,7,12,12,14-*hexamethyl*-1,4,8,11-*tetra-azacyclotetradeca*-7,14-*diene*)*cobalt*(III) *perchlorate monohydrate*, *trans*-$[CoBr(CN)L^1][ClO_4]\cdot H_2O$. This complex was similarly prepared with a similar yield to its chloro-analogue except that a stoicheiometric amount of $[NH_4]Br$ was used instead of $[NH_4]Cl$ (Found: C, 36.2; H, 6.1; Br, 13.9; N, 12.4. Calc. for $C_{17}H_{34}BrClCoN_5O_5$: C, 36.3; H, 6.1; Br, 14.2; N, 12.4%), $\lambda_{max.}$ 452 (ε 121), $\lambda_{min.}$ 386 nm (ε 52 $dm^3\ mol^{-1}\ cm^{-1}$).

Kinetics.—The acid and base hydrolyses were followed spectrophotometrically *in situ* using Unicam SP 700 or SP 8000 recording spectrophotometers, separately equipped with a thermostatted cell holder and a suitable set of scale-expansion accessories as described previously.[4] The reaction was started by adding a drop of a cold concentrated aqueous solution of the complex to the appropriate reaction medium (0.01 mol dm^{-3} HNO_3 or a buffer solution) previously brought to the reaction temperature in a 4-cm open-top silica cell. The solution was rapidly stirred with a thin glass paddle which had also been brought to the reaction temperature. After removing the glass paddle and putting a cover on the cell, the instrument was switched on to record the changing absorbances at a fixed wavelength [acid hydrolysis, at 480 (X = Cl) and 500 nm (Br); base hydrolysis, at 480 (X = Cl) and 340 nm (Br)]. The change in

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* **CAUTION:** the method is potentially hazardous and should only be carried out in a good fumehood.

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

[12] P. W. Mak and C. K. Poon, *Inorg. Chem.*, 1976, **15**, 1949.

temperature on adding the drop of complex solution to the reaction medium was estimated to be negligible. For the very fast reactions, kinetic runs were repeated four or five times to obtain the best average value of the observed rate. The pH of buffer solutions in the silica cell was measured with a set of microelectrodes, type K4112 (calomel) and G222C (glass), using a Radiometer type PHM26 pH meter. The Radiometer set-up was calibrated against a standard buffer solution contained in the reference cell which was housed in the same temperature-controlled cell holder and hence kept at the same reaction temperature.

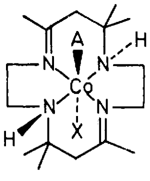
RESULTS

Attempted syntheses of these *trans*-$[Co(CN)(L^1)X]^+$ complexes by treating the appropriate dihalogeno-complex with a stoicheiometric amount of cyanide were unsuccessful. Analytically pure samples of these complexes were prepared *via* the sulphito-intermediate with an overall yield of *ca.* 38%, as represented in the Scheme.

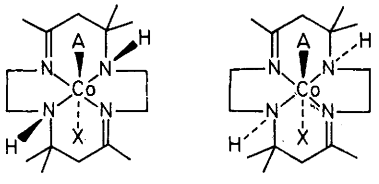
$$trans\text{-}[CoCl_2L^1][ClO_4] \xrightarrow{HClO_4} trans\text{-}[Co(Cl)L^1(OH_2)][ClO_4]_2$$
$$\xrightarrow[+\ Ag[ClO_4]]{Na_2[SO_3]} trans\text{-}[CoL^1(OH_2)(SO_3)][ClO_4]\cdot H_2O$$
$$\xrightarrow[+\ HClO_4]{Na[CN]} trans\text{-}[Co(CN)L^1(OH_2)][ClO_4]_2\cdot 2H_2O$$
$$\xrightarrow{[NH_4]X} trans\text{-}[Co(CN)L^1X][ClO_4]\cdot H_2O$$

SCHEME Synthesis of *trans*-$[Co(CN)(L^1)X]^+$ (X = Cl or Br)

Complexes of the general type *trans*-$[CoA(L^1)X]^+$ can have several diastereoisomers. The N-meso(*RS*) configuration gives one isomer whereas the N-*rac*(*RR,SS*) gives two.



N-*meso(RS)*



N - *rac(RR,SS)*

In the present case, all the L^1 complexes are prepared (Scheme) from isomerically pure *trans*-(*RS*)-$[CoCl_2L^1]$-$[ClO_4]$.[13] Only one single isomer was isolated during every intermediate step of preparation as shown by chromatography using Dowex 50W-X8 (20—50 mesh) and Sephadex C25 cation exchangers. These complexes are not sufficiently soluble in most common solvents for n.m.r. study. In the absence of other isomers of the same complex for comparison, it is rather difficult to decide unambiguously the configuration of the complexes prepared. It is, however, reasonable to assume that they are isomerically pure and probably have the same configuration [N-*meso*(*RS*)] as the starting dichloro-complex. We are currently growing suitable crystals of some of these complexes in order to confirm their configuration by *X*-ray analysis.

Preliminary spectrophotometric studies showed that the changing visible-absorption spectra for the acid hydrolysis of *trans*-$[Co(CN)(L^1)X]^+$ maintained isosbestic points at 443 (X = Cl) and 449 nm (Br) throughout the entire reactions. The final spectrum was identical with that of an authentic sample of *trans*-$[Co(CN)L^1(OH_2)]^{2+}$. Volhard's titration confirmed that the release of halide was complete from both complexes. The first-order aquation rate constants were, therefore, obtained from gradients of standard semilogarithmic plots of $\ln(D_t - D_\infty)$ against time, where D_t and D_∞ represent absorbances at time *t* and after 10 aquation half-lives respectively. These plots were linear to three half-lives and the rate constants were found to be independent of acid (0.01—0.05 mol dm^{-3}) and complex (1.0×10^{-3}—4.0×10^{-3} mol dm^{-3}) concentrations. Most of the kinetic runs were carried out at 0.01 mol dm^{-3} HNO_3. The data are collected in Table 1.

TABLE 1

First-order rate constants for the acid hydrolysis of *trans*-$[Co(CN)(L^1)X]^+$ in 0.01 mol dm^{-3} HNO_3 [a]

X	θ_c/°C	10^3k_1 [b]/s^{-1}
Cl	18.0	1.10
	20.6	1.45
	24.4	2.35
	26.2	3.00
	29.3	3.90
	25.0	2.5 [c]
Br	8.1	1.45
	10.9	2.10
	14.1	3.10
	17.3	4.40
	20.6	6.30
	25.0	10.0 [c]

[a] These reactions were independent of the acid (0.01—0.05 mol dm^{-3}) and complex concentrations (1.0×10^{-3}—4.0×10^{-3} mol dm^{-3}). [b] Each entry represents an average from two to six different determinations. [c] Obtained by extrapolation from data at other temperatures.

The base hydrolysis of these complexes was most conveniently studied in buffer solutions. Isosbestic points were maintained at 445 and 372 nm for the chloro- (in 2,4,6-trimethylpyridine–HNO_3 buffer system) and at 448 and 387 nm for the bromo-complex (in 2,6-dimethylpyridine–HNO_3 buffer system). The initial spectrum was identical, in each case, with that of the starting complex while that of the final acidified solution was identical with that of *trans*-$[Co(CN)L^1(OH_2)]^{2+}$. Since general-base catalysis has been detected [12] for the hydrolysis of *trans*-$[CoA(L^1)X]^+$ (A = Cl or NCS, X = Cl or Br) in these amine buffers, reactions of these two cyano-complexes were, therefore, followed in buffer solutions of relatively low base (1×10^{-3}—1×10^{-2} mol dm^{-3}) and complex concentrations (1×10^{-4}—4×10^{-4} mol dm^{-3}) and at a constant ionic strength of 0.10 mol dm^{-3}. At these low base concentrations the contribution by these amine bases to catalysis of the hydrolysis of these complexes was effectively negligible. Pseudo-first-order rate constants, $k_{obs.}$, were obtained from standard semilogarithmic plots. The hydroxide-ion concentration for each kinetic run was obtained from the pH of the reaction solution and the ionic product of water at the same temperature.[14] Activity coefficients of hydroxide ion, $\gamma_\pm$, were calculated by the following approximate Debye–Hückel equation for a 1 : 1 electrolyte [15] at $I \leqslant 0.1$ mol dm^{-3}, where D represents the dielectric constant of

$$\log \gamma_\pm = \frac{-1.824 \times 10^6 I^{\frac{1}{2}}}{(1 + I^{\frac{1}{2}})(DT)^{\frac{3}{2}}}$$

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[13] N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, 1967, **6**, 770.

[14] ' Handbook of Chemistry and Physics,' 48th edn., ed. R. C. Weast, Chemical Rubber Co., Ohio, 1968, D-92.

[15] S. Glasstone, ' Text Book of Physical Chemistry,' 2nd edn., 1951, p. 967.

water at a temperature T on the absolute scale at $I = 0.10$ mol dm^{-3}; the activity coefficient is virtually constant (*ca.* 0.76—0.74) over the range 5—60 °C. The second-order base-hydrolysis rate constants, obtained from least-squares plots of $k_{obs.}$ against $[OH^-]$, are collected in Table 2. These plots did not pass through the origin and their intercepts agreed reasonably well with the aquation data extrapolated to the same temperature.

TABLE 2

Second-order base-hydrolysis rate constants of *trans*-$[Co(CN)(L^1)X]^+$ in buffer solutions and at $I = 0.10$ mol dm^{-3}

X	θ_c/°C	pH	$10^8[OH^-]$/mol dm^{-3}	$10^2 k_{obs.}$/s^{-1}	$10^{-5} k_{OH}$/dm^3 mol^{-1} s^{-1}
Cl [a]	11.6	7.22	7.4	0.44	0.52 ± 0.04
		7.59	17.0	1.0	
		7.80	28.0	1.5	
		7.94	39.0	2.1	
	15.9	7.15	9.0	0.80	0.74 ± 0.05
		7.54	22.0	1.8	
		7.74	35.0	2.7	
		7.85	45.0	3.5	
	21.1	7.38	23.0	2.8	1.15 ± 0.06
		7.58	37.0	4.5	
		7.74	54.0	6.4	
	25.1	6.95	12.0	2.3	1.6 ± 0.12
		7.32	28.0	5.0	
		7.52	45.0	7.3	
		7.64	59.0	9.8	
Br [b]	13.3	6.51	1.7	1.0	4.3 ± 0.15
		6.99	5.0	2.4	
		7.19	8.0	3.7	
	20.1	6.40	2.2	2.3	7.2 ± 0.7
		6.74	5.0	4.1	
		6.94	7.9	6.4	
	24.9	6.32	2.8	4.0	10.5 ± 1.0
		6.66	6.1	6.9	
		6.84	9.2	10.5	
		6.97	12.5	14	

[a] In 2,4,6-trimethylpyridine-HNO_3 buffer system. [b] In 2,6-dimethylpyridine-HNO_3 buffer system.

DISCUSSION

A plot of log k_{CNX} against log k_{N_3X} over an extensive series of L [L = L^1, L^4, L^5, $(en)_2$ (en = ethylenediamine), or $(NH_3)_4$] was linear with gradient = 1.0 (Figure 1). A similar plot with gradient *ca.* 1 has also been observed [5] between log k_{NCSX} and log k_{N_3X} [L = L^1, L^2, L^3, L^4, L^5, or $(en)_2$] (Figure 2). These observations imply that the electronic effects of $[CN]^-$, $[N_3]^-$, and $[NCS]^-$ in affecting the lability of these complexes respond similarly to changes of the common *cis*-amine ligands, independent of the nature of the leaving halide (Cl^- or Br^-). A plot of log k_{NO_2X} against log k_{N_3X} was linear with gradient = 0.9 for saturated *cis*-amine ligands [L = L^4, L^5, or $(en)_2$] (Figure 3). The deviation of points for L = L^2 and L^3 below the linear plot has been explained in terms of the co-operative π-conjugative effect.[7]

Comparison of Figures 1 and 3 shows quite clearly that these cyano-complexes do not behave in the same way as the corresponding π-accepting nitro-complexes in their response to increased unsaturation of the amine macrocycles. If the behaviour of the $[NO_2]^-$ ligand is 'normal' insofar as the co-operative π-conjugative effect is concerned, it is not clear why the $[CN]^-$ ligand should be 'abnormal'. However, it is worth noting

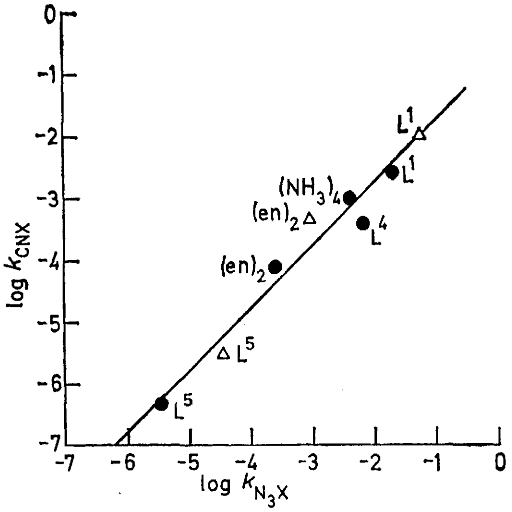

FIGURE 1 Least-squares plot of log k_{CNX} against log k_{N_3X} for the acid hydrolysis of *trans*-$[CoA(L)X]^+$ (A = CN and N_3 respectively): X = Cl (●) or Br (△)

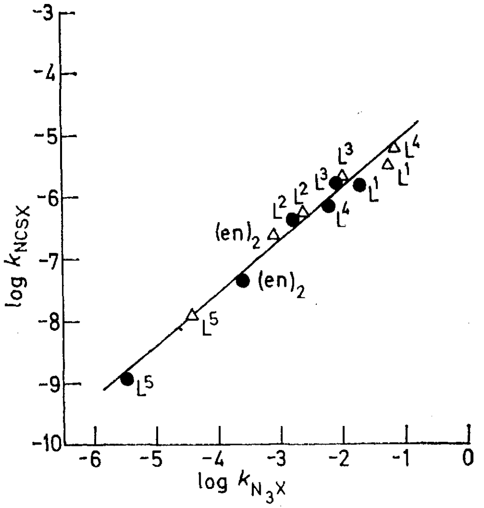

FIGURE 2 A similar plot to Figure 1 of log k_{NCSX} against log k_{N_3X}

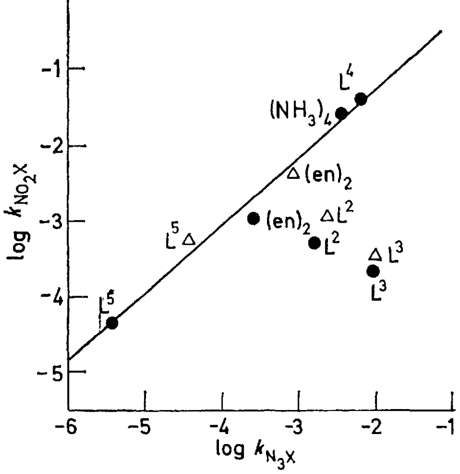

FIGURE 3 A similar plot to Figure 1 of log k_{NO_2X} against log k_{N_3X}

that these cyano-complexes are rather exceptional in that the $k_{Br} : k_{Cl}$ ratio of the L^1 complexes (4.0) is nearly equal to that of the corresponding saturated L^5 complexes (5.8 : 1), suggesting that the presence of some π conjugation in the former does not prominently affect the ' hardness ' of the cobalt(III) ion in the latter complexes.

TABLE 3

Second-order rate constants, k_{OH}, at 25.0 °C and activation parameters for the base hydrolysis of some complexes of the type *trans*-$[CoA(L)X]^+$

L	A	X	k_{OH} / $dm^3 mol^{-1} s^{-1}$	$\Delta H^‡$ / kJ mol^{-1}	$\Delta S^‡$ / J $K^{-1} mol^{-1}$
L^1	Cl [a]	Cl	2.2×10^5		
L^1	NCS [b]	Cl	1.3×10^5	51.5 ± 1.5	25 ± 12
L^1	NCS [b]	Br	2.9×10^5	52.8 ± 2.0	37 ± 15
L^1	CN [c]	Cl	1.6×10^5	56.5 ± 1.0	44 ± 8
L^1	CN [c]	Br	1.1×10^6	52.4 ± 1.0	46 ± 8
L^5	Cl [d]	Cl	6.7×10^4	56.5 ± 1.5	37 ± 12
L^5	NCS [e]	Cl	9.0×10^2	87.8 ± 1.5	106 ± 12
L^5	NCS [b]	Br	1.1×10^4	78.8 ± 1.3	97 ± 8
L^5	CN [f]	Cl	2.8×10	94.6 ± 1.0	100 ± 8
L^5	CN [g]	Br	5.0×10^2	84.1 ± 1.5	88 ± 12

[a] At 19.8 °C; J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, 1970, **9**, 1504. [b] Ref. 12. In that paper, no allowance was made for the deviation from unity of the activity coefficient of the hydroxide ion at $I = 0.10$ mol dm^{-3}. From the primary data in Table 2 of the paper the hydroxide-ion concentrations were recalculated as described here in the text and the new entries for k_{OH}, $\Delta H^‡$, and $\Delta S^‡$ are presented in this Table. It should be noted that the k_{OH} values are effectively decreased by a factor of *ca.* 0.75 while $\Delta H^‡$ values remain virtually unchanged. [c] This work. [d] C. K. Poon, Ph.D. Thesis, University of London, 1967; data recalculated by the method of least squares. [e] K. S. Mok, C. K. Poon, and H. W. Tong, *J.C.S. Dalton*, 1972, 1701. [f] C. K. Poon and H. W. Tong, *J.C.S. Dalton*, 1973, 1301. [g] Ref. 9.

The present investigation of the base hydrolysis of *trans*-$[Co(CN)(L^1)X]^+$ confirmed that the second-order rate constants of these L^1 halogeno-complexes are indeed virtually independent of the nature of orientating $[CN]^-$, $[NCS]^-$, and Cl^- ligands (Table 3). The activation enthalpies lie in a narrow range (*ca.* 54 ± 3 kJ mol^{-1}) and activation entropies are *ca.* 35 ± 10 J K^{-1} mol^{-1}. These values of the rate constants and activation parameters are very similar to those of the amine proton-exchange reactions of most cobalt(III) amine complexes.[12,16] All these observations have been taken to indicate a ' limiting ' $S_N1(CB)$ mechanism for the base hydrolysis of these L^1 halogeno-complexes (cyano, isothiocyanato, and chloro), in which the deprotonation of the L^1 ligand (amine proton) becomes the rate-determining step.[11,12,16] For the L^5 series of complexes, the dichloro-complex has been shown to react by a ' limiting,' while the cyano- and isothiocyanato-halogeno-complexes react by the ' normal,' $S_N1(CB)$ mechanism.[16] Here the rate constants are definitely dependent on the nature of both the orientating and leaving groups with much greater activation enthalpies (78—95 kJ mol^{-1}) and entropies (88—106 J K^{-1} mol^{-1}).

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[16] M. L. Tobe, *Accounts Chem. Res.*, 1970, **3**, 377.