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Synthesis and Aquation Kinetics of Some *cis*-Dihalotetra-ammine Chromium(III) Complexes

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Salts of the previously unknown cis-$Cr(NH_3)_4X_2^+$ (X = Cl, Br) cations have been synthesized in high yield from reaction between cis-$[Cr(NH_3)_4F_2]ClO_4$ and dry gaseous HX in 2-methoxyethanol. Both cations aquate in dilute acid (HCl or HNO_3, $\mu = 0.42$) with strict retention; X = Cl, $k_{25} = 3.30 \times 10^{-4}$ sec^{-1}, $\Delta H^{\ddagger} = 20.0$ kcal mol^{-1}, $\Delta S^{\ddagger} = -5.9$ cal mol^{-1} deg^{-1}; X = Br, $k_{25} = 3.80 \times 10^{-3}$ sec^{-1}, $\Delta H^{\ddagger} = 19.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -5.7$ cal mol^{-1} deg^{-1}. The retentive aquation of trans-$Cr(NH_3)_4Br_2^+$ is also reported; $k_{25} = 9.8 \times 10^{-4}$ sec^{-1}, $\Delta H^{\ddagger} = 19.3$ kcal mol^{-1}, $\Delta S^{\ddagger} = -7.2$ cal mol^{-1} deg^{-1}. The spontaneous and Hg^{2+} promoted hydrolysis of several cis- and trans-CrN_4AX^{n+} cations (N = NH_3, $^1/_2en$; A = Cl, Br, OH_2, OH; X = Cl, Br) have been found to proceed with >99% retention.

Introduction

Recent interest has been directed to the preparation[1–10] and aquation kinetics[5–11] of tetra-ammine chromium(III) complexes. These studies include *trans*-$Cr(NH_3)_4ClI^+$ [8], -$Cr(NH_3)_4Cl_2^+$ [6], -$Cr(NH_3)_4ClBr^+$ [6], *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ [6], -$Cr(NH_3)_4(OH_2)Br^{2+}$ [11] and $Cr(NH_3)_4(OH_2)I^{2+}$ [8,11]. The labile *cis*- and *trans*-$Cr(NH_3)_4(OH)X^+$ (X = Cl^- [7], Br^- [8,11], I^- [8,11]) have also been studied. We report here the synthesis and primary aquation kinetics of the new complexes *cis*-$Cr(NH_3)_4Cl_2^+$ and -$Cr(NH_3)_4Br_2^+$, and primary aquation of *trans*-$Cr(NH_3)_4Br_2^+$ [4]. This work completes the dibromo[11] and dichloro[6] systems and permits comparison with the bis(ethylenediamine) chemistry.[12–14,23] We have also measured the steric course of spontaneous and Hg^{2+} promoted aquation of these and other tetra-amine chromium(III) complexes in an attempt to find an authentic case of Cr(III) substitution proceeding with stereochemical change.

Results

Aquation of cis- and trans-$Cr(NH_3)_4Br_2^+$

Nitrate and to a lesser extent chloride media were used due to the sparing solubility of the perchlorate salts.

For the *cis* isomer spectral scans revealed that the violet to red (20 °C, min) and red to orange (hr) colour changes correspond to the sequence:

$$cis\text{-}Cr(NH_3)_4Br_2^+ \xrightarrow[H_2O]{\text{fast}} cis\text{-}Cr(NH_3)_4(OH_2)Br^{2+} + Br^-$$

$$\xrightarrow[H_2O]{\text{slow}} cis\text{-}Cr(NH_3)_4(OH_2)_2^{3+} + 2Br^-$$

Kinetic overlap between the two stages is small; sharp isosbestic points (Table I) persist for almost the complete duration of the first step (Figure 1). Prior isomerization to *trans*-$Cr(NH_3)_4Br_2^+$ or direct aquation to *trans*-$Cr(NH_3)_4(OH_2)Br^{2+}$ would be most readily detected as a shift in the 529 nm isosbestic point (Figure 1). The results (Table I) place an upper limit of 2% on the formation of either *trans* species. A result of equal definition is provided by the identity between the spectral changes for the second stage and those observed with the isolated and independently investigated[11] *cis*-$Cr(NH_3)_4(OH_2)Br^{2+}$ intermediate. The final spectrum (100 ± 1% *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$) confirms the assigned retention and indicates also that Br^- loss is sensibly complete, excluding even transient formation of *trans* species which are less reactive, and furthermore which give *trans* product *(vide infra)*.

Similarly, a two stage aquation is found for *trans*-$Cr(NH_3)_4Br_2^+$ (green to blue–violet to orange):

$$trans\text{-}Cr(NH_3)_4Br_2^+ \xrightarrow[H_2O]{\text{fast}} trans\text{-}Cr(NH_3)_4(OH_2)Br^{2+} + Br^-$$

$$\xrightarrow[H_2O]{\text{slow}} trans\text{-}Cr(NH_3)_4(OH_2)_2^{3+} + 2Br^-$$

Figure 2 reproduces typical changes observed during the initial step. The isosbestic points (Table I) are in excellent agreement with the above scheme but are not precisely definitive of steric course (Figures 1 and 2); up to 10% *cis* product can be accommodated by experimental error, albeit small (ε, ± 1%). The infinite spectrum provides better definition (>98% retention). At low acidity (0.005 *M* HNO_3), secondary Br^- loss is accelerated *via* *trans*-$Cr(NH_3)_4(OH)Br^+$, enabling

TABLE I. Isosbestic Points and Steric Course for the Primary Aquation of Some Dihalochromium(III) Complexes in Dilute Nitric Acid.

Complex	ε,λ (M^{-1} cm^{-1}, nm)		% Steric Change
	Observed	Predicted	
cis-$Cr(NH_3)_4Br_2^+$	11.5, 350	11.5, 350	<2
	37.1, 389	37.0, 389	
	14.0, 460	14.0, 460	
	42.1, 529	42.0, 529	
trans-$Cr(NH_3)_4Br_2^+$	11.6, 347	11.4, 347	<2[a]
	27.8, 422	27.0, 423	
	16.8, 455	16.7, 455	
	~16, ~482[b]	15.8, 481	
	21.7, 582	21.8, 582	
cis-$Cr(NH_3)_4Cl_2^+$	33.5, 387	33.7, 387	<2
	10.6, 453	10.4, 453	
	40,0, 525	40.0, 525	

[a] From product spectra analysis (see text). [b] Region of tangency–"touch" isosbestic point.

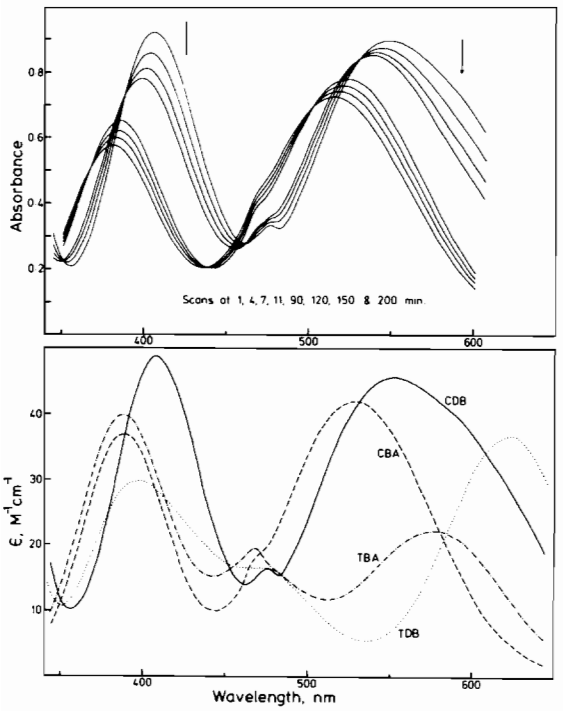

Figure 1. Upper: Spectral changes characterizing aquation of *cis*-$Cr(NH_3)_4Br_2^+$ in 0.1 *M* HNO_3 at 14.8° C. Lower: Pure component spectra: CDB, *cis*-$Cr(NH_3)_4Br_2^+$; TDB, *trans*-$Cr(NH_3)_4Br_2^+$; CBA, *cis*-$Cr(NH_3)_4(OH_2)Br^{2+}$; TBA, *trans*-$Cr(NH_3)_4(OH_2)Br^{2+}$.

trans-$Cr(NH_3)_4(OH_2)_2^{3+}$ to be identified free of subsequent but slow interfering side reaction (*trans* to *cis* isomerization and NH_3 loss[11,19,20]). It has been established that *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Br^{2+}$ and

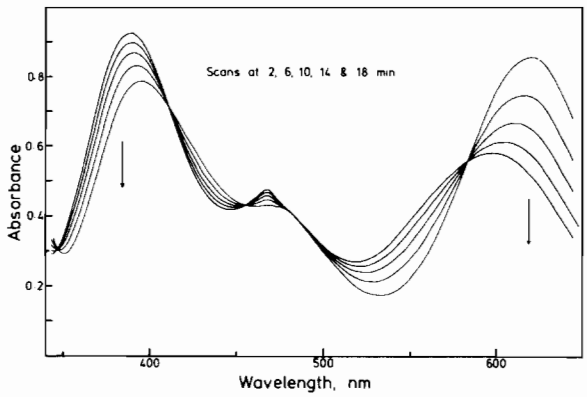

Figure 2. Spectral changes characterizing first-stage aquation of *trans*-$Cr(NH_3)_4Br_2^+$ in 0.1 *M* HNO_3 at 27.0° C.

$Cr(NH_3)_4(OH)Br^+$ hydrolyses proceed with full retention[11].

First-order rate constants determined for varied conditions of temperature, pH and ionic strength are given in Table II. For the *cis* isomer, primary Br^- loss was treated as a discrete step. Plots of $\ln|D-D_\infty|$ *vs.* time where D_∞ correspond to 100% *cis*-$Cr(NH_3)_4(OH_2)Br^{2+}$ were linear for *ca.* two $t_{1/2}$ at 410 and 607 nm despite large absorbance changes at these wavelengths for secondary aquation. Moreover, k_{obs} values obtained at 368 and 437 nm, isosbestic points for product aquation[11] (Fig. 1), are within 2–8% of these numbers. The wavelength independence of k_{obs} supports the proposed stoichiometry of primary aquation since ε values for the alternative products hold widely differing relationships with one another at these wavelengths (Figure 1).

Kinetic overlap between the two aquation stages is more pronounced for the *trans* isomer and accordingly

TABLE II. Observed First-Order Rate Constants for the Primary Aquation of *cis*- and *trans*-$Cr(NH_3)_4Br_2^+$ and *cis*-$Cr(NH_3)_4Cl_2^+$.

Temp., °C	$[H^+]$, *M*	μ, *M*[a]	10^3k, sec^{-1}	λ, nm[b]
cis-$Cr(NH_3)_4Br_2^+$[c]				
15.5	0.40	0.40 (0.42)	1.26	437
15.5	0.40	0.40 (0.42)	1.29	607
15.5	0.20	0.20 (0.22)	1.25 ± 0.02[d]	437
15.5	0.20	0.20 (0.22)	1.25 ± 0.01[d]	607
20.1	0.40	0.40 (0.43)	2.09	437
20.1	0.40	0.40 (0.43)	2.27	607
25.2	0.40	0.40 (0.42)	3.78	437
25.2	0.40	0.40 (0.43)	3.86	607
25.2	0.40	0.40 (0.44)	4.11	368
25.2	0.40	0.40 (0.44)	4.01	410
25.2	0.040	0.40 (0.42)	4.02 ± 0.03[d]	437
25.2	0.040	0.04 (0.06)	3.87	437
25.2	0.20	0.20 (0.42)	3.81	437
25.2	0.20	0.20 (0.42)	3.98	368
trans-$Cr(NH_3)_4Br_2^+$[e]				
20.3	0.10	0.10 (0.13)	0.577 ± 0.05[d]	370
20.3	0.10	0.10 (0.13)	0.564[e]	370
25.2	0.10	0.10 (0.13)	0.970 ± 0.01[d]	370
34.8	0.10	0.10 (0.13)	2.96	370
34.8	0.10	0.10 (0.12)	2.86	540
39.4	0.10	0.10 (0.13)	4.38	540
39.4	0.10	0.10 (0.13)	4.32	370
39.4	0.005	0.10 (0.13)	4.52	540
39.4	0.005	0.005 (0.03)	4.48	370
39.4	0.10	0.10 (0.12)	4.68[f]	540
39.4	0.40	0.40 (0.42)	4.62[f]	540
cis-$Cr(NH_3)_4Cl_2^+$[g]				
19.7	0.40	0.40 (0.43)	1.72 ± 0.02[d]	600
19.7	0.40	0.40 (0.43)	1.68	434
25.2	0.40	0.40 (0.43)	3.39 ± 0.07[h]	600
25.2	0.40	0.40 (0.44)	3.30	434
35.2	0.40	0.40 (0.43)	10.3	600
35.2	0.40	0.40 (0.44)	10.6	434
35.2	0.040	0.40 (0.43)	10.6	600
35.2	0.010	0.40 (0.43)	10.3	600
35.2	0.040	0.04 (0.07)	9.93	600
44.6	0.40	0.40 (0.43)	27.4 ± 0.4[d]	434

[a] Nominal value for added electrolyte; value in parenthesis includes initial complex concentration. [b] Constant λ run wavelength. [c] $[Cr] = (1.8–3.6) \times 10^{-2} M$. [d] Mean of duplicate runs, and average deviation. [e] $[Cr] = (2.1–3.7) \times 10^{-2} M$. [f] Acidity and ionic strength controlled with HCl; media HNO_3–$NaNO_3$ otherwise. [g] $[Cr] = (2.7–4.0) \times 10^{-2} M$. [h] Mean of triplicate runs, and average deviation.

(accurate) rate data were obtained only at wavelengths coinciding with isosbestic points for the second stage. Again, k_{obs} values from initially linear rate plots (one to two $t_{1/2}$) were wavelength independent (Table I) which served to confirm the primary aquation stoichiometry.

The aquation rates show no significant acid (0.04–0.4 *M* HNO_3, *cis;* 0.005–0.1 *M* HNO_3, *trans*) nor ionic strength dependence (Table II). The *trans* rate is unaffected also by the transfer from NO_3^- to Cl^- media.*

This can be taken as evidence against possible nitrate catalysis (which requires prior coordination, usually *via* aqua substitution)[19–21].

Trans-$Cr(NH_3)_4Br_2^+$ reacts at about $^1/_{40}$th the *cis* isomer rate and also, since no *cis* species appear as products, a pre-isomerization mechanism can be ruled out; *trans* to *cis* isomerization must be at most 2% of

* In strong HNO_3, oxidation of co-ordinated Br^- (to Br_2) leads to accelerated aquation, as found for analogous tetra-amine-cobalt(III) complexes.

the *trans* aquation rate. Similar considerations of rate and stereochemistry apply to *cis* aquation and to aquation of other tetra-ammine complexes reported previously[6–9, 11].

Aquation of cis-$Cr(NH_3)_4Cl_2^+$

The comments above again apply here. Fixed wavelength kinetic measurements and repetitive scan spectrophotometry established Cl^- release to be both completely retentive and first order. Details are included in Figure 3 and Table I and II. Aquation of *trans*-$Cr(NH_3)_4Cl_2^+$ and of *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ has been reported previously.[6]

Mercury(II) Promoted Aquation

The following reactants were studied: *cis*- and *trans*-$CrN_4X_2^+$ (N = NH_3, $^1/_2$en; X = Cl, Br) and *cis*- and *trans*-Cr $en_2(OH_2)X^{2+}$ (X = Cl, Br). The aquation stereochemistry is $100 \pm 1\%$ retentive in each case, in 0.02, 0.1 or 1.0*M* Hg^{2+} (see Experimental).

Spontaneous Aquation of cis- and trans-$Cren_2(OH)X^+$ (X = Cl, Br)

The solid aqua complexes dissolved in pH 9.4 or 10.2 buffers rapidly hydrolyse (Br > Cl, *cis* ~ *trans*) at [OH^-] independent rates. We infer the formation and aquation of the labile hydroxo complexes. Constant final spectra were observed only in *en* media. In the time scale of these hydrolyses (1–10 min) *cis*- and *trans*-Cr $en_2(OH)_2^+$ are unreactive; we can confirm very slow isomerization in en buffers and en loss in NaOH media[22]. The steric course of hydrolysis was easily established as >99% retentive since the spectra of the *cis* and *trans* products differ widely (see Experimental). *Trans*-$Cren_2(OH)Cl^+$ has been studied previously and reported as giving 13% *cis* product[22]. The present observations resolve an obvious stereochemical anomaly.

Aquation Stereochemistry

The absence of stereochemical change is consistent with all other reliable observations on Cr(III) amine complexes[15]. Similar simple Co(III) complexes show significant rearrangement, *e.g.*, the spontaneous aquation of *trans*-Co $en_2(OH)X^+$ (X = Cl, Br; 73% *cis* product)[24] and Hg^{2+} promoted aquation of *cis*-Co $en_2X_2^+$ (X = Br, 43%; X = Cl, 24% *trans* product[24]). The present augments our previous work[11] on the directly analogous Cr(III) complexes and further emphasizes the strict retention of simple Cr(III) aquation.

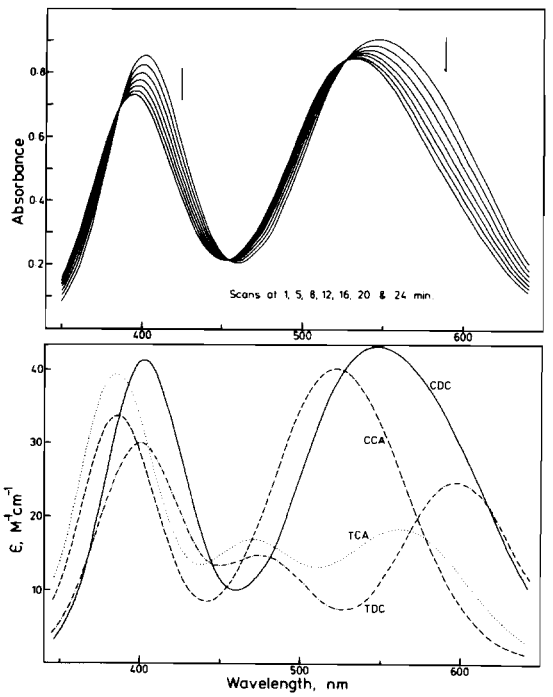

Figure 3. Upper: Spectral changes characterizing first-stage aquation of *cis*-$Cr(NH_3)_4Cl_2^+$ in 0.1*M* HNO_3 at 29.7° C. Lower: Pure component spectra in dilute acid: CDC, *cis*-Cr $(NH_3)_4Cl_2^+$; TDC, *trans*-$Cr(NH_3)_4Cl_2^+$; CCA, *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$; TCA, *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$.

General Discussion

Table III summarizes kinetic data for $Cr(NH_3)_4$ and $Cr(en)_2$ complexes. These results reveal the usual[25] leaving group rate order $I^- > Br^- > Cl^-$, the differences being about an order of magnitude. A similar pattern obtains for $Cr(NH_3)_5X^{2+}$ and $Cr(OH_2)_5X^{2+}$ aquations where the total rate variations (I^- to Cl^-, 25° C) are 110- and 300-fold, respectively.

In addition to the Cr–X bond factor, anion hydration will be important. Since the hydration enthalpies of X^- decrease from Cl^- to I^- [27–29], this contribution serves to compress the effects of differential bond strengths ($Cl^- > Br^- > I^-$). In dmf and dmso where anion solvation is weaker and in the reverse order, greater rate differences are found between Cl^- and Br^- solvolysis[30], supporting a case for dissociative reaction.

Rate data for $Cr(NH_3)_4AX^{n+}$ (including $Cr(NH_3)_5X^{2+}$ [29]) as a function of varied A, X and geometry are compared in Table IV.

The most significant feature is the overall uniformity of the series, irrespective of A and X, and this argues strongly for a common mechanism. Equally importantly, this uniformity extends to the broad class of aqua and aqua-amminechromium(III) systems[31].

The anticipated[25, 32] order of assisting ligands (A) is $OH^- \gg NH_3 > OH_2 > I^-, Br^-, Cl^-$. Considering first the *trans* series, the trends are qualitatively those expected for a dissociative process.

TABLE III. Comparison of Rates and Activation Parameters for the Aquation of Some Chromium(III) Tetra-amine Complexes*.

Complex	Medium	$10^5 k_{25}$, sec^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal mol^{-1} deg^{-1}	Reference
cis-$Cr(NH_3)_4Cl_2^+$	$NaNO_3$–HNO_3	33 ± 1.5	20.0	–5.9	This work
trans-$Cr(NH_3)_4Cl_2^+$	$NaClO_4$–$HClO_4$	4.9[a]	21.0	–7.8	6
cis-$Cr(NH_3)_4Br_2^+$	$NaNO_3$–HNO_3	380 ± 14	19.2	–5.7	This work
trans-$Cr(NH_3)_4Br_2^+$	$NaNO_3$–HNO_3	98 ± 4	19.3	–7.2	This work
trans-$Cr(NH_3)_4ICl^+$	$NaClO_4$–$HClO_4$	330[b] ≦9[d]	18.6[b,c]	–7.7[b,c]	8
trans-$Cr(NH_3)_4ClBr^+$	$NaClO_4$–$HClO_4$	29[e] ≦3.4[d]	20.2[e]	–6[e]	6
cis-$Cren_2Cl_2^+$	HNO_3	33	20.5	–6	23
trans-$Cren_2Cl_2^+$[f]	HNO_3	2.3	22.6	–7	23
cis-$Cren_2Br_2^+$	$HClO_4$	230	18.6	–8	12, 13
trans-$Cren_2Br_2^+$	$HClO_4$	33	21.8	–1.4	12, 14

[a] Value calculated for k_{45} and E_a of rcf. 6. [b] Value for loss of I^-. [c] Published figures incorrect; recalculated from quoted k_{obs}, T data. [d] Value for loss of Cl^-. [e] Value for loss of Br^-. [f] Complex reaction involving en release and isomerization; data for Cl^- release only.

* Data for this work were calculated from the fit of k values to the Absolute Rate Equation. Errors in k_{25}, ΔH^* and ΔS^* are standard deviations; ΔH^*, ±0.5 kcal mol^{-1}; ΔS^*, ±1.5 cal mol^{-1} deg^{-1}.

TABLE IV. Comparison of Rate Constants for Aquation of Tetra-amminechromium(III) Complexes.[a]

	trans-$Cr(NH_3)_4ACl^{n+}$					
A =	OH^- ≫	I^- >	Br^- >	Cl^- >	NH_3 >	OH_2
$10^5 k_{25}(sec^{-1})$ =	~10^5	9	3.4	2.5	1.1	0.07
	cis-$Cr(NH_3)_4ACl^{n+}$					
	OH^- ≫	Cl^- >	NH_3 >	OH_2		
	~2×10^4	17	1.1	0.5		
	trans-$Cr(NH_3)_4ABr^{n+}$					
	OH^- ≫	Br^- >	Cl^- >	NH_3 >	OH_2	
	~10^4	50	30	10	1	
	cis-$Cr(NH_3)_4ABr^{n+}$					
	OH^- ≫	Br^- >	NH_3 ~	OH_2		
	~10^5	190	10	8		
	trans-$Cr(NH_3)_4AI^{n+}$					
	OH^- ≫	Cl^- >	NH_3 >	OH_2		
	~2×10^5	330	105	9.5		
	cis-$Cr(NH_3)_4AI^{n+}$					
	OH^- ≫	OH_2 ~	NH_3			
	~5×10^5	107	105			

[a] Rates statistically corrected where A = X.

Strong labilization by the hydroxo group is typical of both Cr(III) and Co(III) chemistry. The major departure from expectation is the placement of the halides but here the additional effect of net charge would account for their observed activating ability. Charge separation in dissociative aquation is more energetically favourable the lower the substrate charge.

The importance of electron displacement *vis à vis* charge effects is seen in the similar "*trans* activation" of Cl^- and NH_3. Cr(III) more closely resembles Pt(II) than Co(III) in this regard. For example, the aquation rate ratios $k_{n+}/k_{(n+1)+}$ for the couples *trans*-$M(NH_3)_m Cl_2^{n+}/M(NH_3)_{m+1} Cl^{(n+1)+}$ have the respective values 2.4 and 3.8 for Cr(III) and Pt(II)[33], but 2700 for Co(III)[34].

Intriguing is the lack of significant *trans* labilization by the iodo group, counter to its clear accelerating effect in $Cr(OH_2)_5I^{2+}$,[35–37] and possibly *trans*-$Cr(NH_3)_4$

$(OH_2)I^{2+}$.[9] However, the latter reactions involve neutral leaving groups whereas an anionic leaving group is considered here (Table IV). Moreover, the substrate charges are different. In dissociative activation its electronic influence is therefore expected to depend upon the degree of charge separation.

Basically the same pattern of A effects obtains with *cis*-$Cr(NH_3)_4AX^{n+}$ as with the *trans* series. The main difference lies in the higher position (magnitude) of A = NH_3, *i.e.*, a *cis* isomer reacts faster than its *trans* form. This amounts to about an order of magnitude. Accumulated data[25,16,38] show that an amine donor *trans* to the leaving group is necessary for the rate order *cis* > *trans*. Indeed, the isomers of $Cr(OH_2)_4Cl_2^+$ aquate at very similar rates[39], as do $Cr(OH_2)_4(NCS)_2^+$.[40] Some form of specific *trans* activation by amine donors is clear.

Cis/trans reactivity has been discussed previously in connection with variation in solvent dipole and leaving group solvation[30]. Other factors affecting relative reaction rates of isomers are chelate ring strictures[41], and steric interactions between adjacent A and X groups. Striking examples of the latter are provided by *cis*-$CrN_4(ONO)Cl^+$ (N = NH_3, $^1/_2$en), $Cr(NH_3)_5C_2O_4^+$ and $Cr(NH_3)_5(ONO_2)^{2+}$ aquations[10,42–44]. None of these effects presently apply to the $Cr(NH_3)_4$ complexes. Further, simple repulsive arguments fail to explain why the *cis/trans* reactivity ratio favours the dichloro over the dibromo species, and it is difficult to see why this ratio is independent of the size of X in $Cr(NH_3)_4(OH_2)X^{2+}$ (Table III and IV). Finally, consideration of the series of *cis*- and *trans*-halohydroxo ions[8,11,32] indicates that the relative effectiveness of OH^- is the same whether in a *cis* or *trans* position, despite the fact that OH^- is potentially a powerful π-donor. Conventional π-bonding for *cis* labilization[32] is clearly not the only relevant factor.

Comparison of data for the tetra-ammine and bis (ethylenediamine) complexes (Table III) reveals little correlation with the order expected for the so-called kinetic chelate effect ($NH_3 \gg$ en, based on Co(III) data[33]). Only the *trans* substrates follow the anticipated sequence although the rate differences are small, less than a factor of three.

It remains to note that for Co(III) the most pronounced effects of chelation are seen with *trans* substrates, substrates which aquate with geometric change[33]. Thus the fall in rate between the $(NH_3)_4Co$ and $(en)_2Co$ complexes could arise from chelate strictures retarding the motions required to generate the trigonal bipyramidal structure. This would not apply to Cr(III) where aquations occur with no apparent reorganization of the basis octahedral framework[15]. Recent studies on other Cr(III) chelates, $Cr(tn)_2$ in particular[45], emphasize the lack of chelate acceleration in Cr(III) aquation. These investigations include both neutral[46] and anionic leaving groups[45], in both aquation and solvolysis.

Experimental

Electronic spectra were recorded on a Hitachi EPS-3T auto-recording instrument. Kinetic and analytical techniques have been described[11,38,47]. Complexes used were freshly prepared, and light was excluded routinely in all experiments. Purified HgO in Analar $HClO_4$ provided Hg^{2+}.[11] Analar HCl, HNO_3 and $HClO_4$ were standardized against Analar HgO and diluted with doubly distilled water for kinetic studies. Ionic strength was adjusted with Analar $NaClO_4 \cdot H_2O$ or $NaNO_3$. *En* buffers (μ = 1.0, pH 9.4 and 10.2) were prepared from Analar $HClO_4$ and diamine dried and distilled from KOH[11].

Cis-$[Cr(NH_3)_4F_2]ClO_4$

Details of the preparation of the difluoro isomers have not been published previously*. *Trans*-$[Crpy_4F_2]I$ (170 g)[17] was dried (70°C, 12 hr), placed in an autoclave with liquid NH_3 (500 ml), and heated (100°C, 2 hr). The red violet solid collected on cooling

*We thank Professor C. E. Schäffer, Copenhagen, for providing the essential details (ref. 4).

TABLE V. Comparison of Tetra-ammine and Bis(ethylenediamine) Chromium(III) Visible Spectra.

Complex	ε,λ (M^{-1} cm^{-1}, nm)[a,b]		
	Max[e]	Min[f]	Max[e]
cis-$Cr(NH_3)_4Br_2^+$	48 ± 1.5, 408 10.5 ± 0.5, 356	16.7 ± 0.5, 477 14.2 ± 0.5, 462	45.7 ± 1.5, 553 15.6 ± 0.6, 483
cis-$Cren_2Br_2^+$[c]	83.0, 415	29.2, 468	89.4, 544
cis-$Cr(NH_3)_4Cl_2^+$	41.4 ± 2, 402	10.0 ± 0.7, 459	43.3 ± 2, 546
cis-$Cren_2Cl_2^+$[d]	68.5, 402	20.7, 456	70.6, 528

[a] In 0.05–1.0*M* HNO_3 or $HClO_4$. [b] λ,± (0.5–1.0) nm. [c] Ref. 12. [d] Ref. 23. [e] Maxima. [f] Minima.

was washed with liquid NH_3 (5 × 200 ml) leaving a brown residue of *trans*-$[Cr(NH_3)_4F_2]I$ which was set aside. NH_3 was allowed to evaporate from the combined filtrates and washings *(well ventilated fume hood!)*. The collected residue was washed with ethanol and recrystallized from a minimum volume of $HClO_4$ (0.01*M*, 30° C) by filtration, dropwise addition of $HClO_4$ (70%, 15 ml), and cooling (0° C, 4 hr). Violet–red *cis*-$[Cr(NH_3)_4F_2]ClO_4$ which deposited was filtered, washed with dilute $HClO_4$ and then methanol, and air dried.

Trans-$[Cr(NH_3)_4F_2]ClO_4$

The crude iodide salt set aside above was recrystallized from a minimum volume of $HClO_4$ (0.01*M*, 70° C) by filtration, dropwise $HClO_4$ (60%) addition and cooling (0° C, 2 hr). The collected brown-red crystals were methanol and then ether washed, and air dried.

Cis-$Cr(NH_3)_4Br_2^+$ Salts

Cis-$[Cr(NH_3)_4F_2]Cl_4$ (1.6 g) was suspended in 2-methoxyethanol (15 ml). The mixture, cooled to −15° C, was saturated with dry HBr gas. The resultant red solution was warmed to 20° C under pressure in a sealed reaction vessel *(HF!)* and stirred magnetically until precipitation was essentially complete (2 hr). The finely divided grey–blue product was collected and washed with ethanol. The yield was essentially quantitative. Royal-blue crystals were recovered from a saturated aqueous solution (0° C) on addition of HBr (48%) (Caution: accumulated *cis*-$[Cr(NH_3)_4(OH_2)Br]Br_2$ tends to separate out unless recrystallization is performed quickly). Final purification was achieved by recovery from water as the perchlorate ($NaClO_4$ or $HClO_4$), then reconversion to the bromide by the addition of NaBr or $N(C_2H_5)_4Br$ to a solution in DMF, as described for the $Cr(en)_2$ analogue[30]. *Anal.* Calcd for $Cr(NH_3)_4Br_2 \cdot Br \cdot H_2O$: Cr, 13.8; H, 3.73; N, 14.8; Br, 63.4. Found: Cr, 13.6; H, 3.77; N, 14.9; Br, 63.0%. Vacuum drying (120° C, 1 hr) yielded the anhydrous salt. *Anal.* Calcd for $Cr(NH_3)_4Br_2 \cdot Br$: Cr, 14.5; H, 3.36; N, 15.6; Br, 66.6. Found: Cr, 14.5; H, 3.39; N, 15.5; Br, 66.2%.

Cis-$Cr(NH_3)_4Cl_2^+$ Salts

The crude chloride was obtained from the reaction between *cis*-$[Cr(NH_3)_4F_2]ClO_4$ and dry HCl gas in 2-methoxyethanol, as detailed for the dibromo complex above. Blue–violet needles were obtained on recrystallization from water (0° C) and HCl (37%, 0° C). The product was washed with cold dilute HCl followed by methanol and finally ether. *Anal.* Calcd for $Cr(NH_3)_4Cl_2 \cdot Cl \cdot H_2O$: Cr, 21.3; H, 5.77; N, 22.9; Cl, 43.5. Found: Cr, 21.1; H, 5.74; N, 22.8; Cl, 43.8%. The perchlorate was obtained from water (0° C, $HClO_4$). *Anal.* Calcd for $Cr(NH_3)_4Cl_2 \cdot ClO_4$: Cr, 17.9; H, 4.17; N, 19.3; Cl, 36.6. Found: Cr, 18.0; H, 4.20; N, 19.3; Cl, 36.8%.

Trans-$[Cr(NH_3)_4Br_2]Br \cdot H_2O$

Commencing with *trans*-$[Cr(NH_3)_4F_2]ClO_4$ the synthesis was analogous to that described for the *cis* isomer above. Aqueous HBr (48%) may be substituted for 2-methoxyethanol/HBr[4]. The product recrystallized from water (0° C, NaBr) as grass-green needles. *Anal.* Calcd for $Cr(NH_3)_4Br_2 \cdot Br \cdot H_2O$: Cr, 13.8; H, 3.73; N, 14.8; Br, 63.4. Found: Cr, 13.7; H, 3.67; N, 15.0; Br, 62.9%.

Trans-$[Cr(NH_3)_4Cl_2]Cl \cdot H_2O$

This was prepared and recrystallized as described[16]. An identical material is obtained *via trans*-$[Cr(NH_3)_4F_2]ClO_4$ and HCl *(vide supra)*. *Anal.* Calcd for $Cr(NH_3)_4Cl_2 \cdot Cl \cdot H_2O$: Cr, 21.3; H, 5.77; N, 22.9; Cl, 43.5. Found: Cr, 21.1; H, 5.72; N, 22.6; Br, 43.4%. Salts (Cl^-, Br^-, ClO_4^-) of *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ and $Cr(NH_3)_4(OH_2)Br^{2+}$ were prepared for concurrent work[11] and analysed satisfactorily. Both *trans* isomers were purified by conversion (NO^+) to and acid ($HClO_4$) decomposition of *trans*-$[Cr(NH_2)_3(ONO)X]ClO_4$ (X = Cl, Br)[10,11].

Cis- and trans-$Cren_2X_2^+$, $Cren_2(OH_2)X^{2+}$ (X = Cl, Br), $Cren_2(OH_2)(OH)^{2+}$ and $Cren_2(OH_2)_2^{3+}$ Salts

These were obtained as detailed elsewhere[16,30]. *Anal.* Calcd for $Cren_2Cl_2 \cdot Cl \cdot H_2O$: Cr, 17.5; C, 16.2; H, 6.1; N, 18.8; Cl, 35.8. Found *(cis)*: Cr, 17.7; C, 16.3; H, 6.2; N, 18.7; Cl, 36.0. Found *(trans)*: Cr, 17.7; C, 16.2; H, 6.2; N, 18.9; Cl, 35.8%. Other analyses were given earlier[16,30].

Characterization

Cis/trans distinctions are clear since isomeric pairs are known in all cases. The $Cr(NH_3)_4$ complexes have very similar but less intense electronic spectra (Table V). Isomeric purity was established according to recorded criteria.[24]

Hg^{2+} Promoted Aquation

The essential techniques have been described in detail[11,23]. In every case the stereochemistry was determined from final $CrN_4(OH_2)_2^{3+}$ spectra (20° C) which change only slowly with time. The contribution to reaction from the spontaneous process was always negligible. In slower reactions (*e.g.*, *trans*-$CrN_4(OH_2)Cl^{2+}$), rapid spectral scanning revealed isosbestic points in agreement with those predicted for retentive aquation. The steric course for the more reactive *cis*-$CrN_4X_2^+$ species was determined more accurately and conveniently by rapidly generating $CrN_4(OH_2)_2^{3+}$ with excess Hg^{2+}. In each case the product spectra were superimposable (ε, ±1%) upon those of the pure isomer, *i.e.*, the reactions were retentive.

Base Hydrolysis

The stereochemistry (20° C) of *cis*- and *trans*-$Cren_2(OH)X^+$ (X = Cl, Br) aquation was also determined simply from final spectra (X = Cl, $t_{1/2}$ ~3 min; X = Br, $t_{1/2}$ <20 sec, 20° C). Product $Cren_2(OH)_2^+$ spectra, and $Cren_2(OH_2)_2^{3+}$ by careful $HClO_4$ acidification (to 0.1 *M*), were very closely (ε ±1%) those corresponding to the pure isomers, indicating complete retention.

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