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Base Hydrolysis, Racemisation and Proton Exchange Rates for some *trans*-Dihalo(tetraamine)chromium(III) Complexes

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Kinetic parameters (k_{OH}, M^{-1} s^{-1}; E_a, *kJ* mol^{-1}; $\Delta S^{\#}_{298}$, *J* K^{-1} mol^{-1}) *obtained for the base hydrolysis* (μ = *0.1* M) *of* trans-$CrCl_2(en)_2^+$, trans-*(RR,SS)*-$CrBr_2$*(tnentn)*$^+$ *and* trans-*(RSSR)*-$CrBr_2$*(cyclam)*$^+$ *are 3.62* × 10^{-2}*; 98.3; +49: 80.9; 127; +211: 140; 123; +200 respectively at 298.2 K. The rates of sec-NH proton exchange* (k_{exch}, M^{-1} s^{-1}) *for* trans-*(RR,SS)*-CrX_2*(tnentn)*$^+$, *X = F, Cl and* trans-*(RSSR)*-$CrCl_2$*(teta)*$^+$ *are 1* × 10^2, *1* × 10^3 *and 3.5* × 10^2 *respectively at 298.2 K.* trans-*(SS)*-CrF_2*(tnentn)*$^+$ *racemises* (k_{rac}, M^{-1} s^{-1}; μ = *0.13* M) *with kinetic parameters 0.27; 88.7; +33 at 298.2 K. Corresponding parameters* (k_{rac}) *for X = Br are estimated to be 20; 89; +70. These data allow considerable insight into the mechanistic pathways for the base hydrolysis of* trans-$CrX_2(N_4)^+$ *complexes.*

Introduction

The rates of base hydrolysis of Cr(III) chloro amine complexes are often 10^4–10^5 times slower than those of analogous Co(III) complexes of the same stereochemistry [1–5].

The generally accepted mechanism for the base hydrolysis of Co(III) chloro amine complexes involves the formation of a conjugate base, followed by a rate determining decomposition of this intermediate (the S_N1CB mechanism, eqn. (1)).

$$\begin{array}{c} \mathrm{CoCl(NH_3)_5^{2+} + OH^- \overset{K}{\rightleftharpoons} CoCl(NH_3)_4(NH_2)^{2+} + H_2O} \\ \downarrow k \\ \text{products} \end{array} \qquad (1)$$

If such a mechanism is appropriate for analogous Cr(III) and Co(III) complexes, then either the NH protons adjacent to Cr(III) are less acidic, or the resulting Cr(III) conjugate base is less labile.

Proton exchange rates have previously been used to determine M–NH acidities and for $M(NH_3)_6^{3+}$ or $M(en)_3^{3+}$ (M = Co, Cr) systems there is little difference between Cr(III) and Co(III) [6]. For many chloro pentaamine Co(III) complexes $k_{exchange}$:k_{OH} is 10^5–10^6:1 [7]. However, for certain very labile Co(III) complexes, the rates of base hydrolysis approach those of proton exchange and the base hydrolysis reaction is subject to general base catalysis [8]. Thus, in terms of the S_N1CB mechanism, every act of deprotonation results in product formation.

We have recently determined the rates of base hydrolysis of some Cr(III) analogues [1, 2] of these very labile Co(III) complexes[†] *e.g.* *trans*-(RR,SS)-$CrCl_2$(tnentn)$^+$ and *trans*-(RSSR)-$CrCl_2$(te*ta*) and have again found the expected decrease of ~10^5 in base hydrolysis rates. This rate difference was interpreted as due to a lowering in the acidity of the Cr–NH protons relative to Co(III) but this interpretation could be questioned on the basis that $M(en)_3^{3+}$ and $M(NH_3)_6^{3+}$ (M = Co, Cr) have similar proton exchange rates [6].

In this paper we present kinetic data for proton exchange rates, base catalysed racemisation (proton inversion) and base hydrolysis for several *trans*-$CrX_2(N_4)^+$ systems.

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[†] Abbreviations used: en = $NH_2(CH_2)_2NH_2$, tnentn = $NH_2CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$, cyclam = 1,4,8,11-tetraazacyclotetradecane, te*ta* = C(7,14)-*meso*-5,5,7,12,12,14-hexamethylcyclam, ox = oxalato, DMF = dimethylformamide, DMSO = dimethylsulphoxide.

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Experimental

trans-(RR,SS)-[$CoCl_2$(tnentn)]Cl [9, 10], *trans*-(RR,SS)-[$CrCl_2$(tnentn)]Cl [1], *trans*-(RR,SS)-[CrF_2(tnentn)]ClO_4 [11], *trans*-[$CrF_2(en)_2$]ClO_4 [11, 12], *trans*-(RSSR)-[$CrCl_2$(te*ta*)]Cl [2, 13], *cis*-β-(RR,SS)- and Δ(−)$_{589}$-*cis*-β-(RR)-[Cr(ox)(tnentn)]-ClO_4 [1] were prepared as previously described.

CAUTION: Although we have experienced no difficulty with the perchlorate salts described, these should be regarded as potentially explosive and handled accordingly.

*(−)$_{589}$-*trans*-(RR)- and *trans*-(RR,SS)-[$CrBr_2$(tnentn)]ClO_4*

These grass green salts were prepared by heating the chiral or racemic *cis*-β-oxalato complexes (1 g/30 ml) in 20% HBr solution at 80 °C for 10 min, followed by addition of 60% $HClO_4$ (5 ml/1 g) to the hot solution. The perchlorate salts are almost insoluble in water but can be recrystallised from DMF by the addition of saturated aqueous $NaClO_4 \cdot H_2O$ solution. The racemic salt can also be prepared by heating (10 min. 80 °C) *trans*-(RR,SS)-[CrF_2(tnentn)]ClO_4 (2 g) with HBr (25 ml, 60%) followed by the addition of $HClO_4$ (5 ml, 60%). *Anal.*: Calcd. for $CrC_8H_{22}N_4Br_2ClO_4$: C, 19.79; H, 4.57; N, 11.54. Found: C, 20.05; H, 5.17; N, 11.17.

Visible absorption spectra: (DMF); λ, (nm), (ε) (M^{-1} cm^{-1}): 615 max (34.7), 540 min (6.7), 372 sh (49.7), 448 max (56.6), 390 sh (35.7), 347 min (11.7). Circular dichroism spectra: (DMF); λ(nm), (Δε) (M^{-1} cm^{-1}): 620 (−0.102), 520 (−0.015), 460 (−0.191), 410 (−0.10), 370 (−0.266). Optical rotatory dispersion spectra: (DMF); λ(nm), [*M*] (° M^{-1} m^{-1}): 660 (+255), 600 (0), 589 (−22), 500 (−376), 550 (0), 430 (+64), 416 (0), 395 (−227), 371 (0), 350 (+589).

trans-[$CrCl_2(en)_2$]ClO_4

trans-[$CrF_2(en)_2$]ClO_4 was gently heated (40 °C) in 12 *M* HCl (1g/15 ml) for 10–15 min and 60% $HClO_4$ (5 ml/1 g) was added to the hot solution. Purple-green dichroic crystals were precipitated in good yield. The yield is considerably reduced if more dilute HCl is used in the substitution reaction. DMF is again an excellent solvent for this water-insoluble salt. *Anal.* Calcd. for $CrC_4H_{16}N_4Cl_3O_4$: C, 14.03; H, 4.71; N, 16.36. Found: C, 14.18; H, 4.86; N, 16.20.

trans-(RSSR)-[$CrBr_2$(cyclam)]ClO_4

trans-[$CrCl_2$(cyclam)]Cl is formed in about a 20% yield (along with *cis*-[$CrCl_2$(cyclam)]Cl) when $CrCl_3 \cdot 6H_2O$ (dehydrated in DMF) is reacted with cyclam [14–17]. The *trans*-dichloro perchlorate salt is easily separated by dissolving the crude reaction product in 0.1 *M* HCl (1.5 g/100 ml, 80 °C) and adding 60% $HClO_4$ (10 ml) to the hot solution. The pale green water-insoluble salt (0.3 g) that deposited was suspended in water (15 ml) and NaOH (0.5 g) was added. The solid dissolved to produce an orange solution as the temperature was raised to 80 °C. An equal volume of 60% HBr, and 5 ml of 60% $HClO_4$, was then added and grass green crystals (0.2 g) slowly deposited from the hot orange-green solution. This salt is slowly soluble in room temperature DMSO (*e.g.* 35 mg in 10 ml DMSO over 30 min.). *Anal.* Calcd. for $CrC_{10}H_{24}N_4Br_2ClO_4$: C, 23.48; H, 4.73; N, 10.95. Found: C, 24.28; H, 5.15; N, 10.34. Visible absorption spectra: (DMSO); 605 max (29.4), 512 min (3.0), 435 sh (16.7), 405 sh (31.5), 358 max (50.5), 345 min (48.4).

Resolution of trans-(RR,SS)-[CrF_2(tnentn)]ClO_4

The racemic perchlorate salt (3 g) was dissolved in sodium formate/formic acid buffer (50 ml, 1 *M*, pH ≈ 3.7) and a solution (3 g, H_2O 50 ml) of dihydrogenbenzoyl-(+)-tartrate plus LiOH, adjusted to pH ~ 7 with formic acid, was added. A solid material, that can only be described as similar to macerated filter paper, slowly deposited over two days at room temperature in an open beaker. This pale orange solid was collected by filtration, washed with 2-propanol and ether, and air dried. An aqueous solution showed a strong positive circular dichroism at 522 nm (Δε = +0.28 M^{-1} cm^{-1}) and the visible absorption spectrum corresponded to *trans*-CrF_2-(tnentn)$^+$ [11].

A small portion of this material was heated at 80–90 °C in 6 *M* HCl/2 *M* $HClO_4$ for 2 hr during which time green crystals deposited. The visible absorption spectra (DMF) of this green solid corresponded to *trans*-$CrCl_2$(tnentn)$^+$ and the CD spectrum to the (SS)-isomer [1]. A suitable amount (*e.g.* 60 mg) of the less soluble monohydrogenbenzoyl-(+)-tartrate salt was dissolved in water (25 ml) and run through an anion exchange resin (Amberlite, IRA-400, standard grade, 8% DVB, Cl^- form, 10 × 1 cm column). The CD and ORD spectrum of the orange coloured effluent (50 ml) was recorded (5 cm cells) and the complex concentration was determined from the visible absorption spectra. Circular dichroism spectra: (H_2O); 522 (+0.28), 465 (+0.18), 407(0), 385 (−0.03), 354(0). Optical rotatory dispersion spectra: H_2O); 589 (+474), 565 (+519), 522(0), 500 sh (−260), 430 (−623), 365 (−286).

Proton Exchange Reactions

40 mg of the complex salts were dissolved in 1 ml D_2O and the appropriate weights of tris HCl and tris (free base) were added in that order. (160 mg and 12 mg respectively for pH = 7.1: 80 mg and 60 mg respectively for pH = 8.1). These solutions were maintained at 25.0 °C for various time intervals and the complex cations precipitated by the addition

of *ca.* 1 g $NaClO_4 \cdot H_2O$ (*trans*-(RR,SS)-MCl_2-(tnentn)$^+$, M = Co, Cr) or 3–5 drops of saturated K_2HgI_4 solution (*trans*-(RR,SS-CrF_2(tnentn)$^+$). At pH = 8.1, Cr–Cl bond rupture was observed at long time intervals, for *trans*-(RSSR)-$CrCl_2$(tet*a*)$^+$. Here, the reactant solution was quenched by addition of 1 ml 12 *M* HCl and the solution warmed (60 °C on a water bath for 5–10 min) to chloride anate the aqua products. Addition of 1 g $NaClO_4 \cdot H_2O$ to the cooled solution gave quantitative precipitation of *trans*-[$CrCl_2$(tet*a*)]ClO_4.

The precipitated salts were collected by filtration, washed with 2-propanol and then ether and air dried. The extent of deuteration (Table I) for the *trans*-MX_2(tnentn)$^+$ salts (M = Co, X = Cl; M = Cr, X = Cl) was estimated from the infrared spectrum of the solids (KBr disc, Pye Unicam Spectraset) using the 620 cm^{-1} ClO_4^- band as an estimate of the complex concentration, and a band at 760 cm^{-1}, increasing with time, as an estimate of the amount of deuteration. Appropriate bands for the HgI_4^{2-} salt of *trans*-(RR,SS)-CrF_2(tnentn)$^+$ and ClO_4^- salt of *trans*-$CrCl_2$-(tet*a*)$^+$ were: 555 cm^{-1} (Cr–F band); 620 cm^{-1} (ClO_4^-) for complex ion concentration: 2400 cm^{-1} (N–D band); 2400 cm^{-1} (N–D band) for extent of reaction, respectively.

Base Hydrolysis Kinetics

The rate of base hydrolysis of *trans*-$CrCl_2(en)_2^+$ was determined from spectrophotometric scans of the complex dissolved in sodium hydroxide solution. Small amounts of the perchlorate salt were placed in a 1 cm spectrophotometer cell that had been rinsed with DMF. The complex dissolved in the residual solvent and the cell was then filled with 0.01 *M* NaOH (μ = 0.1 *M* NaCl) at the appropriate temperature. Spectral scans (using temperature controlled cell holders) showed a two step reaction and initial isobestic points at 435 and 460 nm were lost after 3 half lives to give an envelope of spectral curves increasing at all wavelengths (700–350 nm). Pseudo-first-order rate constants (k_{obs}) were obtained for the first reaction step using an 'infinity' absorbance that gave the best linear fit for a plot of $\ln(A_o - A_\infty)/(A_o - A_t)$ *vs.* t at 520 nm. Conversion to k_{OH} ($k_{obs} = k_{OH}[OH^-]^{-1}$) and extrapolation to 25 °C (Table II) gave a value of $k_{OH} = 3.62 \times 10^{-2}$ M^{-1} s^{-1} in acceptable agreement with 3.7×10^{-2} M^{-1} s^{-1} obtained titrimetrically by Pearson, Munson and Basolo [4].

Pseudo-first-order rate constants for the base hydrolysis of *trans*-(RR,SS)-$CrBr_2$(tnentn)$^+$ and *trans*-(RSSR)-$CrBr_2$(cyclam)$^+$ were obtained from the uptake of OH^- (0.1 *M*) with time using a pH-stat. Small samples of the complex (*ca.* 10 mg) were dissolved in one ml of DMF or DMSO (cyclam complex) and this solution was added to aqueous 0.1 *M* NaCl solution (50 ml) previously adjusted to the desired pH and temperature. In both cases, two moles of OH^- were consumed for every mole of complex, without any noticeable break in the OH^- uptake *vs.* time curve. This suggests that the rate of bromide release from *trans*-CrBr(OH)$(N_{(4)})^+$ (N_4 = tnentn, cyclam) is faster than, or synchronous with, the loss of the first bromide ion.

The set pH was converted to [OH^-] using the expression $-\log[OH^-] = pK_{wc} + \log \gamma_\pm -$ set pH, where $\log \gamma_\pm = 0.105$ for $\mu = 0.1$ *M* (NaCl) and pK_{wc} = 13.779 at 25.0 °C. The pH-meter was calibrated using 0.01 *M* borax solution (pH = 9.18 at 25.0 °C).

Racemisation Kinetics

Small samples of the less soluble monohydrogen benzoyl-(+)-tartrate salt of $(+)_{589}$-(SS)-CrF_2(tnentn)$^+$ (12 mg) were dissolved in 10 ml of 0.13 *M* en/enH$^+$ buffer (pH = 9.93 at 25.0 °C) and this solution was transferred to a 5 cm jacketed spectrophotometer cell. Changes in the CD spectrum were recorded at 525 nm and the final CD spectrum (6–7 half-lives) corresponded to the base line.

Attempts to measure the racemisation of $(-)_{589}$-*trans*-(RR)-$CrBr_2$(tnentn)$^+$ were frustrated by extensive base hydrolysis of the complex (causing mutarotation to *trans*-(RR)-$Cr(OH)_2$(tnentn)$^+$).

Results and Discussion

Transition-metal amine complexes, when dissolved in D_2O, exchange N–H protons according to the rate law [18]:

$$-d(NH)/dt = k_{exch}[\text{complex}][OD^-].$$

The rate of reaction can be controlled by the pD of the solution, and at fixed pD, pseudo-first-order kinetics are observed.

Among the methods used to monitor the extent of deuteration are infrared spectroscopy [19], the OH overtone band at 1600 nm [20] and proton NMR [21]. The latter method is not suitable for paramagnetic Cr(III) complexes and we have used the 'classical' method of infrared (IR) spectroscopy for our systems.

For *trans*-MX_2(tnentn)$^+$ complexes, there are two possible sec-NH proton configurations, and the systems used in this work have been shown by resolution to be the RR,SS (N-racemic) forms. For *trans*-$CrCl_2$-(tet*a*)$^+$ the sec-NH proton configuration is less certain, but a single crystal X-ray analysis of *trans*-[Cr(Cl)-(tet*a*)(OH_2)]$(NO_3)_2$ (an hydrolysis product of *trans*-$CrCl_2$(tet*a*)$^+$ in water) shows the configuration to be (RSSR). Although there is no structural evidence, the stereochemistry of the most stable *trans*-[$CoCl_2$(cyclam)]ClO_4 isomer is believed to have the (RSSR)-secNH configuration [23]. The infrared

TABLE I. Extent of Deuteration with Time for some *trans*-MX_2(tetramine)$^+$ Complexes.[a]

(RR,SS)-$CrCl_2$(tnentn)$^+$				(RR,SS)-CrF_2(tnentn)$^+$			
pH = 7.1		pH = 8.1		pH = 7.1		pH = 8.1	
T (min)	% D_{exch}	T (min)	% D_{exch}	T (min)	% D_{exch}	T (min)	% D_{exch}
5	10	5	34	40	7	12	10
20	20	10	56	120	10	30	27
60	39	20	86			65	39
120	65					90	48
160	73					156	63
						300	83
$t_{1/2}$ = 80 min		$t_{1/2}$ ~ 8 min		$t_{1/2}$ ~ 15 hr		$t_{1/2}$ = 90 min	

(RSSR)-$CrCl_2$(tet*a*)$^+$				(RR,SS)-$CoCl_2$(tnentn)$^+$	
pH = 7.1		pH = 8.1		pH 5	
T (min)	% D_{exch}	T (min)	% D_{exch}	T (min)	% D_{exch}
60	23	12	42	5	8
110	37	30	47	60	35
120	44	61	73	180	63
260	51	128	78		
460	60				
1330	88				
$t_{1/2}$ = 260 min		$t_{1/2}$ ~ 30 min		$t_{1/2}$ ~ 120 min	

[a] Ionic strengths at pH 5, 7.1 and 8.1 were approximately 10^{-2}, 1.0 and 0.5 *M* respectively.

spectrum of this complex, and *trans*-[$CrCl_2$(cyclam)]-ClO_4 are almost identical, and, as base hydrolysis followed by anation with HCl leads to a product with retained stereochemistry (both for Co(III) and Cr(III)), we believe that the *trans*-[$CrBr_2$(cyclam)]-ClO_4 used in this work also has the (RSSR) stereochemistry.

The IR spectra of salts precipitated from D_2O/buffer solutions show the expected changes with time. For *trans*-(RSSR)-$CrCl_2$(tet*a*)$^+$, the intensity of the single band at 3225 (N–H band) decreases and is replaced by a single band at 2400 (N–D band). There are also other changes in the IR spectra with additional bands appearing in the 760–820 cm^{-1} region.

For the (RR,SS)-MX_2(tnentn)$^+$ systems, there are two types of exchangeable protons in the ligand – the sec NH and the terminal NH_2. The changes in the IR spectrum suggest that only the sec NH protons are extensively exchanged in the pD regions studied and the reaction can be conveniently monitored by the appearance of a single sharp band at 760 cm^{-1}.

Plots of ln 100/(100 – %D_{exch}) *vs.* time (Table I) were reasonably linear and values of k_{obs} (±10%) (Table II) were estimated from the slope. The rate of base hydrolysis for the loss of the first chloro ligand in *trans*-(RR,SS)-$CoCl_2$(tnentn)$^+$ [10] (and in *trans*-(RSSR)-$CoCl_2$(cyclam)$^+$) [22, 23] approaches that of proton exchange. This is not the case for *trans*-(RR,SS)-$CrCl_2$(tnentn)$^+$ where the rate ratios $k_{exch}:k_{rac}$ [1] $:k_{OH}$ [1] are in the ratio 1700:10:1, but is almost the situation for *trans*-(RSSR)-$CrCl_2$(tet*a*)$^+$ where $k_{exch}:k_{OH}$ [2] = 2.4:1.

Thus for the tet*a* system at least, the decrease in reactivity towards base hydrolysis in Cr(III) relative to Co(III) is almost entirely due to a decrease in N–H proton acidity (assuming $k_{exch} \sim k_{OH}$ for the Co(III) complex).

For the tnentn system it appears that both a reduced N–H acidity and a reduced lability of the conjugate base contribute, with the Cr(III) conjugate base being about 1700X less reactive. Our estimate for the RSSR cyclam system again suggests a less reactive Cr(III) conjugate base, this time by a factor of about 300.

The kinetic parameters now determined for the base hydrolysis of several *trans*-$CrX_2(N_4)^+$ systems (Tables II and III) reval some interesting trends.

TABLE II. Rate Constants for the Base Hydrolysis, Proton Exchange and Racemisation of some *trans*-$CrX_2(N_4)^+$ complexes at $\mu = 0.1$ *M* (NaCl).

Racemisation

N_4	X	T (°C)	pH[a]	10^4 OH^- (*M*)	10^4 k_{obs} (s^{-1})	k_{rac} (M^{-1} s^{-1})	k_{rac} (calc)[b] (M^{-1} s^{-1})
(SS)-tnentn	F	25.0	9.93	1.11	0.303	0.273	0.267
					0.298	0.268	
		34.9	9.64	1.19	0.960	0.806	0.830
		35.6	9.64	1.19	1.04	0.874	0.897
		45.5	9.35	1.18	3.05	2.58	2.56
					3.09	2.62	

Base Hydrolysis

N_4	X	T (°C)	pH[c]	OH^- (*M*)	10^4 k_{obs}	k_{OH}	k_{OH} (calc)[b]
$(en)_2$	Cl	25.0					3.62×10^{-2}
		26.0		0.01	4.18	4.18×10^{-2}	4.13×10^{-2}
		28.0		0.01	5.36	5.36×10^{-2}	5.37×10^{-2}
		35.5		0.01	13.5	1.35×10^{-1}	1.39×10^{-1}
		40.5		0.01	26.2	2.62×10^{-1}	2.56×10^{-1}
(RR,SS)-tnentn	Br	20.0	9.4	2.21×10^{-5}	7.70	34.8	33.6
			9.6	3.50×10^{-5}	11.7	33.4	
		25.0	9.1	1.64×10^{-5}	13.1	79.9	80.9
			9.0	1.31×10^{-5}	11.0	84.0	
		30.0	8.8	1.22×10^{-5}	21.0	172	189
			8.6	7.73×10^{-6}	14.0	181	
		35.0	8.3	5.13×10^{-6}	23.1	450	429
			8.1	3.44×10^{-6}	15.3	445	
(RSSR)-cyclam	Br	25.0	8.8	8.24×10^{-6}	11.6	140	
		35.0	8.0	2.74×10^{-6}	19.3	705	

Proton Exchange[d]

N_4	X	T (°C)	pH[e]	10^4 k_{obs}	k_{exch}
(RR,SS)-tnentn	Cl[f]	25.0	~5.0	~1	~1×10^5
(RR,SS)-tnentn	Cl	25.0	7.1	1.3	1.0×10^3
			8.1	14	1.0×10^3
(RR,SS)-tnentn	F	25.0	7.1	~0.1	~0.8×10^2
			8.1	1.3	1.0×10^2
(RSSR)-teta	Cl	25.0	7.1	0.44	3.5×10^2
			8.1	~4	~3.2×10^2

[a] 0.01 mol en2HCl added to 150 ml 0.1 *M* NaOH. pK_1(en) = 9.93 at 25.0 °C with $dpK_a/dT = -0.029$ [32]. [b] Calculated from the activation parameters listed in Table III. [c] Maintained using a pH-stat. [d] See footnote a Table I. [e] Maintained using tris buffer (see experimental). [f] Co(III) complex in unbuffered D_2O.

Dibromo complexes react about 100 times faster than the corresponding dichloro analogues, despite a higher (less favourable) activation energy, a feature commented on previously [2]. Thus activation entropy makes a major contribution in determining the reaction characteristics. Indeed, where compari-

TABLE III. Activation Parameters for the Base Hydolysis (k_{OH}), Racemisation (k_{rac}) and Proton Exchange (k_{exch}) for some *trans*-$MX_2(N_4)^+$ Complexes at 298.2 K ($\mu = 0.1$ *M*).[a]

N_4	M	X	k_{OH} (M^{-1} s^{-1})	k_{rac} (M^{-1} s^{-1})	k_{exch} (M^{-1} s^{-1})
$(en)_2$	Co	Cl	3.2×10^3 (94.5, +140)[b]		
	Co	Br	1.2×10^4 [c]		
	Cr	Cl	3.7×10^{-2} [d]		
			3.62×10^{-2} (98.3, +49)[e]		
	Cr	Br	6.4(123, +175)[f]		
(RRSS)-tnentn	Co	Cl	1.0×10^5 [g]		
	Cr	F		0.27(87.5, +29)[e]	1×10^2 [e]
	Cr	Cl	0.58(87.7, +36)[h]	6(88.7, +59)[h]	1×10^3 [e]
	Cr	Br	80.9(127, +211)[e]	[20(89, +70)][i]	[1.6×10^3][i]
(RSSR)-cyclam	Co	Cl	6.5×10^4 (45, 0)[j]		
	Cr	Cl	1.6[k]		
	Cr	Br	140 (123, +200)[e,l]		
(RSSR)-te*ta*	Co	Cl	1.5×10^6 [m]		
	Cr	Cl	145 (116, +79)[n]		3.5×10^2 [e]

[a] Values in parenthesis are E_a (kJ mol^{-1}) and $\Delta S^{\#}_{298}$ (J K^{-1} mol^{-1}) respectively. [b] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962). [c] F. Basolo, W. R. Matoush and R. G. Pearson, *J. Am. Chem. Soc., 78*, 4883 (1956). [d] Ref. 5. [e] This research. [f] M. S. Nozari and J. A. McLean, Jr., in 'Coordination Chemistry Papers Presented in Honour of John C. Bailar, Jr.', Plenum Press (1969). [g] Ref. 10. [h] Ref. 1. [i] Data in square brackets are estimated. [j] Ref. 23. [k] Ref. 15. [l] Activation parameters determined from only two temperatures. [m] J. A. Kernohan and J. F. Endicott, *Inorg. Chem., 9*, 1504 (1970). [n] Ref. 2.

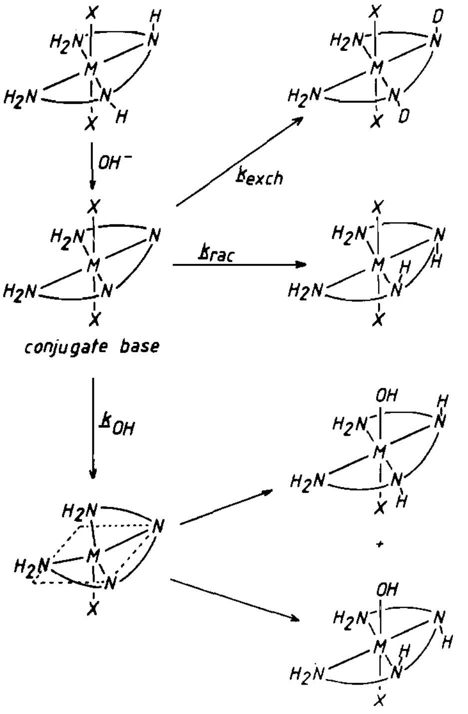

Fig. 1. Conjugate base mechanism for the rates of proton exchange, racemisation and base hydrolysis of *trans*-$MX_2(N_4)^+$.

sons are avilable between Cr(III) and Co(III), it is the large positive value of $\Delta S^{\#}_{298}$ that contributes to the increased rate of base hydrolysis in the Co(III) systems. (Data from the $MX(NH_3)_5^{2+}$; M = Co, Cr; systems [24] also reflect this observation).

Swaddle [25] has elegantly summarised the present state of the art in the interpretation of activation entropy and the hypothesis that "a relatively positive $\Delta S^{\#}$ reflects extensive desolvation of the square pyramid intermediate as it rearranges to the trigonal bipyramid form" is especially pertinent [26].

In terms of the conjugate base mechanism (1) (Fig. 1) proposed for the base hydrolysis of Co(III) amine complexes [6], an integral component is the stabilisation of a trigonal bipyramid transition state by the deprotonated amido group [27–29].

Thus we would equate labilisation of the conjugate base, generation of a trigonal bipyramid transition state and increase in $\Delta S^{\#}$ as all reflecting the driving force contributing to base hydrolysis.

For the stereochemically more rigid Cr(III) systems, the lower $\Delta S^{\#}$ values (as compared to Co(III)) and hence the smaller k_{OH} values, are explicable in terms of a less well developed trigonal bipyramid transition state. The large increase in $\Delta S^{\#}$ for Cr–Br systems when compared to the Cr–Cl analogues, is perhaps reflected in a steric distortion towards the trigonal bipyramid, by the remaining bromo ligand, despite the subsequent *trans* labilisation of the resulting hydroxobromo complex.

The overall kinetic parameters for base hydrolysis, will of course, reflect contributions from the initial deprotonation as well as the subsequent rate determining halide release. Our measurements of the kinetic parameters for the racemisation of *trans*-$CrX_2(tnentn)^+$ show that the activation energy for this deprotonation/protonation process to be independent of X (for X = F, Cl) and, making a reasonable estimation of k_{rac} (X = Br) = 20 M^{-1} s^{-1} (25 °C, μ = 0.1 *M*), the entropy of activation can also be estimated (Table III).

The entropy pattern observed for k_{rac} (X = F, Cl, Br; $\Delta S^{\#}$ = 29, 59, 70) can again be interpreted in terms of desolvation, with the bromo complex being expected to lose water molecules in the deprotonation process more easily than the analogous fluoro.

We note that for X = Cl, the equivalence of E_a (k_{OH}) and E_a (k_{rac}) suggests that there is little further energy required for bond reorganisation beyond the deprotonation process. This is not the situation for the dibromo, where the higher energy of activation for base hydrolysis is offset by a more labile conjugate base (more positive $\Delta S^{\#}$).

Extrapolation of these trends to *trans*-$CrF_2(N_4)^+$ systems would suggest that here, negative $\Delta S^{\#}$ values might be expected in the base hydrolysis. Such reactions are observed to be very slow and *trans*-(RR,SS)-$CrF_2(tnentn)^+$ remains unchanged in 0.1 *M* NaOH over several weeks at room temperature. Assuming a value of k_{OH} 1000 times less than that for the dichloro analog, and a similar activation energy, $\Delta S^{\#}$ is calculated to be –20 JK^{-1} mol^{-1}. Chan and Hui [30] report a negative $\Delta S^{\#}$ value for the base hydrolysis of $CrF(NH_3)_5^{2+}$ and it is interesting to note that the Al^{3+}-assisted aquation of this complex [31] also has a negative $\Delta S^{\#}$.

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