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## The synthesis and X-ray structure of *trans*- $[CrCl_2(nPrNH_2)_4]BF_4 \cdot H_2O$ and the thermal and $Hg^{2+}$ -assisted chloride release kinetics from some *trans*- $[CrCl_2(N)_4]^+$ complexes

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### Abstract

Complexes of the type *trans*-[CrCl<sub>2</sub>(RNH<sub>2</sub>)<sub>4</sub>]Cl (R = Et, nPr, nBu) are readily formed from [CrCl<sub>3</sub>(thf)<sub>3</sub>] and four equivalents of the amine in tetrahydrofuran (thf). The structure of *trans*-[CrCl<sub>2</sub>(nPrNH<sub>2</sub>)<sub>4</sub>]BF<sub>4</sub>·H<sub>2</sub>O (triclinic, P1, a = 5.828(3), b = 10.030(10), c = 10.403(4) Å,  $\alpha = 73.34(6)$ ,  $\beta = 89.37(3)$ ,  $\gamma = 87.78(7)$ , V = 582.1(7) Å<sup>3</sup>, Z = 1) has been determined by single crystal X-ray diffraction. The two Cr–Cl bonds are approximately equivalent (Cr–Cl(1) = 2.325(3), Cr–Cl(2) = 2.326(3)) and two of the (*cis*) nPrNH<sub>2</sub> 'arms' are above and two below the Cr(N)<sub>4</sub> plane. The rates of loss of the first chloro ligand from *trans*-[CrCl<sub>2</sub>(RNH<sub>2</sub>)<sub>4</sub>]<sup>+</sup> (R = Et, nPr, nBu) are about 16 times slower than that for R = H. Spectrophotometrically determined kinetic parameters (0.05 M HNO<sub>3</sub>, 25 °C) are R = H: 10<sup>6</sup> k (s<sup>-1</sup>) = 45.9,  $\Delta H^{\neq}$  (kJ mol<sup>-1</sup>) = 94.9,  $\Delta S^{\neq}$  (J K<sup>-1</sup> mol<sup>-1</sup>) = -10; R = Et: 10<sup>6</sup> k = 2.88,  $\Delta H^{\neq} = 116$ ,  $\Delta S^{\neq} = +39$ ; R = nPr: 10<sup>6</sup> k = 6.70,  $\Delta H^{\neq} = 101$ ,  $\Delta S^{\neq} = -6$ ; R = nBu: 10<sup>6</sup> k = 4.90,  $\Delta H^{\neq} = 116$ ,  $\Delta S^{\neq} = +43$ . Hg<sup>2+</sup>-assisted chloride release kinetics for the first step in the aquation of several *trans*-[CrCl<sub>2</sub>(N)<sub>4</sub>]<sup>+</sup> systems have been measured in 50:50 dmf:aq. HClO<sub>4</sub> (*I*=0.5 M). The activation entropy data suggest that the thermal aquation processes for *trans*-[CrCl<sub>2</sub>(N)<sub>4</sub>]<sup>+</sup> are more widely spread across the interchange mechanistic spectrum than those for the analogous Co(III) systems.

Keywords: Crystal structures; Kinetics and mechanism; Chromium complexes; Amine complexes

## 1. Introduction

A curious feature of the first step in the acid hydrolysis rate of *trans*-[CrCl<sub>2</sub>(N)<sub>4</sub>]<sup>+</sup> complexes is the relative insensitivity of the reaction rate constant ( $k_{\rm H}$ ) to the non-replaced ligand. Thus, for a series of *trans*-[CrCl<sub>2</sub>(N)<sub>4</sub>]<sup>+</sup> systems (Table 1),  $k_{\rm H}$  spans a range of about 14 whereas for the analogous Co(III) complexes the range is about 5500. It has also been recognised that the Cr(III) systems are stereochemically inert, while those of Co(III) can give variable amounts of *cis*-product [1] and this stereolability is reflected in a positive value for the activation entropy ( $\Delta S_{\rm H}^{\pm}$ ) [2].

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To extend the kinetic data available we have synthesised salts of *trans*-[CrCl<sub>2</sub>(RNH<sub>2</sub>)<sub>4</sub>]<sup>+</sup> (R = Et, nPr, nBu) in good yield and measured the rate of loss of the first chloro ligand in 0.05 M HNO<sub>3</sub> (Eq. (1)). We have also measured the rate of the first step for the Hg<sup>2+</sup>-assisted chloride release (Eq. (2)) from a series of *trans*-[CrCl<sub>2</sub>(L)<sub>4</sub>]<sup>+</sup> complexes (Table 1) in 50% aqueous acidic dimethyl formamide (dmf) solution (I=0.5 M).

$$trans - [CrCl_{2}(RNH_{2})_{4}]^{+} + H_{2}O \xrightarrow{H^{+}} [CrCl(RNH_{2})_{4}(OH_{2})]^{2+} + Cl^{-} \qquad (1)$$
$$trans - [CrCl_{2}(L)_{4}]^{+} + Hg^{2+} + H_{2}O \xrightarrow{H^{+}}$$

$$[CrCl(L)_4(OH_2)]^{2+} + HgCl^+ \quad (2)$$

## 2. Experimental

### 2.1. Syntheses

Caution: perchlorate salts of amine complexes are potentially explosive and should be handled accordingly.

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Table 1

L <sub>4</sub>	$10^5 k_{\rm H}  ({\rm Cr})$ (s <sup>-1</sup> )	$\Delta H^{\neq}$ (kJ mol <sup>-1</sup> )	$\Delta S^{\neq}$ (J K <sup>-1</sup> mol <sup>-1</sup> )	Ref.	$10^{2} k_{Hg}$ (Cr) <sup>a</sup> (M <sup>-1</sup> s <sup>-1</sup> )	Δ <i>H</i> <sup>≠</sup> (kJ mol <sup>-1</sup> )	$\frac{\Delta S^*}{(J \text{ K}^{-1} \text{ mol}^{-1})}$	$\frac{10^5 k_{\rm H}}{({\rm S}^{-1})}$	$\Delta H^{\star}$ (kJ mol <sup>-1</sup> )	$\frac{\Delta S^{\star}}{(J \text{ K}^{-1} \text{ mol}^{-1})}$	Ref.
(3,3-tri)(OH <sub>2</sub> )	1.61	119±1.3	$+63\pm4$	b	26.8	81.1±1.6	+ 16 ± 3				
$(nBuNH_2)_4$	0.490	116±3	$+43 \pm 6$	c	2.73	$77.2 \pm 2.3$	$-16 \pm 5$				
(EtNH <sub>2</sub> ) <sub>4</sub>	0.288	$116 \pm 3$	$+39 \pm 6$	d							
	0.544	$115 \pm 3$	$+40 \pm 6$	c							
$(Me_2tn)_2$	2.25	101	+5	[3]	10.1	$70.9 \pm 1.5$	$-26 \pm 3$	557	94	+28	[3]
(tn) <sub>2</sub>	2.08	100	+1	[5]	35.4	$63.8 \pm 4.1$	$-39 \pm 8$	5530	87	+29	[6]
(2,3,2-tet)	0.323	107	0	[7]	1.34	$74.0 \pm 1.5$	$-32\pm3$	1.5	102	+4	[8]
(3,3,3-tet)	0.74	102	-2	[16]	3.05	$76.5 \pm 1.0$	$-17\pm2$				
(nPrNH <sub>2</sub> ) <sub>4</sub>	0.670	$101 \pm 3$	$-6\pm6$	d	3.01	$69.8 \pm 2.0$	$-40\pm4$				
	1.44	$96 \pm 5$	$-15 \pm 10$	c							
(NH <sub>3</sub> ) <sub>4</sub>	4.59	$95 \pm 3$	$-10 \pm 6$	<sup>d</sup> , [9]	203	74.3±3.2	$+10\pm6$	224	87	-6	[8]
(tn)(en)	1.93	95	-15	[10]	28.2	$60.0\pm2.2$	$-54 \pm 5$	43.3	99	+21	[10]
$(en)_2$	2.25	95	-17	[1]	18.0	$63.5\pm3.0$	$-46\pm 6$	3.2	112	+44	[8]
(tet-a)	1.26	93	- 37	[11]	4.04	$74.9 \pm 1.5$	$-20 \pm 3$	93	107	+ 54	[12]
(3,2,3-tet)	0.106	95	-50	[13]	0.357	$74.1 \pm 1.5$	$-43\pm5$	5.6	106	+ 29	[8]
$(2,3-tri)(OH_2)$	7.25	79	- 69	[14]	16.2	$88.6 \pm 1.2$	$+37\pm3$	400	90	+ 88	[14]

Kinetic parameters for reactions of *trans*-[MCl<sub>2</sub>(L)<sub>4</sub>]<sup>+</sup> complexes in acidic solution at 298.2 K

<sup>a</sup> This research, 50:50 dmf:aqueous HClO<sub>4</sub> (I=0.5 M), Eq. (2).

<sup>b</sup> This research, 0.1 M HClO<sub>4</sub>.

<sup>c</sup> This research, 50:50 dioxane:0.05 M HNO<sub>3</sub>.

<sup>d</sup> This research, 0.05 M HNO<sub>3</sub>.

Perchlorate salts of the complexes were prepared using literature procedures: trans-[CrCl<sub>2</sub>(tn)<sub>2</sub>]ClO<sub>4</sub> [3,4]; trans-[CrCl<sub>2</sub>(en)(tn)]ClO<sub>4</sub> [5]; trans-[CrCl<sub>2</sub>(en)<sub>2</sub>]ClO<sub>4</sub> [15]; trans-[CrCl<sub>2</sub>(Me<sub>2</sub>tn)<sub>2</sub>]ClO<sub>4</sub> [3]; trans-[CrCl<sub>2</sub>(tet-a)]-ClO<sub>4</sub> [18]; trans-[CrCl<sub>2</sub>(3,3,3-tet)]ClO<sub>4</sub> [16]; trans-[CrCl<sub>2</sub>(2,3,2-tet)]ClO<sub>4</sub> [7]; trans-[CrCl<sub>2</sub>(3,2,3-tet)]ClO<sub>4</sub> [13]; trans-[CrCl<sub>2</sub>(3,3-tri)(OH<sub>2</sub>)]ClO<sub>4</sub> [17]; trans-[CrCl<sub>2</sub>(2,3-tri)(OH<sub>2</sub>)]ClO<sub>4</sub> [14].

*Trans*- $[CrCl_2(NH_3)_4]Cl_2 \cdot H_2O[19]$  was kindly supplied by O. Mønsted, University of Copenhagen.

# 2.1.1. Trichlorotris(tetrahydrofuran)chromium(III), [CrCl<sub>3</sub>(thf)<sub>3</sub>]

This complex (an excellent starting material for Cr(III)amine complexes [1,20]) was prepared using a modification of Shamir's method [21].

Hydrated chromium(III) chloride,  $CrCl_3 \cdot 6H_2O$  (20 g) was suspended in 100 ml of tetrahydrofuran in a round bottom flask equipped with side-arm, dropping funnel, magnetic stirrer and condenser in a fume hood. Thionyl chloride (SOCl<sub>2</sub>, 40 ml) was added dropwise to the stirred solution at such a rate that the thf refluxed gently, taking about 30 min. Towards the end of the SOCl<sub>2</sub> addition, the flask was heated to maintain gentle reflux. Purple crystals deposited from the hot solution about 5 min after the SOCl<sub>2</sub> addition was complete. The slightly moisture sensitive product,  $CrCl_3(thf)_3$ , was suction filtered from the ice cooled solution, washed three times with ether and allowed to complete drying over SiO<sub>2</sub> in a desiccator. The yield was routinely 21–22 g (75–78%) and the product is stable for long periods (months) when stored in a dark, dry atmosphere. 2.1.2. Trans-dichlorotetrakis(n-propylamine)chromium(III) chloride, trans- $[CrCl_2(nPrNH_2)_4]Cl$ 

A solution of nPrNH<sub>2</sub> (4.5 ml, 0.054 mol) in thf (30 ml) was added with stirring to solid  $CrCl_3(thf)_3$  (5.0 g, 0.013 mol) in a flask fitted with a condenser. A green solution formed immediately and the reaction mixture was refluxed for 1 h during which time a small amount of the product crystallised. An equal volume of ether was added dropwise to the cooled, stirred reaction mixture and further product deposited. The green solid was collected by suction filtration, washed with ether, and air dried (yield 3.6 g, 68%). The complex is readily soluble in methanol but only sparingly soluble in water.

The chloride, perchlorate, tetrafluoroborate and nitrate salts were obtained by dissolving separate 1.5 g samples of the crude product in 60 ml of warm methanol, acidified with 3 drops of 3 M HCl. These solutions were poured into 50 ml of 1 M HCl (chloride salt):50 ml water plus 3 drops 1 M HClO<sub>4</sub> plus 2 g NaClO<sub>4</sub>·H<sub>2</sub>O (perchlorate salt):50 ml water plus 3 drops 1 M HNO<sub>3</sub> plus 2 g NaNO<sub>3</sub> (nitrate salt). Green crystals of the products were obtained after leaving the solutions for 1 or 2 days to allow the methanol to spontaneously evaporate at room temperature. The filtered products were washed with a little 2-propanol, then ether and air dried.

*Anal.* Calc. for [CrCl<sub>2</sub>(nPrNH<sub>2</sub>)<sub>4</sub>]Cl: C, 36.5; H, 9.20; N, 14.2. Found: C, 35.9; H, 9.10; N 13.9%.

Visible absorption spectra (MeOH): max. (598 nm, 33.9  $M^{-1}$  cm<sup>-1</sup>), min. (544, 19.8), max. (498, 28.0), min. (462, 24.0), max. (412, 54.8).

## 2.1.3. Trans-dichlorotetrakis(n-butylamine)chromium(III) chloride, trans-[CrCl<sub>2</sub>( $nBuNH_2$ )<sub>4</sub>]Cl

This complex was prepared and recrystallised as for the  $nPrNH_2$  analog, except 5.0 ml of  $nBuNH_2$  were used. *Anal.* Calc. for  $[CrCl_2(nBuNH_2)_4]Cl: C, 42.6; H, 9.83; N, 12.4.$  Found: C, 42.5; H, 9.84; N, 12.4%.

Visible absorption spectra (MeOH): max. (598 nm, 34.2  $M^{-1}$  cm<sup>-1</sup>), min. (544, 19.8), max. (496, 28.6), min. (464, 24.3), max. (412, 56.7).

## 2.1.4. Trans-dichlorotetrakis(ethylamine)chromium(III) chloride, trans- $[CrCl_2(EtNH_2)_4]Cl$

Small portions of  $CrCl_3(thf)_3$  (2 g total) were added with stirring to 7 ml of anhydrous ethylamine in a small reaction Dewar flask. Excess amine evaporated spontaneously overnight and the resulting purple gum was dissolved in 3 M HCl (20 ml). After about 4 days at room temperature a small quantity (0.4 g) of dark green crystals (*trans*-[CrCl<sub>2</sub>-(EtNH<sub>2</sub>)<sub>4</sub>]Cl) deposited and these were collected by filtration. On further spontaneous evaporation a material with properties corresponding to  $CrCl_3(EtNH_2)_3$  (grass green needles) deposited as the major product. *Anal.* Calc. for [CrCl<sub>2</sub>(EtNH<sub>2</sub>)<sub>4</sub>]Cl: C, 28.4; H, 8.33; N, 16.5. Found: C, 28.4; H, 8.91; N, 16.8%.

Table 2

Crystal data for trans-[CrCl2(nPrNH2)4]BF4·H2O

Empirical formula	C <sub>12</sub> H <sub>38</sub> BCl <sub>2</sub> CrF <sub>4</sub> N <sub>4</sub> O
Formula weight	464.17
Temperature (K)	130(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	P1
Unit cell dimensions	
a (Å)	5.828(3)
b (Å)	10.030(10)
c (Å)	10.403(4)
α (°)	73.34(6)
β(°)	89.37(3)
γ(°)	87.78(7)
Volume (Å <sup>3</sup> )	582.1(7)
Z	1
Density (calc.) (Mg $m^{-3}$ )	1.324
Absorption coefficient (mm <sup>-1</sup> )	0.759
F(000)	245
Crystal size (mm)	$0.72 \times 0.24 \times 0.13$
$\theta$ Range for data collection (°)	2.04-22.49
Index ranges	$0 \le h \le 6, -10 \le k \le 10,$
	$-11 \le l \le 11$
Reflections collected	1642
Independent reflections	$1641 \ (R_{\rm int} = 0.1564)$
Absorption correction	semi-empirical from $\Psi$ -scans
Max. and min. transmission	0.990 and 0.723
Refinement method	full-matrix least-squares on $F^2$
Data/restraints/parameters	1640/23/251
Goodness-of-fit on $F^2$	1.061
Final R indices $(I > 2\sigma(I))$	R1 = 0.0570, wR2 = 0.1499
R indices (all data)	$R1 = 0.0627, wR2 \approx 0.1594$
Largest difference peak and hole $(e \text{ Å}^{-3})$	0.901  and  -0.888

Visible absorption spectra (MeOH): max. (598 nm, 33.8  $M^{-1}$  cm<sup>-1</sup>), min. (542, 19.8), max. (496, 28.1), min. (462, 24.2), max. (410, 54.8).

### 2.2. X-ray structural determination

Crystallographic information for trans-[CrCl<sub>2</sub>-(nPrNH<sub>2</sub>)<sub>4</sub>]BF<sub>4</sub>·H<sub>2</sub>O, the diffraction data collection procedures (Siemens P4 four-circle diffractometer) and the structure solution details are given in Table 2. Non-hydrogen atom coordinates for the cation are listed in Table 3 and important bond lengths and angles in Table 4.

Table 3

Table 4

Non-hydrogen atom coordinates ( $\times 10^4$ ) for trans-[CrCl<sub>2</sub>(nPrNH<sub>2</sub>)<sub>4</sub>]<sup>+ a</sup>

Atom	<i>x</i>	у	z	$U_{\rm eq}$
Cr	4985(3)	4998(2)	5001(2)	22(1)
Cl(1)	1977(4)	4582(2)	6536(2)	26(1)
Cl(2)	8029(4)	5405(2)	3493(2)	25(1)
N(1)	6918(18)	3228(10)	6079(10)	23(2)
C(11)	6049(25)	2176(13)	7331(13)	33(3)
C(21)	7731(28)	998(18)	7885(16)	69(6)
C(31)	10078(46)	933(36)	7924(36)	59(11)
C(31')	7162(45)	204(29)	9211(30)	57(10)
N(2)	6681(17)	6160(9)	6080(9)	19(2)
C(12)	6411(23)	5886(13)	7542(14)	34(3)
C(22)	7876(27)	6829(15)	8090(13)	39(4)
C(32)	7427(43)	6510(20)	9617(18)	79(7)
N(3)	3116(19)	6823(10)	3945(10)	25(2)
C(13)	4054(25)	7828(13)	2766(13)	32(3)
C(23)	2429(26)	9106(14)	2172(16)	49(4)
C(33)	563(44)	8782(29)	1409(25)	34(7)
C(33')	3142(55)	9904(28)	814(24)	47(7)
N(4)	3289(18)	3830(10)	3927(11)	28(3)
C(14)	3590(24)	4055(13)	2491(11)	28(3)
C(24)	2072(25)	3239(13)	1830(13)	34(3)
C(34)	2490(34)	3553(22)	362(17)	74(6)

<sup>a</sup> See Fig. 1 for the atom labelling scheme.

Selected bond lengths (Å) and angles (°) for trans-[CrCl<sub>2</sub>( $nPrNH_2$ )<sub>4</sub>]BF<sub>4</sub>. H<sub>2</sub>O

Bond lengths (Å)			
<b>Cr–Cl</b> (1)	2.326(3)	Cr-N(2)	2.111(10)
Cr–Cl(2)	2.324(3)	Cr-N(3)	2.112(10)
Cr–N(1)	2.100(10)	Cr-N(4)	2.113(12)
Bond and dihedral angles			
N(2)-Cr- $N(4)$	179.8(5)		
N(1)-CrN(3)	177.9(6)		
Cl(2)-Cr-Cl(1)	179.2(2)		
N(1)-C(11)-C(21)-C(31)	33.7(3.7)		
N(1)-C(11)-C(21)-C(31')	166.6(1.9)		
N(3)-C(13)-C(23)-C(33)	-76.2(1.8)		
N(3)-C(13)-C(23)-C(33')	-164.9(1.8)		
N(2)-C(12)-C(22)-C(32)	178.2(1.3)		
N(4)-C(14)-C(24)-C(34)	179.2(1.3)		
Cl(2)-Cr-Cl(1) N(1)-C(11)-C(21)-C(31) N(1)-C(11)-C(21)-C(31') N(3)-C(13)-C(23)-C(33) N(3)-C(13)-C(23)-C(33') N(2)-C(12)-C(22)-C(32) N(4)-C(14)-C(24)-C(34)	$179.2(2) \\33.7(3.7) \\166.6(1.9) \\-76.2(1.8) \\-164.9(1.8) \\178.2(1.3) \\179.2(1.3)$		

\* See Fig. 1 for the atom labelling scheme.

## 2.3. Kinetics

The rate of thermal solvolysis was measured in either 0.05 M HNO<sub>3</sub> (R = Et, nPr) or 50:50 dioxane 0.05 M HNO<sub>3</sub>. Small samples of the complex (R = Et, nPr) were dissolved in 5.0 ml H<sub>2</sub>O and 5.0 ml of 0.1 M HNO<sub>3</sub> were added. The solution was transferred to a 4.00 cm spectrophotometer cell and temperature was controlled using an electrically heated cell block. Similar procedures were used for the dioxane:0.05 M HNO<sub>3</sub> system except that the complexes were initially dissolved in two drops of MeOH. Once temperature equilibrium was established, fixed wavelength (Table 5) scans were initiated, and the reaction was followed for 6–10 half-lives.

The rate of the first step of the  $Hg^{2+}$ -assisted solvolysis for several *trans*-[CrCl<sub>2</sub>(N)<sub>4</sub>]<sup>+</sup> complexes was measured spectrophotometrically in 50:50 dmf:aq. HClO<sub>4</sub> (I=0.5 M) using absorbance versus time techniques (Table 6). Small samples of the ClO<sub>4</sub><sup>-</sup> or Cl<sup>-</sup> salts were dissolved (or suspended) in 5.00 ml of dmf and 5.00 ml of aq. HClO<sub>4</sub> solution containing various concentrations (0.02–0.08 M) of dissolved Hg(NO<sub>3</sub>)<sub>2</sub> were added. The mixed solution was transferred to a 4.00 cm spectrophotometer cell placed in an electrically heated temperature controlled cell holder and repeat scan or fixed wavelength (380 nm) traces were obtained after the solution reached temperature equilibrium.

The rate of loss of the first chloro ligand from *trans*-[CrCl<sub>2</sub>(3,3-tri)(OH<sub>2</sub>)]<sup>+</sup> was measured spectrophotometrically (393 nm, absorbance increase) in 0.1 M HClO<sub>4</sub> giving mean 10<sup>4</sup>  $k_{\rm H}$  (s<sup>-1</sup>) values of 0.999±0.007, 3.71±0.13, 5.58±0.15, 7.92±0.18 and 13.8±0.6 at 36.5, 45.3, 48.4, 50.8 and 54.6 °C, respectively. Activation parameters calculated from these data are reported in Table 1.

## 3. Results and discussion

### 3.1. Synthesis and structure

Complexes of the type *trans*- $[CrCl_2(RNH_2)_4]^+$  were first described by Mandal [22] but the synthesis (from the HCl decomposition of  $[CrCl(RNH_2)_5]^{2+}$ ) is not very reproducible and the yields are low. We describe here an efficient and direct synthesis by reacting a suspension of the readily available  $[CrCl_3(thf)_3]$  [21] with four equivalents of the

Table 5

Observed and calculated first-order rate constants for the first step in the acid hydrolysis of some trans-[CrCl<sub>2</sub>(RNH<sub>2</sub>)<sub>4</sub>]<sup>+</sup> complexes

<i>T</i> (°C)	$10^4 k_{\rm H}^{\rm a}$ (obs.) (s <sup>-1</sup> )	$10^4 k_{\rm H}^{\rm b}$ (calc.) (s <sup>-1</sup> )	<i>T</i> (°C)	$10^4 k_{\rm H}^{\rm a}$ (obs.) (s <sup>-1</sup> )	$10^4 k_{\rm H}^{\rm b}$ (calc.) (s <sup>-1</sup> )
R = H (595) 0.05 M HNO	c 3		R = nBu (4) 50:50 dioxa	12) ° ane:0.05 M HNO <sub>3</sub>	
35.4	$1.81 \pm 0.02$	1.72	45.5	$1.04 \pm 0.03$	1.07
37.8	$2.24 \pm 0.01$	2.30	48.5	$1.70 \pm 0.04$	1.62
41.0	$3.27 \pm 0.01$	3.39	51.9	$2.49 \pm 0.06$	2.57
44.3	$4.80 \pm 0.1$	4.99	55.0	$3.87 \pm 0.08$	3.91
46.7	$6.98 \pm 0.2$	6.58	58.0	$6.19 \pm 0.14$	5.79
50.2	9.67±0.1	9.87	61.0	$8.18\pm0.18$	8.53
R = Et (604)	c		R = Et (604)	4) <sup>c</sup>	
0.05 M HNO	3		50:50 dioxa	ane:0.05 M HNO <sub>3</sub>	
46.6	$0.764 \pm 0.01$	0.735	45.2	1.05+0.07	1.10
49.2	$1.06 \pm 0.04$	1.05	49.0	$1.94 \pm 0.13$	1.86
51.5	$1.39 \pm 0.04$	1.44	50.5	$2.20 \pm 0.18$	2.13
54.6	2.07 + 0.04	2.18	55.4	$4.22 \pm 0.3$	4.37
57.4	3.22 + 0.05	3.16	58.0	$6.39 \pm 0.5$	6.13
60.6	$4.95 \pm 0.05$	4.79	61.1	$8.84 \pm 0.7$	9.11
R = nPr (604	) <sup>c</sup>		R = nPr (60)	)4) °	
0.03 M HNO	3				
43.0	$0.698 \pm 0.16$	0.714	44.7	$1.55 \pm 0.1$	1.69
45.7	$1.01 \pm 0.06$	0.996	49.0	$3.06 \pm 0.1$	2.78
51.3	$1.98 \pm 0.03$	1.95	52.6	$4.40 \pm 0.4$	4.17
52.7	$2.32 \pm 0.4$	2.30	55.8	$5.86 \pm 0.4$	5.95
60.6	$5.40 \pm 0.1$	5.67	58.3	$7.72 \pm 0.6$	7.81
61.3	$6.99 \pm 0.1$	6.13	61.0	$10.1 \pm 0.3$	10.4
63.0	$6.71 \pm 0.1$	7.40			
63.7	$8.06\pm0.02$	7.99			

<sup>a</sup> Mean ± standard deviation of 10–15 point-by-point calculations from the absorbance vs. time data at fixed wavelength<sup>c</sup> over 3–4 half-lives.

<sup>b</sup> Calculated from the activation parameters cited in Table 1.

<sup>c</sup> Wavelength (nm) used to monitor the reaction.



Fig. 1. A perspective view of the *trans*- $[CrCl_2(nPrNH_2)_4]^+$  cation in *trans*- $[CrCl_2(nPrNH_2)_4]BF_4 \cdot H_2O$ . There is some disorder in the positions of C(31) and C(33).

monoamine in tetrahydrofuran solution or, in the case of R = Et, reaction with the neat monoamine. Good yields of *trans*-[CrCl<sub>2</sub>(RNH<sub>2</sub>)<sub>4</sub>]Cl can be obtained after work up and other salts by metathesis from aqueous HCl-methanol. The visible absorption spectra are entirely consistent with the *trans*-[CrCl<sub>2</sub>(N<sub>4</sub>)]<sup>+</sup> chromophore [1]. To confirm the configuration, an X-ray data set was collected using a single crystal of *trans*-[CrCl<sub>2</sub>(nPrNH<sub>2</sub>)<sub>4</sub>]BF<sub>4</sub>·H<sub>2</sub>O and the structure was solved (Fig. 1).

Appropriate structural information are presented in Tables 2–4. There is some disorder in the position of the terminal carbon in two of the (*trans*) nPrNH<sub>2</sub> 'arms' and Fig. 1 shows one of the three possible positional disordered arrangements. There are four possible arrangements for RNH<sub>2</sub> 'arms' in a square planar  $[M(NH_2R)_4]^{n+}$  complex. If the arm is above the MN<sub>4</sub> plane it can be assigned (+) and below (-). In terms of Fig. 1, in the order N(1)–N(4), the four arrangements are (+-+-), (++--), (+++-) and (++++). Table 7 lists some of the available data. It is obvious that only small energy changes are required to change the orientation, e.g. the change from Cl<sup>-</sup> anion to NO<sub>3</sub><sup>-</sup> anion in  $[CoCl(MeNH_2)_5]X$ .

To check the proposal that Cr–Cl bond lengths and acid hydrolysis rate may be related [31], we have collected in Table 8 the data available for *trans*-[CrCl<sub>2</sub>(L)<sub>4</sub>]<sup>+</sup> systems. Although  $\Delta$ [Cr–Cl] = 0.04 Å, there is no apparent correlation with lability.

#### 3.2. Spontaneous thermal aquation

Although salts of *trans*- $[CrCl_2(RNH_2)_4]^+$  (R = Et, nPr) are only sparingly soluble in aqueous electrolyte solutions we have found that 0.05 M HNO<sub>3</sub> is a suitable solvent for the spectrophotometric determination of the rate of loss of the first chloro ligand for R = H, Et and nPr. The R = nBu complex requires the addition of dioxane (or methanol) and reaction rates in 50:50 dioxane:0.05 M HNO<sub>3</sub> were determined for all three alkylamine complexes (Table 5). Spectrophotometric changes with time showed good isosbestic points (Table 9) indicating only minor interference from the second hydrolysis step and kinetic data were obtained from absorbance versus time traces. The reaction was complete after 6– 8 half-lives as indicated by a constant absorbance value. For

#### Table 6

Observed and calculated rate constants for the first step in the Hg<sup>2+</sup>-assisted chloride release from some *trans*-[CrCl<sub>2</sub>(L)]<sup>+</sup> complexes in 50:50 dmf:aqueous HClO<sub>4</sub> (I = 0.5 M)<sup>a</sup>

T (℃)	Hg <sup>2+</sup> (mM)	$10^4 k_{obs}^{b}$ (s <sup>-1</sup> )	$\frac{10^2 k_{\rm Hg}^{\ c}}{({\rm M}^{-1} {\rm s}^{-1})}$	$10^2 k_{\rm Hg} ({\rm calc.})^{\rm d}$ (M <sup>-1</sup> s <sup>-1</sup> )
L = (]	NH3)4			
14.0	10.0	$63.0 \pm 2$	$63.0 \pm 2$	61.2
		$61.9 \pm 2$	$61.9 \pm 2$	
18.3	10.0	$96.3 \pm 3$	$96.3 \pm 3$	99.6
		$103 \pm 3$	$103 \pm 3$	
		$94.9 \pm 3$	$94.9 \pm 3$	
20.5	10.0	$124 \pm 4$	$124 \pm 4$	126
		$131 \pm 4$	$131 \pm 4$	
		$128 \pm 4$	$128 \pm 4$	
25.0				203
L = (	nPrNH <sub>2</sub> ) <sub>4</sub>			
41.5	10.0	$14.7\pm0.06$	$14.7\pm0.06$	13.9
		$14.5\pm0.05$	$14.5 \pm 0.05$	
	21.5	$29.4\pm0.6$	$13.7 \pm 0.3$	
		$30.0\pm0.6$	$13.9\pm0.3$	
	33.0	$45.4 \pm 1.4$	$13.7 \pm 0.4$	
		$46.7 \pm 1.3$	$14.2 \pm 0.4$	
36.6	21.5	$18.8 \pm 0.3$	$8.74 \pm 0.14$	8.98
		$18.2 \pm 0.2$	$8.46 \pm 0.09$	
	33.0	$29.1 \pm 1.1$	$8.81 \pm 0.33$	
		$28.7 \pm 0.5$	$8.69 \pm 0.15$	
	43.0	$38.5 \pm 0.6$	$8.95 \pm 0.14$	
		$37.8\pm0.7$	$8.79 \pm 0.16$	
31.6	21.5	$12.8 \pm 0.3$	$5.95 \pm 0.14$	5.67
		$12.9 \pm 1.1$	$6.00 \pm 0.5$	
	33.0	$18.6 \pm 0.3$	$5.64\pm0.09$	
		$17.1 \pm 0.5$	$5.18 \pm 0.15$	
	43.0	$26.6 \pm 0.5$	$6.18 \pm 0.11$	
95.0		$23.5 \pm 0.8$	$5.46 \pm 0.18$	2.01
25.0				3.01
L = ( n	$BuNH_2)_4$			
41.5	10.0	$14.4 \pm 1.3$	$14.4 \pm 1.3$	14.7
		$14.8 \pm 1.2$	$14.8 \pm 1.2$	
	21.5	$32.4 \pm 1.4$	$15.1 \pm 0.7$	
		$32.0 \pm 3.0$	$14.9 \pm 1.5$	
36.1	10.0	$8.34 \pm 0.7$	$8.34 \pm 0.7$	8.67
		$8.75 \pm 0.6$	$8.75 \pm 0.6$	
		$7.86 \pm 0.8$	$7.86 \pm 0.8$	
	21.5	$19.2 \pm 0.3$	$8.93 \pm 0.2$	
	20.0	$19.1 \pm 0.2$	$8.88 \pm 0.1$	
	30.0	$25.0 \pm 0.9$	$8.33 \pm 0.3$	
	42.0	$27.5 \pm 0.6$	$9.16 \pm 0.2$	
	43.0	$38.7 \pm 2.0$	$9.00 \pm 0.5$	
21.2	10.0	$57.5 \pm 2.0$	$8.72 \pm 0.3$	5.06
31.2	10.0	$5.13 \pm 0.13$	$5.13 \pm 0.13$	5.20
	21.5	$3.21 \pm 0.00$	$3.21 \pm 0.00$	
	21.5	$10.0 \pm 0.03$	4.93 ± 0.1	
	33.0	$18.2 \pm 0.03$	$4.93 \pm 0.1$ 5 51 ± 0.1	
	55.0	$17.2 \pm 0.7$	$5.18 \pm 0.7$	
	43.0	$25.9 \pm 0.7$	$6.02 \pm 0.2$	
	, 5.0	$22.8 \pm 0.6$	$5.30 \pm 0.1$	
25.0				2.73
L = (e	en),			
41.6	10.0	77.3 + 1.5	77.3 + 1.5	73.5
		$77.0 \pm 1.5$	77.0 + 1.5	
		$79.5 \pm 1.6$	$79.5 \pm 1.6$	
				(continued

Table 6 (continued)

Table 6 (continued)

т (°С)	Hg <sup>2+</sup> (mM)	$\frac{10^4 k_{obs}}{(s^{-1})}^{b}$	$10^2 k_{Hg}^{c}$ (M <sup>-1</sup> s <sup>-1</sup> )	$10^2 k_{\rm Hg} ({\rm calc.})^{\rm d} ({\rm M}^{-1} {\rm s}^{-1})$	<i>Т</i> (°С)	Hg <sup>2+</sup> (mM)	$\frac{10^4 k_{obs}}{(s^{-1})}^{b}$	$10^2 k_{Hg}^{c}$ (M <sup>-1</sup> s <sup>-1</sup> )	10² <i>k</i> (M <sup>-</sup>
39.3	10.0	$60.7 \pm 1.2$	$60.7 \pm 1.2$	61.0	L = 3	,2,3-tet			
		$63.5 \pm 1.3$	$63.5 \pm 1.3$		43.3	43.0	$9.14 \pm 0.2$	$2.14 \pm 0.04$	2.1
		$69.3 \pm 1.4$	$69.3 \pm 1.4$		41.6	43.0	$7.74 \pm 0.1$	$1.80\pm0.02$	1.8
36.7	10.0	$56.1 \pm 1.1$	$56.1 \pm 1.1$	49.3	35.7	43.0	$4.50\pm0.05$	$1.05 \pm 0.01$	1.0
		$50.5 \pm 1.0$	$50.5 \pm 1.0$		30.4	21.5	$1.38\pm0.06$	$0.642 \pm 0.03$	0.6
34.3	10.0	$39.8 \pm 0.8$	$39.8 \pm 0.8$	40.4		43.0	$2.55 \pm 0.09$	$0.593 \pm 0.02$	
		$40.3 \pm 0.8$	$40.3 \pm 0.8$		25.0				0.3
32.1	10.0	$339 \pm 0.7$	$339 \pm 07$	33 5					
02.1	1010	$312 \pm 0.6$	$31.2 \pm 0.6$	0010					
		334+07	334+07		L = 3	,3,3-tet	174.00	17 4 1 0 0	17
29.6	10.0	$246 \pm 0.5$	$246 \pm 0.5$	27.0	42.3	10.0	$17.4 \pm 0.2$	$17.4 \pm 0.2$	17.0
27.0	10.0	$24.0 \pm 0.5$ 25.1 ± 0.5	$24.0 \pm 0.5$ $25.1 \pm 0.5$	21.0	•••	21.5	$37.0 \pm 0.6$	$17.2 \pm 0.3$	
		$25.1 \pm 0.5$	$25.1 \pm 0.5$		38.7	21.5	$26.8 \pm 0.5$	$12.5 \pm 0.2$	12.4
		$25.5 \pm 0.5$	$25.5 \pm 0.5$			33.0	$41.8 \pm 0.8$	$12.7 \pm 0.2$	
		$23.1 \pm 0.3$	$23.1 \pm 0.3$		36.4	21.5	$21.4 \pm 0.3$	$9.95 \pm 0.1$	9.8
		$22.2 \pm 0.4$	$22.2 \pm 0.4$			33.0	$32.8 \pm 0.7$	9.94 ± 0.2	
		$22.4 \pm 0.5$	$22.4 \pm 0.5$	10.0	33.9	21.5	$16.5 \pm 0.2$	$7.67 \pm 0.1$	7.7
25.0				18.0		43.0	$33.9 \pm 0.7$	$7.88 \pm 0.2$	
14.4	33.0	$29.4 \pm 1.0$	$8.89 \pm 0.3$	6.76	31.2	21.5	$12.6 \pm 0.2$	$5.86 \pm 0.1$	5.8
L = 0	en)(tn)						$12.2 \pm 0.06$	$5.67 \pm 0.03$	
45.0	10.0	157 + 4	$157 \pm 4$	137		43.0	$25.2 \pm 0.6$	$5.86 \pm 0.1$	
42.1	10.0	$106 \pm 2$	$106 \pm 2$	110	25.0				3.0
42.1	10.0	$100 \pm 2$	$100 \pm 3$	110					
10.0	10.0	80817	$898 \pm 2$	94.2	I - **	* •			
40.0	10.0	$72.4 \pm 1$	$73.4 \pm 1$	78.2	L - u	21-a 21.5	45 6 1 1 0	212105	20.0
25.2	10.0	73.4 <u>±</u> 1	$73.4 \pm 1$	65.3	41.0	21.5	$43.0 \pm 1.0$	$21.2 \pm 0.3$	20.3
55.5 05.0	10.0	$00.0 \pm 1$	$00.0 \pm 1$	18.5	38.3	21.5	$33.3 \pm 0.7$	$13.3 \pm 0.3$	15.0
23.0	22.0	275105	114:05	20.2	30.1	21.5	$26.8 \pm 0.7$	$12.4 \pm 0.3$	12.4
14.4	33.0	37.3±0.5	$11.4 \pm 0.5$	11.1	32.4	21.5	$18.0 \pm 1.0$	$8.37 \pm 0.4$	8.0
L = (tr	1),				30.4	21.5	$14.8 \pm 0.5$	$6.89 \pm 0.2$	7.0
38.7	10.0	$135 \pm 3$	$135 \pm 3$	114		33.0	$24.1 \pm 0.3$	$7.31 \pm 0.1$	
36.8	10.0	$109 \pm 2$	$109 \pm 2$	97.9		43.0	$30.9 \pm 0.8$	$7.16 \pm 0.2$	
34.5	10.0	$83.7 \pm 2$	$83.7 \pm 2$	80.7			$30.0 \pm 1.0$	$6.98 \pm 0.2$	
32.9	10.0	$64.2 \pm 1$	$64.2 \pm 1$	70.5	25.0				4.(
		$64.2 \pm 2$	$64.2 \pm 2$						
30.9	10.0	$55.0 \pm 1$	$55.0 \pm 1$	59.4	L ≈ (	2,3-tri)(Oł	H_)		
2012	10.0	582+2	582+2		36.8	10.0	64.1 ± 1.3	$64.1 \pm 1.3$	66.0
		$53.2 \pm 2$ 53.1 + 1	$531 \pm 1$				$64.8 \pm 1.3$	64.8 + 1.3	
25.0		55.1 T 1	55.1 ± 1	35 3	34.2	10.0	$48.1 \pm 1.0$	48.1 + 1.0	48.9
14.0	33.0	45 0 + 2	139+05	12.7			$48.3 \pm 1.0$	$48.3 \pm 1.0$	
14.0	55.0	45.7 12	15.9 ± 0.5	12.,	32.3	10.0	$39.0 \pm 0.8$	$39.0 \pm 0.8$	39.3
L = (	$Me_2tn)_2$				31.3	10.0	$37.0 \pm 0.7$	370+07	34 0
37.8	10.0	$36.2 \pm 2$	$36.2 \pm 2$	34.2	51.5	10.0	$35.2 \pm 0.7$	$352 \pm 0.7$	54.
36.4	10.0	$31.1 \pm 0.9$	$31.1 \pm 0.9$	30.0	30.4	10.0	$325\pm0.0$	$325\pm0.7$	31 /
33.6	10.0	$22.8\pm0.3$	$22.8\pm0.3$	23.1	25.0	10.0	$52.5 \pm 0.0$	$52.5 \pm 0.0$	160
33.1	21.5	$39.2 \pm 1.0$	$21.3 \pm 0.5$	22.0	14.3	22.0	124407	106 10 2	10.2
30.3	10.0	$15.6 \pm 0.06$	$15.6 \pm 0.06$	16.9	14.5	33.0	$13.4 \pm 0.7$	$4.00 \pm 0.2$	4.
		$15.8 \pm 0.2$	$15.8\pm0.2$						
	21.5	$34.0 \pm 0.4$	$15.8 \pm 0.2$		L ≈ (	3,3-tri)(OI	H <sub>2</sub> )		
25.0	10.1				38.7	10.0	$118 \pm 2.4$	$118 \pm 2.4$	118
14.0	33.0	$10.5 \pm 0.1$	$3.17\pm0.03$	3.24			$117 \pm 2.4$	$117 \pm 2.4$	
		$11.2 \pm 0.1$	$3.41 \pm 0.03$		36.4	10.0	92.5±1.8	$92.5 \pm 1.8$	92.
	20		····				$95.2 \pm 1.8$	$95.2 \pm 1.8$	
L = 2	,3,2-tet		10 ( ) 0.0	10.4	33.8	10.0	$68.6 \pm 1.4$	$68.6 \pm 1.4$	70.
46.2	21.5	$22.9 \pm 0.4$	$10.6 \pm 0.2$	10.4			$70.7 \pm 1.4$	70.7 ± 1.4	
	33.0	$32.7 \pm 0.6$	9.91±0.2	- · · ·	32.1	10.0	$59.1 \pm 1.2$	$59.1 \pm 1.2$	58.
43.0	33.0	$25.5 \pm 0.6$	$7.72 \pm 0.2$	7.44	30.6	10.0	$50.1 \pm 1.0$	$50.1 \pm 1.0$	50.
40.5	33.0	$20.7 \pm 0.4$	$6.27 \pm 0.2$	6.14	25.0	-			26
	43.0	$26.4\pm0.5$	$6.14 \pm 0.12$						200
38.2	21.5	$10.9 \pm 0.3$	$5.06 \pm 0.13$	4.94					
	43.0	$20.6\pm0.2$	$4.79\pm0.05$		* [ <i>(</i>	] [] (]] ~ I	× 10 <sup>-3</sup> M		
30.2	21.5	$4.80\pm0.2$	$2.23 \pm 0.1$	2.27	יע הי	hserved nee	udo-first-order rete	constant	
25.0				1.34	۰۴	= k [Ho	2+1-1	vonotant.	
				(continued)	^н ⁴ Ca	alculated from	om the activation pa	trameters cited in 7	Table 1.

)	Hg <sup>2+</sup> (mM)	$10^4 k_{obs}^{b}$ (s <sup>-1</sup> )	$10^2 k_{Hg}^{c}$ (M <sup>-1</sup> s <sup>-1</sup> )	$10^2 k_{Hg}$ (calc.) <sup>d</sup> (M <sup>-1</sup> s <sup>-1</sup> )
= 3	,2,3-tet			
3	43.0	$9.14 \pm 0.2$	$2.14 \pm 0.04$	2.13
ŝ	43.0	$7.74 \pm 0.1$	$1.80 \pm 0.02$	1.82
7	43.0	$4.50 \pm 0.05$	$1.05 \pm 0.01$	1.04
1	21.5	$1.38 \pm 0.06$	$0.642 \pm 0.03$	0.618
	43.0	$2.55 \pm 0.09$	$0.593 \pm 0.02$	
)	15.0	2000 ± 0107	0.075 ± 0.05	0.357
= 3	.3.3-tet			
3	10.0	$17.4 \pm 0.2$	$17.4 \pm 0.2$	17.6
	21.5	$37.0 \pm 0.6$	$172 \pm 0.3$	
7	21.5	$268 \pm 0.5$	$125 \pm 0.2$	12.4
	33.0	$418 \pm 0.8$	$12.5 \pm 0.2$ $12.7 \pm 0.2$	12.4
1	21.5	$41.0 \pm 0.0$	$0.05 \pm 0.1$	0.80
•	21.5	$21.4 \pm 0.5$ $22.8 \pm 0.7$	$9.95 \pm 0.1$	2.09
`	33.0	$32.0 \pm 0.7$	$7.94 \pm 0.2$	7 70
,	21.5	$10.3 \pm 0.2$	7.0/±0.1	1.10
	43.0	$33.9 \pm 0.7$	$7.88 \pm 0.2$	5.05
2	21.5	$12.6 \pm 0.2$	$5.86 \pm 0.1$	5.85
		$12.2 \pm 0.06$	$5.67 \pm 0.03$	
	43.0	$25.2 \pm 0.6$	$5.86 \pm 0.1$	
)				3.05
≈ te	et-a			
5	21.5	45.6±1.0	$21.2 \pm 0.5$	20.9
5	21.5	$33.3 \pm 0.7$	$15.5\pm0.3$	15.6
l	21.5	$26.8 \pm 0.7$	$12.4 \pm 0.3$	12.4
1	21.5	$18.0 \pm 1.0$	$8.37 \pm 0.4$	8.60
1	21.5	$14.8 \pm 0.5$	$6.89 \pm 0.2$	7.03
	33.0	$24.1 \pm 0.3$	$7.31 \pm 0.1$	
	43.0	$30.9 \pm 0.8$	$7.16 \pm 0.2$	
		$30.0 \pm 1.0$	$6.98 \pm 0.2$	
)				4.04
= (	2 3-tri)(OH-	)		
રે	10.0	641+13	641+13	66.0
	10.0	$648 \pm 13$	$64.8 \pm 1.3$	00.0
,	10.0	$48.1 \pm 1.0$	$48.1 \pm 1.0$	48 9
~	10.0	$48.3 \pm 1.0$	$48.3 \pm 1.0$	40.9
2	10.0	$39.0 \pm 0.8$	$40.5 \pm 1.0$ $30.0 \pm 0.8$	30.2
, a	10.0	$37.0 \pm 0.3$	$37.0 \pm 0.0$	34.0
,	10.0	$37.0 \pm 0.7$ $35.2 \pm 0.7$	$37.0 \pm 0.7$	J4.7
1	10.0	$33.2 \pm 0.7$	$33.2 \pm 0.7$	21.2
+	10.0	$52.5 \pm 0.0$	52.5±0.0	31.5
2	22.0	124 . 07	4.00 + 0.0	10.2
3	33.0	13.4 <u>±</u> 0.7	4.06±0.2	4.15
= (	3,3-tri)(OH <sub>2</sub>	)		
7	10.0	118±2.4	118 + 2.4	118
	-	$117 \pm 2.4$	117 + 2.4	
4	10.0	$92.5 \pm 1.8$	92.5 + 1.8	92.8
		95.2 + 1.8	$95.2 \pm 1.8$	
8	10.0	$686 \pm 14$	$686 \pm 14$	70 5
	+0.0	$70.7 \pm 1.4$	$70.7 \pm 1.4$	10.5
1	10.0	501+12	501±10	58 7
6	10.0	$50.1 \pm 1.0$	$50.1 \pm 1.2$	50.0
ñ	10.0	50.1 <u>T</u> 1.0	50.1 <u>T</u> 1.0	26.8
v				20.0

Table 7 Conformations of  $RNH_2$  'arms' in  $[M(X)(Y)(NH_2R)_4]^{n+}$  complexes

Complex	Conformation	Ref.
$[Pt(EtNH_2)_4][PtBr_2(EtNH_2)_4]Br_4$	+ + + +	[23]
	+ + + +	
$[CrCl(MeNH_2)_5]Cl_2^{a}$	+ + + -	[24]
[RhCl(MeNH <sub>2</sub> ) <sub>5</sub> ]Cl <sub>2</sub> <sup>a</sup>	+ + + -	[25]
[CoCl(MeNH <sub>2</sub> ) <sub>5</sub> ]Cl <sub>2</sub> <sup>a</sup>	+ + +	[26]
$[CoCl(MeNH_2)_5](NO_3)_2$	+ +	[24]
$[Co(EtNH_2)_5(OH_2)](ClO_4)_3 \cdot 2H_2O$	+ + +	[27]
[Pt(EtNH <sub>2</sub> ) <sub>4</sub> ]PtCl <sub>4</sub>	+ +	[28]
$[CrCl_2(nPrNH_2)_4]BF_4 \cdot H_2O$	+ +	this research

\* An isomorphous series.

#### Table 8

Comparison of Cr--Cl bond lengths and acid hydrolysis ratios

Complex	Cr–Cl ª (Å)	$10^{5} k_{\rm H} (25 {}^{\circ}{\rm C})^{\rm a} ({\rm s}^{-1})$	$10^{2} k_{Hg} (25 \text{ °C}) (M^{-1} \text{ s}^{-1})$
$Trans-[CrCl_2(OH_2)_4]^+$	2.289(1)	4.53	
$Trans - [CrCl_{2}(en)(OH_{2})_{2}]^{+}$	2.286(1) 2.320(1)	3.10	
Trans-[ $CrCl_2(NH_3)_4$ ] <sup>+</sup>	2.298(1)	4.59 °	203 <sup>b</sup>
Trans-[CrCl <sub>2</sub> (nPrNH <sub>2</sub> ) <sub>4</sub> ] <sup>+</sup>	2.325(3)	0.670 <sup>c</sup>	3.01 <sup>b</sup>
$Trans-[CrCl_2(en)_2]^+$	2.330(1)	2.25	18.0 <sup>b</sup>

<sup>a</sup> Data from Ref. [29].

<sup>b</sup> This research, 50:50 dmf:aq. HClO<sub>4</sub> (I = 0.5 M).

° This research, 0.05 M HNO3.

R = H and nBu, there was slight drifting of the end absorbance but good first order rate constants over 3–4 half-lives were obtained using an assumed 'infinity' value. Rate constants determined over a 15 °C temperature range allowed the calculation of the associated activation parameters (Table 1).

One disturbing feature of the absorbance versus time specscans for the thermal hydrolysis of transtral  $[CrCl_2(RNH_2)_4]^+$  (Eq. (1)) (R = nPr, nBu) is that neither the direction of absorbance change at  $\sim 410$  nm, nor the position of the isosbestic points correspond to those determined for the Hg<sup>2+</sup>-assisted process (Eq. (2)) (Table 9) (Fig. 2). The thermal process is characterised by a decrease in absorbance with time at 420 nm, whereas for the  $Hg^{2+}$ assisted process the absorbance at 390 nm increases with time. The absorption spectra at the completion of the reaction are also different. For most of the *trans*- $[CrCl_2(N_4)]^+$  systems where data are available, the two processes have isosbestic points identical within experimental error (Table 9), so we do not believe that the addition of dmf is causing the problem. (Similar differences are observed for trans- $[CrCl_2(nPrNH_2)_4]^+$  in 50:50 dioxane:HClO<sub>4</sub>.)

Previous experience would suggest that the Hg<sup>2+</sup>-assisted process leads to retention of configuration and the final absorption spectra from the Hg<sup>2+</sup>-assisted process (Fig. 2) is characteristic of a *trans*-[CrCl(OH<sub>2</sub>)(N<sub>4</sub>)]<sup>2+</sup> species. Thus the thermal reaction could be complicated by either a concurrent change in stereochemistry or competitive amine loss. As changes in stereochemistry are hardly ever observed in *trans*- $[CrCl_2(N_4)]^+$  substitution processes [1], we believe that amine loss is the best explanation, and this aspect of the reaction is being investigated further.

As with the  $[CrCl(RNH_2)_5]^{2+}$  series [32], the change from R = H to R = Et in *trans*- $[CrCl_2(RNH_2)_4]^+$  results in a marked (16 times) reduction in reaction rate (Table 1). This rate reduction was previously interpreted in terms of an associative interchange process [33] but it is now thought that a direct comparison of rate constants is not mechanistically significant and a more detailed analysis of the activation parameters is required [34].

An interchange mechanism is now believed to operate for all substitution process illustrated by Eqs. (1) and (2) [35]. In an attempt to quantify the extent of interchange, the activation entropy ( $\Delta S^{\neq}$ ) has been proposed as a measure of the extent of the penetration of the approaching water molecule into the coordination sphere of the complex during the interchange process [34]. Large negative values (~ - 80 J K<sup>-1</sup>)

Table 9

Isosbestic points for the first step in the thermal and  $Hg^{2+}$ -assisted chloride release from some *trans*-[CrCl<sub>2</sub>(L<sub>4</sub>)]<sup>+</sup> complexes

	the second s		the second s	
$(en)_2$	Hg <sup>2+</sup> -assisted	a	405, 420, 560	b
-	thermal	с	470, 550	[30]
$(Me_2tn)_2$	Hg <sup>2+</sup> -assisted	a	409, 429, 574	ъ
	thermal	c	408, 435, 585	[3]
$(tn)_2$	Hg <sup>2+</sup> -assisted	а	407, 443, 571	b
	thermal	c	407, 445, 571	[5]
(en)(tn)	Hg <sup>2+</sup> -assisted	а	402, 451, 559	b
	thermal		405, 454, 560	[10]
3,3,3-tet	Hg <sup>2+</sup> -assisted	а	410, 422, 581	ъ
	thermal	с		<sup>d</sup> [16]
2,3,2-tet	Hg <sup>2+</sup> -assisted	a	e, e, 564	ъ
	thermal			d [7]
3,2,3-tet	Hg <sup>2+</sup> -assisted	a	e, e, 568	b
	thermal	c	456, 435, 568	[13]
tet-a	Hg <sup>2+</sup> -assisted	a	380, 404, 552	b
	thermal	f	392, 414, 561	[11]
$(2,3-tri)(OH_2)$	Hg <sup>2+</sup> -assisted	a	417, 449, 562	ь
	thermal	с	422, 454, 569	[14]
(3,3-tri)(OH <sub>2</sub> )	Hg <sup>2+</sup> -assisted	a	414, 450, 569	ъ
	thermal	j	413, 458, 566	b
$(nPrNH_2)_4$	Hg <sup>2+</sup> -assisted	а	410, 447, 586	b
	thermal	g	395, 495, 576	b
(nBuNH <sub>2</sub> ) <sub>4</sub>	Hg <sup>2+</sup> -assisted	а	414, 439, 593	ь
	thermal	h	392, 504, 580	ь
$(EtNH_2)_4$	thermal	g	396, 495, 577	ъ
		h	394, 498, 581	b
(NH <sub>3</sub> ) <sub>4</sub>	thermal	g	397, 453, 558	b
		ì	402, 440, 566	[9]

 $^a$  This research,  $[\,Hg^{2\,+}\,]=0.01$  M,  $HClO_4=0.45$  M in 50% aqueous dmf.

<sup>b</sup> This research.

<sup>c</sup> 0.1 M HNO<sub>3</sub>

<sup>d</sup> Isosbestic points not reported.

e Close contacts only.

<sup>f</sup> 0.05 M H<sub>2</sub>SO<sub>4</sub>.

<sup>g</sup> 0.05 M HNO<sub>3</sub>.

<sup>h</sup> 50:50 dioxane:0.05 M HNO<sub>3</sub>.

<sup>1</sup> 1.0 M HClO<sub>4</sub>.

<sup>j</sup> 0.1 M HClO<sub>4</sub>.



Fig. 2. Spectral scans (180 s intervals) for *trans*-[CrCl<sub>2</sub>(nPrNH<sub>2</sub>)<sub>4</sub>]<sup>+</sup>. (a) Upper curves in 50:50 dmf:0.0215 M Hg<sup>2+</sup>, 0.5 M HClO<sub>4</sub> at 36.7 °C. Isosbestic points at 410, 447 and 586 nm with absorbance increasing at 400 nm. (b) Lower curves in 0.05 M HNO<sub>3</sub> at 60.0 °C. Isosbestic points at 395, 495 and 576 nm with absorbance decreasing at 410 nm.

 $mol^{-1}$ ) indicate an associatively favourable situation and large positive values (~ + 120 J K<sup>-1</sup> mol<sup>-1</sup>) indicate an associatively restricting process.

The activation entropy data  $(\Delta S_{\rm H}^{\neq})$  for the first step in the thermal acid hydrolysis of *trans*-[CrCl<sub>2</sub>(N<sub>4</sub>)]<sup>+</sup> cover a considerable range and the complexes in Table 1 are ranked in order, from  $\Delta S_{\rm H}^{\neq}$  positive to negative. It should be noted that there are many more associatively favourable cases ( $\Delta S_{\rm H}^{\neq}$  negative) for Cr(III) than there are for Co(III) and for the present series of N<sub>4</sub> ligands, the approaching water molecule can distinguish between the two metal centres.

Although the non-replaced ligands in the *trans*- $[CrCl_2(N_4)]^+$  series do not appear to have a major influence on reactivity, as indicated by  $k_H$  (25 °C) values, they do

Table 10		
Variation of k <sub>Hg</sub> with dmf conce	entration at 36.5 °C for t	rans-[CrCl <sub>2</sub> (nPrNH <sub>2</sub> ) <sub>4</sub> ] +

appear to have considerable influence on the extent of water penetration into the coordination sphere as indicated by the  $\Delta S_{\rm H}^{\pm}$  data. With regard to the specific set of *trans*-[CrCl<sub>2</sub>(RNH<sub>2</sub>)<sub>4</sub>]<sup>+</sup> complexes,  $\Delta S_{\rm H}^{\pm}$  values are in the order -10, +39, -6, +43 J K<sup>-1</sup> mol<sup>-1</sup> for R = H, Et, nPr, nBu. As with the [CrCl(RNH<sub>2</sub>)<sub>5</sub>]<sup>2+</sup> series, the R = H complexes appear to be the least associatively restricting in an interchange process (most negative  $\Delta S^{\pm}$ ) but the R = nPr value appears to be out of line. It should be noted that the  $\Delta S_{\rm H}^{\pm}$ values for the corresponding reaction with *trans*-[RhCl<sub>2</sub>(RNH<sub>2</sub>)<sub>4</sub>]<sup>+</sup> are -55, +33, -53, -33 J K<sup>-1</sup> mol<sup>-1</sup> for R = H, Me, Et, nPr, respectively [36,38], where the large  $\Delta S_{\rm H}^{\pm}$  change from R = H to R = Me is not continued for R = Et or nPr.

## 3.3. $Hg^{2+}$ -assisted chloride release rates

The  $Hg^{2+}$ -assisted chloride release kinetics for Eq. (2) were measured in 50:50 dmf:aqueous  $HClO_4$  containing dissolved  $Hg(NO_3)_3$ . Most *trans*- $[CrCl_2(N)_4]ClO_4$  salts are readily soluble in dmf (an exception is *trans*- $[CrCl_2(cyclam)]ClO_4$ ) and the complex remains in solution on the addition of an equal volume of aqueous  $HClO_4/Hg^{2+}$  (I=1.0 M). *Trans*- $[CrCl_2(NH_3)_4]Cl \cdot H_2O$  is not soluble in dmf, but solution was achieved on the addition of the aqueous acidic phase. For *trans*- $[CrCl_2(nPrNH_2)_4]Cl$ , kinetic data were obtained at various dmf:aq.  $HClO_4/Hg^{2+}$  ratios (Table 10) to allow extrapolation to zero dmf. Although the ionic strength was also varying with solvent composition, we can use the expression (3).

$$2.41k_{Hg}(50:50, dmf:aq. HClO_4, I=0.5 M)$$

$$=k_{\rm Hg}({\rm aq.~HClO_4}, I=1.0~{\rm M})$$
 (3)

Our previous investigations [37] involving Hg<sup>2+</sup>-assisted acid hydrolysis in various media suggest that  $\Delta H^{\neq}$  values are media independent and we will assume that is the situation for the present systems. For most purposes, however, we will use the kinetic parameters determined in the mixed solvent (Table 1).

% dmf *	[Hg <sup>2+</sup> ] (mM)	[H <sup>+</sup> ] (M)	<i>I</i> (M)	$\frac{10^3 k_{obs}}{(s^{-1})}$	$10^2 k_{\rm Hg}^{\rm b}$ (M <sup>-1</sup> s <sup>-1</sup> )	$10^2 k_{\rm Hg} ({\rm calc.})^{\rm c}$ (M <sup>-1</sup> s <sup>-1</sup> )
0			1.0			20.5 <sup>d</sup>
10	18.0	0.85	0.9	$3.37 \pm 0.09$	$18.7 \pm 0.5$	18.1
20	34.3	0.72	0.8	$5.19 \pm 0.07$	$15.1 \pm 0.2$	15.7
30	30.1	0.63	0.7	$3.95 \pm 0.2$	$13.1 \pm 0.7$	13.3
40	25.8	0.54	0.6	$2.68\pm0.08$	$10.4 \pm 0.3$	10.8
50	21.5	0.45	0.5	$1.86 \pm 0.02$	$8.65 \pm 0.1$	8.45
60	17.2	0.36	0.4	$1.04\pm0.01$	$6.04 \pm 0.1$	6.04

\* % dmf by volume.

<sup>b</sup>  $k_{\text{Hg}} = k_{\text{obs}} [\text{Hg}^{2+}]^{-1}.$ 

<sup>c</sup> Calculated from the expression  $k_{Hg}$  (M<sup>-1</sup> s<sup>-1</sup>) = 20.5 - 0.241 (% dmf).

<sup>d</sup> [ $k_{\text{Hg}}$  (zero dmf)][ $k_{\text{Hg}}$  (50% dmf)]<sup>-1</sup>=2.41.

The rate constant associated with the  $Hg^{2+}$ -assisted chloride release reaction (Eq. (2)) is considerably more sensitive to the effects of the non-replaced ligands than is the case with the thermal reaction and again *trans*-[CrCl<sub>2</sub>(NH<sub>3</sub>)<sub>4</sub>]<sup>+</sup> reacts about 60–70 times faster than *trans*-[CrCl<sub>2</sub>-(RNH<sub>2</sub>)<sub>4</sub>]<sup>+</sup> (R = nPr, nBu).

Although  $\Delta S_{\rm H}^{\neq}$  and  $\Delta S_{\rm Hg}^{\neq}$  cannot be directly compared, the relative trends should be the same if  $\Delta S^{\neq}$  is discriminating for solvent interchange penetration. No particular pattern emerges and most  $\Delta S_{Hg}^{\neq}$  data line in the range  $-30 \pm 10$  J  $K^{-1}$  mol<sup>-1</sup> suggesting a similar position for these complexes in the interchange mechanistic spectrum for Hg<sup>2+</sup>-assisted chloride release. This is, perhaps, to be expected if M-ClHg is regarded as a better leaving group than M-Cl [39], as the non-replaced ligands will have less influence on the trajectory of the entering water molecule. On the basis of the  $\Delta S_{Hg}^{\neq}$ comparisons, the interchange process for the trans- $[CrCl_2(N_3)(OH_2)]^+$  systems would appear to be more associatively restricting than for the trans- $[CrCl_2(N_4)]^+$ compounds and within the latter group, trans- $[CrCl_2(NH_3)_4]^+$  seems to be out of line.

### 4. Conclusions

The interpretation of activation entropy  $(\Delta S^{\neq})$  as a measure of solvent penetration into the coordination sphere during a substitution reaction provides considerable insight into the interchange process. For thermal aquation reactions of *trans*- $[\operatorname{CrCl}_2(N)_4]^+$  complexes there is good spread of  $\Delta S_{\rm H}^{\neq}$  values and hence a range of interactions across the mechanistic spectrum. For the corresponding Co(III) complexes, however, only a limited range of the mechanistic spectrum is involved, and the process is generally more dissociatively activated ( $\Delta S_{\rm H}^{\neq}$  in a reasonably narrow positive range).

Again only a limited range of the mechanistic spectrum is involved for the first step in the Hg<sup>2+</sup>-assisted chloride release from *trans*-[CrCl<sub>2</sub>(N<sub>4</sub>)]<sup>+</sup>, but with this set of complexes the reaction may be more associatively activated with  $\Delta S_{Hg}^{+} = \sim -30 \pm 10 \text{ J K}^{-1} \text{ mol}^{-1}$ .

These conclusions provide an explanation for the observation that while  $k_{\rm H}$  and  $k_{\rm Hg}$  show good correlation for Co(III) complexes [37], the corresponding correlation in Cr(III) systems is poor [40]. In the Cr(III) case, the thermal process is operating over a wide range of the mechanistic spectrum, whereas the Hg<sup>2+</sup>-assisted process takes place within a narrow region.

One of the more intriguing questions raised in this analysis is to what extent does the approaching water molecule 'recognise' a change in the central atom in a series of homoleptic complexes. Relatively constant  $\Delta S^{\neq}$  (J K<sup>-1</sup> mol<sup>-1</sup>) data for the thermal acid hydrolysis of [MCl(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup>:Co<sup>III</sup> (-44), Ru<sup>III</sup> (-45), Cr<sup>III</sup> (-50), Rh<sup>III</sup> (-51), Ir<sup>III</sup> (-101) were originally cited [34] as suggesting a rather small central metal dependence. However, other systems, including the present *trans*- $[MCl_2(NH_3)_4]^+$ : Ru<sup>II</sup> (-3), Co<sup>III</sup> (-6), Cr<sup>III</sup> (-10), Rh<sup>III</sup> (-38), Ru<sup>III</sup> (-50); *trans*- $[MCl_2(en)_2]^+$ : Co<sup>III</sup> (+44), Cr<sup>III</sup> (-17), Ru<sup>III</sup> (-21), Ir<sup>III</sup> (-25), Rh<sup>III</sup> (-54); and *trans*- $[MCl_2(tn)_2]^+$ : Co<sup>III</sup> (+29), Cr<sup>III</sup> (+1), Rh<sup>III</sup> (-33), have a much greater  $\Delta S^{\neq}$  spread. Here the central metals, especially Co<sup>III</sup> versus Rh<sup>III</sup>, appear to contribute to factors affecting the degree of penetration of the approaching water molecule.

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