Inorganica Chimica Acta, 54 (1981) L145–L147

The Base Hydrolysis of the *trans*-Dichloro(C-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)chromium(III) Cation

D. A. HOUSE

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

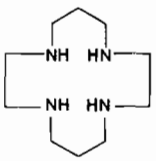
and R. W. HAY

Department of Chemistry, University of Stirling, Stirling, U.K.

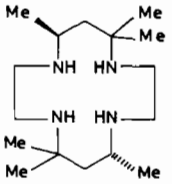
Received May 13, 1981

Introduction

Currently very little synthetic or mechanistic work has been carried out on chromium(III) complexes of macrocyclic ligands. Ferguson and Tobe [1] have described the preparation of a number of *cis*- and *trans*- complexes of the type $[CrX_2(cyclam)]^+$ (cyclam = 1,4,8,11-tetraaxacyclotetradecane(I), X = Cl^-, Br^-, NCS^-, NO_2^- and N_3^-). Further synthetic work on the *trans*-$[CrX_2(cyclam)]^+$ complexes has been recently described [2], and Sperati [3] has also



(I)
cyclam



(II)
teta (C-meso)

reported the preparation of a number of Cr(III) complexes of macrocyclic ligands. The kinetics and steric course of aquation and base hydrolysis of *cis*- and *trans*-$CrCl_2(cyclam)]^+$ have been studied [4], base hydrolysis occurred with a second order rate law and values of k_{OH} were reported to be very much less than those of the corresponding cobalt(III) complexes. As part of a continuing study of amine complexes of Cr(III) [5–10] we have prepared *trans*-$[CrCl_2(teta)](NO_3)_2$ (teta = C-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane = (II)) and determined its base hydrolysis rate. For the analogous cobalt(III) derivatives steric acceleration of base hydrolysis due to the ring methyl groups occurs [11] consistent with a dissociative SN_1CB mechanism.

Experimental

Trans-*Dichloro(teta)chromium(III) Nitrate*, trans-*[CrCl$_2$(teta)](NO$_3$)[3, 12, 13]*.

Solutions of $CrCl_3 \cdot 6H_2O$ and teta$\cdot 2H_2O$ in DMF were dehydrated by boiling [14, 15] and then mixed. Green crystals of the crude chloride salt were slowly deposited from the hot solution as the volume was reduced. This green solid was dissolved in water and addition of excess 2 *M* $NaNO_3$ solution resulted in the precipitation of the nitrate salt. Satisfactory elemental analysis data have been obtained for this complex, and the full details of the preparation of this and other Cr(III) complexes of teta and tetb [13] will be described in a subsequent publication.

Kinetics

The rate of the reaction between *trans*-$CrCl_2(teta)^+$ and OH^- was measured using a Radiometer pH-stat. About 20 mg of the solid complex was added to a stirred solution (50 ml) of 0.1 *M* NaCl (previously adjusted to slightly above the desired pH) in a temperature controlled reaction vessel. As the complex dissolved (complete within 1 min), the pH dropped, and was maintained at the set value by automatic addition of 0.1 *M* NaOH (less than 1 ml for complete reaction). The extent of reaction *vs.* time trace was recorded directly from the uptake of OH^- [16–18].

Results and Discussion

In the reaction between *trans*-$CrCl_2(teta)^+$ and OH^-, approximately two moles of OH^- are consumed for every mole of complex (pH = 7.8–9.4) and the final visible absorption spectrum if identical to that obtained from *trans*-$[Cr(teta)(OH_2)_2](ClO_4)_3$ dissolved in 0.01 *M* NaOH.

Thus *trans*-$CrCl_2(teta)^+$ and *trans*-$CrCl(OH)(teta)^+$ are reacting with OH^- at comparable rates (eqns. 1–3).

$$t\text{-}CrCl_2(teta)^+ + OH^- \xrightarrow{k_1} t\text{-}CrCl(OH)(teta)^+ + Cl^- \quad (1)$$

$$t\text{-}CrCl(OH)(teta)^+ + OH^- \xrightarrow{k_2} t\text{-}Cr(OH)_2(teta)^+ + Cl^- \quad (2)$$

$$k_1 \sim k_2 \quad (3)$$

Spectrophotometric scans (pH = 6.3, carbonate buffer, T = 35 °C) show drifting of initial isosbestic

TABLE I. Observed and Calculated Rate Constants for the Base Hydrolysis of *trans*-[$CrCl_2$(tet*a*)]NO_3 at μ = 0.1 *M* NaCl.[a]

T °C [K]	pH[b] (10^6 [OH^-], *M*)	10^4 k_{obs}[c] s^{-1}	$k_{OH\ obs}$[d] $M^{-1}\ s^{-1}$	$k_{OH\ calc}$[e] $M^{-1}\ s^{-1}$
20.4 [293.6]	9.40 (22.8)	17.7	77.6	69.3
		16.5	72.2	
24.7 [297.9]	8.50 (4.04)	5.70	141	139
		4.93	122	
	8.70 (6.40)	8.34	130	
	8.90 (10.1)	13.0	129	
28.3 [301.5]	8.50 (5.37)	12.5	233	242
		13.6	253	
		12.8	238	
		13.0	242	
	8.60 (6.76)	16.5	244	
		15.8	234	
30.1 [303.3]	8.40 (4.91)	16.8	342	320
		16.2	323	
35.3 [308.5]	7.80 (1.76)	12.8	727	696
		12.2	693	

[a]Loss of first chloride ion. [b]$-\log[OH^-] = pK_{wc} + 0.105$ – set pH [16]. [c]Observed pseudo-first-order rate constant as determined from the trace of OH^- uptake *vs.* time, using the $t_{1/2}$ and $t_{3/4}$ method [17]. [d]$k_{OH} = k_{obs}\ [OH^-]^{-1}$. [e]Calculated using the activation parameters: E_a = 116 ± 3 kJ mol^{-1}, log*PZ* = 22.584, $\Delta S^{\#}_{298}$ = 179 ± 6 J K^{-1} mol^{-1}.

TABLE II. Kinetic Data for the Base Hydrolysis of Some Analogous Co(III) and Cr(III) Complexes.[a]

Complex	k_{OH} (298.2), $M^{-1}\ s^{-1}$ [b]			10^3 Co(III)/Cr(III)	Ref.[c]
	Cr(III)	Co(III)			
trans-$MCl_2(en)_2^+$	0.037		0.31×10^4	84	d; e
trans-MCl_2(2,3,2-tet)$^+$		(RS)[a]	3.4×10^4		f
		(RR,SS)	6.8×10^4		f
trans-MCl_2(3,2,3-tet)$^+$		(RR,SS)	10.2×10^4		g
trans-MCl_2(cyclam)$^+$	(?)[a] 1.3	(RSSR)	6.5×10^4	51	h; f
		(RRRR, SSSS)	15.7×10^4		f
trans-MCl_2(tet*a*)$^+$	(?) 145	(?)	$\sim 150 \times 10^4$	~10	i; j
$MCl(NH_3)_5^{2+}$	1.8×10^{-3}		1.58	0.85	k; k
sym-fac-cis-MCl(en)(dien)$^{2+}$	7.3×10^{-3}		7.3	1.0	l; m
sym-fac-cis-MCl(tn)(dien)$^{2+}$	7.7×10^{-3}		10.6	1.4	l; m

[a]Configuration of the secondary NH protons (where known) are indicated in parentheses. [b]Loss of first chloride ion. See original references for ionic strength conditions. [c]First reference for Cr(III); second reference for Co(III). [d]Ref. 20. [e]Cited in ref. 4. [f]Cited in ref. 28. [g]D. A. House, *Inorg. Chim. Acta, 48*, 193 (1981). [h]Ref. 4. [i]This research. [j]Ref. 29. k_{OH} = 5.7×10^5 at 19.8 °C. [k]Ref. 21, Table 2. [l]Ref. 6. [m]Ref. 21, Table 26.

points towards the latter stages of the reaction and log (extent of reaction) *vs.* time plots for the hydroxide uptake *vs.* time data were linear for only two half lives. This initial rate data represents k_1, but the values of k_2 have not yet been determined. Rather than attempts the mathematical analysis of the combined rate data, we are first attempting to prepare *trans*-CrCl(tet*a*)$(OH_2)^{2+}$, and measure k_2 directly.

The fact that less than the expected two moles (1.8 observed) of OH^- were used in the total reaction is probably due to some OH^- contribution from the reaction *t*-$Cr(OH)_2$(tet*a*)$^+$ + H_2O → Cr(OH)(tet*a*)-$(OH_2)^{2+}$ + OH^- (4), with an estimated pK_2 of about 8.

Table I lists the kinetic data corresponding to reaction (1) and similar data for related Cr(III) and Co(III) complexes are presented in Table II. The data in Table I, together with a satisfactory linear

activation energy plot, show that the rate of loss of the first chloride ion can be expressed by the relation

$$\frac{d[Cl^-]}{dt} = k_1 [Cr(III)] [OH^-] \quad (5)$$

over a greater than 10 fold variation in $[OH^-]$.

The mechanism of the base hydrolysis of Cr(III) amine complexes has been the basis of considerable discussion and speculation [5]. The reaction rates are usually several orders of magnitude slower than those of analogous Co(III) complexes, and *trans*-$CrCl_2(teta)^+$ is no exception (Table II). Thus, in terms of the normally accepted SN_1CB mechanism for the base hydrolysis of Co(III) amine complexes, either the acidity of the NH(amine) protons must be lower, or the derived conjugate base less labile for Cr(III), than for Co(III). Nevertheless, following the argument of Edwards *et al.* [19], an SN_1CB mechanism is favoured for Cr(III) on the basis of the large positive activation entropies observed for this type of reaction [20] (Table I, footnote e). We would, however, also favour an SN_1CB mechanism for the base hydrolysis of Cr(III) amine complexes on the basis of the trends of k_{OH} observed in Table II, where the rate ratios Co(III)/Cr(III) are about 10^4 for tetraamines and 10^3 for pentaamines. The steric acceleration due to C-methyl substitution observed in the base hydrolysis of *trans*-$CrCl_2(teta)^+$ relative to *trans*-$CrCl_2(cyclam)^+$ (Table II) is also consistent with an SN_1CB mechanism [11].

The other observation we would make here (and at present unexplained) is that the base hydrolysis rate ratio Cr–Br/Cr–Cl ~ 100 [20], is much greater than that of Co–Br/Co–Cl ~ 6 [21].

One final problem that has not always had due recognition in complex ion macrocyclic chemistry, is that of the assignment of the stereochemistry of the NH protons. There is no doubt that different stereochemistries are kinetically significant, especially for aquation reactions [22, 23] and different orientations can facilitate or inhibit the generation of suitable transition states [23]. In base hydrolysis reactions, where deprotonation is believed to preceed halide release, the stereochemistry of the NH protons is not expected to be as significant in determining the stereochemistry of the transition state. Nevertheless, where base hydrolysis rates have been determined for epimerically related systems [24] *e.g.* α- and β-$CoCl(en)(dpt)^{2+}$ [25] or α- and β-$CoCl(tetren)^{2+}$ [26], there is a factor of about 2 between k_{OH} for the two isomers. (See also Table II). Such contributions may well be missed if isomeric mixtures are used.

Preliminary aquation rate data suggests that the *trans*-$[CrCl_2(teta)]NO_3$ used in the base hydrolysis studies may have non equivalent chloro ligands [27] but the assignment of the stereochemistry of the sec-NH protons remains speculative at this stage.

Acknowledgements

We thank the New Zealand Universities Grants Committee for providing funds to purchase instruments used in this research.

References

1 J. Ferguson and M. L. Tobe, *Inorg. Chim. Acta, 4,* 109 (1970).
2 C. K. Poon and K. C. Pun, *Inorg. Chem., 19,* 568 (1980).
3 C. R. Sperati, *Ph.D. Thesis, Ohio State University* (1971); *Diss. Abs., 32B,* 6282 (1972); *Chem. Abs., 77,* 107189K (1972).
4 E. Campi, J. Ferguson and M. L. Tobe, *Inorg. Chem., 9,* 1781 (1970).
5 C. S. Garner and D. A. House, *Transition Metal. Chem., 6,* 59 (1970).
6 B. S. Dawson and D. A. House, *Inorg. Chem., 16,* 1354 (1977).
7 D. A. House, *Inorg. Nucl. Chem. Lett., 12,* 259 (1976).
8 I. J. Kindred and D. A. House, *J. Inorg. Nucl. Chem., 37* 1320 (1975), *37,* 13559 (1975).
9 D. A. House, *J. Inorg. Nucl. Chem., 35,* 3103 (1973).
10 R. W. Hay, B. Jeragh and P. R. Norman, unpublished research.
11 C. K. Poon and P. W. Mak, *J. Chem. Soc. Dalton,* 216 (1978), and references cited therein.
12 J. Glerup, H. C. Ørsted Inst., University of Copenhagen, personal communication.
13 B. Jeragh, *Ph.D. Thesis, University of Stirling* (1979).
14 J. C. Chang, *J. Indian Chem. Soc., 54,* 98 (1977).
15 E. Pedersen, *Acta Chem. Scand., 24,* 3362 (1970).
16 A. J. Cunningham, D. A. House and H. K. J. Powell, *J. Inorg. Nucl. Chem., 33,* 572 (1971).
17 J. McKenzie and D. A. House, *J. Inorg. Nucl. Chem., 39,* 1843 (1977).
18 D. A. House, P. R. Norman and R. W. Hay, *Inorg. Chim. Acta Lett., 45,* L117 (1980).
19 J. O. Edwards, F. Monacelli and G. Ortaggi, *Inorg. Chim. Acta, 11,* 47 (1974).
20 Ref. 5, Table 26.
21 D. A. House, *Coord. Chem. Rev., 23,* 223 (1977).
22 C. J. Cooksey and M. L. Tobe, *Inorg. Chem., 17,* 1558 (1978).
23 R. W. Hay, P. R. Norman, D. A. House and C. K. Poon, *Inorg. Chim. Acta,* accepted for publication.
24 A. R. Gainsford and D. A. House, unpublished research.
25 Ref. 21, Table 26.
26 Ref. 21, Table 11.
27 M. C. Couldwell and D. A. House, *Inorg. Chem., 13,* 2949 (1974).
28 J. Lichtig and M. L. Tobe, *Inorg. Chem., 17,* 2442 (1978).
29 D. P. Rillema, J. F. Endicott and J. R. Barber, *J. Am. Chem. Soc., 95,* 6987 (1973).