Kinetics of Base Hydrolysis of *cis*-Aminebromobis(ethylenediamine)-cobalt(III) Complexes in Aqueous Solution at 25 °C

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Rate constants, k_{OH}, are reported for the base hydrolysis of 11 penta-aminebromocobalt(III) complexes, *cis*-$[CoBr(en)_2(NH_2R)]^{2+} + [OH]^- \longrightarrow [Co(OH)(en)_2(NH_2R)]^{2+} + Br^-$, at 25 °C and I = 0.1 mol dm^{-3}. For the straight-chain amines (R = Me, Et, Pr^n, Bu^n, n-pentyl, or n-hexyl) the values of k_{OH} are essentially constant at 82 ± 3 dm^3 mol^{-1} s^{-1}. These results are in contrast to previous reports that the Pr^n derivative undergoes base hydrolysis 5—6 times faster than the methyl and ethyl derivatives. For the straight-chain amines the value of k_{OH}^{Br}/k_{OH}^{Cl} is *ca.* 6.2. Activation parameters for the base hydrolysis of the Pr^n derivative are $\Delta H^\ddagger$ = 89 ± 2 kJ mol^{-1} and $\Delta S^\ddagger$ = 96 ± 4 J K^{-1} mol^{-1} at 298 K. The positive $\Delta S^\ddagger$ is consistent with an S_N1(CB) mechanism. Bulky amines such as cyclopropylamine and 2,2-dimethoxyethylamine lead to significant increases in the rates of base hydrolysis, probably due to steric acceleration of the ionisation step. With α,ω-aminoalkanols there is evidence for specific hydrogen-bonding effects leading to increased base-hydrolysis rates.

A PREVIOUS paper[1] dealt with the base hydrolysis of a variety of penta-aminechlorides of the type *cis*-$[CoCl(en)_2(NH_2R)]^{2+}$ (en = ethylenediamine). In contrast to previous work,[2-4] it was found that within experimen-

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[1] R. W. Hay and P. L. Cropp, *J. Chem. Soc.* (*A*), 1969, 42.

[2] S. C. Chan and F. Leh, *J. Chem. Soc.* (*A*), 1966, 126.

[3] S. C. Chan and F. Leh, *J. Chem. Soc.* (*A*), 1966, 129.

[4] S. C. Chan and F. Leh, *J. Chem. Soc.* (*A*), 1966, 134.

tal error the straight-chain amine derivatives (R = Me, Et, Pr^n, or Bu^n) hydrolysed at the same rate with k_{OH} = 12.75 ± 0.4 $dm^3 mol^{-1} s^{-1}$ at 25 °C and I = 0.1 mol dm^{-3}. The simple amine derivative (R = H) hydrolysed at a somewhat slower rate (k_{OH} 8.1 ± 0.4 $dm^3 mol^{-1} s^{-1}$), while the branched-chain derivative (R = Pr^i) hydrolysed *ca.* four times faster than the straight-chain derivative (R = Pr^n), probably due to steric acceleration of halide loss in an S_N1 process. Chan *et al.*[5] studied the base hydrolysis of a variety of penta-aminebromides of the type *cis*-$[CoBr(en)_2(NH_2R)]^{2+}$ over the range 0—20 °C and I = 0.1 mol dm^{-3}, and reported quite marked differences in the rates of hydrolysis of straight-chain amine derivatives; thus for R = Pr^n, k_{OH} = 141 dm^3 $mol^{-1} s^{-1}$ at 20.3 °C and for R = Et, k_{OH} = 24.2 dm^3 $mol^{-1} s^{-1}$ at 20.3 °C. For this reason we have studied the base-hydrolysis rates of a variety of penta-aminebromides, to complement the previous work on the penta-aminechlorides.

EXPERIMENTAL

Materials.—*trans*-Dibromobis(ethylenediamine)cobalt(III) bromide was prepared essentially as described by Werner[6] (Found: C, 11.8; H, 4.1; N, 13.6. Calc. for $C_4H_{16}Br_3CoN_4$: C, 11.5; H, 3.9; N, 13.4%). The penta-aminebromides were synthesised essentially as described by Bailar and Clapp.[7] For R = Et, Pr^n, Bu^n, n-pentyl, and n-hexyl a typical preparation was as follows. The complex *trans*-$[CoBr_2(en)_2]Br$ (4.18 g, 0.01 mol) and water (2 cm^3) were ground to a paste, with the addition of a small excess of the appropriate amine. The paste rapidly changed from bright green to the characteristic purple-red of the penta-aminebromide. After *ca.* 0.5 h the coagulated mixture was filtered on sintered glass, and the *product* washed with methanol until the washings were colourless. The crude complex was recrystallised from the minimum volume of hot water (*ca.* 60 °C) containing a few drops of concentrated hydrobromic acid. Even after recrystallisation, the complexes were contaminated by $[Co(en)_3]^{3+}$ which was removed by gel filtration as follows. The complex was dissolved in the minimum volume of water (60 °C) acidified with HBr, and pipetted on to a column of Sephadex G-10. The complexes were eluted with dilute HBr (*ca.* 0.01 mol dm^{-3}). Two major bands were normally obtained. The first, faster-moving, orange-yellow band due to $[Co(en)_3]^{3+}$ was discarded and the second purple-red band of the desired complex was collected and concentrated on a rotatory evaporator to *ca.* 5 cm^3. Cooling gave the required complex. The other complexes were prepared similarly but in some cases it was necessary to extend the reaction period during grinding to *ca.* 1 h or more. Analytical data for the various penta-aminebromides are summarised in Table 1.

cis-Aqua(n-butylamine)bis(ethylenediamine)cobalt(III) trinitrate monohydrate, *cis*-$[Co(en)_2(OH_2)(NH_2Bu^n)][NO_3]_3{\cdot}H_2O$, was prepared by mercury(II)-catalysed aquation. Mercury(II) nitrate (36 g) in nitric acid (100 cm^3, 2 mol dm^{-3}) was added to a suspension of *cis*-$[CoBr(en)_2(NH_2Bu^n)]Br_2$ (5 g) in nitric acid (110 cm^3, 2 mol dm^{-3}) at 60 °C. The resulting solution was stirred for 15 min and filtered while hot. Ethanol–diethyl ether (200 cm^3, 1 : 1) was added to the cold solution which was then placed in a refrigerator overnight. The orange-red crystalline *product* was recrystallised from nitric acid (1 mol dm^{-3}) at 60 °C, after gel-filtration on Sephadex G-10 (Found: C, 20.8; H, 4.9; N, 24.5. Calc. for $C_8H_{22}CoN_8O_{11}$: C, 20.65; H, 4.8; N, 24.1%).

TABLE 1

Analytical data (%) for *cis*-$[CoBr(en)_2(NH_2R)]Br_2$

	Calc.			Found		
R	C	H	N	C	H	N
H	11.0	4.4	16.05	10.8	4.6	15.8
Me	13.3	4.7	15.5	13.1	4.8	15.3
Et	15.5	5.0	15.0	15.5	5.2	15.0
Pr^n	17.6	5.5	14.6	17.5	5.4	14.6
Bu^n	19.5	5.5	14.2	19.8	5.7	14.3
n-Pentyl	21.4	5.8	13.8	21.5	5.9	13.7
n-Hexyl	23.1	6.0	13.5	23.2	6.0	13.3
$CH_2CH(OMe)_2$	18.3	5.2	13.45	18.5	5.4	13.8
Cyclopropyl	17.7	4.9	14.7	17.4	4.9	14.5
$(CH_2)_3OH$	17.1	5.1	14.2	17.1	5.1	14.1
$(CH_2)_6OH$	22.4	5.8	13.1	22.2	5.8	13.0
$CH_2CH(OMe)_2$ [a]	24.6	6.95	17.9	24.3	6.9	18.0
Cyclopropyl [b]	23.3	7.0	19.4	23.6	6.9	19.5

[a] The penta-aminechloride was isolated as the chloride salt. Analytical data are based on the anhydrous complex. [b] For *cis*-$[CoCl(en)_2\{NH_2(C_3H_5)\}]Cl_2{\cdot}H_2O$.

cis-Chloro(cyclopropylamine)bis(ethylenediamine)cobalt(III) dichloride monohydrate was prepared essentially as described by Chan and Cheung.[8] The crude complex was recrystallised from hot water (*ca.* 60 °C) containing a few drops of concentrated hydrochloric acid. The brick-red crystalline product was dried *in vacuo* (Found: C, 23.6; H, 6.9; N, 19.5. Calc. for $C_5H_{17}Cl_3CoN_3O$: C, 23.3; H, 7.0; N, 19.4%). Visible spectrum: $\lambda_{max.}$ 527 (73) and 348 nm (ε 82 $dm^3 mol^{-1} cm^{-1}$).

cis-*Chloro*(2,2-*dimethoxyethylamine*)*bis*(*ethylenediamine*)-*cobalt*(III) *Dichloride.*—The complex *trans*-$[CoCl_2(en)_2]Cl$ (2.86 g) was ground to a paste with water and an equimolar amount of 2,2-dimethoxyethylamine added dropwise with continuous grinding for 30 min. The coagulated *product* was crystallised by addition of methanol (30 cm^3) and purified by gel filtration. The complex was then recrystallised from dilute HCl and dried *in vacuo* (Found: C, 24.3; H, 6.9; N, 18.0. Calc. for $C_8H_{28}Cl_3CoN_5O_2$: C, 24.6; H, 6.95; N, 17.9%). Visible spectrum: $\lambda_{max.}$ 528 (78) and 368 nm (ε 90 $dm^3 mol^{-1} cm^{-1}$).

Kinetics and Measurements.—The kinetics of base hydrolysis were studied in the range pH 8.5—9.5 at I = 0.1 mol dm^{-3} ($Na[ClO_4]$). Sodium tetraborate–boric acid buffers were used for pH 8.5—9.2 and sodium tetraborate–potassium hydroxide buffers for pH 9.3—9.7,[9] the buffers being adjusted to the appropriate ionic strength by the addition of sodium perchlorate. The reactions were monitored spectrophotometrically on a Gilford 2400S instrument using the absorbance decrease at 315 nm. Plots of log $(A_t - A_\infty)$ were linear in each case for at least three half-lives. The pH of the buffers was determined prior to the run and normally checked on completion. The pH values were determined with a Radiometer 26 pH meter equipped

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[5] S. C. Chan, C. Y. Cheng, and F. Leh, *J. Chem. Soc.* (*A*), 1967, 1586.

[6] A. Werner, *Annalen*, 1912, **386**, 118.

[7] J. C. Bailar and L. B. Clapp, *J. Amer. Chem. Soc.*, 1945, **67**, 171.

[8] S. C. Chan and T. L. Cheung, *Austral. J. Chem.*, 1970, **23**, 707.

[9] D. D. Perrin, *Austral. J. Chem.*, 1963, **16**, 572.

with a G202B high-alkalinity glass electrode and a K401 calomel electrode. Values of the hydroxide-ion concentration were obtained from the pH using a molar activity coefficient of 0.772 and a value of pK_w 13.997 at 25 °C.[10] The activity coefficients at 30 and 35 °C were estimated from the Davies' equation [11] using literature values [12] of the Debye–Hückel parameter A. The requisite activity coefficients are 0.770 (30) and 0.768 (35 °C). The appropriate values of pK_w are [10] 13.883 (30) and 13.680 (35 °C).

Visible spectral measurements were made with a Perkin-Elmer 402 instrument using 1-cm cells. Infrared spectra were determined as KBr discs with a Perkin-Elmer 457 instrument. Hydrogen-1 n.m.r. spectra were determined at 90 MHz using perdeuteriodimethyl sulphoxide as solvent and tetramethylsilane as internal reference.

RESULTS AND DISCUSSION

General.—The *cis* configuration of the penta-aminebromides was established by a variety of physical measurements. Two spin-allowed *d–d* transitions are normally observed for octahedral cobalt(III) complexes ($^1A_{1g}\rightarrow{}^1T_{1g}$ at lower energy, and $^1A_{1g}\rightarrow{}^1T_{2g}$ at higher energy). For the CoN_5Br chromophore the shorter-wavelength band is obscured by the charge-transfer band so that a single *d–d* band is observed (Table 2).

TABLE 2

Visible spectra of *cis*-$[CoBr(en)_2(NH_2R)]Br_2$ complexes

R	$\lambda_{max.}$ nm	ε dm³ mol⁻¹ cm⁻¹	$\lambda_{min.}$ nm	ε dm³ mol⁻¹ cm⁻¹
H	544	75	425	18
Me	548	71	431	20
Et	547	72	429	22
Pr^n	549	81	430	23
Bu^n	546	78	428	21
n-Pentyl	546	79	431	24
n-Hexyl	545	80	429	23
$CH_2CH(OMe)_2$	546	79		
Cyclopropyl	548	81		
$(CH_2)_3OH$	547	84		
$(CH_2)_6OH$	545	76		
$CH_2CH(OMe)_2$ [a]	528	78	368 [b]	90
Cyclopropyl [a]	527	73	348 [b]	82

[a] For penta-aminechloride. [b] $\lambda_{max.}$ value.

All the complexes have $\lambda_{max.}$ 546 ± 2 nm with absorption coefficients in the range 70—80 dm³ mol⁻¹ cm⁻¹, fully consistent with the *cis* configuration.[13] The *trans* complexes normally have absorption coefficients of 40—50 dm³ mol⁻¹ cm⁻¹ for the lowest-energy ligand-field band. The i.r. spectra also support this assignment (Table 3). The splitting of the δ(NH) bands of the NH_2 groups of the ethylenediamine ligands gives two bands at *ca.* 1 612w and 1 574vs cm⁻¹, consistent with a *cis* stereochemistry. The more symmetrical *trans* complexes generally display a single band.[14] In addition, Baldwin [15] has shown that the most consistent difference in the i.r. spectra of *cis* and *trans* isomers of bis(ethylenediamine)cobalt(III) complexes occurs in the CH_2-rocking region between 870 and 900 cm⁻¹. In this region the *cis* isomer commonly displays two bands and the *trans* isomer only one. The splitting is due to the lower symmetry of the *cis* derivatives. All the penta-aminebromides show two bands in this region (Table 3).

TABLE 3

Characteristic i.r. bands (cm⁻¹) [a] for penta-aminebromides

R	CH_2 rock	$\delta(NH_2)$
Me	890, 878	1 587, 1 610w
Et	892, 876	1 573, 1 618w
Pr^n	894, 873	1 559, 1 613w
Bu^n	902, 894	1 578, 1 594w
n-Pentyl	896, 872	1 580, 1 608w
n-Hexyl	895, 877	1 582, 1 609 (sh)
$CH_2CH(OMe)_2$	890, 875	1 580
Cyclopropyl	880, 860	1 572
$(CH_2)_3OH$ [b]	890, 876	[c]
$(CH_2)_6OH$ [d]	894, 885	[e]

[a] All the spectra were determined as KBr discs. [b] ν(OH) at 3 360s,br cm⁻¹. [c] Bands at 1 959 and 1 545 cm⁻¹. [d] ν(OH) at 3 420s, br cm⁻¹. [e] Broad band at 1 570 cm⁻¹ due to δ(NH) and δ(OH).

N.m.r. measurements can be of particular value in assigning stereochemistry. The chemical shift of the NCH_2CH_2N protons provides a useful criterion of stereochemistry. Lantzke and Watts [16] have noted that for *cis*-bis(ethylenediamine) complexes the NCH_2CH_2N signal occurs below δ 3.0 (mean 2.88) p.p.m. whereas the *trans* isomers have signals at δ >3.0 p.p.m. Although the position of the NH signals is a function of the ligand-field strength of the other ligands in the complex,[17] the NCH_2CH_2N signal is unaffected; thus in *cis*-$[CoCl_2(en)_2]^+$ and *cis*-$[Co(CN)_2(en)_2]^+$ the NCH_2CH_2N signals occur at δ *ca.* 3.2 p.p.m. in CF_3CO_2H as solvent.[17] In addition, the position of the NCH_2CH_2N resonance is almost independent of the solvent (water Me_2SO, CF_3CO_2H, or D_2SO_4) used in the measurement.[16,17] In the n.m.r. spectra [in $(CD_3)_2SO$] of all the penta-aminehalides reported here the NCH_2CH_2N signal is at δ <3.0 p.p.m., fully consistent with a *cis* stereochemistry.

Kinetics.—The base hydrolysis of the penta-aminebromides can be summarised by equation (1). The

$$cis\text{-}[CoBr(en)_2(NH_2R)]^{2+} + [OH]^- \xrightarrow{k_{OH}} [Co(OH)(en)_2(NH_2R)]^{2+} + Br^- \quad (1)$$

reaction was normally studied in the range pH 8.6—9.6 using a sodium tetraborate–boric acid buffer adjusted to $I = 0.1$ mol dm⁻³. Values of $k_{obs.}$ (the observed first-order rate constant at constant pH) for the various penta-aminehalides are listed in Table 4. In each case, the values of $k_{obs.}/[OH^-] = k_{OH}$ are effectively constant, confirming a first-order dependence on the hydroxide-ion concentration. Conversion of the penta-aminebromide into the penta-aminehydroxide leads to a significant visible spectral change. Thus an N_5Br donor system has $\lambda_{max.}$ at *ca.* 546 ± 2 nm for the lowest-energy

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[11] C. W. Davies, *J. Chem. Soc.*, 1938, 2093.

[12] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' 2nd edn., Butterworths, London, 1959.

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[14] M. L. Morris and D. H. Busch, *J. Amer. Chem. Soc.*, 1960, **82**, 1521.

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[16] J. R. Lantzke and D. W. Watts, *Austral. J. Chem.*, 1967, **20**, 35.

[17] H. Yoneda and Y. Nakashima, *Bull. Chem. Soc. Japan*, 1974, **47**, 669.

TABLE 4

Rate constants for the base hydrolysis of $[CoBr(en)_2(NH_2R)]^{2+}$ at 25 °C and $I = 0.1$ mol dm^{-3} ($Na[ClO_4]$)

R	pH	$10^3k_{obs.}/s^{-1}$	$k_{OH}/$ dm^3 mol^{-1} s^{-1}
H	8.59	0.371	73.6
	8.77	0.510	66.8
	8.98	0.831	67.1
	9.18	1.30	66.3
	9.18	1.41	71.9
	9.35	1.89	65.2
	9.59	3.56	70.6
	$k_{OH} = 69 \pm 4$ dm^3 mol^{-1} s^{-1}		
Me	8.59	0.418	83.0
	8.79	0.663	83.1
	8.98	0.990	80.0
	9.19	1.60	82.3
	9.38	2.55	82.0
	$k_{OH} = 82 \pm 3$ dm^3 mol^{-1} s^{-1}		
Et	8.54	0.368	82.0
	8.73	0.525	75.4
	8.98	0.923	74.6
	9.19	1.63	81.1
	9.30	1.95	75.3
	9.57	3.72	77.2
	$k_{OH} = 78 \pm 3$ dm^3 mol^{-1} s^{-1}		
Pr^n	8.53	0.338	77.0
	8.73	0.548	78.8
	8.97	0.970	78.5
	9.17	1.48	77.6
	9.32	2.23	82.6
	9.32	2.21	81.8
	9.57	3.87	80.5
	$k_{OH} = 79.5 \pm 3$ dm^3 mol^{-1} s^{-1}		
Bu^n	8.53	0.363	82.6
	8.73	0.571	82.0
	9.01	1.12	84.6
	9.18	1.51	77.5
	9.32	2.11	78.1
	9.57	3.95	81.8
	$k_{OH} = 81 \pm 3$ dm^3 mol^{-1} s^{-1}		
n-Pentyl	8.55	0.391	85.0
	8.55	0.388	84.3
	8.99	1.09	83.1
	9.27	2.15	88.0
	9.58	4.18	85.0
	$k_{OH} = 85 \pm 3$ dm^3 mol^{-1} s^{-1}		
n-Hexyl	8.56	0.383	83.3
	8.74	0.575	80.7
	8.98	1.09	88.0
	9.27	2.00	83.0
	9.58	4.06	82.5
	9.59	4.40	87.3
	$k_{OH} = 84 \pm 4$ dm^3 mol^{-1} s^{-1}		
$CH_2CH(OMe)_2$ (X = Br)	7.98	1.96	1 584
	8.33	4.55	1 642
	8.66	9.71	1 640
	8.98	20.1	1 625
	$k_{OH} = 1\,623 \pm 20$ dm^3 mol^{-1} s^{-1}		
(X = Cl)	8.98	1.05	85
	9.17	1.71	90
	9.37	2.75	90
	9.54	3.55	78
	$k_{OH} = 86 \pm 4$ dm^3 mol^{-1} s^{-1}		
Cyclopropyl (X = Br)	8.55	2.48	539
	8.75	4.31	592
	8.97	7.20	596
	9.28	12.6	510
	$k_{OH} = 560 \pm 30$ dm^3 mol^{-1} s^{-1}		
Cyclopropyl (X = Cl)	8.52	0.56	130
	9.08	1.96	127
	9.28	3.23	131
	9.37	3.80	125
	$k_{OH} = 128 \pm 5$ dm^3 mol^{-1} s^{-1}		
$(CH_2)_3OH$	8.64	0.86	153
	8.77	1.16	152
	8.97	1.76	146
	9.18	3.05	155
	9.31	3.86	146
	9.39	4.81	151
	$k_{OH} = 150.5 \pm 5$ dm^3 mol^{-1} s^{-1}		
$(CH_2)_6OH$	8.53	0.47	107
	8.53	0.45	103
	8.83	0.95	108
	9.03	1.55	111
	9.44	3.86	110
	9.44	4.08	114
	$k_{OH} = 109 \pm 5$ dm^3 mol^{-1} s^{-1}		

ligand-field band, compared with $\lambda_{max.}$ *ca.* 504 ± 3 nm for the N_5OH donor system on Co^{III}. A sample of *cis*-$[Co(en)_2(NH_2Bu^n)(OH_2)]^{3+}$ was prepared by mercury(II)-catalysed aquation of the penta-aminebromide. It has been established that mercury(II)-catalysed aquations occur with retention of configuration.[18] The spectrum of the penta-aminehydroxide obtained by base hydrolysis of *cis*-$[CoBr(en)_2(NH_2Bu^n)]^{2+}$ has $\lambda_{max.}$ 504 (114) and 358 nm (ε 101 dm^3 mol^{-1} cm^{-1}). This spectrum is almost identical to that of the *cis*-penta-aminehydroxide obtained by dissolving *cis*-$[Co(en)_2(NH_2Bu^n)(OH_2)]^{3+}$ in 0.1 mol dm^{-3} sodium hydroxide [$\lambda_{max.}$ 502 (113) and 354 nm (ε 109 dm^3 mol^{-1} cm^{-1})]. Base hydrolysis in these systems thus occurs predominantly with retention of configuration, suggesting a square-pyramidal intermediate.

The values of k_{OH} obtained for the various penta-aminebromides are summarised in Table 5, together with the rate constants[1] for the analogous penta-aminechlorides. For the straight-chain amines (R = Me, Et, Pr^n, Bu^n, *n*-pentyl, or *n*-hexyl) the values of $k_{OH}{}^{Br}$ are remarkably constant with $k_{OH}{}^{Br} = 82 \pm 3$ dm^3 mol^{-1} s^{-1} at 25 °C and $I = 0.1$ mol dm^{-3}. The value for R = H is somewhat lower (69 dm^3 mol^{-1} s^{-1}) and for the linear amines there appears to be a rough correlation between the pK_a of the substituent amine and the value of k_{OH}; the lower the pK_a the lower is the value of k_{OH}. The present results contrast sharply with those of Chan *et al.*[5] who reported that the Pr^n derivative underwent base hydrolysis some 5—6 times faster than the Me and Et derivatives at 20.3 °C and $I = 0.1$ mol dm^{-3}. In addition, the values of $k_{OH}{}^{Br}/k_{OH}{}^{Cl}$ lie in the range 6.1—6.4 for the Me, Et, Pr^n, and Bu^n derivatives, although Chan *et al.*[5] have reported that the values of $k_{OH}{}^{Br}/k_{OH}{}^{Cl}$ are significantly greater for Pr^n than for the Me or Et substituents. For R = Et the quoted value is 7.2, but for R = Pr^n the value is 25.

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[18] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 1960, 4812; S. C. Chan and M. L. Tobe, *ibid.*, 1963, 514; A. M. Sargeson, *Austral. J. Chem.*, 1963, **16**, 352.

Activation parameters were determined for the base hydrolysis of *cis*-$[CoBr(en)_2(NH_2Pr^n)]^{2+}$. At $I = 0.1$ mol dm^{-3} the values of k_{OH} at 30.1 and 39.8 °C are 141.3 and 467.7 dm^3 mol^{-1} s^{-1} respectively. These constants give $\Delta H^‡ = 89$ kJ mol^{-1} and $\Delta S^‡ = 96$ J K^{-1} mol^{-1} at 298 K. A positive $\Delta S^‡$ value is predicted for an $S_N1(CB)$ mechanism and calculations[19] suggest that a value of *ca.* 142 J K^{-1} mol^{-1} should be observed. Most of the experimental values obtained for hydrolysis of penta-aminehalides fall within the range 87—174 J K^{-1} mol^{-1}. For an S_N2 process a value of $\Delta S^‡$ of *ca.* −63 J K^{-1} mol^{-1} is predicted.[19]

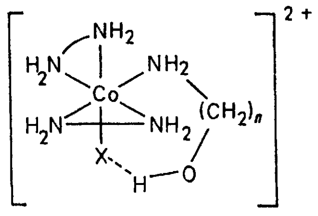
TABLE 5

Summary of base-hydrolysis rate constants (k_{OH}) for *cis*-$[CoX(en)_2(NH_2R)]^{2+}$ (X = Cl or Br) at 25 °C and $I = 0.1$ mol dm^{-3}

R	pK_a [a]	k_{OH}^{Br} / dm^3 mol^{-1} s^{-1}	k_{OH}^{Cl} / dm^3 mol^{-1} s^{-1}	k_{OH}^{Br}/k_{OH}^{Cl}
H	9.27	69 ± 4	8.1 ± 0.4 [b]	8.7
Me	10.67	82 ± 3	12.8 ± 0.4 [b]	6.4
Et	10.67	78 ± 3	12.8 ± 0.4 [b]	6.1
Pr^n [c]	10.69	79 ± 3	12.8 ± 0.4 [b]	6.2
Bu^n	10.66	81 ± 3	12.8 ± 0.4 [b]	6.4
n-Pentyl	10.64	85 ± 3		
n-Hexyl	10.64	84 ± 4		
$CH_2CH(OMe)_2$	<9.45 [d]	1 623 ± 20	86 ± 5	18.9
Cyclopropyl	9.10 [e]	560 ± 30	128 ± 5	4.3
$(CH_2)_3OH$	9.96	150 ± 5		
$(CH_2)_6OH$	10.60 (21 °C)	109 ± 5		

[a] Data from D. D. Perrin, ' Dissociation Constants of Organic Bases,' Plenum, New York, 1965; values at 25 °C. [b] From ref. 1. [c] For hydrolysis of the penta-amine bromide: $\Delta H^‡ =$ 89 kJ mol^{-1}; $\Delta S^‡ = 96$ J K^{-1} mol^{-1}. [d] The value for 2-methoxyethylamine is 9.45, *cf.* the reported value of 10.67 for ethylamine; thus the pK_a of 2,2-dimethoxyethylamine is expected to be *ca.* 8.2. [e] J. J. Christensen, R. M. Izatt, D. P. Wrathall, and L. D. Hansen, *J. Chem. Soc.* (*A*), 1969, 1212.

The present results are consistent with an $S_N1(CB)$ process involving rate-determining halide ionisation to give a five-co-ordinate intermediate. Steric acceleration of an ionisation process is expected to occur. Quite significant rate enhancements are observed with bulky amines such as cyclopropylamine and 2,2-dimethoxyethylamine. Steric compression in the complex leads to steric acceleration of the ionisation process, and would be expected to be greater with the larger bromide ion than with chloride, which may account for the high value of $k_{OH}^{Br}/k_{OH}^{Cl} = 18.9$ observed for the complex containing 2,2-dimethoxyethylamine. Steric compression should also be manifested in changes in $\Delta H^‡$. However, in these reactions there appears to be a close interplay between enthalpy and entropy changes and it might be that for R = cyclopropyl a decrease in $\Delta H^‡$ is outweighed by a more negative $\Delta S^‡$, so that the somewhat anomalous k_{OH}^{Br}/k_{OH}^{Cl} value of 4.3 is observed. Hydrogen-bonding effects are also important in determining relative reactivities: hydrogen bonding[20] between water and the outgoing halogen is expected to follow the order Br < Cl. The somewhat higher reactivities observed for the complexes with the α,ω-aminoalkanols suggest that intramolecular hydrogen bonding of the type shown in (I) may also assist the loss of halide ion in the ionisation step.



(I)

The effect is more marked for $n = 3$ (eight-membered ring) than for $n = 6$ (11-membered ring). The ν(OH) band for hydroxyl groups which are completely ' free ' (*i.e.* both intra- and inter-molecular hydrogen bonding is absent) is usually sharp and for alcohols occurs at 3 625 ± 10 cm^{-1}. Bands of ν(OH) which are broader and at values lower than 3 625 cm^{-1} indicate hydrogen bonding. For the penta-aminebromides, when R = $(CH_2)_3OH$, ν(OH) occurs at 3 360 cm^{-1} while for R = $(CH_2)_6OH$ the ν(OH) is at 3 420 cm^{-1}. Both bands are strong and relatively broad. Δν values of 50—200 cm^{-1} indicate medium hydrogen bonding, while Δν > 200 cm^{-1} indicates strong hydrogen bonding. The i.r. measurements thus support the view that intramolecular hydrogen bonding might be of kinetic importance in these systems.

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