Aquation of Formato-, *NN*-Dimethylformamide-, and Fluoro-penta-amminechromium(III) Complexes. Identification of Reaction Paths and Kinetic Studies †

By **Najat Al-Shatti, T. Ramasami,** and **A. Geoffrey Sykes,*** Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT

The formato- and *NN*-dimethylformamide (DMF) complexes $[Cr(NH_3)_5(O_2CH)]^{2+}$ and $[Cr(NH_3)_5(OCHNMe_2)]^{3+}$ have been prepared and characterized. Ion-exchange separation of the aquation products in the case of the formato-complex indicates that ammonia loss features prominantly. With the DMF complex a single process corresponding to aquation of DMF is observed. Kinetic studies give $k_1 = 1.79 \times 10^{-4}\ s^{-1}$ at 50 °C, $I = 1.00$M ($LiClO_4$), with activation parameters $\Delta H^\ddagger = 20.2 \pm 0.5$ kcal mol^{-1} and $\Delta S^\ddagger = -13.5 \pm 1.7$ cal K^{-1} mol^{-1}. Aquation of $[Cr(NH_3)_5F]^{2+}$ yields $[Cr(NH_3)_5(H_2O)]^{3+}$ (k_2) and $[Cr(NH_3)_4(H_2O)F]^{2+}$ (k_3) with the latter predominating over the conditions $[H^+] = 0.01$—1.00M investigated. From product analyses and kinetic studies at different $[H^+]$ rate constants have been obtained at 50 °C, $I = 1.00$M ($LiClO_4$). Aquation of fluoride is $[H^+]$-dependent, $k_2 = a + b[H^+]$, with $a = 2.1 \times 10^{-6}\ s^{-1}$ and $b = 2.9 \times 10^{-6}$ l mol^{-1} s^{-1}, while k_3 for ammonia loss is independent of $[H^+]$, $k_3 = 7.7 \times 10^{-6}\ s^{-1}$.

RECENT studies on the aquation of $[Cr(NH_3)_5X]^{(3-n)+}$ complexes has indicated that compared with analogous Co^{III} complexes they exhibit considerable variation in behaviour with aquation of ammonia often being a predominant feature.[1-4] The need to define reaction paths by careful product analyses is clearly indicated in the aquation of $[Cr(NH_3)_5F]^{2+}$, which has previously been assumed to yield only $[Cr(NH_3)_5(H_2O)]^{3+}$ as product.[5]

EXPERIMENTAL

Preparation of Penta-ammineaquochromium(III).—The ammonium nitrate salt, $[Cr(NH_3)_5(H_2O)][NO_3]_3{\cdot}NH_4NO_3$,[6] was first prepared. This was converted into the perchlorate salt by dissolution (10 g) in 0.1M-$HClO_4$ (50 ml) at *ca.* 50 °C, followed by the slow addition of $NaClO_4$. When the solution became turbid addition of $NaClO_4$ was stopped, the solution was re-heated until it became clear, and then cooled slowly in the dark. The crude perchlorate salt thus obtained was recrystallized twice from 0.1M-$HClO_4$ by addition of solid $NaClO_4$, to give $[Cr(NH_3)_5(H_2O)][ClO_4]_3$, $\lambda_{max.}$ 360 (ε 30.5) and 480 nm (35.7 l mol^{-1} cm^{-1}).

Preparation of Penta-ammineformatochromium(III).—Sodium formate (AnalaR; 5 g) was dissolved in water (15 ml) to which formic acid (AnalaR, 3.5 ml) had been added. The solution was warmed to 40 °C, $[Cr(NH_3)_5(H_2O)][ClO_4]_3$ (5 g) was added, and the temperature maintained for 20 min. Sodium perchlorate was then added until an orange complex began to crystallize. At this stage the solution was warmed again to 40—45 °C and cooled slowly. The orange crystals were filtered off and washed with ethanol and diethyl ether. The sample was stirred with methanol (AnalaR; 300 ml) and since the $[Cr(NH_3)_5(O_2CH)]^{2+}$ component is soluble it was easily separated from $[Cr(NH_3)_5(H_2O)]^{3+}$. The methanolic solution was concentrated on a rotary evaporator at *ca.* 30 °C. To precipitate the complex a large excess of diethyl ether was added. The precipitate was dried and recrystallized from 0.1M-$HClO_4$ at 30 °C by addition of $NaClO_4$ (Found: C, 3.5; H, 4.25; Cl, 18.6; Cr, 13.5; N, 18.4. Calc. for $[Cr(NH_3)_5(O_2CH)][ClO_4]_2$: C, 3.2; H, 4.20; Cl, 18.7; Cr, 13.6; N, 18.4%).

*Preparation of Penta-ammine-*NN*-dimethylformamide-chromium*(III).—The complex $[Cr(NH_3)_5(H_2O)][ClO_4]_2$ (6 g) was dissolved in water-free *NN*-dimethylformamide (*ca.* 40 ml). Molecular sieve 4A XW, 1/16 inch pellets, (0.5 g) was added and the mixture maintained at *ca.* 20 °C for 15 min. The molecular sieve was filtered off and the solution poured into ice-cold acetone (AnalaR; 100 ml); precipitation was completed by addition of diethyl ether (AnalaR; *ca.* 150 ml). The solid was filtered off and washed with acetone, ethanol, and diethyl ether. The orange solid was dissolved in 0.05M-$HClO_4$ (20 ml) and recrystallized by addition of $NaClO_4$ (Found: C, 7.6; H, 4.35; Cr, 10.0; N, 16.7. Calc. for $[Cr(NH_3)_5\{OCHN(CH_3)_2\}][ClO_4]_3$: C, 7.1; H, 4.33; Cr, 10.2; N, 16.6%).

Preparation[7] *of Fluoropenta-amminechromium*(III).—Ammonium hydrogen fluoride (B.D.H. Reagent Grade; 1.5 g) and $[Cr(NH_3)_5(H_2O)][ClO_4]_3$ (10 g) were dissolved in warm water (60 ml) and heated on a water-bath at *ca.* 60 °C for 30 min in a Polythene beaker. A saturated solution of $NaClO_4$ was added slowly to this solution which was then cooled to 0 °C when red crystals were obtained. The crystals were recrystallized twice from 0.1M-$HClO_4$ by the addition of a saturated solution of $NaClO_4$. Absorption maxima $\lambda_{max.}$ 365 (ε 21) and $\lambda_{max.}$ 505 nm (ε 42.6 l mol^{-1} cm^{-1}) are in satisfactory agreement with literature values; $\lambda_{max.}$ (± 1 nm), ε ($+3\%$).

U.v.–Visible Spectra.—The formato-complex gives $\lambda_{max.}$ 362 (ε 33.7) and 488 nm (52.5 l mol^{-1} cm^{-1}). Similarities in the spectra of penta-amminecarboxylatochromium(III) complexes with regard to peak positions 364 ± 4 and 488 ± 6 nm and absorption coefficients 34 ± 2 and 51 ± 3 l mol^{-1} cm^{-1} respectively are noted. The DMF complex $[Cr(NH_3)_5(OCHNMe_2)]^{3+}$ gives $\lambda_{max.}$ 360 (ε 37.0) and 490 nm (55.4 l mol^{-1} cm^{-1}).

I.r. Spectra.—The spectrum of $[Cr(NH_3)_5\{OCHN(CH_3)_2\}]^{3+}$ shows a band at 1 662 cm^{-1} which can be assigned to ν(C=O). The corresponding band in the free ligand occurs at 1 746 cm^{-1}. This shift of ν(C=O) by 84 cm^{-1} is indicative of (C=O)

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† No reprints available.

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TABLE 1

Reaction products for the aquation of $[Cr(NH_3)_5F]^{2+}$ (*ca.* 6×10^{-3}M) at 50 °C, $I = 1.00$M ($LiClO_4$). Percentages are expressed relative to initial made-up Cr^{III} concentration

$[H^+]$/M	Reaction time (*t*/min)	$[Cr(NH_3)_5(H_2O)]^{3+}$ (%)	$[Cr(NH_3)_4(H_2O)F]^{2+}$ (%)	$[Cr(NH_3)_5F]^{2+}$ [a] (%)
0.01	450	4.74	17.8	79
0.10	420	4.30	12.5	83
0.10	450	4.72	14.6	81
0.20	540	6.80	19.3	74
0.50	540	11.1	23.6	65
0.70	450	8.1	15.5	76
0.98	450	13.6	20.8	65

[a] Unchanged complex.

co-ordination.[8] For $[Cr(NH_3)_5(O_2CH)]^{2+}$ peaks at 1 650 and 1 340 cm^{-1} can be assigned to $\nu_{as}(C{=}O)$ and $\nu_2(C{=}O)$ respectively,[9] and co-ordination of the carboxy group can be inferred.

Aquation Products.—Solutions, $I = 1.0$M ($LiClO_4$), were separated after 7—9 h reaction time using a Dowex 50W-X2 (100—200 mesh) cation-exchange resin column (12 cm × 1 cm diam.) at 0 °C. Solutions were first diluted five-fold with water at 0 °C and then loaded onto the column. Complexes were eluted with 0.1M-$HClO_4$–0.2M-$NaClO_4$ (50—75 ml), 0.1M-$HClO_4$–0.4M-$NaClO_4$ (50—100 ml), and finally 0.1M-$HClO_4$–0.9M-$NaClO_4$. The NH_3 content of the different bands was determined using the micro-Kjeldahl technique.[10] Determination of Cr was carried out spectrophotometrically after it had been oxidized to chromate(VI) with H_2O_2 in NaOH, $\lambda_{max.}$ 372 nm (ε 4.82×10^3 l mol^{-1} cm^{-1}).

RESULTS

Reaction Paths.—The complex $[Cr(NH_3)_5(O_2CH)]^{2+}$ undergoes concurrent reactions as indicated by a shift of the absorption maxima towards longer wavelengths and non-retention of isosbestic points for a run at $[H^+] = 0.1$M and $I = 1.00$M ($LiClO_4$). Ion-exchange separation of products was carried out on a solution $[Cr(NH_3)_5(O_2CH)^{2+}] = 8.3 \times 10^{-3}$ M at $[H^+] = 0.1$M, $I = 1.00$M ($LiClO_4$), after 30 min of reaction at 45 °C. Four chromatographic bands (three orange and one pink) were observed. Two of the orange bands were identified as $[Cr(NH_3)_5(H_2O)]^{3+}$ and unchanged $[Cr(NH_3)_5(O_2CH)]^{2+}$ by their elution characteristics and spectra. Of the remaining products one (orange) complex exhibits 3+ charged elution characteristics and the other (pink) complex 2+ charged behaviour. The analyses for both gave an NH_3 : Cr ratio of 4 : 1 (3.83 : 1.0 in the case of the 3+ species, and 3.92 : 1.0 for the 2+ species). The spectrum of the 3+ species is in satisfactory agreement with the known spectrum of *cis*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$, $\lambda_{max.}$ 366 (ε 26.6) and 495 nm (36.1 l mol^{-1} cm^{-1}).[11] The 2+ pink complex with $\lambda_{max.}$ 375 and 520 nm is most probably $[Cr(NH_3)_4(H_2O)(O_2CH)]^{2+}$. Quantitative estimates at $[H^+] = 1.0 \times 10^{-2}$ M indicate that 21% NH_3 per Cr undergoes aquation in 30 min at 25 °C. No kinetic studies were attempted.

The complex $[Cr(NH_3)_5\{OCHN(CH_3)_2\}]^{3+}$ undergoes aquation giving $[Cr(NH_3)_5(H_2O)]^{3+}$ as the only detectable product at 45 °C, $[H^+] = 0.1$—1.0M, $I = 1.00$M ($LiClO_4$). The final spectrum corresponded with that of $[Cr(NH_3)_5(H_2O)]^{3+}$, and the reaction can therefore be formulated as in equation (1).

More than one product is indicated in the aquation of $[Cr(NH_3)_5F]^{2+}$ by the non-retention of isosbestic points (cross-over point initially at 525 nm). A solution of $[Cr(NH_3)_5F]^{2+}$ (6.0×10^{-3}M) at $[H^+] = 0.1$M, $I = 1.00$M ($LiClO_4$) was thermostatted for 7 h at 50 °C and product

$$[Cr(NH_3)_5\{OCHN(CH_3)_2\}]^{3+} \xrightarrow{k_1} [Cr(NH_3)_5(H_2O)]^{3+} + OCHN(CH_3)_2 \quad (1)$$

separation and analyses were carried out. Three bands (pink, red, and orange) were observed in the ion-exchange column. The pink complex moved faster than unchanged red $[Cr(NH_3)_5F]^{2+}$. The NH_3 : Cr ratio for the pink 2+ species (3.94 : 1.0) is consistent with the formulation $[Cr(NH_3)_4(H_2O)F]^{2+}$. Spectra of the three species are given in Figure 1. Visible scan spectra also indicated that the predominant process is not aquation of F^- at $[H^+] = 0.1$M and 50 °C, because in the region 430—530 nm spectrophotometric changes were in the opposite direction to those expected had the product been solely $[Cr(NH_3)_5(H_2O)]^{3+}$. Therefore the reported polarographic study[5] on the F^- aquation of $[Cr(NH_3)_5F]^{2+}$ does not take into account the process involving loss of NH_3, and reassessment of rate constants for fluoride aquation is required. The reaction paths (and related rate constants) are as indicated in equations (2) and (3). The dependence of reaction products

$$[Cr(NH_3)_5F]^{2+} \xrightarrow{k_2} [Cr(NH_3)_5(H_2O)]^{3+} + F^- \quad (2)$$

$$[Cr(NH_3)_5F]^{2+} \xrightarrow[H^+]{k_3} [Cr(NH_3)_4(H_2O)F]^{2+} + NH_4^+ \quad (3)$$

on $[H^+]$ is indicated in Table 1.

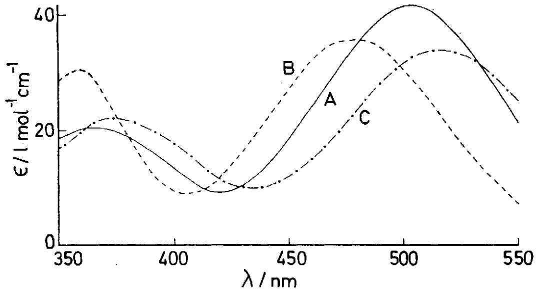

FIGURE 1 U.v.–visible absorption spectra of $[Cr(NH_3)_5F]^{2+}$ (A), $[Cr(NH_3)_5H_2O]^{3+}$ (B), and $[Cr(NH_3)_4(H_2O)F]^{2+}$ (C); $[HClO_4] = 0.1$M, $I = 1.0$M ($LiClO_4$)

Kinetic Studies.—No kinetic studies were attempted for

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the complex $[Cr(NH_3)_5(O_2CH)]^{2+}$ in view of the complexity of the system. Rate constants k_1 for the aquation of the DMF complex are given in Table 2. Activation parameters are $\Delta H^\ddagger = 20.2 \pm 0.5$ kcal mol^{-1} and $\Delta S^\ddagger = 13.5 \pm 1.7$ cal K^{-1} mol^{-1}. Rate constants k_{obs} (Table 3) for the aquation of $[Cr(NH_3)_5F]^{2+}$ were obtained by monitoring absorbance changes at the isosbestic point at 498 nm for $[Cr(NH_3)_5(H_2O)]^{3+}$ and $[Cr(NH_3)_4(H_2O)F]^{2+}$ and correspond to $(k_2 + k_3)$. Plots of log (O.D.$_t$ − O.D.$_\infty$) against time using O.D.$_\infty$ calculated were linear over an extended (two day) period representing at least 72% reaction. By consideration of data in Figures 2 and 3 it is possible to evaluate k_2 and k_3. The linearity of Figure 2 suggests that the [H$^+$] dependence is introduced by the k_2 term, (4).

TABLE 2

Rate constants for the aquation of $[Cr(NH_3)_5(OCHNMe_2)]^{3+}$ (1.82×10^{-3}M except as stated), $\lambda = 260$ nm, $I = 1.00$M ($LiClO_4$)

Temp. (t/°C)	[H$^+$] M	10^4k_1 s^{-1}
40.0	0.10	0.58
	0.99	0.56
45.0	0.10	1.04
	0.99	1.02
50.0	0.02	1.79
	0.10	1.79
	0.99	1.77
	0.99	1.79 [a]
	0.99	1.79 [b]
55.0	0.10	2.66
	0.99	2.50
60.0	0.10	4.34
	0.99	4.34

[a] $[Cr^{III}] = 0.45 \times 10^{-3}$M. [b] $\lambda = 290$ nm.

TABLE 3

Rate constants for the combined aquation processes, (2) and (3), for the complex $[Cr(NH_3)_5F]^{2+}$ at 50 °C, $\lambda = 498$ nm, $I = 1.00$M ($LiClO_4$)

[H$^+$] M	$10^3[Cr^{III}]$ M	10^5k_{obs} s^{-1}
0.010	2.8	1.04
0.050	2.8	1.00
0.10	1.4	1.01
0.15	2.8	1.00
0.20	2.8	1.04
0.30	2.8	1.07
0.50	2.8	1.07
0.70	2.8	1.22
0.80	1.8	1.27
0.90	1.8	1.26
0.99	1.8	1.28

$$k_2 = a + b[H^+] \qquad (4)$$

If this is the case then the dependence in Figure 2 is given by equation (5),

$$\frac{[Cr(NH_3)_5(H_2O)^{3+}]}{[Cr(NH_3)_4(H_2O)F^{2+}]} = \frac{a + b[H^+]}{k_3} \qquad (5)$$

and that in Figure 3 by equation (6).

$$k_{obs} = a + b[H^+] + k_3 \qquad (6)$$

From an unweighted least-squares treatment Figure 2 gives $a/k_3 = 0.28 \pm 0.01$, $b/k_3 = 0.37 \pm 0.01$ l mol^{-1}, and Figure 3 gives $(a + k_3) = (9.8 \pm 0.2) \times 10^{-6}$ s^{-1} and $b = (2.9 \pm 0.3) \times 10^{-6}$ l mol^{-1} s^{-1}. Thus we conclude that $a = 2.1 \times 10^{-6}$ s^{-1}, $b = 2.9 \times 10^{-6}$ l mol^{-1} s^{-1}, and $k_3 = 7.7 \times 10^{-6}$ s^{-1}.

DISCUSSION

Product analyses carried out during the aquation of the fluoro-complex have indicated that aquation of both NH_3 and F^- ligands occurs. The former is dominant over the [H$^+$] range 0.01—1.00M (Table 1). Rate constants previously reported [5] for fluoride aquation therefore require modification. As in other studies involving aquation of fluoride an [H$^+$] dependence is observed indicating the relative ease of aquation of protonated fluoride. Protonation constants for co-ordinated fluoride have not been measured and are believed to be small.

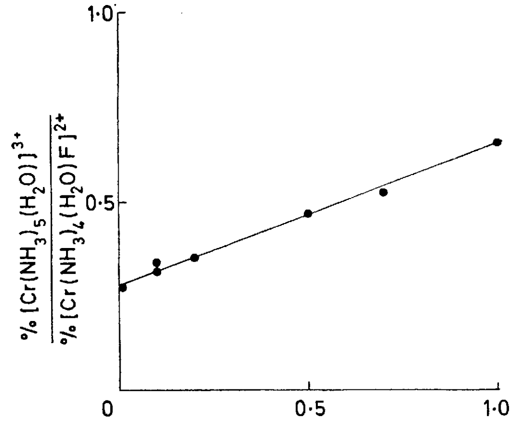

FIGURE 2 The dependence of the product ratio $[Cr(NH_3)_5H_2O]^{3+}/[Cr(NH_3)_4(H_2O)F]^{2+}$ on [H$^+$], for reactions carried out at 50 °C, $I = 1.00$M ($LiClO_4$)

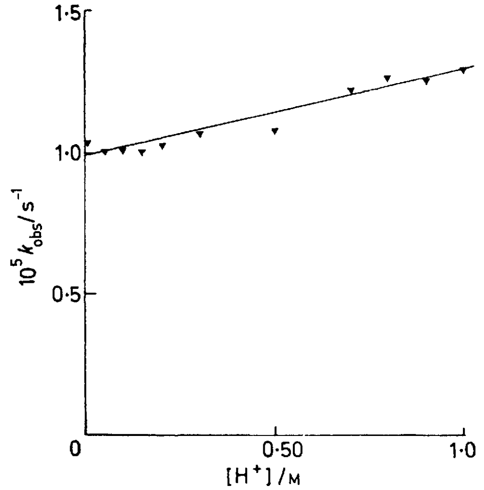

FIGURE 3 Combined rate constants k_{obs} for the aquation of $[Cr(NH_3)_5F]^{2+}$, where two processes are involved, equations (2) and (3). Temperature 50.0 °C, $I = 1.00$M ($LiClO_4$)

With limited data available for neutral ligands it is not possible to assign any definite mechanism for the aquation of $[Cr(NH_3)_5\{OCHN(CH_3)_2\}]^{3+}$. Although it is tempting to consider an I_d mechanism based on other results for the aquation of 1— ligands,[12] other factors (*e.g.* cleavage of the C=O bond) may be relevant. It is interesting to note that $[Cr(NH_3)_5(OCHNMe_2)]^{3+}$ behaves differently from other complexes of the type $[Cr(NH_3)_5X]^{(3-n)+}$ when $X^{n-} = HCO_2^-$, $CH_3CO_2^-$, $CH_2ClCO_2^-$, $CHCl_2CO_2^-$, $HC_2O_4^-$, $^+NH_3CH_2CO_2^-$, SO_4^{2-}, and NO_3^- is bonded *via* oxygen.[2-4] The labilization of *cis*-ammonia has been invoked when $X^{n-} = NO_3^-$, $CH_3CO_2^-$, $CH_2ClCO_2^-$, $CHCl_2CO_2^-$,[2,3] on the grounds that more than an equivalent of NH_3 per Cr is released into solution. Also the complex prepared by treating *cis*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$ with glycine has a spectrum identical to that of the primary product in the aquation of $[Cr(NH_3)_5(O_2CCH_2NH_3)]^{3+}$.[4,13] Furthermore, for one of the reaction paths involving $[Cr(NH_3)_5(O_2CH)]^{2+}$ the product is *cis*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$ and the reaction sequence $[Cr(NH_3)_5(O_2CH)]^{2+} \longrightarrow$ *cis*-$[Cr(NH_3)_4(H_2O)(O_2CH)]^{2+} \longrightarrow$ *cis*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$ is implied. It has been reported that the isomerization of *trans*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$ to *cis*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$ is slow and not detectable.[14] If the product $[Cr(NH_3)_4(H_2O)(O_2CH)]^{2+}$ is a *trans*-isomer and undergoes aquation to give *trans*-$[Cr(NH_3)_4(H_2O)_2]^{3+}$ as the primary product it would certainly have been detected. Normally the aquation reactions of acido-groups in acidoaquotetra-aminechromium(III) complexes are stereoretentive.[15] The above scheme implies that unless stereochemical changes occur during processes involving loss of ammonia from complexes $[Cr(NH_3)_5X]^{(3-n)+}$, the geometric position of the labilized NH_3 is *cis* to the co-ordination oxy-anion, X^{n-}.

The participation of an unbound oxygen in *cis*-labilization can be readily appreciated from the differences in behaviour of $[Cr(NH_3)_5(OCHNMe_2)]^{3+}$ and $[Cr(NH_3)_5X]^{(3-n)+}$ complexes where $X^{n-} = HCO_2^-$, $CH_3CO_2^-$, $CH_2ClCO_2^-$, $CHCl_2CO_2^-$, $^+NH_3CH_2CO_2^-$, SO_4^{2-}, and NO_3^-. The unbound oxygen can assist loss of ammonia either by direct co-ordination to the metal (forming a seven-co-ordinated intermediate),[2,16,17] or by hydrogen bonding to an adjacent NH_3.[3] The original suggestion was that the H-bonding weakened the Cr^{III}–N bond. An alternative view[4] is that such partial transfer of H^+ from NH_3 to the carboxy-group will strengthen the Cr^{III}–N bond of the NH_3 ligand involved, and weaken the Cr^{III}–O bond. Alternatively H-bonding could introduce an intramolecular conjugate-base effect and lead to the loss of another NH_3. Though an H-bonding mechanism could be operative in some cases, the behaviour of $[Cr(NH_3)_5(NO_3)]^{2+}$ is difficult to explain in this way since NO_3^- is only very weakly basic.

The results to date strongly suggest that ligands capable of participating in transient seven-co-ordinate intermediate formation (*e.g.* NO_3^-) are much more effective than ligands which cannot participate in any form of chelation (*e.g.* F^-). The effectiveness of various X^{n-} groups in labilizing ammonia ligands (25 °C, $[H^+] = 0.1$M, 30 min period) is in the order $NO_3^- > CH_3CO_2^- \approx SO_4^{2-} > HCO_2^- > CH_2ClCO_2^- > CHCl_2CO_2^- > {}^+NH_3CH_2CO_2^- > F^-$. Hydroxide is also able to labilize NH_3,[4] as in the conjugate-base mechanism, by a mechanism which is generally presumed to involve π-donation from the ligand to metal, and it is likely that F^- functions in a similar fashion. It is evident from the above that loss of ammonia in the complexes $[Cr(NH_3)_5X]^{(3-n)+}$ is more efficient when seven-co-ordinate intermediate formation can occur. In the case of ammonia loss from $[Cr(NH_3)_5F]^{2+}$ it is not known whether the *cis* or *trans* aquofluoro-product is obtained.

Finally, difficulties experienced in isolating complexes of the type $[Cr(NH_3)_5X]^{(3-n)+}$ because of processes involving loss of ammonia can be overcome in some cases by using non-aqueous solvents, for example methanol.* The observation that the complex $[Cr(NH_3)_5(OCHNMe_2)]^{3+}$ undergoes loss of the DMF in preference to NH_3 opens up the possibility of using DMF as a solvent for the preparation of new penta-ammine complexes.

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* See for example the preparation of $[Cr(NH_3)_5(C_2O_4H)][ClO_4]_2$ in ref. 4.

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