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Aquation of Chromium(III) Ammines in Aqueous Perchlorate Solutions

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The kinetics of aquation of $Cr(NH_3)_6{}^{3+}$, $Cr(NH_3)_5OH_2{}^{3+}$, *trans*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$, *cis*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$, *mer*-$Cr(NH_3)_3(OH_2)_3{}^{3+}$, "*trans*"-$Cr(NH_3)_2(OH_2)_4{}^{3+}$, and $CrNH_3(OH_2)_5{}^{3+}$ have been examined in acidic 1.0 M perchlorate solutions. In 1.0 M $HClO_4$ at 75.0°, the first-order rate coefficients for the loss of the first ammine ligands are respectively (sec^{-1}, $\times 10^5$) 7.8, 7.7, 7.5, 5.0, 2.6, 0.71, and 0.11; for the first four species and the last, $\Delta H^* = 24.6$, 24.6, 25.0, 26.7, and 30.3 kcal mol^{-1}, and the corresponding ΔS^* values are −6.9, −7.0, −5.9, −1.8, and +1.0 cal deg^{-1} mol^{-1}. The corresponding rates reported by Bjerrum and Jorgensen (*Acta Chem. Scand.*, **12**, 1047 (1958)) for acidic nitrate media are all markedly faster, except for the hexaammine, and this is interpreted in terms of cis activation of the NH_3 ligands by coordinated nitrate. Isomerization in perchlorate solution is unimportant compared with aquation, which is stereoretentive. Approximate kinetic data for the base hydrolyses of the tetraammines are also reported.

Introduction

In a recent preliminary communication,[1] we reported that nitrate coordinated to chromium(III) activates ammine ligands in the cis positions toward aquation and that this effect results in the acceleration of loss of coordinated NH_3 from chromium(III) aquoammines in nitrate media, relative to perchlorate solutions, apparently because nitrate can complex Cr(III) significantly while perchlorate does so only very slightly, if at all. The only systematic study of the stepwise aquation of the chromium(III) ammines reported to date is that of Bjerrum and Jorgensen,[2,3] who used nitrate media exclusively; accordingly, it is necessary to reexamine the products, rates, and steric course of these aquations in perchlorate media.

We report here the rates and steric courses of the aquations in 1.0 M perchlorate solutions of $Cr(NH_3)_6{}^{3+}$, $Cr(NH_3)_5OH_2{}^{3+}$, *cis*- and *trans*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$, and $CrNH_3(OH_2)_5{}^{3+}$ in some detail and, in outline, the aquations of *mer*-$Cr(NH_3)_3(OH_2)_3{}^{3+}$ and "*trans*"-$Cr(NH_3)_2(OH_2)_4{}^{3+}$. A full study of the properties of the lower ammines has been postponed because of uncertainties surrounding the identities and isomeric purities of various preparations of the triammines and diammines (see below and ref 4).

Experimental Section

Materials. Reagent grade perchloric acid (72%, "Baker Analyzed"), sodium perchlorate (Anachemia Chemicals), and sodium hydroxide were used without further purification. Distilled water was passed through Barnstead deionizer and organic removal cartridges before use. The purity of each of the solid ammine salts, prepared as described below, was established by microanalysis for nitrogen, and their visible absorption spectra in 1.0 M $HClO_4$ were found to be in agreement with published data.[4]

$[Cr(NH_3)_6](ClO_4)_3$ was prepared as previously described;[5] the visible spectrum showed maxima at λ_{max} 462 nm (molar absorbancy index ϵ 40.0 M^{-1} cm^{-1}) and 350 nm (ϵ 33.0 M^{-1} cm^{-1}). *Anal.* Calcd for $[Cr(NH_3)_6](ClO_4)_3$: N, 18.6. Found: N, 18.7.

$[Cr(NH_3)_5OH_2](ClO_4)_3$ was made by treatment of aqueous $[Cr(NH_3)_5OH_2](NO_3)_3 \cdot NH_4NO_3$[6] with perchloric acid and was recrystallized from very dilute $HClO_4$; λ_{max} 476 (ϵ 35.5) and 358 nm (30.7 M^{-1} cm^{-1}). *Anal.* Calcd for $[Cr(NH_3)_5OH_2](ClO_4)_3$: N, 15.5. Found: N, 15.5.

cis-$[Cr(NH_3)_4(OH_2)_2](ClO_4)_3 \cdot 0.5H_2O$ was obtained from *cis*-$[Cr(NH_3)_4Cl(OH_2)]Cl_2$[7] and was recrystallized from the minimum amount of water at ambient temperature by addition of 72% $HClO_4$, followed by cooling to 0°; λ_{max} 493 (ϵ 36.9) and 366 nm (ϵ 28.5 M^{-1} cm^{-1}); λ_{min} 417 nm (ϵ 8.6 M^{-1} cm^{-1}). *Anal.* Calcd for $[Cr(NH_3)_4(OH_2)_2](ClO_4)_3 \cdot 0.5H_2O$: N, 12.1. Found: N, 12.1.

trans-$[Cr(NH_3)_4(OH_2)_2](ClO_4)_3 \cdot 0.5H_2O$ was made from $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5$ by the method of Hoppenjans and Hunt;[7] λ_{max} 472 (ϵ 22.7) and 368 nm (ϵ 32.7 M^{-1} cm^{-1}); λ_{min} 415 nm (ϵ 11.5 M^{-1} cm^{-1}). The first band is broad and irregularly shaped and probably represents the sum of two regular bands with maxima near 470 and 520 nm, the mean of which wavelengths corresponds to the peak of the first absorption band of the cis isomer. *Anal.* Calcd for $[Cr(NH_3)_4(OH_2)_2](ClO_4)_3 \cdot 0.5H_2O$: N, 12.1. Found: N, 12.1.

Aqueous *mer*-$Cr(NH_3)_3(OH_2)_3{}^{3+}$ was made by heating a solution of 0.200 g of *trans*-$[Cr(NH_3)_4(OH_2)_2](ClO_4)_3$ in 20 ml of 0.1 M $HClO_4$ at 75° for 10.5 hr (about 4 half-lives for the aquation of the first NH_3 from the latter complex). The solution was cooled to room temperature and passed through a column (30 cm long × 1 cm in diameter) of Dowex 50W-X4 cation-exchange resin (200–400 mesh, H^+ form). Elution with 1 M $HClO_4$ at a rate of 2 ml min^{-1} produced four distinct bands, which were identified spectroscopically: (1) a small quantity of $CrNH_3(H_2O)_5{}^{3+}$; (2) a mixture of $Cr(NH_3)_2(OH_2)_4{}^{3+}$ isomers; (3) the desired *mer*-$Cr(NH_3)_3(OH_2)_3{}^{3+}$ (2.5×10^{-3} M); (4) unchanged *trans*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$. The spectrum of the third fraction agreed with that of the apparently authentic, pure *mer*-triammine, obtained by different methods:[4,8] λ_{max} 507 (ϵ 26.6) and 373 nm (ϵ 25.6 M^{-1} cm^{-1}); λ_{min} 431 nm (ϵ 8.1 M^{-1} cm^{-1}).

"*trans*"-$Cr(NH_3)_2(OH_2)_4{}^{3+}$ was obtained as a 9×10^{-3} M solution in 3 M $HClO_4$ by House's method;[9] λ_{max} 520 (ϵ 20.8) and 382 nm (ϵ 18.5 M^{-1} cm^{-1}); λ_{min} 440 nm (ϵ 6.0 M^{-1} cm^{-1}).

Aqueous $CrNH_3(OH_2)_5{}^{3+}$ (0.01–0.02 M) was made by oxidation of aqueous chromium(II) with hydrazoic acid in the presence of chloride[10] and was purified by elution from Dowex 50W-X8 with 3 M $HClO_4$; λ_{max} 544 (ϵ 20.4) and 394 nm (ϵ 19.0 M^{-1} cm^{-1}); λ_{min} 460 nm (ϵ 4.9 M^{-1} cm^{-1}).

All preparations were stored in the dark until needed, the solids in desiccators over P_2O_5, and the solutions in sealed flasks at 0°.

Warning! Chromium(III) ammine perchlorates, in solid form or in solution in concentrated $HClO_4$, present a potential explosion hazard, though no such mishap occurred in the conduct of the work described here.

Procedures. The chromium contents of the various solutions were estimated spectrophotometrically as $CrO_4{}^{2-}$, after oxidation with alkaline H_2O_2.[11]

The ion-exchange chromatographic separations described below were each carried out at 20° (except as stated) with new resin which had been washed with the appropriate eluent until the eluate was spectroscopically clean in the visible region. In no case was a chromium(III) ammine observed to decompose significantly on the resin

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in the course of ion-exchange chromatography; nevertheless, fractions eluted with 1.5 *M* NaOH were acidified with $HClO_4$ immediately on leaving the column, to obviate possible decomposition of the hydroxoammines. The various aquation products so isolated were characterized by their visible absorption spectra in aqueous $HClO_4$.

All spectroscopic measurements were made using a Cary Model 15 spectrophotometer.

Kinetics. All aquations were carried out with the exclusion of light, over durations of 2 half-lives or more.

The aquation of $Cr(NH_3)_6^{3+}$ was followed using 0.004–0.010 *M* solutions, containing $HClO_4$ and $NaClO_4$ such that $[H^+] = 0.1\text{–}1.0$ *M* at ionic strength $I = 1.0$ *M*, in sealed vessels which were immersed in the thermostat (±0.03°). Samples (20 ml) were withdrawn periodically, cooled to 20°, and treated with 10 *M* NaOH and solid $NaClO_4$ until the solution became 1.0 *M* in OH^- and 3.0 *M* in ClO_4^-; under these conditions, $[Cr(NH_3)_6](ClO_4)_3$ was precipitated quantitatively, while the various hydroxoammines remained in solution. The precipitate was recovered with a fine filter, redissolved in 20.0 ml of water, and the $Cr(NH_3)_6^{3+}$ content was measured by its visible spectrum. The linear plot of log $[Cr(NH_3)_6^{3+}]$ *vs.* time gave the first-order rate coefficient $k_{6\rightarrow5}$ for the disappearance of $Cr(NH_3)_6^{3+}$ in the reaction mixture.

The aquation of $Cr(NH_3)_5OH_2^{3+}$ (0.005–0.010 *M*, with $[H^+] =$ 0.1–1.0 *M* at $I = 1.0$ *M*) was followed by separating the aquation products from the unreacted pentaammine by ion-exchange chromatography under alkaline conditions, so utilizing the charge differences between $Cr(NH_3)_5OH^{2+}$, $Cr(NH_3)_4(OH)_2^+$, and so on, to effect clean separations of the ammine species. Aliquots of the acidic reaction mixture from the thermostat were chilled to 0°, rendered alkaline with 10 *M* NaOH, and passed through Dowex 50W-X2 resin (50–100 mesh, Na^+ form, prewashed with 2 *M* NaOH) in jacketed columns at 0°. Elution with 0.1 *M* NaOH released species presumed to be $Cr(NH_3)_3(OH)_3^0$, while 1.5 *M* NaOH eluted $Cr(NH_3)_4(OH)_2^+$; $Cr(NH_3)_5OH^{2+}$ remained on the resin. The eluted Cr was determined spectrophotometrically[11] as CrO_4^{2-}, and the concentration of unreacted $Cr(NH_3)_5OH_2^{3+}$ in the original sample was then calculated by difference and used to compute the rate coefficient $k_{5\rightarrow4}$ for the disappearance of $Cr(NH_3)_5OH_2^{3+}$.

The aquation rates of *cis*- and *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$ were measured as described for $Cr(NH_3)_5OH_2^{3+}$, except that the concentrations of $Cr(NH_3)_4(OH_2)_2^{3+}$ were calculated in duplicate (directly from the Cr content of the 1.5 *M* NaOH fraction and indirectly from that of the 0.1 *M* NaOH eluate) with excellent agreement. From these data, the rate coefficients $k_{4c\rightarrow3}$ and $k_{4t\rightarrow3}$ for the disappearance of the *cis*- and *trans*-tetraammines were calculated.

The aquation of *mer*-$Cr(NH_3)_3(OH_2)_3^{3+}$ was carried out using the stock solution directly ($[H^+] = I = 1.0$ *M*) or diluted with an equal volume of 1 *M* $NaClO_4$ ($[H^+] = 0.5$ *M*). Aliquots (25 ml) were passed directly through Dowex 50W-X2 resin (H^+ form, 50–100 mesh, 25 cm × 1-cm diameter column) at 20° and eluted with about 500 ml of 1.0 *M* $HClO_4$ at a rate of 2 ml min^{-1} to achieve separation on the resin of the various tripositive species present. The topmost band on each column (unreacted *mer*-$Cr(NH_3)_3(OH_2)_3^{3+}$) was removed mechanically and reeluted separately with 3 *M* $HClO_4$. The Cr contents of these fractions were estimated spectrophotometrically[11] as CrO_4^{2-} and used to calculate the first-order rate coefficient $k_{3m\rightarrow2}$ for disappearance of the meridional triammine.

The rate coefficient $k_{2t\rightarrow1}$ for the disappearance of $Cr(NH_3)_2(OH_2)_4^{3+}$ (presumed trans isomer) was obtained as described for the *mer*-triammine.

The rate of aquation (first-order coefficient $k_{1\rightarrow0}$) of $CrNH_3(OH_2)_5^{3+}$ was so slow that samples were aquated at 100–110° in sealed Pyrex ampoules, and the progress of the reaction was followed from the changing visible spectrum of the solutions, measured at 20°. The product was $Cr(H_2O)_6^{3+}$, and good isosbestic points were maintained at 419, 456, and 592 nm.

The decompositions of *cis*- and *trans*-$Cr(NH_3)_4(OH)_2^+$ in NaOH–$NaClO_4$ ($I = 0.5$ *M*, $[OH^-] = 0.05\text{–}0.5$ *M*) were followed by recording (at 20°) the progressive spectral changes in aliquots taken from reaction vessels in the thermostat.

Results

Characterization of Aquation Products. (1) Aquation of $Cr(NH_3)_6^{3+}$. After 5 hr at 75.0°, a solution (100 ml) of hexaamminechromium(III) perchlorate (0.0100 *M*) and $HClO_4$ (1.0 *M*) precipitated the unchanged hexaammine perchlorate (26%) on cooling to 0°, and addition of 20 ml of 72% $HClO_4$ at 0° brought down $[Cr(NH_3)_5OH_2](ClO_4)_3$ (40%). The solution phase was made alkaline ($[OH^-] \approx 0.5$ *M*) and was chromatographed at 0° on Dowex 50W-X2 (Na^+ form) as described above for the aquation kinetics of $Cr(NH_3)_5OH_2^{3+}$, to yield on acidification $Cr(NH_3)_4(OH_2)_2^{3+}$ (15%, mainly the cis isomer) and $Cr(NH_3)_3(OH_2)_3^{3+}$ (15%). Thus, the rate coefficients $k_{6\rightarrow5}$, $k_{5\rightarrow4}$, and $k_{4\rightarrow3}$ are of comparable magnitude in perchloric acid solution at 75°.

(2) Aquation of $Cr(NH_3)_5OH_2^{3+}$. This was carried out as described for $Cr(NH_3)_6^{3+}$ and gave $Cr(NH_3)_3(OH_2)_3^{3+}$ and lower ammines (29%), $Cr(NH_3)_4(OH_2)_2^{3+}$ (43%), and unchanged pentaammine (28%). The relative amounts of *cis*- and *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$ were calculated from the absorption spectrum of the mixture in the region 480–520 nm in acidic solution, using the relation

$$\%\ \text{cis} = \frac{\epsilon_{\text{app}} - \epsilon_{\text{trans}}}{\epsilon_{\text{cis}} - \epsilon_{\text{trans}}} \times 100 \qquad (1)$$

and amounted to 77 ± 3% cis and 23 ± 3% trans in the whole tetraammine fraction. The trans isomer content was slightly higher in the first portions of the tetraammine fraction to leave the column and lower in the last, so that *trans*-$Cr(NH_3)_4(OH)_2^+$ is more easily eluted by alkali than the cis isomer, there being no evidence for isomerization on the resin.

(3) Aquation of *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$. In an experiment like that just described, the triammine product (see Experimental Section) gave spectra essentially identical with those reported[4] for the meridional isomer prepared by different procedures. Thus, if these characterizations[4] of the meridional isomer are correct (see under the aquation of *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$, below), the aquation of the *trans*-tetraammine is stereoretentive and is much faster than cis-trans or fac-mer isomerization. The latter conclusion is reinforced by the observation that, when *trans*-$[Cr(NH_3)_4(OH_2)_2](ClO_4)_3$ (200 mg) was aquated for 2.6 hr at 75.0° in 20 ml of 1.0 *M* $HClO_4$ and chromatographed on Dowex 50W-X4 (H^+ form, 200–400 mesh) using 1.0 *M* $HClO_4$ as eluent, the products (identified spectroscopically) were pure unchanged *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$ (50%), pure *mer*-$Cr(NH_3)_3(OH_2)_3^{3+}$ (43%), and a fraction (7%) having the same spectrum as the aquation products of *mer*-$Cr(NH_3)_3(OH_2)_3^{3+}$; thus, neither the *trans*-tetraammine nor the *mer*-triammine had undergone detectable isomerization even though aquation was proceeding apace. Finally, when the spectroscopic changes accompanying the aquation of *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$ during its first half-life were examined directly, the optical absorption at 482 nm was seen to remain constant, whereas a marked increase would have accompanied any significant trans → cis isomerization.

(4) Aquation of *mer*-$Cr(NH_3)_3(OH_2)_3^{3+}$. A solution of *mer*-$Cr(NH_3)_3(OH_2)_3^{3+}$ (2.54×10^{-3} *M*, 50 ml) in 1.0 *M* $HClO_4$ was heated at 75.0° for 6 hr and chromatographed on Dowex 50W-X4 (H^+ form) as described for the *trans*-tetraammine. Three species separated on elution with 1.0 *M* $HClO_4$: (a) $CrNH_3(OH_2)_5^{3+}$, (b) a diammine fraction with spectral maxima at 523 (ϵ 23.8) and 385 nm (ϵ 20.4 M^{-1} cm^{-1}) and a minimum at 442 nm (ϵ 6.6 M^{-1} cm^{-1}); (c) unchanged *mer*-$Cr(NH_3)_3(OH_2)_3^{3+}$ (which again indicates that the mer isomer does not isomerize under these conditions).

(5) Aquation of "*trans*"-$Cr(NH_3)_2(OH_2)_4^{3+}$. An aliquot of the stock solution (see Experimental Section) was maintained at 75.0° for 24 hr and then cooled to room temperature and chromatographed on Dowex 50W-X4 (200–400 mesh, H^+ form). Only two bands were separated, these being $CrNH_3(OH_2)_5^{3+}$ (47%) and seemingly unchanged "*trans*"-$Cr(NH_3)_2(OH_2)_4^{3+}$.

(6) **Aquation of *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$.** The perchlorate salt of the *cis*-tetraammine (200 mg) was aquated at 75.0° in 20 ml of 1.0 *M* $HClO_4$ for 18.8 hr, and the products were chromatographed on Dowex 50W-X4 (200-400 mesh, H^+ form) with 1.0 *M* $HClO_4$ as eluent, as described for the *trans*-tetraammine. Four bands were isolated: (a) a small amount of $CrNH_3(OH_2)_5^{3+}$, (b) a diammine having absorption maxima at 523 (ϵ 28.7) and 383 nm (ϵ 23.4 M^{-1} cm^{-1}) (fractions (a) and (b) represent 42% of the available Cr), (c) a triammine having absorption maxima at 511 (ϵ 39.0) and 374 nm (ϵ 28.0 M^{-1} cm^{-1}) and a minimum at 428 nm (ϵ 8.5 M^{-1} cm^{-1}) (42%), and (d) unchanged *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$. The last item indicates that *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$ does not isomerize appreciably on the time scale of the aquation reactions, a conclusion which is supported by the observation that the spectrum of aquating *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$ tends continuously toward that of the aquation products and not that of *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$.

The spectrum of the triammine of fraction (c) resembles that reported by Schaffer and Andersen[12] for the presumed facial isomer, although the ratio of the height of the longer wavelength absorption peak to that at the shorter wavelength is 1.39 in our product and 1.55 in theirs. The wavelengths of these maxima are not greatly different in the supposed fac and mer isomers, and so, if we take the peak height ratio for the meridional isomer to be 1.02, an adaptation of eq 1 indicates that our product contained about 70% *fac*- and 30% *mer*-$Cr(NH_3)_3(OH_2)_3^{3+}$. The absolute values of ϵ are less reliable than the peak height ratios for this purpose, but, no matter how the isomeric distribution is estimated, it appears that the fac isomer is predominant, and furthermore the differences between the spectra of the triammine products from *cis*- and *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$ leave no doubt that they contain different amounts of the fac and mer isomers. However, there is considerable disagreement in the literature[4] as to the spectrum of the fac isomer; our results suggest that the data of Schaffer and Andersen[12] are the most reliable, but the triammine isomer distribution percentages given above should be regarded as crude estimates at best.

There was no change in the spectra of successive portions of fraction (b) as the elution progressed, which could mean that it contained a single isomer, but the close similarities among the peak height ratios of fraction (b), the diammine product of the aquation of *mer*-$Cr(NH_3)_3(OH_2)_3^{3+}$ (above), and the supposed "*trans*"-diammine prepared from the Reineckate ion suggest that the spectra of the *cis*- and *trans*-diammines may be too closely similar to permit distinction between them on this basis. An alternative explanation, that the aquations of the higher ammines and the oxidation of the Reineckate ion all lead to the same mixture of diammine isomers, seems highly improbable; nor is it likely (on the basis of our experience with the higher ammines) that the diammines undergo isomerization rapidly on the time scale of our experiments. Inconsistencies between the various published spectral data for the diammines,[3,4,9,12-14] including our own, serve to emphasize the need for improved characterization of these diammines (and also the triammines).

Kinetics. The aquation rates were accurately first order in the original complexes over at least 2 half-lives, and the corresponding rate coefficients collected in Table I are precise to ±2%. There is no significant dependence of rates upon acidity in the range $[H^+] = 0.1\text{-}1.0\,M$.

Because some of the ion-exchange separations required the use of strongly alkaline conditions, some rough, direct spectrophotometric measurements were made on the base hydrolysis of *cis*- and *trans*-$Cr(NH_3)_4(OH)_2^+$. The spectrum of the pure cis species in 0.5 *M* NaOH showed maxima at 383 (ϵ 39.5) and 527 nm (ϵ 39.5 M^{-1} cm^{-1}), with a minimum at 453 nm (ϵ 18.7 M^{-1} cm^{-1}); the corresponding data for the trans isomer are 403 (30.3), 522 (29.3), and 456 (15.2), and, for the green final solutions (presumably $Cr(OH)_4^-$), 423 (29.4), 584 (26.8), and 500 nm (10.0 M^{-1} cm^{-1}). Isosbestic points were not quite strictly maintained in the course of the base hydrolyses, but the largest decrease in absorption for the trans complex (at 520 nm) occurred according to first-order kinetics, within the experimental error, and precluded any significant trans → cis isomerization, which would have resulted in an obvious rise in the absorption.

The first-order rate coefficients for base hydrolysis (Table II) showed no dependence on $[OH^-]$ over the range 0.05-0.50 *M*. Extrapolation of these data to 0° indicated that the half-lives of *cis*- and *trans*-$Cr(NH_3)_4(OH)_2^+$ under the conditions of our ion-exchange experiments would be 72 and 143 hr, respectively, which are much longer than the time scale of the elutions (~0.5 hr); data[15] on the base hydrolysis of $Cr(NH_3)_5OH^{2+}$ indicate an even longer half-life (~10^4 hr) for this species in strongly alkaline solutions at 0°. The rates of ammonia loss from *cis*- and *trans*-$Cr(NH_3)_4(OH)_2^+$ are some 10^3 times greater than from the corresponding aquo species because ΔS^* is much more positive for the hydroxo compounds. The relative reactivities of the cis and trans isomers are reversed.

Discussion

The ion-exchange techniques described above yield rate data (Table I) for the disappearance of several of the individual species produced in the stepwise aquation of $Cr(NH_3)_6^{3+}$ in 1.0 *M* acidic perchlorate media and also reveal the steric courses of these reactions in cases where the spectral properties of the products are known with sufficient certainty. Thus, $Cr(NH_3)_5OH_2^{3+}$ aquates to yield ~20% *trans*- and ~80% *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$; the trans isomer may actually be formed initially in rather greater relative amount than this, since it aquates a little faster than the cis, but the isomeric ratio is close to that expected statistically if all the ammine ligands were equivalent.

If the reported spectra[4] of *mer*-$Cr(NH_3)_3(OH_2)_3^{3+}$ are truly representative of this species (as seems likely), then the first aquation of the *trans*-tetraammine yields the mer product exclusively and is therefore stereoretentive. The *cis*-tetraammine must therefore yield at least some *fac*-triammine, since the triammine spectrum is not that accepted for the mer form, and indeed one would expect 50% facial and 50% meridional isomers in the aquation of the *cis*-tetraammine if this were stereoretentive and if all the ammine ligands were equivalent. In fact, the *fac*-triammine seems to predominate, which may mean that NH_3 exerts a noticeable trans-activating effect relative to H_2O.

The kinetic data of Table I show that the loss of an ammine ligand occurs with equal ease from $Cr(NH_3)_6^{3+}$, $Cr(NH_3)_5OH_2^{3+}$, and *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$; this means that a slight activation of the ammines occurs when one and then two aquo groups are introduced, since the rate coefficients

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Table I. First-Order Rate Coefficients k and Activation Parameters for the Replacement of One NH_3 by H_2O in $Cr(NH_3)_n(OH_2)_{6-n}^{3+}$ in $HClO_4$–$NaClO_4$ Solutions of Ionic Strength 1.0 *M*

Complex	$[H^+]$, *M*	Temp, °C	[Cr], *M*	10^5k, sec^{-1}	ΔH^*,[a] kcal mol^{-1}	ΔS^*,[b] cal deg^{-1} mol^{-1}
$Cr(NH_3)_6^{3+}$	1.0	75.0	0.010	7.8	24.6	−6.9
	0.1	75.0	0.004	7.7		
	1.0	65.0	0.004	2.84		
	1.0	55.0	0.004	0.84		
$Cr(NH_3)_5OH_2^{3+}$	1.0	75.0	0.005	7.7	24.6	−7.0
	0.1	75.0	0.010	7.8		
	1.0	65.0	0.010	2.62		
	1.0	55.0	0.010	0.83		
trans-$Cr(NH_3)_4(OH_2)_2^{3+}$	1.0	75.0	0.010	7.5	25.0	−5.9
	0.1	74.8	0.005	7.6		
	1.0	65.1	0.010	2.46		
	1.0	55.1	0.010	0.79		
cis-$Cr(NH_3)_4(OH_2)_2^{3+}$	1.0	75.1	0.010	5.0	26.7	−1.8
	0.1	75.1	0.005	5.1		
	1.0	65.1	0.010	1.67		
	1.0	55.2	0.010	0.46		
mer-$Cr(NH_3)_3(OH_2)_3^{3+}$	1.0	75.0	0.0025	2.60		
	0.5	75.0	0.0013	2.54		
"*trans*"-$Cr(NH_3)_2(OH_2)_4^{3+}$	1.0	75.0	0.0029	0.71		
	0.5	75.0	0.0010	0.73		
$CrNH_3(OH_2)_5^{3+}$	1.0	110.6	0.0013	7.3	30.3	+1.0
	0.3	109.8	0.0004	6.3		
	1.0	99.8	0.0013	2.19		
	1.0	75.0		0.11[c]		

[a] Uncertainty ±0.3 kcal mol^{-1}, except for monoammine (±0.7). [b] Uncertainty ±1.0 cal deg^{-1} mol^{-1}, except for monoammine (±2.0). [c] Extrapolated value.

Table II. First-Order Rate Coefficients for the Decomposition of *cis*- and *trans*-$Cr(NH_3)_4(OH)_2^+$ in NaOH-$NaClO_4$ Solution of Ionic Strength 0.5 *M*[a]

Temp, °C	$[OH^-]$, *M*	10^3k,[b] sec^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1} mol^{-1}
		Cis Isomer		
60.9	0.05	14.1	24.6 ± 0.5	6.2 ± 1.5
61.4	0.5	13.9		
51.3	0.5	3.9		
40.9	0.5	1.16		
40.1	0.5	1.03		
		Trans Isomer		
61.3	0.05	9.6	25.6 ± 0.5	8.5 ± 1.5
61.4	0.5	9.5		
51.5	0.5	2.62		
40.4	0.5	0.68		

[a] [Complex] = 3.0 × 10^{-3} *M*. [b] ±3%.

of Table I are not statistically corrected for the number of available ammonias. The *cis*-tetraammine, however, is markedly less reactive than the trans form, which again suggests that the NH_3 ligands possess some degree of trans-labilizing power relative to H_2O. From *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$ to $CrNH_3(OH_2)_5^{3+}$, a decrease in reactivity is increasingly apparent, which may once again be attributed, at least in part, to the progressive loss of trans pairs of ammonias.

The decrease in rate coefficients as we descend Table I originates in an increase in the activation enthalpy ΔH^*. However, this is offset partially by a concomitant increase in ΔS^*, a phenomenon which is frequently attributable to solvation effects. The relatively low ΔS^* values recorded for the higher ammines may reflect the comparatively low degree of solvation of ammines *vis a vis* aquo complexes in the initial state,[16] which would be increased in the transition state when an aquo group is introduced to replace an NH_3. ΔS^* is about the same for the aquation of the monoammine as for aquo exchange[16] in $Cr(H_2O)_6^{3+}$ and $Cr(NH_3)_5OH_2^{3+}$.

Table III. Rate Coefficients $k_{n\rightarrow(n-1)}$ (sec^{-1}) for the Aquation of $Cr(NH_3)_n(OH_2)_{6-n}^{3+}$ in Nitrate and Perchlorate Media at 40°

	>0.1 *M* HNO_3[a]	1.0 *M* $HClO_4$[b]	(*k* in HNO_3)/(*k* in $HClO_4$)
$k_{6\rightarrow5}$	1.4 × 10^{-6}	1.4 × 10^{-6}	1
$k_{5\rightarrow4}$	2.5 × 10^{-5}	1.3 × 10^{-6}	19
$k_{4c\rightarrow3}$	2.8 × 10^{-5}	6.1 × 10^{-7}	46
$k_{4t\rightarrow3}$	~2.8 × 10^{-4}	1.2 × 10^{-6}	233
$k_{1\rightarrow0}$	2.5 × 10^{-6}	7.6 × 10^{-9}	330

[a] Reference 3. [b] This work.

The rate coefficient $k_{5\rightarrow4}$ for the aquation of the pentaammine is clearly the sum of two components, one ($k_{5\rightarrow4c} \approx 6 \times 10^{-5}$ sec^{-1} at 75°) giving rise to the *cis*-tetraammine and the other ($k_{5\rightarrow4t} \approx 1.5 \times 10^{-5}$ sec^{-1}) to the trans isomer. Similarly, for the aquation of *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$ at 75°, we can make the provisional crude estimates of $k_{4c\rightarrow3f} \approx 3.5 \times 10^{-5}$ sec^{-1} and $k_{4c\rightarrow3m} \approx 1.5 \times 10^{-5}$ sec^{-1} for the production of the *fac*- and *mer*-triammines, respectively.

The coefficient $k_{4t\rightarrow3}$ apparently represents $k_{4t\rightarrow3m}$ exactly, but $k_{3m\rightarrow2}$ is likely to be the sum of the unresolved components $k_{3m\rightarrow2t}$ and $k_{3m\rightarrow2c}$, with the latter presumably predominating for both statistical and "trans-activational" reasons, if these reactions are again stereoretentive. Thus, we may expect that the main product of aquation of the meridional triammine is the *cis*-diammine, despite the apparent spectroscopic resemblance to the supposed "*trans*"-diammine prepared as described above. The data we quote for the latter species should therefore be regarded with due circumspection.

The most striking feature of our results is the contrast with the data obtained by Jorgensen and Bjerrum[3] using nitrate media at 40°, which are summarized in Table III along with extrapolations to 40° of our rate data obtained

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(16) T. W. Swaddle and D. R. Stranks, *J. Amer. Chem. Soc.*, **94**, 8357 (1972).

in 1.0 *M* $HClO_4$. It will be seen that aquations of all the listed species *except the hexaammine* are markedly accelerated in nitrate media; thus, we may conclude that this effect originates in replacement of an aquo ligand by nitrate, rather than in ion-pair formation or some medium effect, and that the coordinated nitrate activates an ammine group cis to it as described previously.[1] As would be expected on this basis, the effect becomes more important as the number of available aquo groups increases and as the rates of the uncatalyzed aquations decrease.

Espenson and Carlyle[17] have also noted a marked nitrate catalysis of the aquation of $CrNH_3(OH_2)_5{}^{3+}$. Our extrapolated rate data for this reaction at 45° in 1.0 *M* $HClO_4$ are slower than their stated upper limits (allowing for medium effects) by a factor of up to 3, but close agreement is not expected since our extrapolation is a large one and also because Espenson and Carlyle studied only the first few per cent of reaction.

Nitrate catalysis is more effective in the aquation of *trans*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$ than in the cis isomer, by a factor of 5.1. This may explain why Jorgensen and Bjerrum[3] concluded that the stepwise aquation of $Cr(NH_3)_6{}^{3+}$ in nitrate media proceeds mainly *via* the *trans*-tetraammine, whereas our data indicate that, in perchlorate solutions, aquation proceeds predominantly *via cis*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$. If the cis-activating properties of the nitrato ligand operated by a purely electronic mechanism such as that suggested for halo ligands,[18] we might expect the nitrate effect to be greater in the *trans*-tetraammine relative to the cis by a purely statistical factor of 1.33. The much larger observed factor is more easily rationalized on the basis of an associative bidentate ring closure of coordinated nitrate,[1,19] since, in the cis complex, the tendency of a coordinated nitrato group to chelate can be mostly easily accommodated by displacement of the relatively reactive remaining aquo ligand cis to it, without NH_3 loss, but in the trans complex, ring closure by coordinated nitrate must necessarily occur at the expense of the ammine ligands.

Catalysis of the decomposition of $Cr(NH_3)_5OH_2{}^{3+}$ at 45° by 1.5 *M* $NaNO_3$ or Na_2SO_4 has been noted by Duffy and Earley,[20] whose optical absorbance data (Figure 1 of ref 20) actually suggest the formation of a sulfato complex prior to ammine loss. Presumably, bound sulfate can activate the ligands cis to it in much the same way as nitrate, and it is significant that we have so far been unable to isolate $Cr(NH_3)_5SO_4{}^+$, either as solid salts or as the unique Cr-containing species in a solution.[21]

Complete information on the steric course of the aquations of chromium(III) aquoammines must await unambiguous syntheses and characterizations of the *fac*-triammine and the diammines, but our results indicate that the aquations are stereoretentive and that isomerization is negligibly slow compared with aquation. Since $H_2{}^{18}O$ exchange between aquochromium(III) complexes and bulk solvent is evidently fast compared with ammine replacement (*e.g.*, aquo exchange is more than 300 times faster than aquation for $Cr(NH_3)_5OH_2{}^{3+}$ in dilute $HClO_4$ at 40°),[16,20] it follows that aquo exchange is also completely stereoretentive.

This is consistent with our contention[22] that simple substitution processes in chromium(III) ammines occur by an associative (I_a or SN2) attack on Cr at the flank of the ligand being displaced. Isomerization of Cr(III) complexes can then be expected to occur only by some intramolecular "twist" mechanism[23] or, in chelates, by ring opening followed by reclosure at a new site. Significantly, the only reported cases of isomerization of chromium(III)-amine complexes concern chelates in which isomerization and amine loss are competitive,[8] so that twist mechanisms probably do not operate in these species. We may note that the mercury(II)-catalyzed hydrolysis of *trans*-$Cr(en)(tmd)Cl_2{}^+$ yields *cis*-$Cr(en)(tmd)(OH_2)_2{}^{3+}$,[24] but such "induced" hydrolyses of chromium(III) species appear to be essentially dissociatively activated,[25] in contrast to "spontaneous" aquations.[22] For cobalt(III)-amine complexes such as *trans*-$Co(en)(tmd)Cl_2{}^+$,[24] extensive stereochemical change is frequently encountered even in spontaneous aquation, and this is attributable to the prevalence of dissociative activation at Co(III) centers.

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Registry No. $Cr(NH_3)_6{}^{3+}$, 14695-96-6; $Cr(NH_3)_5OH_2{}^{3+}$, 15975-47-0; *trans*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$, 36834-73-8; *cis*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$, 42402-01-7; *mer*-$Cr(NH_3)_3(OH_2)_3{}^{3+}$, 23774-35-8; *trans*-$Cr(NH_3)_2(OH_2)_4{}^{3+}$, 22941-62-4; $CrNH_3(OH_2)_5{}^{3+}$, 42402-03-9.

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(19) A similar mechanism, involving coordinated carbonate, has been suggested by J. E. Earley, D. J. Surd, L. Crone, and D. Quane, *Chem. Commun.*, 1401 (1970), to explain CO_2 catalysis of replacement of NH_3 by EDTA in $Cr(NH_3)_5OH^{2+}$.

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(21) J. A. Duffy and W. J. D. Macdonald, *J. Chem. Soc. A*, 2066 (1970), have found that $Cr(NH_3)_5OH_2{}^{3+}$ can be recovered essentially unchanged after as much as 3 days in 100% H_2SO_4 at 40°; but here the anion concerned is $HSO_4{}^-$, which is analogous to $ClO_4{}^-$ and is a poor complexing agent accordingly, and in any event the sulfuric acid solvent system is scarcely comparable with water.

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