Kinetics of Hydrolysis of *trans*-Dichloro- and *trans*-Dibromo-(*N-meso*-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene)cobalt(III) Cations

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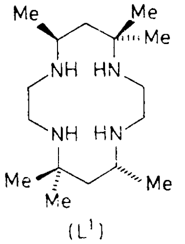
The kinetics of hydrolysis of the title cations *trans*-$[CoX_2(N\text{-}meso\text{-}L^4)]^+$ (X = Cl or Br; L^4 = 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene) have been studied at I = 0.1 mol dm^{-3} over the range pH 3.0—4.5. Hydrolysis of the first halogen ligand obeys a rate expression of the form $k_{obs.} = k_{OH_2} + k_1^{OH}[OH^-]$, where $k_{obs.}$ is the observed first-order rate constant at constant pH. The values of k_1^{OH} are 8.5×10^7 (X = Cl) and *ca.* 1×10^9 dm^3 mol^{-1} s^{-1} (X = Br) at 25 °C. The base-hydrolysis rates are the highest yet reported for halogenocobalt(III) complexes of the $[CoX_2(N_4)]^{2+}$ type. The pH-independent process is represented by $k_{OH_2} = 5.4 \times 10^{-3}$ s^{-1} for the chloro-complex. Hydrolysis of the second halogen ligand proceeds more slowly and in this case $k_{obs.} = k_2^{OH}[OH^-]$ with $k_2^{OH} = 5.9 \times 10^6$ (X = Cl) and 1.2×10^7 dm^3 mol^{-1} s^{-1} (X = Br) at 25 °C. The thermodynamic activation parameters for the hydrolysis of the second halogen ligand are $\Delta H^\ddagger$ = 57 kJ mol^{-1} and $\Delta S_{298}^\ddagger$ = 75 J K^{-1} mol^{-1} (X = Cl) and $\Delta H^\ddagger$ = 56 kJ mol^{-1} and $\Delta S_{298}^\ddagger$ = 80 J K^{-1} mol^{-1} (X = Br). These values may indicate rate-determining deprotonation of the substrate in the base-hydrolysis reactions.

RECENTLY there has been considerable interest in the substitution reactions of cobalt(III) complexes of macrocyclic ligands. Poon [1] has reviewed the area with particular emphasis on the hydrolysis of unidentate ligands in cobalt(III) complexes containing macrocyclic N_4 ligands. Previous studies [1-5] have dealt primarily with cobalt(III) complexes of *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane, tet *a* (L^1), 1,4,8,11-tetra-azacyclotetradecane, cyclam (L^2), and 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene, *trans*-[14]-diene (L^3).

The present paper deals with the base hydrolysis and aquation rates of complexes of 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene, L^4. Complexes of this ligand have two chiral nitrogen centres and two diastereoisomers occur, the *N-rac* [*i.e. RR*(*SS*)] diastereoisomer (I) and the *N-meso* (*i.e. RS*) diastereoisomer (II). The *N-meso* and *N-rac* diastereoisomers have been isolated and characterised in the case of $[CoCl_2(L^4)]^+$ (ref. 6) and $[NiL^4]^{2+}$; [7] the *N-rac* diastereoisomer is the most thermodynamically stable.[6,7] The configuration of these complexes has been established by resolution [8] of $[Ni(N\text{-}rac\text{-}L^4)]^{2+}$ on potato starch and by crystallography [9] of $[Co(N\text{-}rac\text{-}L^4)(SCN)_2][SCN]\cdot H_2O$.



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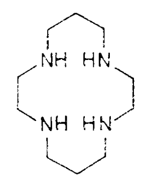

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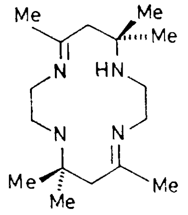

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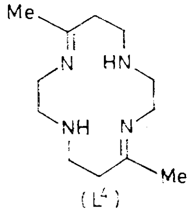

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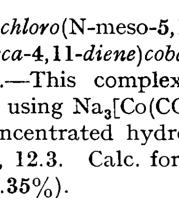
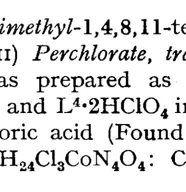


(I)



(II)

EXPERIMENTAL

trans-*Dichloro*(N-meso-5,12-*dimethyl*-1,4,8,11-tetra-aza-*cyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate*, *trans*-$[CoCl_2(L^4)][ClO_4]$.—This complex was prepared as previously described [6] using $Na_3[Co(CO_3)_3]$ and $L^4\cdot 2HClO_4$ in the presence of concentrated hydrochloric acid (Found: C, 32.0; H, 5.4; N, 12.3. Calc. for $C_{12}H_{24}Cl_3CoN_4O_4$: C, 31.8; H, 5.3; N, 12.35%).

trans-*Dibromo*(N-meso-5,12-*dimethyl*-1,4,8,11-*tetra-aza-cyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate Monohydrate*, *trans*-$[CoBr_2(L^4)][ClO_4]\cdot H_2O$.—This complex was prepared by treating the dichloro-complex with methanolic hydrobromic acid as previously described [6] and was isolated as the perchlorate salt (Found: C, 25.5; H, 4.4; N, 9.8. Calc. for $C_{12}H_{26}Br_2ClCoN_4O_5$: C, 25.7; H, 4.7; N, 10.0%).

trans-*Aquachloro*(5,12-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*cobalt*(III) *Perchlorate Dihydrate*, *trans*-$[CoCl(L^4)(OH_2)][ClO_4]_2\cdot 2H_2O$.—The complex *trans*-$[CoCl_2(N\text{-}meso\text{-}L^4)][ClO_4]$ (0.4 g) was dissolved in the minimum volume of hot water (*ca.* 60 °C) and filtered rapidly through a sintered glass filter after complete dissolution had occurred. Concentrated perchloric acid (*ca.* 2 cm^3) was then added to the filtrate, which was allowed to stand in an open beaker for several days. After this time, the green crystals which had slowly grown were collected, washed with ice-cold ethanol then diethyl ether, and dried in a vacuum desiccator for a short period. The visible absorption spectrum measured using aqueous perchloric acid as solvent had maxima at 588 (ε 52) and 425 nm (ε 44 dm^3 mol^{-1} cm^{-1},

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

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

[3] D. P. Rillema, J. F. Endicott, and J. R. Barber, *J. Amer. Chem. Soc.*, 1973, **95**, 6987.

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

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

[6] R. W. Hay and G. A. Lawrance, *J.C.S. Dalton*, 1975, 1466.

[7] R. A. Kolinski and B. Korybut-Daszkiewicz, *Inorg. Chim. Acta*, 1975, **14**, 237.

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shoulder) (Found: C, 25.4; H, 5.4; N, 9.5. $C_{12}H_{30}Cl_3CoN_4O_{11}$ requires C, 25.2; H, 5.3; N, 9.8%). When the *trans*-aquachloro-complex is dissolved in acetonitrile at room temperature the colour of the solution rapidly changes from green to red-purple. A concentrated solution of the complex in acetonitrile slowly (*ca.* 30 min) precipitates purple-red needles of the acetonitrile chloro-complex. The crystals are stable in dry air and the i.r. spectrum (Nujol mull) confirms the presence of co-ordinated acetonitrile. The acetonitrile ligand is very labile and is immediately displaced on dissolution in water to give the green aquachloro-complex.

Kinetic Measurements.—Base-hydrolysis kinetics were monitored using a Gilford 222 modified Unicam SP 500 spectrophotometer. The cell compartment was thermostatted to ±0.1 °C. In general, the reactions were initiated by injecting a small aliquot portion (50 μl) of the requisite complex, dissolved in acetonitrile, into the appropriate buffer solution which had previously been equilibrated to the required temperature. Absorbance changes were monitored at 325 nm. The final concentration of the complex was in the range 0.5×10^{-3}—1.0×10^{-3} mol dm^{-3}. Formate or chloroacetate buffers were employed, the ionic strength being adjusted to 0.1 mol dm^{-3} with sodium perchlorate. The dihalogeno-complexes are stable in dry acetonitrile for long periods.

Since the *trans*-aquachloro-complex reacts with acetonitrile, in this case a weighed amount of the solid complex was added rapidly with stirring to the equilibrated buffer solution. The concentration of acetonitrile (*ca.* 2% v/v) used in the runs with the dihalogeno-complexes had no effect on the reaction. Rate constants were obtained from plots of log $(A_t - A_\infty)$ against time. As the base hydrolysis of the dihalogeno-complexes involves two consecutive reactions, plots in these cases showed marked initial curvature, becoming linear at longer times. Such plots were resolved into two straight lines by conventional procedures.[10] Plots for the aquachloro-complex were linear for at least four half-lives. Values of the hydroxide-ion concentrations were obtained using the appropriate pK_w value [11] and activity coefficients were estimated from the Davies' equation.[12]

RESULTS AND DISCUSSION

The reaction of $L^4 \cdot 2HClO_4$ with $Na_3[Co(CO_3)_3]$ followed by treatment with HCl gives *trans*-$[CoCl_2(N\text{-}meso\text{-}L^4)]^+$. The analogous dibromo-derivative was prepared by treating the dichloro-complex with methanolic hydrobromic acid. The metastable *N-meso* nitrogen configuration will be retained under acidic conditions. Studies [8] of the racemisation of $(-)_{436}[NiL^4]^{2+}$ in 0.5 mol dm^{-3} phosphate buffer at pH 6.20 and 20 °C indicate that $k_{obs.} = 1.7 \times 10^{-5}$ s^{-1} ($t_{\frac{1}{2}}$ *ca.* 680 min). The reaction is first order in the hydroxide-ion concentration with $k = 1.1 \times 10^3$ dm^3 mol^{-1} s^{-1} at 20 °C. No information is available for the cobalt(III) complexes, but nitrogen inversion is expected to be relatively slow at pH < 4.

Buckingham *et al.*[13] have compared the rates of proton exchange and racemisation of a number of co-ordinated secondary amines on Co^{III} and showed that the rate constant for exchange, in aqueous solution, is generally many orders of magnitude greater than that for racemisation. Previously we have shown that base hydrolysis of *trans*-$[CoCl_2(N\text{-}meso\text{-}L^4)]^+$ at high pH followed by treatment with HCl to regenerate the dichloro-complex gave *trans*-$[CoCl_2(N\text{-}rac\text{-}L^4)]^+$. Halogeno-complexes of macrocyclic-Co^{III} undergo very rapid base hydrolysis.[1-3] For complexes of the type $[CoX_2(L^4)]^+$ (X = Cl or Br) two consecutive hydrolytic reactions are expected. Figure 1 shows plots of log $(A_t - A_\infty)$ for the dichloro-derivative at pH 3.54. The plots show initial curvature and become linear at longer times. Using the procedures described by Frost and Pearson,[10] it is possible to resolve the initial curved plots into two straight lines corresponding to the two hydrolytic reactions. Values of $k_{obs.}$ at constant pH for the two processes could then be obtained. Table 1 lists values of k_1(obs.) for the first

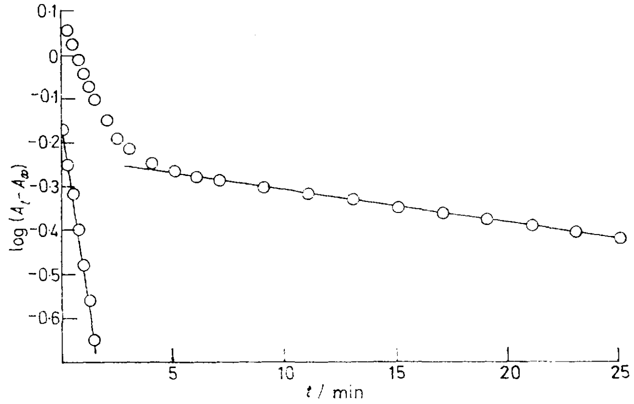

FIGURE 1 Base hydrolysis of *trans*-$[CoCl_2(L^4)]^+$ at pH 3.54, I = 0.1 mol dm^{-3}, and 25 °C, showing resolution into two consecutive reactions

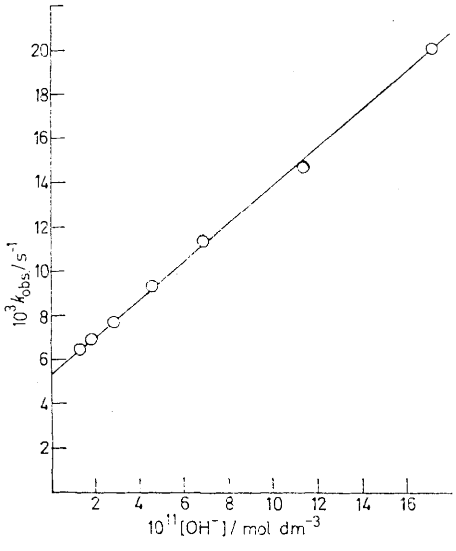

FIGURE 2 Plot of k_1(obs.) against $[OH^-]$ for the hydrolysis of $[CoCl_2(L^4)]^+$ in the range pH 3.00—4.12

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[10] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanisms,' 2nd edn., John Wiley, London, 1961.

[11] R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' 2nd edn., Butterworths, London, 1965.

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hydrolytic step of the dichloro-complex over the range pH 3.00—4.30. A plot of k_1(obs.) against the hydroxide-ion concentration (Figure 2) was linear with a positive intercept due to a reaction independent of the hydroxide-ion concentration. The rate constant k_1(obs.) can be represented by the equation $k_1(\text{obs.}) = 5.4 \times 10^{-3} + 8.5 \times 10^{7}\,[\text{OH}^-]$. Very good agreement between the values of k_1(obs.) obtained and those calculated from the above expression were obtained (Table 1). In the range pH 3.00—4.30 both aquation and base hydrolysis were observed. Base hydrolysis contributes to the extent of some 17% at pH 3.00, rising to 80% at pH 4.30.

TABLE 1

Hydrolysis kinetics for the loss of the first chloride ligand from *trans*-$[\text{CoCl}_2(\text{L}^4)]^+$ at 25 °C and I = 0.1 mol dm^{-3}

pH	$10^{11}[\text{OH}^-]$ / mol dm^{-3}	10^3k_1(obs.)/dm^3 mol ^{1} s^{-1}	
		a	*b*
3.00	1.31	6.58	6.51
3.13	1.76	7.00	6.90
3.33	2.79	7.75	7.77
3.54	4.53	9.33	9.25
3.72	6.85	11.33	1.22
3.94	11.37	14.67	15.06
4.12	17.21	20.00	20.03
4.30	26.05	26.10	27.54

[a] Average value of at least three kinetic runs. [b] Calculated from the equation $k_{\text{obs.}} = 5.4 \times 10^{-3} + 8.5 \times 10^{7}\,[\text{OH}^-]$.

Values of k_2(obs.) for hydrolysis of the second chloride ligand are listed in Table 2. There is excellent agreement between the values obtained above by the resolution technique and those obtained using an authentic sample of the intermediate *trans*-$[\text{CoCl}(\text{L}^4)(\text{OH}_2)]^{2+}$; thus at pH 3.13 the resolved plot gives $k_2(\text{obs.}) = 1.05 \times 10^{-4}$ s^{-1}, while a value of 1.04×10^{-4} s^{-1} is obtained with the intermediate (Table 2). Plots of k_2(obs.) against the hydroxide-ion concentration were linear and passed through the origin (Figure 3), indicating that base hydrolysis is the only kinetically important process at pH > 3.0. The value of the second-order rate constant for base hydrolysis of the second chloro-ligand is 5.9×10^6 dm^3 mol^{-1} s^{-1} at 25 °C and I = 0.1 mol dm^{-3}. The temperature dependence of this reaction was studied over five temperatures in the range 15.6—35.0 °C (Table 3). The values $\Delta H^\ddagger = 57$ kJ mol^{-1} and $\Delta S_{298}^\ddagger = 75$ J K^{-1} mol^{-1} were obtained from these data.

TABLE 2

Base hydrolysis of the second chloro-ligand, *trans*-$[\text{CoCl}(\text{L}^4)(\text{OH}_2)]^{2+} + \text{OH}^- \longrightarrow$ *trans*-$[\text{CoL}^4(\text{OH}_2)_2]^{3+} + \text{Cl}^-$, at 25 °C and I = 0.1 mol dm^{-3}

pH	$10^{11}[\text{OH}^-]$ / mol dm^{-3}	10^4k_2(obs.) * / s^{-1}	$10^{-6}k_2$(obs.)/$[\text{OH}^-]$ / dm^3 mol^{-1} s^{-1}
3.00	1.31	0.80	6.10
3.13	1.76	1.05 (1.04)	5.96 (5.91)
3.33	2.79	1.65	5.92
3.54	4.53	2.75	6.07
3.72	6.85	4.00 (3.98)	5.84 (5.81)
3.94	11.37	6.50	5.72
4.12	17.21	10.05 (10.07)	5.84 (5.85)
4.30	26.05	14.90	5.72

* Values in parentheses were obtained using an authentic sample of *trans*-$[\text{CoCl}(\text{L}^4)(\text{OH}_2)]^{2+}$. The rate constants quoted are the average values of at least three kinetic runs.

Similar measurements to those described above were made with the dibromo-complex. Loss of the first bromide ligand occurs very rapidly and it is difficult to obtain precise rate constants by conventional spectrophotometric techniques. As with the chloro-complex, $k_{\text{obs.}} = k_{\text{OH}_2} + k_1^{\text{OH}}[\text{OH}^-]$ over the range pH 2.2—3.0 (chloroacetate buffers); k_1^{OH} is *ca.* 1×10^9 dm^3 mol^{-1} s^{-1} at I = 0.1 mol dm^{-3}. Precise values of the rate constant were obtained for the base hydrolysis of the second bromo-ligand (Table 4). The average value for bromide hydrolysis is 1.22×10^7 dm^3 mol^{-1} s^{-1} at 25 °C and I = 0.1 mol dm^{-3}. The requisite activation parameters for this reaction are $\Delta H^\ddagger = 56$ kJ mol^{-1} and $\Delta S_{298}^\ddagger = 80$ J K^{-1} mol (Table 3).

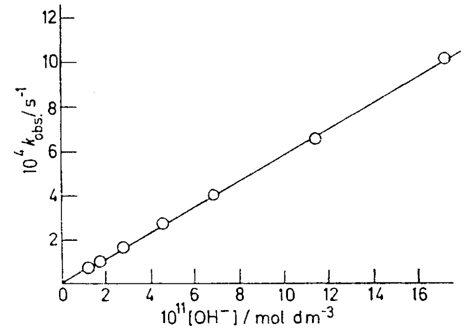

FIGURE 3 Plot of k_2(obs.) against $[\text{OH}^-]$ for the hydrolysis of the second chloro-ligand of $[\text{CoCl}_2(\text{L}^4)]^+$ in the range pH 3.00—4.12

TABLE 3

Temperature dependence of the base hydrolysis of the second chloro-ligand and the second bromo-ligand at I = 0.1 mol dm^{-3}

θ_c / °C	$10^{11}[\text{OH}^-]$ / mol dm^{-3}	10^4k_2(obs.) / s^{-1}	$10^{-6}k_2$(obs.)/$[\text{OH}^-]$ / dm^3 mol^{-1} s^{-1}
(*a*) Chloride hydrolysis [a]			
15.6	1.98	0.56	2.82
19.0	2.70	0.93	3.45
25.0	4.53	2.75	6.07
30.5	7.02	6.10	8.69
35.0	9.76	12.77	13.09
(*b*) Bromide hydrolysis [b]			
15.5	7.09	3.83	5.4
20.1	10.75	8.00	7.4
25.0	16.44	20.00	12.2
29.9	24.30	40.83	16.8
34.6	35.05	84.67	24.1

[a] Measured in formate buffer (pH 3.54) at 25 °C. Hydroxide-ion concentrations were calculated from the measured pH at the temperature of the reaction using the appropriate values of pK_w and γ_1. Each rate constant is the average of at least three kinetic runs. [b] Measured in formate buffer (pH 4.10) at 25 °C

The base-hydrolysis rates for the $[\text{CoX}_2(\text{L}^4)]^{2+}$ complexes appear to be the most rapid reported for halogenocobalt(III) complexes of the $[\text{CoX}_2(\text{N}_4)]^{2+}$ type (Table 5).

Thus *trans*-[CoCl$_2$(L^4)]$^+$ with $k_1^{\mathrm{OH}} = 8.5 \times 10^7$ dm^3 mol^{-1} s^{-1} at 25 °C undergoes base hydrolysis *ca.* 3.7 × 10^4 times faster than *trans*-[CoCl$_2$(en)$_2$]$^+$, *ca.* 4.7 × 10^3 faster than *trans*-[CoCl$_2$(L^5)]$^+$,[14] and *ca.* 1.3 × 10^3 times faster than *trans*-[CoCl$_2$(L^2)]$^+$ (at 20 °C)[1] [en = ethylenediamine, L^5 = *RS*-3,7-diazanonane-1,9-diamine (*RS*-2,3,2-tet)]. Much evidence [15] now supports the view that the base hydrolysis of amine complexes of Co$^{\mathrm{III}}$ involves deprotonation of an amine ligand followed by a slow dissociative reaction of the amido-conjugate base and a rapid aquation of the five-co-ordinate intermediate which is believed to have a trigonal-bipyramidal geometry [S_N1(CB) mechanism]. The kinetically significant reactions can be represented as in equations (1) and (2).

$$\text{Complex} + \text{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Amido} + \text{H}_2\text{O} \qquad (1)$$

$$\text{Amido} \xrightarrow{k_2} \text{Products} \qquad (2)$$

TABLE 4

Base hydrolysis of the second bromo-ligand, *trans*-[CoBr(L^4)(OH$_2$)]$^{2+}$ + OH$^-$ ⟶ *trans*-[CoL^4(OH$_2$)$_2$]$^{3+}$ + Br$^-$, at 25 °C and I = 0.1 mol dm^{-3}

pH	10^{11}[OH$^-$] / mol dm^{-3}	10$^4k_2$(obs.) * / s^{-1}	10$^{-7}k_2$(obs.)/[OH$^-$] / dm^3 mol^{-1} s^{-1}
2.97	1.21	1.44	1.19
3.28	2.49	3.12	1.24
3.68	6.25	7.60	1.21
4.10	16.44	20.00	1.22
4.55	46.35	57.65	1.24

* Average of at least three independent kinetic runs.

TABLE 5

Rate constants for the hydrolysis of macrocyclic halogeno-complexes of Co$^{\mathrm{III}}$ at 25 °C

Complex	k_{OH}/ dm^3 mol^{-1} s^{-1}	$k_{\mathrm{H_2O}}$/s^{-1}
(*a*) Chloride hydrolysis		
trans-[CoCl$_2$(L^1)]$^+$	5.7 × 10^5 [a]	9.3 × 10^{-4}
trans-[CoCl$_2$(L^3)]$^+$	2.17 × 10^5 [a]	3.7 × 10^{-2}
trans-[CoCl$_2$(L^2)]$^+$	6.70 × 10^4	1.1 × 10^{-8}
trans-[CoCl$_2$(en)$_2$]$^+$	2.3 × 10^3	3.5 × 10^{-5}
trans-[CoCl$_2$(*N-meso*-L^4)]$^+$	8.5 × 10^7	5.4 × 10^{-3}
trans-[CoCl(L^4)(OH$_2$)]$^{2+}$	5.9 × 10^6	
trans-[CoCl(NO$_2$)(*N-meso*-L^4)]$^+$ [b]	2.5 × 10^2	4.4 × 10^{-4}
trans-[CoCl(NO$_2$)(L^3)]$^+$	2.2 × 10^2	5.5 × 10^{-4}
(*b*) Bromide hydrolysis		
trans-[CoBr$_2$(L^1)]$^+$		3.3 × 10^{-2}
trans-[CoBr$_2$(L^3)]$^+$	(1 × 10^6)	5.1 × 10^{-2}
trans-[CoBr$_2$(L^2)]$^+$		2 × 10^{-5}
trans-[CoBr$_2$(*N-meso*-L^4)]$^+$	1 × 10^9	
trans-[CoBr(OH$_2$)(L^4)]$^+$	1.2 × 10^7	

[a] At 19.8 °C. Data taken from ref. 1, 3, and R. W. Hay and G. A. Lawrance, *J.C.S. Dalton*, 1975, 1556. [b] In the last reference in *a* we discussed the aquation and base-hydrolysis rates of the chloronitro-derivative *trans*-[CoCl(NO$_2$)(L^4)]$^+$. This complex was prepared from the dichloro-complex which has the *N-meso* configuration, *i.e.* prepared by the carbonato-route (ref. 6). Only one chloronitro-isomer is expected from the *N-meso* configuration, while two isomers can occur with the *N-rac* configuration. The previous paper thus refers to the hydrolysis of the *N-meso* complex and not to the *N-rac* complex as we presumed.

Usually the proton-transfer steps, (1), are reversible and much faster than the dissociative step (k_2). However, Ahmed *et al.*[14] have shown that with *trans*-[CoCl$_2$(L^5)]$^+$ the rate constant k_2 for the dissociation of the conjugate base is considerably greater than its reprotonation rate k_{-1}, so that deprotonation of the substrate becomes the rate-determining step in the base-hydrolysis reaction. In this case {as with *trans*-[CoCl$_2$(L^2)]$^+$} [15] it is possible to observe general base catalysis with a Brønsted exponent, $\beta = 0.67$.

It has been suggested [14,15] that low values of $\Delta H^\ddagger$ (*ca.* 56 kJ mol^{-1}) compared with the 'normal' values of *ca.* 96 kJ mol^{-1} and lower positive values of $\Delta S^\ddagger$ can be used as a mechanistic probe for a change in rate-determining step to slow deprotonation of the substrate. The activation parameters for loss of the second chloride ligand from [CoCl$_2$(L^4)]$^+$ are $\Delta H^\ddagger$ = 57 kJ mol^{-1} and $\Delta S_{298}{}^\ddagger$ = 75 J K^{-1} mol^{-1}, values very similar to those suggested for rate-determining deprotonation of the substrate. Edwards *et al.*[16] recently reviewed ligand-displacement reactions in complexes of M$^{\mathrm{III}}$. For an S_N1(CB) mechanism the estimated value of $\Delta S^\ddagger$ is *ca.* 142 J K^{-1} mol^{-1}, while for an S_N2 reaction $\Delta S^\ddagger$ is *ca.* −63 J K^{-1} mol^{-1}. Substantial positive entropies of activation indicate an S_N1(CB) process. The bulk of the experimental data for the base hydrolysis of aminechloro-complexes of Co$^{\mathrm{III}}$ have $\Delta S^\ddagger$ values in the range 84—167 J K^{-1} mol^{-1} consistent with an S_N1(CB) mechanism. Reactions with low $\Delta H^\ddagger$ values and $\Delta S_{298}{}^\ddagger$ values of *ca.* 80 J K^{-1} mol^{-1} may involve rate-determining deprotonation of the substrate.

Few studies have been made to investigate the extent to which the configuration of the chiral nitrogen centres affects the kinetics and steric course of the base-hydrolysis *trans*-[CoX$_2$(N$_4$)]$^+$ type complexes and this aspect has been largely ignored in previous kinetic studies of macrocyclic complexes. Tobe and his co-workers,[14,17] however, carried out an elegant investigation of the base hydrolysis of *trans*-[CoCl$_2$(*N-meso*-L^5)]$^+$ and *trans*-[CoCl$_2$(*N-rac*-L^5)]$^+$. Base hydrolysis of the *N-rac* diastereoisomer is twice as fast as the *N-meso* diastereoisomer. Both complexes give the same *trans-N-meso*-chlorohydroxo-product and every act of base hydrolysis of the *N-rac* diastereoisomer leads to the *trans-N-meso*-chlorohydroxo-product.

Studies of the base hydrolysis of *trans*-[CoX$_2$(*N-rac*-L^4)]$^+$ and of the stereochemical course of these reactions is currently in progress. Only then will it be possible to consider the mechanisms of these reactions in detail.

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