The pH and Temperature-dependent Hydrolyses of [*N,N*-Bis(2-aminoethyl)-1,2-ethanediamine]bis(solvent)cobalt(III) and Bis(dimethylformamide)(1,4,7,10-tetra-azacyclododecane)cobalt(III) Complexes

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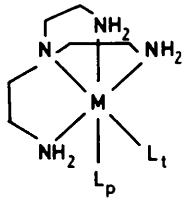
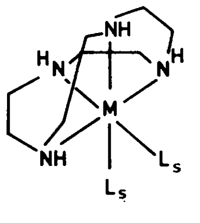
The pH dependence of the hydrolysis of the stereochemically rigid [*N,N*-bis(2-aminoethyl)-1,2-ethanediamine]bis(solvent)cobalt(III) ions (solvent = dimethyl sulphoxide, dimethylformamide, or trimethyl phosphate) in water has been studied. The two successive observed rate constants show, respectively, dependences of the form $k_1 + k_1'[OH^-]$ and $k_2 + k_2'K_a/(K_a + [H^+])$, where a limiting deprotonation of a water molecule operates in the second stage of the reaction. Whereas ^1H n.m.r. of the dimethylformamide complex in acid shows two intermediates, indicating that loss from the two non-equivalent (p and t) sites occurs at similar rates, only one intermediate is observed under base hydrolysis, and lability at one site is apparently greater in this case. Comparisons of data with published results available for other amine complexes are made. The complex bis(dimethylformamide)(1,4,7,10-tetra-azacyclododecane)cobalt(III) is also stereochemically rigid, but both leaving sites are equivalent, and two simple sequential rate constants with k_1/k_2 *ca.* 5:1 are observed in aqueous acid. This ratio is similar to the value of 5.5:1 determined for the composite observed k_1 and k_2 for the *N,N*-bis(2-aminoethyl)-1,2-ethanediamine analogue, and much smaller than ratios reported when ionic (halogeno) leaving groups are involved.

In our previous paper,[1] we discussed the preparations, characterizations, and aspects of the spontaneous hydrolyses of some *N,N*-bis(2-aminoethyl)-1,2-ethanediamine (tren) complexes of cobalt(III) (**I**). The geometry of the tren system is such that the two vacant co-ordination sites are unique, with one (L_p) *trans* to a primary nitrogen, and the other (L_t) *trans* to a tertiary amine. While the molecule is stereochemically rigid, the two leaving group sites are non-equivalent. In the stereochemically rigid cobalt(III) complexes of 1,4,7,10-tetra-azacyclododecane (cyclen) (**II**), the two vacant co-ordination sites (L_s) are both *trans* to secondary amines and equivalent.



(I)



(II)

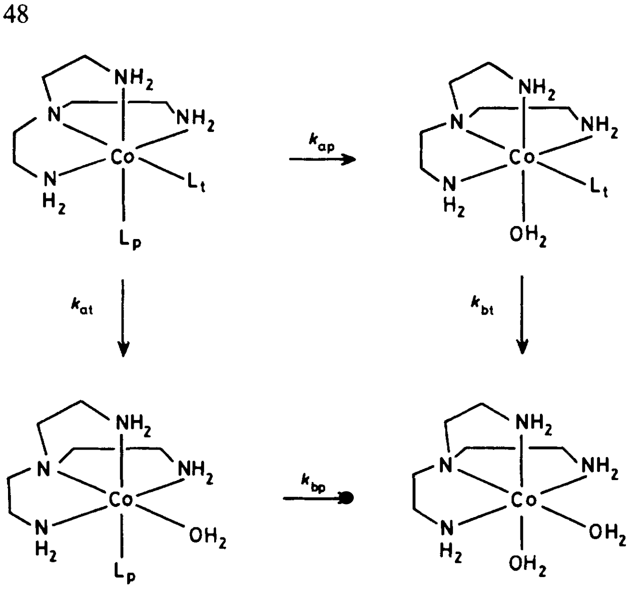
In the cobalt(III) tren complexes, the two sites were readily differentiated, though not identified, by ^1H n.m.r. spectroscopy, which clearly showed the presence of two sets of signals for the ligands in the non-equivalent positions.[1] Further, we found that for the spontaneous hydrolyses to the aqua species, the two sites were of comparable lability since in most cases two intermediates were seen by n.m.r. spectroscopy. Finally, it was determined that the two rates seen, which corresponded to the stepwise loss of the two ligands, differed by no more than a factor of ten at 50 °C. This was in marked contrast to the dibromo and dichloro analogues which showed ratios of 2 660:1 [2,3] and 470:1 [4,5] respectively.

In the present paper we have examined the hydrolyses of these complexes in detail, in particular the kinetics and mechanistic aspects of the reaction of higher pH. Further, to permit comparison with a stereochemically rigid molecule with equivalent leaving sites, the temperature dependence of the acid hydrolysis of the $[Co(cyclen)(HCONMe_2)_2]^{3+}$ complex ion has been investigated.

Experimental

Synthesis of $[Co(tren)L_2]X_3$ (L = dimethyl sulphoxide, dimethylformamide, trimethyl phosphate, or acetonitrile; X = perchlorate or trifluoromethanesulphonate) have been described.[1] Products were isolated as analytically pure solids. The complex $[Co(cyclen)(HCONMe_2)_2][CF_3SO_3]_3$ was prepared in an exactly analogous manner from $[Co(cyclen)(OSO_2CF_3)_2][CF_3SO_3]$, and isolated as an analytically pure solid.[6]

Hydrolysis reactions were followed by spectrophotometry in thermostatted (±0.1 °C) cell holders of Hitachi 220A or Hewlett-Packard 8450A spectrophotometers. Acid-aquation reactions were followed in 0.1 mol dm^{-3} HX–0.9 mol dm^{-3} NaX (X = ClO_4^- or $CF_3SO_3^-$) aqueous solutions. The pH-dependent hydrolysis reactions of the O-bound ligand complexes were pursued in solutions with usually I(buffer) = 0.1 mol dm^{-3} and of total ionic strength 1.0 mol dm^{-3} adjusted with HX–NaX (X = ClO_4^- or $CF_3SO_3^-$). Buffers employed were 2-(*N*-morpholino)ethanesulphonic acid (mes; pH 5.5—6.5), *N*-(2-hydroxyethyl)piperazine-*N'*-ethanesulphonic acid (hepes; pH 6.8—7.45), and tris(hydroxymethyl)methylamine (Tris; pH 7.74—9.00). Samples were dissolved directly into pre-equilibrated buffers in a cell in the spectrophotometer, and reactions were monitored to *ca.* four half-lives of the second reaction continuously, with the final absorbance routinely recorded



Scheme.

separately after >98% reaction. Separation into two components to yield two sequential rate constants was performed by conventional graphical or computational methods, with the fit in the latter determined by an iterative program.[1] In general, computed rate constants showed a precision of $< \pm 5\%$ [k_1(obs.)] and $< \pm 10\%$ [k_2(obs.)]. In calculating hydroxide concentrations, usual literature values of pK_w and $\gamma_\pm$ (0.6288) in 1.0 mol dm^{-3} ClO_4^- were employed. There is apparently no literature value of $\gamma_\pm$ in 1.0 mol dm^{-3} $CF_3SO_3^-$, so in the one case where it was necessary to employ this anion due to solubility problems in perchlorate (with the trimethyl phosphate complex only) values for perchlorate were assumed.

Reaction of $[Co(tren)L_2]^{3+}$ in both acidic and basic solution proceeds to yield only one product, $[Co(tren)(OH_2)_2]^{3+}$, after acidification; this can be separated chromatographically on cationic Dowex or SP-Sephadex resin and ascertained as the only detectable product. For $[Co(cyclen)L_2]^{3+}$, the product is likewise the diaqua complex. Hydrolysis proceeds in two sequential steps, the rate constants for the two being sufficiently different to permit graphical or computational separation in all cases.

Results

In the previous paper,[1] we proposed that the hydrolyses of $[Co(tren)L_2]^{3+}$ followed parallel, consecutive paths as shown in the Scheme. A strict kinetic analysis of such a scheme shows that the kinetics should be characterized by three exponentials α, β, and γ. These correspond to the rates shown in the Scheme as follows: $\alpha = k_{ap} + k_{at}$, $\beta = k_{bp}$, and $\gamma = k_{bt}$. Despite this analysis, in the present and previous work [1] all kinetics could be adequately analyzed in terms of only two exponentials. By analysis of n.m.r. spectra, it was clear that one of these was due to the initial loss of ligand (*i.e.* $k_{ap} + k_{at}$), and we assumed that the other corresponded to the loss of the second ligand. There are several obvious possibilities as to the absence of one exponential, which must be associated with k_{bp} or k_{bt}. For instance, one may have been somewhat faster than the other and was too fast to measure. This possibility is unlikely given the appearance of two intermediates. More likely would be that two of the rates were close in magnitude; for instance, k_{bt} or k_{bp} with ($k_{at} + k_{ap}$), or k_{bt} with k_{bp}. Another possibility could be that if the initial reaction favoured one route, say by a factor of three, then the subsequent reaction *via* the minor route could have been swamped by the absorbance changes due to the major path. It is expected, therefore, that the slower rate seen corresponds to k_{bp} or k_{bt}, although in reality the data may only have been good enough to give an 'average' value.

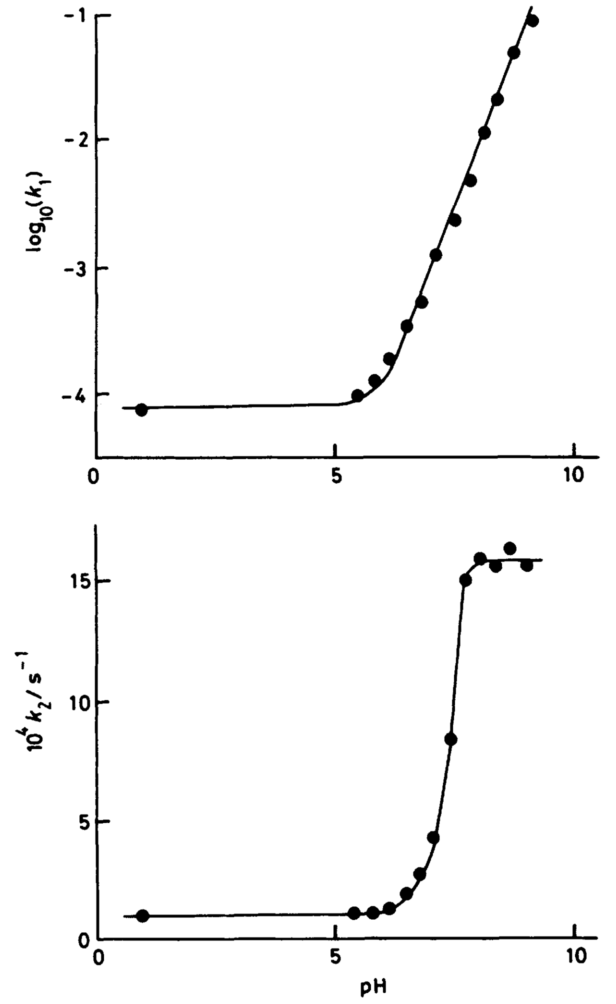


Figure 1. The pH dependence of the observed hydrolysis steps in $[Co(tren)(OSMe_2)_2]^{3+}$ in aqueous solution at 25 °C

The empirical rate equations are straightforward. At all pH values, a two-term rate law, equation (1), applied. The pH dependence of these terms was as in equations (2) and (3).

$$k_{obs.} = k_1(obs.) + k_2(obs.) \tag{1}$$

$$k_1(obs.) = k_1 + k_1'[OH^-] \tag{2}$$

$$k_2(obs.) = k_2 + \frac{k_2' K_a}{K_a + [H^+]} \tag{3}$$

Equation (2) is similar to the usual two-term rate law with components for spontaneous (k_1) and base catalyzed (k_1') hydrolyses. Whilst equation (3) is similar, a limiting deprotonation governs the base catalysis term, with pK_a in the region 7—8; this is illustrated for one example in Figure 1. The data were not of sufficient quality to warrant a graphical solution, so instead visual inspection was used for estimates of pK_a. Values of k_1(obs.) and k_2(obs.) are collected in Table 1 and the

Table 1. Rate constants for hydrolysis of $[Co(tren)L_2]^{3+}$ cations with O-bound ligands[a]

pH	k_1(obs.)/s^{-1} [b]	10^5k_2(obs.)/s^{-1} [b]
L = $OSMe_2$		
1.0[c]	7.4×10^{-5}	1.05
5.50	9.9×10^{-4}	1.10
5.80	1.30×10^{-4}	1.15
6.15	1.95×10^{-4}	1.25
6.50	3.55×10^{-4}	1.90
6.80	5.60×10^{-4}	2.65
7.10	1.25×10^{-3}	4.20
7.45	2.50×10^{-3}	8.35
7.75	4.95×10^{-3}	15.0
8.10	1.29×10^{-2}	15.8
8.35	2.1×10^{-2}	15.6
8.70	5.2×10^{-2}	16.1
9.00	9.9×10^{-2}	15.6
L = $HCONMe_2$		
1.0[c]	1.4×10^{-5}	0.105
5.50	1.5×10^{-5}	0.145
5.80	1.65×10^{-5}	0.20
6.15	1.9×10^{-5}	0.37
6.50	2.55×10^{-5}	0.51
6.80	3.60×10^{-5}	0.82
7.10	6.00×10^{-5}	1.4
7.45	1.15×10^{-4}	1.8
7.75	1.97×10^{-4}	2.5
8.10	4.20×10^{-4}	2.9
8.35	8.5×10^{-4}	3.1
8.70	1.8×10^{-3}	2.9
9.00	3.5×10^{-3}	3.0
L = $OP(OMe)_3$		
1.0[c]	4.3×10^{-4}	8.9
5.50	1.0×10^{-3}	12.2
5.80	1.67×10^{-3}	15.0
6.15	3.00×10^{-3}	30.0
6.50	7.20×10^{-3}	36.5
6.80	1.35×10^{-2}	51
7.10	2.60×10^{-2}	72
7.45	5.3×10^{-2}	101
7.75	1.1×10^{-1}	112
8.10	2.15×10^{-1}	120
8.35	4.2×10^{-1}	124

[a] 25 °C; buffers used were mes, hepes, and tris; total ionic strength = 1.0 mol dm^{-3}, adjusted with $NaClO_4$ or $NaOSO_2CF_3$. [b] Observed rate constants defined in equation (1). [c] Extrapolated data (Table 3).

derived rate and equilibrium constants in Tables 2 and 3. Variable-temperature data (Table 4) were used to determine thermodynamic quantities at pH 1 (Table 5).

The hydrolysis of the bis(dimethylformamide) complex was also studied at acid and higher pH by ^1H n.m.r. In a 1:1 Tris–Tris/$DClO_4$ buffer in D_2O, the peaks due to the unique formyl protons of the starting material at 7.42 and 7.69 p.p.m. decreased at the same rate and were replaced by a peak due to free dimethylformamide (7.93 p.p.m.) and a single intermediate peak at 7.53 p.p.m. (Figure 2). Quenching of this reaction by the addition of a large amount of acid gave a spectrum with only four formyl peaks and not five, as seen for the acid hydrolysis of the same compound (Figure 2). In the acid case, two peaks due to two intermediates were observed at 7.54 and 7.60 p.p.m., but for the base hydrolysis only the former was visible. The implication here is that the reaction only gives one observable intermediate under base hydrolysis.

Table 2. Spontaneous rate constants (s^{-1}) for $[Co(tren)L_2]^{n+}$ and related cobalt(III) complexes $[Co(NH_3)_5L]^{n+}$ and $[Co(NH_2Me)_5L]^{n+}$ at 25 °C, I = 1.0 mol dm^{-3}

L	k_1(tren)	k_2(tren)	k(5NH$_3$)	k(5NH$_2$Me)
$OP(OMe)_3$	4.3×10^{-4}	8.9×10^{-5}	2.5×10^{-4} [a]	2.8×10^{-2} [b]
$OSMe_2$	7.4×10^{-5}	1.1×10^{-5}	1.8×10^{-5} [c]	2.8×10^{-3} [b]
$HCONMe_2$	1.4×10^{-5}	1.1×10^{-6}	1.6×10^{-6} [d]	1.2×10^{-4} [b]
NCMe	7.2×10^{-7}		*ca.* 2×10^{-8} [b]	1.1×10^{-5} [b]
Cl	3.0×10^{-3} [e]	2.7×10^{-5} [f] 2.4×10^{-6} [f]	1.7×10^{-6} [g]	4.0×10^{-5} [h]
Br	2.8×10^{-2} [i]	3.3×10^{-6} [j]		
p-Cl(NH$_3$)	2.5×10^{-6} [k]			
t-Cl(NH$_3$)	1.2×10^{-6} [k]			

[a] W. Schmidt and H. Taube, *Inorg. Chem.*, 1963, **2**, 698. [b] Ref. 8. [c] W. L. Reynolds, M. Birus, and S. Asperger, *J. Chem. Soc., Dalton Trans.*, 1974, 716. [d] W. L. Reynolds and M. A. Knoll, *Int. J. Chem. Kinet.*, 1976, **8**, 389. [e] S. K. Madan, W. M. Reiff, and J. C. Bailar, *Inorg. Chem.*, 1965, **4**, 1366. [f] Two isomers, ref. 3. [g] A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, 1955, **9**, 1261. [h] D. A. Buckingham, F. R. Keene, and A. M. Sargeson, *J. Am. Chem. Soc.*, 1973, **95**, 5649. [i] Ref. 4. [j] Ref. 5. [k] C-H. L. Yang and M. W. Grieb, *J. Chem. Soc., Chem. Commun.*, 1972, 656; as corrected by ref. 9.

Table 3. Base catalysed rate constants for $[Co(tren)L_2]^{n+}$ and related cobalt(III) complexes $[Co(NH_3)_5L]^{3+}$ at 25 °C, I = 1.0 mol dm^{-3}

L	k_1'(tren)/ dm^3 mol^{-1} s^{-1}	k_2'(tren)/ s^{-1}	pK_a	k_{OH}(5NH$_3$)/ dm^3 mol^{-1} s^{-1}	Ref.
$OP(OMe)_3$	115 000	1.2×10^{-3}	7.0	79	*a*
$OSMe_2$	6 200	1.6×10^{-4}	7.5	5.4	*a*
$HCONMe_2$	220	3.0×10^{-5}	7.2	1.1	*b*
p-Cl(NH$_3$)	400				*c*
t-Cl(NH$_3$)	0.02				*c*
p-SCN(NH$_3$)	11 000				*d*
t-SCN(NH$_3$)	0.03				*d,e*

[a] This work; N. E. Dixon, W. G. Jackson, W. Marty, and A. M. Sargeson, *Inorg. Chem.*, 1982, **21**, 688. [b] This work; D. A. Buckingham, J. MacB. Harrowfield, and A. M. Sargeson, *J. Am. Chem. Soc.*, 1974, **96**, 1726. [c] D. A. Buckingham, P. J. Cresswell, and A. M. Sargeson, *Inorg. Chem.*, 1975, **14**, 1485. [d] Ref. 15. [e] Four products identified.

Table 4. Temperature dependence of the rate constants for hydrolyses at pH 1.0 for $[Co(tren)L_2]^{3+}$, I = 1.0 mol dm^{-3}

L	Temperature (°C)	10^4k_1(obs.)/s^{-1}	10^5k_2(obs.)/s^{-1}
$OSMe_2$	31.6	1.66	2.50
	38.3	3.64	6.40
	43.5	6.05	11.3
	49.7	12.5	25.5
	60.0	33.0	86.5
$HCONMe_2$	40.3	0.75	1.10
	49.6	2.00	3.65
	57.2	4.15	9.8
$OP(OMe)_3$	25.0	4.28	8.92
	30.0	8.67	17.2
	35.0	15.9	31.5
	40.0	31.0	59
	45.0	58	111
	50.0	106	184
	55.0	209	332
NCMe	50.8	0.38	0.37
	56.7	0.89	0.77
	66.0	3.20	2.43
	78.5	15.3	10.0

Acid aquation from $[Co(cyclen)(HCONMe_2)_2]^{3+}$ is faster than from the tren analogue, but is simplified by the equivalence of the two leaving sites. The kinetic data analyzed well in terms of only two exponentials, as expected, although the observed rate constants (Table 6) are separated by only a factor of 5 near

Table 5. Activation parameters for aquation of $[Co(tren)L_2]^{3+}$ cations at pH 1.0, I = 1.0 mol dm^{-3}*

L	10^5k_1(obs.)/s^{-1}	$\Delta H_1^‡$	$\Delta S_1^‡$	10^5k_2(obs.)/s^{-1}	$\Delta H_2^‡$	$\Delta S_2^‡$
$OSMe_2$	7.4	86.5 (±2.0)	−33	1.05	102.2 (±1.4)	+2
$HCONMe_2$	1.4	86.1 (±1.3)	−49	0.105	110.8 (±1.9)	+13
$OP(OMe)_3$	43.0	101.7 (±1.2)	+32	8.9	95.3 (±0.7)	−3
NCMe	0.072	125.2 (±1.0)	+50	0.012	110.5 (±1.5)	−8

* Units: $\Delta H^‡$, kJ mol^{-1}; $\Delta S^‡$, J K^{-1} mol^{-1}.

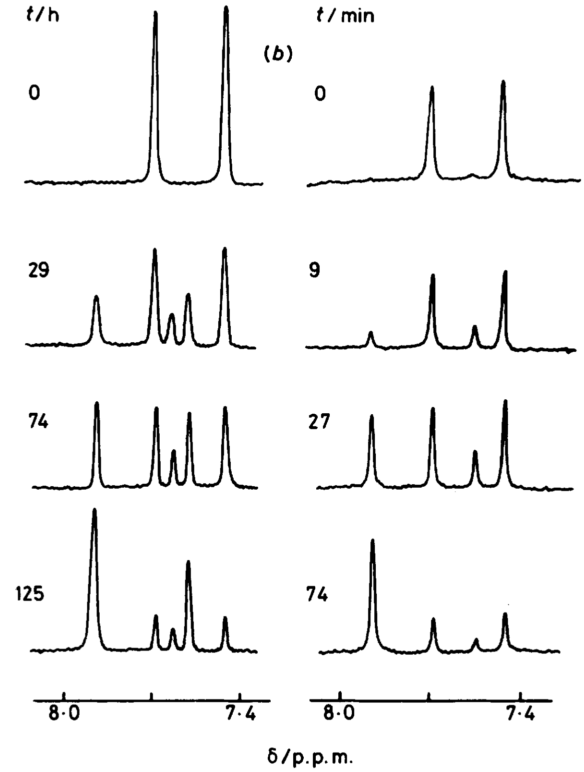


Figure 2. Time-dependent 200-MHz ^1H n.m.r. of the formyl proton region of $[Co(tren)(HCONMe_2)_2]^{3+}$ in (*a*) 0.1 mol dm^{-3} $DClO_4$ and (*b*) 1:1 Tris–Tris/$DClO_4$ buffer

50 °C, a ratio similar to the value of 5.5 determined from the albeit composite k_1(obs.) and k_2(obs.) for the tren analogue at that temperature. While thermodynamic quantities determined for the tren complexes are of limited value since they relate to composite rate terms, the values determined for the cyclen complex refer to single processes. Activation entropies in the cyclen case are near zero, not unexpected for reactions involving displacement of neutral ligands. For the tren system, activation entropies for the second rate also are near zero (Table 5), although results from the composite first step vary with ligand, probably reflecting the composite nature of k_1(obs.). Perhaps the behaviour of k_2(obs.) with temperature like the genuine single steps for the cyclen system support our view that k_2(obs.) corresponds closely to one of k_{bp} or k_{bt}.

Table 6. Rate constants for aquation of $[Co(cyclen)(HCONMe_2)_2]^{3+}$ in 0.1 mol dm^{-3} perchloric acid*

Temperature (°C)	10^4k_1/s^{-1}	10^5k_2/s^{-1}
25.0	0.48	0.82
33.0	1.40	2.35
39.5	2.75	5.3
46.0	6.7	13.5

* Activation parameters determined for k_1, $\Delta H^‡$ 95.5 (±3) kJ mol^{-1}, $\Delta S^‡$ −8 J K^{-1} mol^{-1} and for k_2, $\Delta H^‡$ 102.2 (±1) kJ mol^{-1}, $\Delta S^‡$ +1 J K^{-1} mol^{-1}; k_1/k_2 = 5.0.

Discussion

The kinetics of the initial hydrolytic processes (k_1 and k_1') was not remarkable and was to some extent routine. The rate constants are shown in Tables 2 and 3 and compared with some similar complexes. The order of ligand lability, *i.e.* $OP(OMe)_3$ > $OSMe_2$ > $HCONMe_2$ > NCMe, was preserved in all cases. At 25 °C, the rate constants (k_1) for tren hydrolyses were intermediate between those for the equivalent penta-ammine[7] and pentakis(methylamine)[8] complexes. Whilst the values for k_1 were generally within an order of magnitude for the tren and their penta-amine analogues, the base catalysed rates (k_1') exhibited much larger differences, with the tren compounds being considerably more labile. These differences ranged from a factor of 200 for the dimethylformamide (dmf)[9] complexes to 1 500 for the trimethyl phosphate equivalent.[10] The second step, corresponding to the measured rate constants k_2 and k_2', was more interesting kinetically. As noted before,[1] k_1 and k_2 (for the tren complexes) only varied a little, and large ratios for k_1/k_2 seen for the dibromo and dichloro analogues were not seen for the neutral ligands. Again the same order of lability was found for these ligands.

Whereas the rate law [equation (2)] for the pH dependence of the first step was conventional, that of the second stage [equation (3)] exhibited a maximum rate at pH values above 8. This was best interpreted in terms of an ionization on the complex which governed the kinetics. Given that the observed pK_a values lie in the range 7.0—7.5, it was reasonable to assume that co-ordinated water was responsible. Thus, in these cases, co-ordinated hydroxide was acting as a conjugate base. This behaviour was analogous to that of co-ordinated amide[11] in penta-amine complexes, though in that case the high pK_a of *ca.* 15 precludes the observation of a maximum kinetic rate in water. Indeed, deviations in observed rate constants are rarely seen, though they have been observed for cases where the leaving group contains an acidic proton, for instance O-bonded urea.[10,12]

Comparison between the observed values of k_2' for tren, which are first order, and the usual second-order base hydrolysis rate k_{OH} in penta-amine (and with k_1' for these tren compounds) is difficult. It can be simply seen that k_{OH} for penta-amine complexes is obtained in the region where $[H^+] \gg K_a$; thus the base-catalysed hydrolysis term in equation (3) reduces to $k_2'K_a/[H^+]$ (or $k_2'K_a[OH^-]/K_w$) where $k_2'K_a$ has the units mol dm^{-3} s^{-1} but $k_2'K_a/K_w$ has the second-order units dm^3 mol^{-1} s^{-1}. Values of $k_2'K_a/K_w$ for the tren compexes can be derived from the data given in Table 3 (assuming pK_w = 13.77) and are: 7.1 × 10^3 [$OP(OMe)_3$], 3.0 × 10^2 ($OSMe_2$), and 1.1 × 10^2 dm^3 mol^{-1} s^{-1} ($HCONMe_2$). These figures are similar in magnitude to those derived for a co-ordinated amide mediated reaction and the values lie between those for k_1'(tren) and k_{OH} of the penta-amine equivalents. No special difference in reactivity between the two types of conjugate base was indicated.

Whereas the influence of the base dependent term on the second step of hydrolysis due to the effect of the conjugate base [equation (3)] was also noticed at pH values of greater than 5 for the neutral ligands, the aqua bromo[3] and aqua chloro[5] complexes exhibited this effect at somewhat lower pH values. Values of $k_2'K_a$ of 1.1×10^{-6} mol dm^{-3} s^{-1} and 9.3×10^{-7} mol dm^{-3} s^{-1} for bromo and chloro respectively were obtained at 65 °C and ionic strength 1.0 mol dm^{-3}. Recalculation of the data for the aqua bromo complex, using the inverse of equation (3), gave $k_2' = 1.4 \times 10^{-3}$ s^{-1} and $k_2'K_a = 1.3 \times 10^{-6}$ mol dm^{-3} s^{-1}, from which a pK_a of *ca.* 3.0 can be deduced. Although the value of k_2' at 65 °C is difficult to compare with results at 25 °C, we may confidently expect a rate diminution of the order 100. This would give a value consistent with those found at 25 °C for the neutral leaving groups (Table 3). Similarly, since the temperature dependence of pK_a of the co-ordinated water in complexes of this type has not been addressed in detail, it is again difficult to compare the somewhat lower pK_a value obtained for the aqua bromo complex at higher temperatures with the values obtained in the present study at 25 °C. However, because of the known reduction in K_w with temperature, the pK_a of co-ordinated water will surely rise in value at 25 °C in the former case.

Next we assess the relative reactivity of the two sites under the conditions of base hydrolysis. This was studied in detail using the bis(dimethylformamide) complex, although we have no reason to expect that the other derivatives would behave differently. Without doubt, only one intermediate was observed in the n.m.r. experiment. Three obvious explanations may be proposed. First, one of the intermediates may be much more labile than the other. However, the fact that in the early stages of the reaction the concentrations of the intermediate and free dmf are approximately the same indicates that the latter proposition is unlikely. If this mechanism were in operation, then the concentration of dmf would increase at a faster rate than that of the less labile intermediate. Secondly, the hydrolysis may give only the one product due to unique reactivity or thirdly, the two sites are labile but the equilibrium lies leavily in favour of one of the two putative intermediates. The relative merits of these latter two propositions are difficult to judge given the present data.

Literature evidence supports the view that under base hydrolysis conditions the two isomers of $[Co(tren)(NH_3)X]^{2+}$ do exhibit different reactivity. The p-chloro isomer is some 20 000 times more reactive than the t-chloro form under base hydrolysis[13] whilst the two species are of approximately equal reactivity under acid conditions.[14] Recent work on the analogous $[Co(tren)(NH_3)(SCN)]^{2+}$ complexes has shown a similar difference in reactivities of the p and t isomers.[15] In this case the p isomer hydrolysed at least 350 000 times more rapidly than the t isomer.

In both of these cases, the faster reaction of the p isomer gives complete retention of configuration whilst with the t isomer, considerable formation of the p-hydroxy form accompanies the hydrolysis. Indeed, in most of the examples studied, the p-hydroxy isomer is the major one,[16] but in no case yet published is it formed exclusively from a t-X compound. Lower differences in reactivity between the p and t isomers were observed for the much less labile $-NCS$ and $-N_3$ complexes and the reactions were all stereoretentive.[15]

Given this evidence, and noting the fact that only one intermediate was visible, we believe that the best explanation of our results for base hydrolysis is that one ligand position is considerably more reactive than the other. Although such extrapolations are tenuous, it would be tempting to assign the more reactive site as the p-position in the bis(dimethylformamide) case. However, on the basis of n.m.r. it was not possible definitely to assign the stereochemical course of the reaction. To do this would require the preparation of authentic intermediates, which we have not attempted, though an approach through trifluoromethanesulphonate[17] chemistry may be practicable. It should be noted that the kinetics of this system should now only consist of the two exponentials, corresponding to unique step-wise loss of ligands.

This difference in reactivity for the two sites is a somewhat different result to that obtained for spontaneous hydrolysis of the dmf complex, where without doubt two intermediates were seen. We believe that this is a result of the approximate equal lability of the two sites. Unfortunately, analysis of the spontaneous hydrolysis products from p- and t-$[Co(tren)(NH_3)Cl]^{2+}$ has not been published and we are unable to comment on the possibility of non-retention of configuration. In fact, the spontaneous hydrolysis of the $[Co(tren)(HCONMe_2)_2]^{3+}$ ion bears a close resemblance overall to that of the far simpler $[Co(cyclen)(HCONMe_2)_2]^{3+}$ ion. The simple sequential process in the latter ion with $k_1/k_2 = 5.0$ is remarkably similar to the result observed with the former where $k_1(\text{obs.})/k_2(\text{obs.}) = 5.5$. This observation supports the view that there is no special lability ascribable to the p to t sites in the tren system under spontaneous hydrolysis conditions, in apparent contrast to the base hydrolysis situation. A more extensive study of the simpler cyclen system seems warranted.

Acknowledgements

Interest in this study and access to instrumental facilities provided by Professor A. M. Sargeson (Australian National University) facilitated progress and is gratefully acknowledged.

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Received 2nd January 1987; *Paper* 7/004