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The Kinetics of the First Stage of the Acid Hydrolysis of *trans*-Dichloro(C-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)chromium(III) Cation, *trans*-$CrCl_2(teta)^+$

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Introduction

Transition metal complexes of the macrocyclic tetramines, cyclam*, have been the subject of a considerable number of synthetic and kinetic investigations [1, 2]. The 5,7,7,12,14,14-Me_6 derivative of this ligand, first described by Curtis [3–6], can exist in two forms, the C(5,12)-*meso* (tet*a*) or the C(5,12)-*racemic* (tet*b*) and the transition metal complexes derived from these have quite distinct properties [3–6].

We have previously [7] described the preparation of *trans*-$CrCl_2(teta)^+$ and report here the kinetics of aquation for the first chloro ligand. Although we are still uncertain as to the sec-NH proton arrangement in this *trans*-dichloro, preliminary X-ray crystallographic data from the *trans*-hydroxoaqua dinitrate (an hydrolysis product) suggests the RSSR (*meso*) conformation. The aquation kinetic parameters allow a comparison of structure-reactivity factors with other macrocyclic and linear tetraamine Cr(III) complexes.

Experimental

The macrocyclic ligand, tet*a*, was synthesised by the method of Hay, Lawrence and Curtis [8], and *trans*-$[CrCl_2(teta)]NO_3$ was prepared as described previously [7]. *Anal.* Calcd. for $CrC_{16}H_{36}N_5O_3Cl_2$: Cr, 11.1; C, 40.9; H, 7.7; N, 14.9; Cl, 15.1%; Found: Cr 11.1; C, 40.9; H, 7.9; N, 15.0, Cl, 15.1%. Visible absorption spectral parameters: *trans*-$CrCl_2(teta)^+$ in 0.1 *M* HCl: (nm), (ϵ) (M^{-1} cm^{-1}): 576 max (20.8); 436 sh (26.6); 496 min (1.4); 370 max (38.1); 324 min (3.7). *trans*-$CrCl(teta)(OH_2)^{2+}$ in 0.05 *M* H_2SO_4 (*via* the dichloro after 80 min at 61 °C): 523 max (21.7); 474 min (8.9); 420 sh (30.8); 370 max (54.7), 317 min (8.0). *trans*-$Cr(OH)_2(teta)^+$ in 0.1 *M* NaOH (*via* the dichloro after 20 min at room temperature): 471 max (25.5); 431 min (20.6); 396 max (27.8); 350 min (8.3); 320 max (16.7). *trans*-$Cr(teta)(OH_2)_2^{3+}$ in 1.0 *M* HNO_3 (*via* acidification of the dihydroxo): 514 max (14.5); 469 min (11.0); 419 max (34.4); 399 min (31.2; 354 max (49.4), 337 min (44.7).

TABLE I. Spectrophotometrically Determined Rate Constants (k_H, s^{-1}) for the First Aquation Step for *trans*-(RSSR)-$[CrCl_2(teta)]NO_3$ in 0.05 *M* H_2SO_4 (μ = 0.15 *M*).

T °C (K)	10^4 k_H (s^{-1})	10^4 k_H(calc)^a
55.4 (328.6)	3.84 ± 0.11	3.98
	3.84 ± 0.11	
58.6 (331.8)	5.72 ± 0.23	5.52
	5.69 ± 0.26	
	5.66 ± 0.19	
61.1 (334.3)	6.87 ± 0.16	7.10
	7.35 ± 0.28	
	7.17 ± 0.24	
63.2 (328.6)	8.75 ± 0.18	8.74
	8.27 ± 0.14	
66.1 (339.3)	12.1 ± 0.32	11.6
	12.7 ± 0.36	
68.7 (341.9)	14.1 ± 0.23	14.9
	14.7 ± 0.54	
	14.4 ± 0.32	

^{a}Calculated from the activation parameters cited in Table II.

The rate of loss of the first chloro ligand was determined spectrophotometrically in 0.05 *M* H_2SO_4 (μ = 0.15 *M*). Small amounts of the complex were dissolved in the pre-heated solution and the spectral changes were monitored at 520 nm using the fixed wavelength technique. Isosbestic points for the reaction were observed at 561, 474 and 392 nm. Both reference and sample cells were maintained at the desired temperature with circulating water. Pseudo-first-order rate constants (k_H, s^{-1}) were calculated from the expression:

$$k_H t = \ln \frac{A_\infty - A_o}{A_\infty - A_t}$$

where A_o, A_∞ and A_t are the measured absorbance at time zero, the end of the reaction (7–9 half-lives)

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*Abbreviations used: en = $NH_2(CH_2)_2NH_2$; R,S-pn = (±)-$NH_2CH(CH_3)CH_2NH_2$; tn = $NH_2(CH_2)_3NH_2$; 2,3,2-tet = $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$; 3,2,3-tet = $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$; cyclam = 1,4,8,11-tetraazacyclotetradecane; tet*a* = C-meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

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TABLE II. Activation Parameters for the First Step in the Acid Hydrolysis of Some *trans*-$MCl_2(N_4)^+$ Complexes at 298.2 K.

	M[a]	k_H (s^{-1})	E_a (kJ mol^{-1})	$S^\#$ (JK^{-1} mol^{-1})	Ref.
$(NH_3)_4$	Co(III)	1.8×10^{-3}	98.8	+36	b,c
	Cr(III)	4.5×10^{-5}	91	−25	d
$(en)(NH_3)_2$	Co(III)	2.3×10^{-4}			b
$(en)_2$	Co(III)	3.5×10^{-5}	110	+59	e
	Cr(III)	2.2×10^{-5}	97	−17	f
$(R,S\text{-}pn)_2$	Co(III)	6.2×10^{-5}			b
	Cr(III)	$\sim 3 \times 10^{-5}$			g
(en)(tn)	Co(III)	3.96×10^{-4}	101	+21	h
	Cr(III)	1.93×10^{-5}	98	−15	h
$(tn)_2$	Co(III)	5.33×10^{-2}	89	+29	i
	Cr(III)	2.08×10^{-5}	103	+1	j
$(NH_3)(dien)^k$	Co(III)	5.21×10^{-4}	97	+8	l
(RR,SS)-(trien)	Co(III)	3.18×10^{-3}	109	+65	m
(RR,SS)-(2,3,2-tet)	Co(III)	2.9×10^{-4}	108	+50	n,o,p
(R,S)-(2,3,2-tet)	Co(III)	1.5×10^{-5}	102	+4	o,p
	Cr(III)?	3.23×10^{-6}	107	0	q
(RR,SS)-(3,2,3-tet)	Co(III)	5.4×10^{-5}	103	+17	p
	Cr(III)	1.06×10^{-6}	95	−50	r
(RRRR,SSSS)-(cyclam)	Co(III)	1.75×10^{-3}	101	+42	s
(RSSR)-(cyclam)	Co(III)	1.1×10^{-6}	103	−13	t
	Cr(III)?	2×10^{-8}	116	−8	u
(RSSR)-(tet*a*)	Co(III)?	9.3×10^{-4}	107	+54	v,w
	Cr(III)?	1.26×10^{-5}	92.6 ± 2.4	−37 ± 5	x
(SRSR)-(tet*b*)[k]	Co(III)?	4.2×10^{-3}	118	+105	v,w

[a] A question mark following the parenthesis indicates that the sec-nH proton stereochemistry is uncertain. [b] R. G. Pearson, C. R. Boston and F. Basolo, *J. Phys. Chem., 59,* 304 (1955). [c] R. C. Link, *Inorg. Chem., 8,* 1016 (1969). [d] D. W. Hoppenjans, J. B. Hunt and C. R. Gregoire, *Inorg. Chem., 7,* 2506 (1968). [e] S. C. Chan, *Austral. J. Chem., 20,* 595 (1967). [f] D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem., 18,* 219 (1961). [g] R. R. Barona and J. A. McLean, *Inorg. Chem., 10,* 286 (1971), estimated from the data at 35 °C using the activation parameters for *trans*-$CrCl_2(en)_2^+$. [h] M. C. Couldwell, D. A. House and H. K. J. Powell, *Inorg. Chem., 12,* 627 (1973). [i] I. R. Jonasson, R. S. Murray, D. R. Stranks and Y. K. Yandell, *Proc. Int. Conf. Coord. Chem., 12,* 32 (1969). [j] M. C. Couldwell and D. A. House, *Inorg. Nucl. Chem. Lett., 7,* 947 (1971); *Inorg. Chem., 11,* 2024 (1972). [k] Non-equivalent chloro ligands. [l] M. C. Couldwell and D. A. House, *Inorg. Chem., 13,* 2949 (1974). [m] A. M. Sargeson and G. H. Searle, *Inorg. Chem., 6,* 2172 (1967). [n] M. L. Tobe, *Inorg. Chem., 7,* 2131 (1969). [o] R. Niththyananthan and M. L. Tobe, *Inorg. Chem., 8,* 2131 (1969). [p] M. D. Alexander and H. G. Hamilton, *Inorg. Chem., 8,* 2131 (1969). [q] C. Kutal and A. W. Adamson, *Inorg. Chem., 12,* 1990 (1973). [r] D. Yang and D. A. House, unpublished research. [s] C. J. Cooksey and M. L. Tobe, *Inorg. Chem., 17,* 1558 (1978). [t] C. K. Poon and M. L. Tobe, *J. Chem. Soc. A,* 2069 (1967). [u] E. Campi, J. Ferguson and M. L. Tobe, *Inorg. Chem., 9,* 1781 (1970). [v] W. K. Chan and C. K. Poon, *J. Chem. Soc. A,* 3087 (1971). [w] J. A. Kernohan and J. F. Endicott, *Inorg. Chem., 9,* 1504 (1970). [x] This research.

and time, t(s). Activation parameters were computer calculated from the variation of *k* with temperature, using standard equations [9].

Results and Discussion

trans-$CrCl_2(teta)^+$ aquates smoothly with excellent isosbestic points to produce *trans*-$CrCl(teta)(OH_2)^{2+}$ in 0.05 *M* H_2SO_4 over the temperature range 55–70 °C. Both nitrate and perchlorate media were unsatisfactory due to unfavourable solubility. Table I lists the pseudo-first-order rate constants obtained for this reaction and Table II lists the activation parameters observed for this, and similar reactions for other *trans*-dichloro(tetraamine)chromium(III) and Co(III) complexes. The visible absorption spectral parameters reported in the experimental section suggest that the *trans*-configuration is preserved throughout all the chemical transformations described. The excellent kinetic data also suggest that the sec-NH protons are symmetrically arranged with respect to the chloro ligands (*i.e.* both ligands equivalent) as two rate processes could be expected if this were not the case [1]. We have discussed earlier our preference for the RSSR (*meso*) configuration. Unfortunately, the sec-NH stereochemistry for *trans*-$CrCl_2(cyclam)^+$ is not well established. Poon [10] has found that *cis*-$CrCl_2(cyclam)^+$ can be isomerised in base to the *trans*-dichloro, and, provided the sec-NH proton configuration at the folded nitrogens is preserved, the resulting *trans*-complex will have the (RRRR, SSSS) (*racemic*) arrangement.

However, basic conditions are well known to invert sec-NH protons and the above proviso is very speculative, especially as the more thermodynamically stable *trans*-$CoCl_2(cyclam)^+$ has the (RSSR) (*meso*) configuration [2].

Following the work of Cooksey and Tobe [2], we would expect *trans*-$CrCl_2(cyclam)^+$ to aquate more rapidly than observed [11], if the (RRRR, SSSS) stereochemistry was maintained.

Although the mechanism of aquation of Cr(III) amine complexes is believed to have considerable associative character [12], it is possible that axial methyl acceleration can still account for the difference in aquation rate between *trans*-$CrCl_2(cyclam)^+$ and *trans*-$CrCl_2$(tet*a*)$^+$ (Table II) as has been proposed for the Co(III) analogues [1].

The situation with regard to sec-NH configuration for the *trans*-$CrCl_2$(linear tetramine)$^+$ is also uncertain. *trans*-$CrCl_2$(3,2,3-tet)$^+$ is known to have the (RR,SS) (racemic) configuration [13, 14] but the stereochemistry of the *trans*-$CrCl_2$(2,3,2-tet)$^+$ is not known. Although *trans*-CrF_2(2,3,2-tet)$^+$ has the (R,S) (*meso*) configuration [16], this has not been established for the *trans*-dichloro, which was synthesised by an entirely different procedure [16].

Nevertheless, there is a decrease in aquation rate of about 10 for these (linear tetramine) chromium(III) complexes relative to the bis(diamines) (Table II), whereas with Co(III), a much more complex pattern of rate variation is evident. This decrease is entirely consistent [17] with the more associative aquation mechanism proposed for Cr(III) complexes.

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