crystal structure of Cs_2PuCl_6.[8,9] It is improbable, but not impossible, that the distortions of the field by the Cs^+ ions, 3.70 Å from the Cl^- ions, could lower the site symmetry sufficiently to split the Γ_3 level by $\sim$5 cm^{-1}. However, the assignment of a Γ_1 ground level to Pu^{4+} in the octahedral $PuCl_6^{2-}$ is preferred as more consistent with crystal structure determinations.

The earlier magnetic susceptibility measurements of Lewis and Elliott[2] on $[(CH_3)_4N]_2PuCl_6$ over the range from 77 to 334°K show a change in slope of a $1/\chi$ *vs.* T graph at about 170°K (120 cm^{-1}). From Table II, $b_4 \approx b_6$ when $E_{\Gamma_1} \approx E_{\Gamma_5}$ and a Γ_4 level would be predicted to be the next higher level. Taking the E_{Γ_4} at 120 cm^{-1}, b_4 is computed as 1.3 cm^{-1}, b_6 = 1.2 cm^{-1}, and the Γ_4 level is calculated to be $\sim$145 cm^{-1} above the ground Γ_1 level.

A total splitting of 145 cm^{-1} for the $^5I_4$ ground state of Pu^{4+} is very small, compared to the ground-state splittings calculated for U^{4+} (2298 cm^{-1})[15] and Np^{4+} (1080 cm^{-1})[16] from the absorption spectra of the analogous Cs_2MCl_6 compounds. However, a crystal field level at $\sim$120 cm^{-1} limits the ground-state splitting to a maximum of $\sim$220 cm^{-1} for Pu^{4+} with a Γ_5 ground level ($b_6 = 0$) and 290 cm^{-1} for a Γ_1 ground level ($b_4 = 0$).

From the b_4, b_6, β, and γ, $A_4\langle r^4\rangle$ and $A_6\langle r^4\rangle$ may be calculated. The $A_n\langle r^n\rangle$ depend only on the environment of the ion in the crystal and should be nearly constant for U^{4+}, Np^{4+}, and Pu^{4+} in analogous compounds. From spectral studies of Cs_2MCl_6, $A_4\langle r^4\rangle$ values of 912 and 540 cm^{-1} are derived for U^{4+} [14] and Np^{4+};[15] $A_6\cdot\langle r^6\rangle = 56$ (U^{4+}) and 150 (Np^{4+}). Neglecting the intermediate coupling corrections to β and γ for Pu^{4+}, $A_4\cdot\langle r^4\rangle = 53$ cm^{-1} and $A_6\langle r^6\rangle = 16$ cm^{-1}, roughly a factor of 10 less than the Np^{4+} values but with nearly the same ratio of fourth- to sixth-order parameters. The agreement between U^{4+} and Np^{4+} parameters is not good, and the Pu^{4+} parameters are certainly wrong. However, intermediate coupling has severe effects on β and γ for Np^{4+} [17] and Pu^{3+} [18] and may also be expected to change β and γ of Pu^{4+} drastically.

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The Mechanisms of Substitution Reactions of Acidopentaaquochromium(III) Complexes

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The use of $(H_2O)_5CrX^{2+}$ at 25.0° in 1.0 *M* HCl produces 22.0, 12.0, and 15.7% $(H_2O)_5CrCl^{2+}$ (corrected for aquation) for X = Br, I, and NO_3, respectively, with small increases in the rate of disappearance of $(H_2O)_5CrX^{2+}$ as compared with the rate in 1.0 *M* $HClO_4$. The volume of activation for the aquation of $(H_2O)_5CrNO_3^{2+}$ in 1.1 *M* $HClO_4$ at 25° is -12.7 ± 1.0 cm^3 mol^{-1} over the pressure range 1–2000 bars, and this is consistent with Cr–O rather than O–N bond breaking. These and other data are best understood in terms of an associative interchange (I_a) mechanism for acid-independent substitution processes in aquochromium(III) complexes, but conjugate-base species such as $Cr(H_2O)_4(OH)X^+$ appear to react by a dissociative interchange (I_d) mechanism.

The mechanism of substitution in complexes of the type $(H_2O)_5Cr^{III}X^{n+}$ remains the subject of controversy.[1-5] Ardon[1] has demonstrated that, when $Cr(H_2O)_5I^{2+}$ is aquated at 30° in the presence of 1.06 *M* chloride ion ($[H^+]$ = 1.00 *M*, *I* = 1.07 *M*), 12.5% of the chromium appears, after about 10 half-periods, as $(H_2O)_5CrCl^{2+}$, with little change in the rate of loss of $(H_2O)_5CrI^{2+}$ as compared with aquation in 1.0 *M* $HClO_4$; this yield of the chloro complex is far in excess of that expected on the basis of anation of the product $Cr(H_2O)_6^{3+}$, and Ardon[1] interpreted these findings in terms of the purely dissociative mechanism (D, or SN1 limiting)[6] of the equations.

$$\mathrm{Cr(H_2O)_5I^{2+}} \overset{\text{slow}}{\rightleftharpoons} \mathrm{Cr(H_2O)_5^{3+} + I^-} \tag{1}$$

$$\mathrm{Cr(H_2O)_5^{3+} + H_2O \longrightarrow Cr(H_2O)_6^{3+}} \tag{2}$$

$$\mathrm{Cr(H_2O)_5^{3+} + Cl^- \longrightarrow Cr(H_2O)_5Cl^{2+}} \tag{3}$$

However, Moore, Basolo, and Pearson[2] subsequently showed that the situation is complicated by the labilization of the aquo group trans to I in $Cr(H_2O)_5I^{2+}$, such that this water molecule undergoes exchange with solvent $H_2{}^{18}O$ about 2.2 times more rapidly than the iodo ligand is replaced (in 1.00 *M* $HClO_4$). The incorporation of Cl^- into a substantial fraction of the reaction products might therefore be interpreted[2] as resulting from the prior formation of some *trans*-$Cr(H_2O)_4ClI^+$, which would decompose to $Cr(H_2O)_5Cl^{2+}$ and I^- sufficiently rapidly to escape detection (eq 4–6, with X = I).

$$\mathrm{Cr(H_2O)_5X^{2+} + Cl^-} \overset{\text{rapid}}{\rightleftharpoons} \{\mathrm{Cr(H_2O)_5X^{2+}, Cl^-}\} \tag{4}$$

$$\{\mathrm{Cr(H_2O)_5X^{2+}, Cl^-}\} \xrightarrow{\text{slow}} trans\text{-}\mathrm{Cr(H_2O)_4ClX^+ + H_2O} \tag{5}$$

$$trans\text{-}\mathrm{ClCr(H_2O)_4X^+ + H_2O} \xrightarrow{\text{rapid}} \mathrm{Cr(H_2O)_5Cl^{2+} + X^-} \tag{6}$$

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[1] M. Ardon, *Inorg. Chem.*, **4**, 372 (1965).

[2] P. Moore, F. Basolo, and R. G. Pearson, *ibid.*, **5**, 223 (1966).

[3] T. W. Swaddle and G. Guastalla, *ibid.*, **7**, 1915 (1968).

[4] J. H. Espenson, *ibid.*, **8**, 1554 (1969).

[5] R. J. Baltisberger and E. L. King, *J. Amer. Chem. Soc.*, **86**, 795 (1964).

[6] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965.

In this interchange scheme, the rate-determining step (eq 5) could involve either predominantly dissociative activation (I_d or S_N1)[6] by the leaving aquo group or a degree of associative activation (I_a or S_N2)[6] by the incoming chloride. The systematics of the substitution kinetics of $(H_2O)_5CrX^{2+}$ species[3,4] suggest that activation requires participation by both the incoming and outgoing ligands (an I_a or S_N2 mechanism[6]), and it has been recognized by Baltisberger and King[5] and by Ardon[1] that the rate of exchange of water between $Cr(H_2O)_6{}^{3+}$ and bulk solvent seems to require that this reaction at least proceeds by an associative mechanism.

We have therefore checked and extended Ardon's experiments to cover X = I, NO_3, and Br. These and the *S*-thiocyanato complex[7] are the only well-characterized $Cr(H_2O)_5X^{2+}$ species which undergo aquation sufficiently more rapidly than the product $Cr(H_2O)_5Cl^{2+}$ and without complications such as protonation of X; the range of X could be extended if NCS^- rather than Cl^- were to be used as the nonbasic anion to be incorporated, but possible linkage isomerism of the thiocyanato ligand could confuse the interpretation. Even so, there is some uncertainty[3] regarding the position of bond breaking (Cr–O or O–N) in the aquation of $(H_2O)_5CrNO_3{}^{2+}$; the obvious approach to this problem, oxygen-18 labeling, presents considerable technical difficulties in this instance, and we have therefore sought an answer indirectly by investigation of the volume of activation ΔV^* of this aquation reaction.

Experimental Section

Bromo-, iodo-, and nitratopentaaquochromium(III) ions were prepared in $HClO_4$ solution as described previously.[8-10]

The absorption spectrum of the bromo complex in 1.0 *M* $HClO_4$ showed maxima at 619 (ϵ 20.3), 430 (ϵ 23.6), and 222 nm (ϵ 8.24×10^3 M^{-1} cm^{-1}). Baker Analyzed $HClO_3$ was used without further purification. Other reagents were Fisher Certified grade. Distilled water was passed through Barnstead ion-exchange and organic-removal cartridges before use.

Kinetic measurements were made spectrophotometrically using a Cary Model 15 spectrophotometer fitted with a jacketed cell which was thermostated (25.00 ± 0.03°) with circulating water from an external Colora bath. The temperature of the cell was monitored with a calibrated Atkins Technical thermistor thermometer. The disappearance of $(H_2O)_5CrBr^{2+}$ was followed using the 222-nm absorption maximum, at which wavelength the molar absorbancy index of $Cr(H_2O)_6{}^{3+}$ is small and that of $(H_2O)_5CrCl^{2+}$ is 1.78×10^3 M^{-1} cm^{-1}; since $(H_2O)_5CrCl^{2+}$ was only a minor reaction product when $(H_2O)_5CrBr^{2+}$ was decomposed in 1.0 *M* HCl and aquated 17 times more slowly than $(H_2O)_5CrBr^{2+}$ under these conditions, the optical density at 222 nm became sensibly constant after about 8 half-periods of the aquation of $(H_2O)_5CrBr^{2+}$. The kinetics of iodo and nitrato complexes were studied as described previously.[8,10] All kinetic measurements were duplicated within 0.5%.

The extent of $(H_2O)_5CrCl^{2+}$ formation when $(H_2O)_5CrX^{2+}$ complexes (X = Br, I, NO_3) were aquated in the presence of chloride ion was determined by cation-exchange chromatography. Solutions were prepared from stock $(H_2O)_5CrX^{2+}$ solutions in $HClO_4$, ailquots of which were mixed with appropriate quantities of HCl and NaCl to give the desired $[H^+]$, $[Cl^-]$, and ionic strength. The initial $(H_2O)_5CrX^{2+}$ content of each reaction mixture was determined with the exclusion of $Cr(H_2O)_6{}^{3+}$ and other forms of Cr(III) by dilution of an aliquot to about 0.1 *M* in H^+, absorption of the cations on a column of Dowex 50W-X8, and elution of $(H_2O)_5CrX^{2+}$ with 1.0 *M* $HClO_4$. All operations utilizing the ion-exchange column were carried out at 0° in a jacketed column maintained at 0° with circulating ice water. Hence, any reactions occurring in the process of absorption and elution can be assumed to be negligible. The $(H_2O)_5CrX^{2+}$ content of the eluate was determined spectrophotometrically as $CrO_4{}^{2-}$ (ϵ 4.82×10^3 M^{-1} cm^{-1} at 372 nm) after oxidation with alkaline hydrogen peroxide. The total content of dipositive Cr(III) species ($CrCl^{2+}$ and residual CrX^{2+}) of these solutions after aquation for 8–9 half-lives of $(H_2O)_5CrX^{2+}$ in the presence of 1.0 *M* Cl^- at 25.0° was determined in the same way; the $(H_2O)_5CrCl^{2+}$ was clearly discernible as a green band during elution. The yield of dipositive Cr(III) species was corrected for residual $(H_2O)_5CrX^{2+}$, either on the basis of the known half-life of this species or by direct measurement of the residual dipositive Cr(III) in control experiments using $HClO_4$ in place of HCl and NaCl.

The aquation of $(H_2O)_5CrNO_3{}^{2+}$ under pressure was studied by withdrawing samples of the solution through a narrow-bore tantalum tube from a 100-ml syringe which was pressurized with Esso Diol N-35 oil in a thermostated (25.00 ± 0.01°) pressure vessel (Autoclave Engineers, Inc., Erie, Pa.) and analyzing for $(H_2O)_5CrNO_3{}^{2+}$ spectrophotometrically at 260 nm.[10] Constant pressure (±10 bars) was maintained in the pressure vessel by an air-driven automatic pump (American Instrument Co., Silver Springs, Md.) which was actuated by a microswitch attached to a 40-cm Heise Bourdon gauge. The sampling device was essentially the same as that described by Osborn and Whalley.[11] The solution in the syringe was left for 1 hr after pressurization before the first sample was withdrawn, so as to ensure full thermal equilibration. Good first-order aquation kinetics were obtained, the correlation coefficient for 10 data points in a least-squares fit being typically of the order of 0.999.

Results

The data of the first row of Table I are the yields of $(H_2O)_5CrCl^{2+}$ obtained when $(H_2O)_5CrX^{2+}$ was aquated for 8–9 half-lives in the presence of 1.00 *M* chloride ion at 25.0° and are corrected for residual $(H_2O)_5CrX^{2+}$. These data represent the percentage yields of $(H_2O)_5CrCl^{2+}$ based on the amount of $(H_2O)_5CrX^{2+}$ present initially and they are the means of several determinations which agreed within ±0.2% of the total available chromium or approximately 1.5% of the eluted chromium. Variation of the initial $(H_2O)_5CrX^{2+}$ concentration over the range 0.13–0.61 m*M* had no significant effect on the data. The yield of $Cr(H_2O)_5Cl^{2+}$ at 25° agrees excellently with Ardon's[1] figure for 30° of 12.5%, if this is adjusted proportionately for Ardon's greater concentration of chloride (1.06 *M*); thus, temperature is not an important factor in these experiments.

TABLE I

PRODUCTS OF AQUATION OF $(H_2O)_5CrX^{2+}$ AFTER 8–9 HALF-PERIODS IN THE PRESENCE OF 1.00 *M* CHLORIDE ION[a]

	X			
	Br	I	NO_3	SCN
% Cr recovered as $(H_2O)_5CrCl^{2+}$	16.3 ± 0.3	11.8 ± 0.2	15.3 ± 0.1	4.3[b]
% $(H_2O)_5CrCl^{2+}$, corrected for loss by aquation	22.0	12.0	15.7	4.4
% aquation directly to $Cr(H_2O)_6{}^{3+}$	63.2	62.5	82.8	77.7
% conjugate-base hydrolysis to $Cr(H_2O)_6{}^{3+}$	14.8	25.5	1.5	17.9
(% $CrCl^{2+}$)/(% direct to Cr^{3+}))	0.35	0.19	0.19	0.057

[a] $[H^+] = [Cl^-] = 1.00 \pm 0.01$ *M*; $I = 1.05$–1.09 *M*; $[CrX^{2+}]_0 = (1.3$–$6.1) \times 10^{-4}$ *M*. [b] From the data of Haim and Sutin,[7] with proportional adjustment for difference in chloride concentrations; percentage of $(H_2O)_5CrCl^{2+}$ calculated with the exclusion of the isomerization pathway yielding $(H_2O)_5CrNCS^{2+}$. Haim and Sutin[7] did not report error limits on their yield of $(H_2O)_5CrCl^{2+}$.

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[7] A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 434 (1966).

[8] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965).

[9] F. A. Guthrie and E. L. King, *ibid.*, **3**, 916 (1964).

[10] T. W. Swaddle, *J. Amer. Chem. Soc.*, **89**, 4338 (1967).

[11] A. L. Osborn and E. Whalley, *Can. J. Chem.*, **39**, 1094 (1961).

Correction of the data of the first row of Table I for aquation of $(H_2O)_5CrCl^{2+}$ in the time span of these experiments can be done using eq 7 with the appropriate first-order aquation rate coefficients k_x (see Table II) and k_{Cl} (3.5×10^{-7} sec^{-1}, by extrapolation of the data of ref 8).

TABLE II

FIRST-ORDER RATE COEFFICIENTS k_x FOR THE AQUATION OF $Cr(H_2O)_5X^{2+}$ AT 25.00°

X	$[H^+]$,[a] *M*	$[Cl^-]$,[b] *M*	*I*, *M*	10^6k_x, sec^{-1}
Br	1.00	0.0	1.08	5.14
	1.00	1.00	1.08	5.86
I[c]	1.01	0.0	1.09	110.1
NO_3	1.00	0.0	1.08	73.5
	1.01	1.00	1.07	78.5

[a] Balance of cations, Li^+ and Cr species. [b] Balance of anions, ClO_4^-. [c] The kinetic effect of added Cl^- at 30° has been fully investigated by Ardon.[1]

$$(\%\ CrCl^{2+}{}_{cor}) = (\%\ CrCl^{2+}{}_{obsd})(k_x - k_{Cl})/k_x(e^{-k_{Cl}t} - e^{-k_xt}) \quad (7)$$

The corrected yields of $(H_2O)_5CrCl^{2+}$ given in the second row of Table I were calculated with the simplifying assumption that the anation of $Cr(H_2O)_6^{3+}$ by Cl^- could be ignored; this is not strictly true, since the formation constant of $(H_2O)_5CrCl^{2+}$ is about 0.11 M^{-1} (extrapolated to the conditions of these experiments[3]), but the error so introduced is small and does not affect the qualitative significance of the data. The rate of anation of $Cr(H_2O)_6^{3+}$ by Cl^- ($k_{an} = 3.0 \times 10^{-8}$ M^{-1} sec^{-1} at 25.0° when $I = [H^+] = 1.0$ *M*)[4] is sufficiently low that less than 3% $(H_2O)_5CrCl^{2+}$ could be produced from $(H_2O)_6Cr^{3+}$ even in the longest of these experiments.

Ardon[1] showed that the incorporation of halide occurred through the acid-independent aquation path only, in $Cr(H_2O)_5I^{2+}$—*i.e.*, the conjugate-base hydrolysis pathway *via* $Cr(H_2O)_4(OH)I^+$ gives only $Cr(H_2O)_6^{3+}$ and I^-. The same presumably holds true for the other $Cr(H_2O)_5X^{2+}$ considered here, but for these the conjugate-base pathway is less important than it is for $Cr(H_2O)_5I^{2+}$, and we have therefore omitted experimental verification of this assumption. We have divided up the yields of $Cr(H_2O)_6^{3+}$ into fractions produced by acid-independent ("direct") aquation (third row of Table I) and fractions originating from the conjugate-base mechanism (fourth row of Table I), on the basis of the published kinetic data relating to these pathways.[7-10,12] The fifth row of Table I presents the fractions of $Cr(H_2O)_5X^{2+}$ decomposition going by the path leading to $Cr(H_2O)_5Cl^{2+}$ relative to the direct aquation path (from rows 2 and 3 of the same table).

The pressure dependence of the rate of aquation of $Cr(H_2O)_5NO_3^{2+}$ at 25.00° in 1.1 *M* $HClO_4$ is illustrated by the data of Table III. The logarithms of the first-order rate coefficients *k* are essentially a linear function of the pressure, *i.e.*, $-1 \times 10^{-3} < (\partial \Delta V^*/\partial P)_T < +1 \times 10^{-3}$ cm^3 mol^{-1}, and we calculate $\Delta V^* = -12.7 \pm 1.0$ cm^3 mol^{-1}.

TABLE III

PRESSURE DEPENDENCE OF THE FIRST-ORDER RATE COEFFICIENT FOR THE AQUATION OF $Cr(H_2O)_5NO_3^{2+}$ AT 25.00° IN 1.1 *M* $HClO_4$

Pressure, kbars	10^5k, sec^{-1}	Pressure, kbars	10^5k, sec^{-1}
0.020	6.82	1.520	14.9
0.456	8.05	2.026	18.5
0.963	10.5		

Discussion

The data of the last row of Table I are evidence against the production of a common, discrete, five-coordinate intermediate, $Cr(H_2O)_5^{3+}$ (eq 1), in the aquation of $Cr(H_2O)_5X^{2+}$ (X = Br, I, NO_3, SCN), because such a purely dissociative (D) mechanism would require that the yield of $Cr(H_2O)_5Cl^{2+}$ by reaction 2, relative to $Cr(H_2O)_6^{3+}$ by reaction 3, be independent of the nature of X. The approximate equality of the relative yields of $Cr(H_2O)_5Cl^{2+}$ when X = I and NO_3 is almost certainly coincidental, in view of the disparity of the data for X = Br and SCN.

On the other hand, if the trans-activation mechanism of eq 4–6 is to explain the chloride-incorporation data for X = NO_3, Br, and SCN, as well as I, we would have to conclude that the trans-activating power of NO_3 is roughly equal to that of I, since the rate coefficients *k* of acid-independent aquation ($10^5k_0 = 7.2$ and 8.4 sec^{-1} at 25.0° for X = NO_3 and I, respectively[8,10,12]) and the relative yields of $Cr(H_2O)_5Cl^{2+}$ are similar. We have been unable[10] to prepare a solid salt (*e.g.*, sulfate) of $Cr(H_2O)_5NO_3^{2+}$ and so cannot obtain an estimate of any trans effect which the NO_3 ligand might exert in this complex, but there is no evidence in the literature[13,14] to suggest that the nitrato ligand is a trans activator comparable with iodide. Baldwin and Bracken[15] found that the order of trans-activating power of X in $Cr(H_2O)_5X^{2+}$ increases in the order $H_2O < NCS < Cl \ll I$, which suggests that in these complexes, as in Co(III) species, the trans-effect sequence follows the nephelauxetic series $F < O \leq N < Cl < C \sim Br < S \sim Se \sim I$;[14] if this is the case, then the trans-activating power of NO_3 will be negligible. This conclusion is reinforced by the observation[16] that, in the absence of π-bonding effects (which are unlikely to be operative in these complexes), the magnitude of the trans effect in octahedral complexes is inversely related to the σ-orbital ionization potential of the activating ligand; since iodide ion is easily oxidized while nitrate is emphatically not, nitrate is unlikely to have a significant trans effect.

By the same reasoning, the *S*-thiocyanato ligand can be expected to have a trans effect comparable with that of I, yet chloride incorporation in the aquation of $(H_2O)_5CrSCN^{2+}$ is relatively slight, despite a slower aquation rate ($k_0 = 4.0 \times 10^{-5}$ sec^{-1} at 25°, *cf.* $k_0 = 8.4 \times 10^{-5}$ for the iodo complex[8]) which would allow more time for a reaction analogous to eq 5 to occur in place of aquation. This time factor could explain the extraordinarily high yield of $Cr(H_2O)_5Cl^{2+}$ obtained in the aquation of $Cr(H_2O)_5Br^{2+}$, which is sufficiently slow[5] ($k_0 = 3.9 \times 10^{-6}$ sec^{-1}) that even the cis aquo ligands could be involved in a reaction similar to eq 5; Baldwin and Bracken[15] have shown that the rate coefficient for the exchange of the cis aquo groups with solvent water is $(2.9 \pm 0.1) \times 10^{-6}$ sec^{-1} for several $Cr(H_2O)_5X^{2+}$ (X = Cl, Br, I, NCS). However, if this

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(12) M. Ardon and N. Sutin, *Inorg. Chem.*, **6**, 2268 (1967).

(13) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962).

(14) J. M. Pratt and R. G. Thorp, *Advan. Inorg. Chem. Radiochem.*, **12**, 375 (1969).

(15) H. W. Baldwin and D. E. Bracken, Chemical Institute of Canada, 50th Canadian Chemical Conference and Exhibition, Toronto, Canada, June 1967, and private correspondence.

(16) R. Mason and A. D. C. Towl, *J. Chem. Soc. A*, 1601 (1970).

cis aquo exchange rate coefficient is valid for all $Cr(H_2O)_5X^{2+}$, cis activation can be discounted as an explanation for chloride incorporation when X = I, NO_3, and SCN.

These difficulties can be avoided, while retaining the hypothesis of a fundamentally similar substitution mechanism for these $Cr(H_2O)_5X^{2+}$ species, if it is assumed that an associative interchange (I_a) mechanism is operating, *i.e.*, that the incoming group (Cl or H_2O) forms a partial bond to the Cr center before the bond to departing ligand X is fully broken. The wide range in relative yields of $Cr(H_2O)_5Cl^{2+}$ in the above experiments is not easily accommodated by supposing that it reflects only the range of formation constants of purely electrostatic ion pairs $\{Cr(H_2O)_5X^{2+}, Cl^-\}$ which undergo dissociative interchange to give first $\{Cr(H_2O)_5{}^{3+}, X^-, Cl^-\}$ and then the chloro, aquo, or X^- complex. The efficiency of Cl^- relative to H_2O in scavenging a transient $Cr(H_2O)_5{}^{3+}$ species would be constant and independent of the scavenging efficiencies of the various X^-, so that the dependence of the relative yield of $Cr(H_2O)_5Cl^{2+}$ upon the nature of X^- cannot be explained in terms of events occurring in an I_d process after the Cr–X bond is broken.

Similarly, Espenson's tabulation[4] of rate coefficients for the anation of $Cr(H_2O)_6{}^{3+}$ by X^{n-} shows a spread of about 10^3-fold, whereas the range for similar anation rates of $Co(NH_3)_5OH_2{}^{3+}$ (for which an extreme I_d mechanism seems assured[6,17–19]) is about a factor of 2;[19] so that an I_d mechanism is possible for the Cr(III) series only if $Cr(H_2O)_6{}^{3+}$ is extraordinarily selective in its ion pairing. In an I_a mechanism, the entering and departing groups both influence the progress of the reaction by electronic interaction through the central metal atom. While trans activation by the departing ligand can obviously be an important influence in an I_a mechanism, it need not be a prerequisite for, *e.g.*, chloride ion incorporation.

No firm conclusions can be drawn regarding the slightly greater rates of disappearance of $(H_2O)_5CrX^{2+}$ in HCl as compared with $HClO_4$, because of the likelihood of medium effects on the reaction rate,[2] but it may be significant that the higher the yield of $(H_2O)_5CrCl^{2+}$, the larger the increase in the rate of loss of $(H_2O)_5CrX^{2+}$, so that chloride incorporation appears to occur in addition to, rather than instead of, normal aquation. This is as expected for an I_a mechanism but could also be accounted for by an I_d process if Cr–X bond fission is facilitated somewhat by ion pairing.

The assignment of an I_a mechanism to substitution in aquochromium(III) complexes and I_d to the analogous reactions of cobalt(III) ammines is in accordance with the predictions made by Spees, *et al.*,[20] on the basis of ligand field theory and explains why direct incorporation of anions into the reaction product is observed in aquation of $Cr(H_2O)_5X^{2+}$ but not in the analogous reactions of $Co(NH_3)_5X^{2+}$ (which give initially only the aquo complex[21]). The calculations of Spees, *et al.*,[20] also serve to explain why the activation energies for the two series of reactions are closely similar (about 25 kcal mol^{-1}), despite the greater ligand field stabilization energy associated with Co(III) ($t_{2g}{}^6$) as compared with Cr(III) ($t_{2g}{}^3$). However it is recognized that changes in solvation will also be a major factor in determining ΔH^*, as will the spherical component (as opposed to the ligand field component) of ΔH^*, since high-spin iron(III) complexes commonly have ΔH^* values around 15 kcal mol^{-1}.

Direct aquation of $Cr(H_2O)_5X^{2+}$ (rate coefficient k_0) is usually accompanied, even in 1 *M* acid, by hydrolysis *via* a pathway with inverse hydrogen ion dependence (rate coefficient k_{-1}), *i.e.*, *via* the conjugate base species $Cr(H_2O)_4(OH)X^+$. Espenson's compilation of data[4] shows that anation rates for $Cr(H_2O)_5OH^{2+}$ span a much smaller range (*ca.* 17-fold, for nonbasic ligands) than do those for $Cr(H_2O)_6{}^{3+}$ (*ca.* 10^3-fold), which suggests that the mechanism of conjugate-base hydrolysis is much closer to I_d than I_a. An alternative but fundamentally similar approach involves plotting the logarithms of k_{-1} against the logarithm of the equilibrium constants for the completed reactions using data from the literature;[3,8–10,12,22] the resulting linear free energy relationship,[2,6] though rough, has a slope greater than 0.9, in accordance with an I_d mechanism.

This explains Ardon's observation[1] that chloride incorporation in the aquation of $(H_2O)_5CrX^{2+}$ occurs *via* the (associative) acid-independent pathway only. It also provides a rationale for the decline in the importance of the conjugate-base pathway, relative to direct aquation, as we move up the spectrochemical series in $(H_2O)_5CrX^{2+}$ (Table IV); Spees, *et al.*,[20] have shown that, for Cr(III), purely dissociative mechanisms will have higher ligand field contributions to their activation energies than will associative processes, so that the essentially dissociative conjugate-base mechanism will compete more effectively with associatively activated direct aquation at the lower ligand field strengths (as measured by the wave number ν_1 of the lowest spin-allowed ligand field transition in the spectrum of $Cr(H_2O)_5X^{2+}$). The anomaly of $Cr(H_2O)_5N_3{}^{2+}$ in Table IV serves to support our contention[23] that the acid-independent aquation of this species proceeds with, in effect, the separation of HN_3 from $Cr(H_2O)_nOH^{2+}$, rather than N_3^- from $Cr(H_2O)_{n+1}{}^{3+}$; this mechanism is unlikely to operate in the conjugate-base pathway, so that the latter path is eclipsed by the former. Table IV also provides an explanation for the failure to observe conjugate-base pathways in the aquation of $Cr(H_2O)_5F^{2+}$ (which probably aquates

TABLE IV

THE RELATIVE IMPORTANCE OF AQUATION (k_0) AND CONJUGATE-BASE HYDROLYSIS (k_{-1}) AS A FUNCTION OF THE WAVE NUMBER ($\bar{\nu}_1$) OF THE FIRST LIGAND FIELD TRANSITION FOR $Cr(H_2O)_5X^{2+}$

X	$10^{-4}\bar{\nu}_1$, cm^{-1}	k_0/k_{-1}, *M*	X	$10^{-4}\bar{\nu}_1$, cm^{-1}	k_0/k_{-1}, *M*
I[a]	1.539	2.45	N_3[d]	1.709	1.0×10^3
SCN[b]	1.613	4.3	NO_3[e,f]	1.733	55
Br[c]	1.616	4.3	NCS[g]	1.739	7.8×10^2
Cl[a]	1.642	9.8	H_2O[e]	1.739	. . .
F[a]	1.681	. . .			

[a] Reference 8. [b] Reference 7. [c] Reference 9 and this work. [d] Reference 23. [e] Reference 10. [f] Reference 12. [g] Reference 22.

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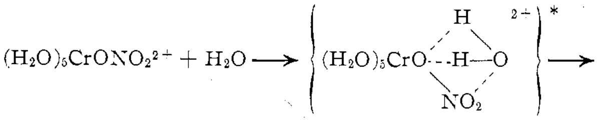
with HF separation[8]) and in the exchange of $Cr(H_2O)_6^{3+}$ with oxygen-18-labeled solvent,[24] in solutions containing about 0.1 *M* acid.

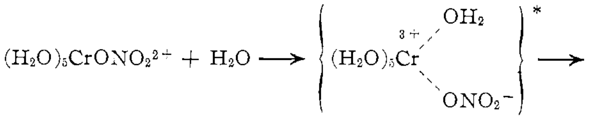
In the above discussion it has been assumed that the mechanism of aquation of $Cr(H_2O)_5NO_3^{2+}$ is the same as for the other $Cr(H_2O)_5X^{2+}$, but the possibility of O–N rather than Cr–O bond breaking must be considered.[3] The measured volume of activation ΔV^* for the aquation of $Cr(H_2O)_5NO_3^{2+}$ can be expressed as the sum of an intrinsic part ΔV_1^* which will be positive if bond-breaking predominates and negative if bond making is the more important and an "electrostrictive" part ΔV_2^* which will be positive if desolvation occurs in the transition state through dissipation of charge density and negative if extra charge is developed in going to the transition state. Four schematic mechanisms can be considered (eq 8–11), representing, respectively, SN1 at N, I_d (SN1) at Cr, SN2 at N, and I_a (SN2) at Cr.

$$(H_2O)_5CrONO_2^{2+} \longrightarrow (H_2O)_5CrO^+ + NO_2^+ \xrightarrow[\text{rapid}]{H_2O}$$
$$(H_2O)_6Cr^{3+} + NO_3^- \quad (\Delta V_1^* \text{ positive, } \Delta V_2^* \text{ positive}) \quad (8)$$

$$(H_2O)_5CrONO_2^{2+} \longrightarrow (H_2O)_5Cr^{3+} + NO_3^- \xrightarrow[\text{rapid}]{H_2O}$$
$$(H_2O)_6Cr^{3+} + NO_3^- \quad (\Delta V_1^* \text{ positive, } \Delta V_2^* \text{ negative}) \quad (9)$$



$$(H_2O)_5CrONO_2^{2+} + H_2O \longrightarrow \left\{ \begin{array}{c} H \\ (H_2O)_5CrO\text{- -}H\text{—}O \\ NO_2 \end{array} \right\}^{2+\,*} \longrightarrow$$
$$(H_2O)_6Cr^{3+} + NO_3^- \quad (\Delta V_1^* \text{ negative, } \Delta V_2^* \text{ positive}) \quad (10)$$



$$(H_2O)_5CrONO_2^{2+} + H_2O \longrightarrow \left\{ (H_2O)_5Cr^{3+} \begin{array}{l} \cdots OH_2 \\ \\ \cdots ONO_2^- \end{array} \right\}^{*} \longrightarrow$$
$$(H_2O)_6Cr^{3+} + NO_3^- \quad (\Delta V_1^* \text{ negative, } \Delta V_2^* \text{ negative}) \quad (11)$$

The observed value of ΔV^* is approximately -13 cm^3 mol^{-1} (Table III), and hence mechanism 8 is obviously eliminated. $|\Delta V_1^*|$ is of the order of 2 cm^3 mol^{-1} in $Co(NH_3)_5X^{n+}$ aquations[18] but $|\Delta V_2^*|$ is much larger. Also the activation volume found[18] for the aquation of $Co(NH_3)_5NO_3^{2+}$, which proceeds by an extreme I_d mechanism with Co–O bond fission,[25] is about 7 cm^3 mol^{-1} less negative (*i.e.*, -6 cm^3 mol^{-1}) than for $Cr(H_2O)_5NO_3^{2+}$. Hence mechanism 11 is to be preferred over 9 or 10, *i.e.*, it is the Co–O bond which is broken, and associative activation by the incoming water molecule is probably important.

The possibility remains that the nitratochromium(II) complex contains bidentate NO_3^- and that reversible ring opening precedes the rate-determining step in aquation. This could explain the deviations of this complex in linear free energy relationships[3] and perhaps account for the chloride-incorporation phenomenon described above. However, such ring-opening and -closing processes have not been investigated but they would have to be very rapid (half-periods of the order of 1 min or less), since they have not been detected by conventional kinetic methods,[10,12] and such rapid reactions are not characteristic of Cr(III) complexes. Anomalies in supposed linear free energy relationships can be ascribed to differences in the relative importance of bond making *vis à vis* bond breaking; there seems to be no reason why these factors should be exactly the same throughout a given series of reactions, and indeed it is probably unreasonable to expect linear free energy relationships to be strictly valid except when their slopes are near unity, *i.e.*, for I_d mechanisms.

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Conversion of Hexaammineruthenium(III) to Sulfamatopentaammineruthenium(III) by Attack on Coordinated Ammonia

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When oxygen is passed through a solution containing $Ru(NH_3)_6^{3+}$ and $S_2O_3^{2-}$ or SPO_3^{3-}, $Ru(NH_3)_5NHSO_3^+$ is produced in good yield. Comparison of the infrared spectra of salts containing this ion or its protonated form with sulfamate complexes of cobalt(III) ammines which are known to be N bonded confirms that the new species are N bonded as well. The value of pK_a for $Ru(NH_3)_5NH_2SO_3^{2+}$ at 25° and $\mu = 0.10$ was measured as 2.6. It is believed that the sulfamate is produced by the transfer of sulfur to coordinated amide, with subsequent oxidation by O_2.

Introduction

Sulfamato complexes have been prepared by the direct reaction of sulfamate with a metal ion.[1-3] While pursuing our interest in the interaction of sulfur ligands with ruthenium ammines, we observed the formation of a sulfamate complex by a novel route. Thiosulfate or thiophosphate in the presence of O_2 and $Ru(NH_3)_6^{3+}$ converts the latter in good yield to

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