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Stoichiometry and Kinetics of the Aquation Reactions of Some Halotetraamminechromium(III) Complexes[1a]

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The stoichiometry and kinetics of the aquation reactions of *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, *trans*-$Cr(NH_3)_4Cl_2^+$, *trans*-$Cr(NH_3)_4BrCl^+$, and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ in $HClO_4$ solutions have been investigated. The replacement of the halide ligands by H_2O occurs with essentially complete retention of configuration. The first step in the aquation of *trans*-$Cr(NH_3)_4BrCl^+$ is the loss of Br^-. First-order rate constants for the aquation reactions in 1.0 *M* $HClO_4$ and activation energies are: $k = (1.8 \pm 0.1) \times 10^{-4}$ sec^{-1} at $70.0 \pm 0.1°$, $E_a = 24 \pm 1$ kcal mol^{-1} for *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$; $k = (9.4 \pm 0.2) \times 10^{-4}$ sec^{-1} at $70.0 \pm 0.1°$, $E_a = 22.0 \pm 0.5$ kcal mol^{-1} for *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$; $k = (2.7 \pm 0.1) \times 10^{-3}$ sec^{-1} at $45.0 \pm 0.1°$, $E_a = 20.8 \pm 0.3$ kcal mol^{-1} for *trans*-$Cr(NH_3)_4BrCl^+$; and $k = (4.8 \pm 0.1) \times 10^{-4}$ sec^{-1} at $45.0 \pm 0.1°$, $E_a = 21.6 \pm 0.3$ kcal mol^{-1} for *trans*-$Cr(NH_3)_4Cl_2^+$. The aquation rates are independent of acidity over the range $[H^+] = 0.1$–1.0 *M*, except for *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, for which the aquation rate is about 50% more rapid at $[H^+] = 0.1$ *M* than at $[H^+] = 1.0$ *M*.

Introduction

The aquation reactions of the halobis(ethylenediamine)chromium(III) complexes have been studied extensively by Garner and coworkers,[2-4] but the analogous ammonia complexes have received almost no attention. A possible reason for this is that syntheses of many of the halotetraammine complexes, particularly the *trans* complexes, have never been reported. We have found that many of the missing complexes occur as products of the acid cleavage of binuclear complexes, such as $(NH_3)_5Cr(OH)Cr(NH_3)_4Cl^{4+}$. Further, we have found it necessary to study the aquation reactions of the monomeric tetraammine complexes in order to understand the cleavage reactions of the binuclear complexes. In this paper we report the results of an investigation of the aquation reactions of the *trans*-dichloro-, *trans*-chloroaquo-, *trans*-bromochloro-, and *cis*-chloroaquotetraamminechromium(III) ions.

Experimental Section

Materials.—To prepare *trans*-$[(NH_3)_4Cr(OH_2)Cl](ClO_4)_2 \cdot n$-$H_2O$, *trans*-$[(NH_3)_4Cr(OH_2)Cl]Cl_2$, prepared by the method of Hoppenjans, Hunt, and DeChant,[5] was triturated carefully with 70% $HClO_4$ to expel the ionic chloride as HCl gas. The perchlorate was recrystallized from a nearly saturated water solution by the addition of 70% $HClO_4$. The perchlorate salt contained varying amounts of crystal water, depending on the conditions of precipitation and drying, so that the ratio moles of NH_3:gram-atoms of bound Cl:gram-atom of Cr was taken as evidence of the quality of the preparation. The *trans* configuration for the complex was assigned on the basis of the similarity of its spectrum to that of the *trans*-chloroaquobis(ethylenediamine)chromium(III) ion. The long-wavelength maximum is split into two peaks typical of *trans* complexes of this type.[6]

Anal. Calcd for $(NH_3)_4Cr(OH_2)Cl^{2+}$: moles of NH_3:gram-atoms of bound Cl:gram-atom of Cr = 4.00:1.00:1. Found: moles of NH_3:gram-atoms of bound Cl:gram-atom of Cr = 4.02:1.01:1.

To prepare *trans*-$[(NH_3)_4CrCl_2]ClO_4$, 10 g of $[(NH_3)_5Cr(OH)Cr(NH_3)_4Cl]Cl_4 \cdot H_2O$, prepared according to the method of Linhard and Weigel,[7] was ground to a fine powder in a mortar. The powder was transferred to a 500-ml flask containing 20 ml of 70% $HClO_4$ and 10 ml of 12 *M* HCl. The flask was stoppered and was allowed to stand until the contents had changed from purple to light brown (3–5 hr). The solid reaction product was separated on a sintered-glass filter and was washed with 1 *M* $HClO_4$ until the filtrate had changed from purple (due to *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$) to orange (due to $Cr(NH_3)_5OH_2^{3+}$) to colorless. The green $[(NH_3)_4CrCl_2]ClO_4$ which remained on the filter was recrystallized twice by dissolution in *ca.* 0.01 *M* $HClO_4$ and reprecipitation with 70% $HClO_4$ after cooling in ice. The product was washed with alcohol and ether and air dried; yield, 4.5 g. The *trans* configuration for the complex was assigned on the basis of the green color and the similarity of the spectrum to that of the *trans*-dichlorobis(ethylenediamine)chromium(III) ion.[4] *Anal.* Calcd for $[Cr(NH_3)_4Cl_2]ClO_4 \cdot H_2O$: Cr, 16.9; bound Cl, 23.0; NH_3, 18.2. Found: Cr, 17.0; bound Cl, 23.0; NH_3, 18.3.

To prepare *trans*-$[Cr(NH_3)_4BrCl]ClO_4$, 10 g of $[(NH_3)_5Cr(OH)Cr(NH_3)_4Cl]Br_4$, prepared from the chloride salt by repeated recrystallization from HBr solution, was added to 20 ml of 70% $HClO_4$ and 10 ml of 47% HBr in a 250-ml lightly stoppered flask. The mixture was allowed to stand for 2 hr at room temperature, during which time it changed from purple to pale green. The solid product was separated on a sintered-glass filter and was washed with small portions of 1 *M* $HClO_4$ until the filtrate was almost clear and the residue was bright green. The residue was dissolved in 100 ml of *ca.* 0.01 *M* $HClO_4$ and was reprecipitated by the addition of 5 ml of 70% $HClO_4$ after cooling in ice. The precipitate was separated on a filter, washed with alcohol and ether, and air dried; yield, 3 g. The green color and the presence of three absorption maxima in the visible region of the spectrum are evidence for the *trans* configuration.[6] *Anal.* Calcd for $[(NH_3)_4CrBrCl]ClO_4$: Cr, 15.8; N, 16.7; Br, 23.8. Found: Cr, 15.8; N, 17.3; Br, 23.6; Br + Cl (excluding ClO_4^-), 1.99 mol/mol of Cr.

To prepare *trans*-$[Cr(NH_3)_4(OH_2)_2](ClO_4)_3$, either reaction with Hg^{2+} or base hydrolysis may be used to remove Cl^- from the *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ ion. The latter approach seemed the more convenient and is the basis of the method described. A 10-g sample of *trans*-$[Cr(NH_3)_4(OH_2)Cl]Cl_2$, prepared as described elsewhere,[5] was dissolved in 120 ml of water and 20

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ml of 2 *M* ammonia was added. The solution was allowed to stand for *ca.* 5 min and then filtered to remove a small amount of pink material, probably $[(NH_3)_5CrCl]Cl_2$, present as an impurity in the starting material. The filtrate was acidified by the addition of about an equal volume of 70% $HClO_4$, upon which *trans*-$[(NH_3)_4Cr(OH_2)_2](ClO_4)_3$ precipitated. The solution was cooled in ice to improve the yield, and the diaquo salt was collected on a filter and washed with alcohol and ether; yield, 16 g. Repeated recrystallization of the salt from water by the addition of 70% $HClO_4$ gave no significant change in the spectrum, so that the salt was considered to be substantially free of *cis*-$[Cr(NH_3)_4(OH_2)_2](ClO_4)_3$. The cation was found to undergo partial loss of ammonia when placed on a cation-exchange column (Dowex 50), so that chromatography could not be used as a measure of isomeric purity. *Anal.* Calcd for $[(NH_3)_4Cr(OH_2)_2](ClO_4)_3$: N, 12.33; Cr, 11.44. Found: N, 12.53; Cr, 11.60.

The salt *cis*-$[Cr(NH_3)_4(OH_2)Cl]Cl_2$ was prepared by a modification[5] of the method of Werner and Surber.[8] *cis*-$[Cr(NH_3)_4(OH_2)Cl](ClO_4)_2$ was prepared from the chloride salt by careful trituration with concentrated $HClO_4$ during which most of the chloride ion was expelled as HCl gas. The perchlorate was recrystallized from the minimum amount of water by the addition of 70% $HClO_4$. As prepared, the *cis*-$[(NH_3)_4Cr(OH_2)Cl](ClO_4)_2$ was contaminated by a small amount of $[(NH_3)_5CrCl](ClO_4)_2$. This impurity was removed by dissolving the salt in methanol, in which the chloropentaammine salt is virtually insoluble, and reprecipitating the salt from the filtered solution with 70% $HClO_4$. The salt was dried with ether before analysis. *Anal.* Calcd for *cis*-$[Cr(NH_3)_4(OH_2)Cl](ClO_4)_2$: Cr, 13.96; N, 15.04; Cl (excluding ClO_4^-), 9.51. Found: Cr, 13.79; N, 14.90; Cl (excluding ClO_4^-), 9.90.

Sodium perchlorate solutions were prepared by neutralization of reagent grade sodium hydroxide with reagent grade perchloric acid. All other chemicals used were J. T. Baker reagent grade.

Analytical Methods.—Complex salts were analyzed for ammonia by a modified Kjeldahl method. The salt was digested with excess NaOH solution and the evolved ammonia was absorbed in boric acid solution, which was then titrated with perchloric acid solution which had been standardized against ammonia derived from standard ammonium chloride by the same digestion procedure. Chromium was determined by titration as dichromate against standard ferrous ammonium sulfate. Oxidation of chromium(III) to chromium(VI) was achieved with alkaline peroxide. Chloride was determined by first digesting the complex with excess NaOH and then titrating the acidified solution to a potentiometric end point with standard $AgNO_3$.[9] When bromide and chloride were both present, total halide content was determined by potentiometric titration against standard $AgNO_3$, and bromide was determined separately as bromate after oxidation with sodium hypochlorite.[10]

Spectra.—Visible absorption spectra of the various complexes were obtained using a Cary Model 15 recording spectrophotometer. In the case of the *trans*-bromochloro ion the spectrum changed by a small amount during the time required for a spectral scan at room temperature, and the spectrum of the complex was obtained by extrapolation to zero time. Molar extinction coefficients were calculated using the recorded absorption spectra and the chromium content of the solution as determined by chemical analysis.

Chromatographic Separations.—As an aid in establishing the stoichiometry of the aquation reactions, solutions in various stages of reaction were placed on columns of Dowex 50W-X2 resin (H^+ form) and the complexes were separated and eluted with perchloric acid. Spectra of the various fractions were recorded, and the chromium content of each fraction was determined by the titration procedure described earlier. Free chloride ion in the effluent was determined by titration against standard $AgNO_3$, and free bromide by titration as BrO_3^- after hypochlorite oxidation.[10]

Kinetic Measurements.—The aquation reactions of *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ were carried out in 1-cm quartz spectrophotometric cells immersed in a small constant-temperature bath built into the cell compartment of the Cary Model 15 spectrophotometer. To begin a run a weighed portion of the appropriate salt was dissolved in an $HClO_4$ or $HClO_4$–$NaClO_4$ solution at the temperature of the run. The solution was diluted to the mark in a volumetric flask, and a portion of the solution was used to fill the spectrophotometric cell. In the cases of *trans*-$Cr(NH_3)_4Cl_2^+$ and *trans*-$Cr(NH_3)_4BrCl^+$ the solubilities were so low as to require the use of longer path length cells, and jacketed 5-cm Pyrex spectrophotometer cells were used as reaction vessels. Because dissolution of the complex salt was slow, an excess of *trans*-$[Cr(NH_3)_4Cl_2]ClO_4$ was shaken together with a measured volume of $NaClO_4$–$HClO_4$ solution at the temperature of the run, the excess solid was allowed to settle for about 5 min, and a portion of the solution was decanted into the cell. A similar procedure was used in preparing the solution of *trans*-$[Cr(NH_3)_4BrCl]ClO_4$, but in this case the excess solid was removed by filtration.

The aquation of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ was followed as the decrease of absorbancy at 390 mμ because of the large absorbance change which accompanies the reaction at this wavelength (see Figure 1). The aquation of *trans*-$Cr(NH_3)_4Cl_2^+$ was followed at 370 mμ, and the aquation of *trans*-$Cr(NH_3)_4BrCl^+$ was followed both as a decrease of absorbancy at 370 mμ and as an increase in absorbancy at 610 mμ. First-order rate constants were determined from the spectrophotometric data by the Guggenheim method,[11] either by graph from the slopes of plots of log $(A_t - A_{t+\tau})$ *vs.* t or by means of a computer programmed to give a nonlinear least-squares fit of the data to the Guggenheim equation.

In the case of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ the progress of the reaction was followed also by chemical analysis of quenched reaction mixtures. A solution of the complex was suspended in a thermostated bath, and aliquots were withdrawn periodically and quenched by rapid cooling to room temperature. The solution was poured onto a column of Dowex 50W-X8 cation-exchange resin, and the free chloride ion was washed from the column with distilled water and titrated against standard $AgNO_3$. The unreacted *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ was removed from the column with *ca.* 1.8 *M* $HClO_4$ and determined spectrophotometrically as CrO_4^{2-} after oxidation with alkaline peroxide. The total chromium concentration of the reaction mixture, as determined by analysis, was taken to be the zero-time concentration of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$. Rate constants were calculated from the fraction of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ remaining at the time of sampling and from the amount of chloride ion released up to that time, assuming first-order kinetics.

Results and Discussion

The change in the visible absorption spectrum of *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ observed during the aquation reaction in 1 *M* $HClO_4$ is shown in Figure 1. Three very sharp isosbestic points are maintained until the primary aquation reaction is about 85% complete. These isosbestic points are at 503 mμ (ε 35.5), at 433 mμ (ε 10.6), and at 368 mμ (ε 28.1). If the only product of the aquation reaction were *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$, then isosbestic points would be expected at 501 mμ (ε 35.2), at 432 mμ (ε 10.0), and at 368 mμ (ε 27.5), which are identical with the observed isosbestic points, within experimental error. The observation of these isosbestic points rules out any significant contribution from two other possible reactions of *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, namely, aqua-

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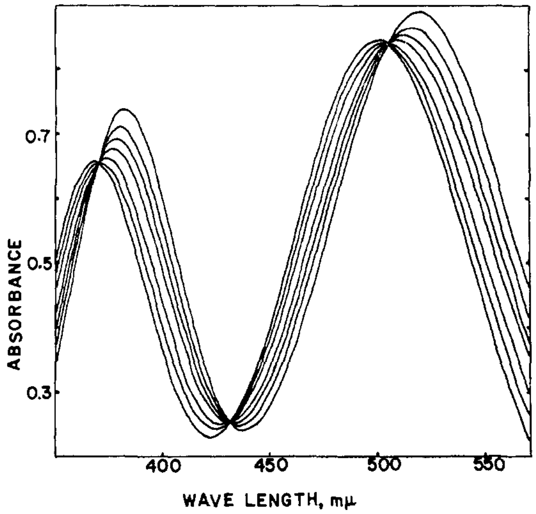

Figure 1.—Change in absorption spectrum with time during the aquation of *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ in 1 *M* $HClO_4$ at 65°. Reading downward at 520 mμ, reaction time is 0, 200, 500, 800, 1400, 2000, and 3200 sec.

tion to *trans*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$ and isomerization to *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$. At 503 mμ the molar extinction coefficients, ε, of *trans*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$ and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ are 23.0 and 15.0, respectively. Thus the conversion of *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ to either of these species would have been accompanied by a large decrease in the absorbancy at 503 mμ. At 432 mμ the molar extinction coefficients of *trans*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$ and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ are 15.5 and 15.0, respectively, which are about 50% higher than the observed isosbestic point. It may then be concluded that the primary product (95% or greater) of the aquation of *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ is *cis*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$ and that the aquation reaction is much more rapid (at least 20 times as rapid) than isomerization to *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$.

Repeated scans of the visible spectra of solutions of *trans*-$(NH_3)_4Cr(OH_2)Cl^{2+}$ undergoing aquation in 1 *M* $HClO_4$ showed three fairly good isosbestic points, which were maintained until the primary aquation reaction was *ca.* 75% complete. These were at 532 mμ (ε 17.6), 431 mμ (ε 13.4), and 366 mμ (ε 30.7), whereas isosbestic points would be expected at 534 mμ (ε 17.4), 430 mμ (ε 13.7), and 366 mμ (ε 26.5) if *trans*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$ were the only reaction product.[12] The agreement between the calculated and observed isosbestic points is quite good, but the small differences are in the direction expected if a small amount of *cis*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$ were formed in the reaction. The extinction coefficients of *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ are not drastically different at these wavelengths, so that nearly 10% of the product could be the *cis* isomer without noticeable effect on the isosbestic points. That *trans*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$ is the major reaction product is indicated also by another line of evidence. The addition of 70% $HClO_4$ to a solution resulting from the aquation of *ca.* 0.1 *M* *trans*-$[Cr(NH_3)_4(OH_2)Cl](ClO_4)_2$ yielded a precipitate having a spectrum which matched that of *trans*-$[Cr(NH_3)_4(OH_2)_2](ClO_4)_3$ which had been recrystallized several times. That the loss of Cl^- from *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ is responsible for the observed spectral changes is supported also by the excellent agreement among the rate constants obtained spectrophotometrically and by titration of released chloride (see Table I). Unfortunately, attempts to separate the reaction products on ion-exchange columns gave ambiguous results, for it was found that loss of NH_3 from *trans*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$ is catalyzed by Dowex 50 ion-exchange resins.

(12) These isosbestic points were determined by comparing the spectrum of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ with that of *trans*-$Cr(NH_3)_4(OH_2)_2{}^{3+}$ generated *in situ* by Hg^{2+}-induced aquation of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$. The spectrum of the diaquo complex so formed differed by less than 0.5% from that of the diaquo complex generated by making a solution of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ basic with NH_3 and then acidic with $HClO_4$.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR AQUATION REACTIONS[a]

Temp, °C	$[H^+]$, *M*	10^4k, sec^{-1}
	trans-$Cr(NH_3)_4(OH_2)Cl^{2+}$	
65.0	1.00	1.13 ± 0.04
70.0	1.00	1.84,[b] 1.78 ± 0.05, 1.73[c]
70.0	0.400	1.92[c]
70.0	0.200	2.11[c]
70.0	0.100	2.6
70.0	0.080	2.94 ± 0.05
75.0	1.00	3.04 ± 0.09
	cis-$Cr(NH_3)_4(OH_2)Cl^{2+}$	
60.0	1.00	3.47[d]
60.0	0.100	3.60[d]
65.0	1.00	5.46[d]
70.0	1.00	9.44
70.0	0.500	9.31[e]
	trans-$Cr(NH_3)_4Cl_2{}^+$	
45.0	1.00	4.82[d]
45.0	0.200	4.93[d]
50.0	1.00	8.5[d]
50.0	0.200	8.8[d]
55.0	1.00	14.0[d]
55.0	0.200	14.2[d]
	trans-$Cr(NH_3)_4BrCl^+$	
35.0	1.00	9.6,[d,f] 9.6[g]
40.0	1.00	16.4[d,f]
40.0	0.200	17.4[d,f]
45.0	1.00	26.7,[d,f] 29.0[g]

[a] Rates measured spectrophotometrically, unless otherwise noted. Errors are standard deviations. $\mu = 1.0$, adjusted with $NaClO_4$. Typical initial concentrations: *cis*- and *trans*-$(NH_3)_4Cr(OH_2)Cl^{2+}$, 0.02 *M*; *trans*-$(NH_3)_4CrCl_2{}^+$ and *trans*-$(NH_3)_4CrBrCl^+$, 0.003 *M*. [b] Followed by retrieval of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$. [c] Titration of released Cl^-. [d] Average of two runs. [e] Average of three runs. [f] At 370 mμ. [g] At 610 mμ.

When *trans*-$Cr(NH_3)_4BrCl^+$ or *trans*-$Cr(NH_3)_4Cl_2{}^+$ is heated in $HClO_4$ solutions at 40–50°, the color of the solution changes fairly rapidly from green to red-violet. Upon prolonged heating, the red-violet color changes to orange. It seemed likely that the change from green to red-violet was associated with the replacement of the first halide ion by water and the red-violet to orange change with the replacement of the second halide ion. Attention was focused on the elucidation of the first reaction, since the aquation reactions of the haloaquo-tetraammine complexes could be studied more conveniently starting with pure complexes.

Repeated scans of the visible spectrum of a solution of $Cr(NH_3)_4Cl_2^+$ undergoing the green to red-violet change revealed isosbestic points at 402 mμ (ε 29), 440 mμ (ε 14), and 566 mμ (ε 17.5), agreeing within experimental error with the isosbestic points expected if *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ were the only reaction product. As a further test of stoichiometry, a sample of *trans*-$[Cr(NH_3)_4Cl_2]ClO_4$ was dissolved in 1 *M* $HClO_4$ and heated at 50° for *ca.* 4500 sec (almost 6 half-lives for the loss of the first Cl^-). The solution was freed of Cr(III) by passage through a cation-exchange column and was found by analysis to have contained 1.04 mol of free Cl^-/mol of Cr. The ion-exchange column was treated with 2.5 *M* $HClO_4$ to remove most of the Cr(III), and the spectrum of the effluent was recorded. Maxima were observed at 555 mμ (ε 19.7), 472 mμ (ε 17.0), and 382 mμ (ε 39.6). Minima were observed at 500 mμ (ε 16.6) and 434 mμ (ε 12.8). From the similarity of this spectrum to that of pure *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ we conclude that *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ is the major product (>92%) of the loss of the first chloride ion from the *trans*-$Cr(NH_3)_4Cl_2^+$ ion.[13]

In the case of the *trans*-$Cr(NH_3)_4BrCl^+$ ion it is of interest to know not only the configuration of the product of the loss of the first halide ion but also which halide, Cl^- or Br^-, is replaced the more readily. Spectral scans recorded during the aquation of *trans*-$Cr(NH_3)_4BrCl^+$ showed isosbestic points at 567 mμ (ε 18.3) and 403 mμ (ε 29.3). If the only reaction product were *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, then isosbestic points would be expected at 568 mμ (ε 19.0) and 406 mμ (ε 29.0). The excellent agreement between the calculated and observed isosbestic points implies that *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ is indeed the major product. The other likely reaction product, *trans*-$Cr(NH_3)_4(OH_2)Br^{2+}$, has extinction coefficients of 24.8 and 31.5 at 567 and 403 mμ, respectively. As a further test of stoichiometry, the first step in the aquation of *trans*-$Cr(NH_3)_4BrCl^+$ was investigated by analysis of partially reacted solutions. The results of a typical experiment follow.

A sample of *trans*-$[Cr(NH_3)_4BrCl]ClO_4$ was allowed to react for 25 min (*ca.* 6 half-times for the first step) at 45° in 1 *M* $HClO_4$. The reaction was quenched by cooling and the sample was allowed to pass through a cation-exchange column to remove Cr(III). The effluent from the column was found to contain 95% of the Br^- (determined as BrO_3^-) originally contained in the $Cr(NH_3)_4BrCl^+$ sample. Perchloric acid (2.5 *M*) was poured through the column, and most of the chromium was eluted. The spectrum of the effluent had maxima at 552 mμ (ε 18.5), 465 mμ (ε 16.5), and 382 mμ (ε 38.6) and minima at 503 mμ (ε 13.7) and 435 mμ (ε 13.1). This is barely distinguishable from the spectrum of a pure sample of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, and the small differences are in the wrong direction to be explained by the presence of the *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ ion.[13] The solution was shown by analysis to contain 0.99 ± 0.01 mol of halide ion/mol of Cr, of which only 0.05 ± 0.01 mol was Br^- ion. From these observations we conclude that in the replacement of the first halide ion of $Cr(NH_3)_4BrCl^+$ by H_2O, Br^- is lost at least 87% of the time. Only a lower limit may be set, since the chromium not recovered from the column may have been $Cr(NH_3)_4(OH_2)_2^{3+}$ arising from the aquation of $Cr(NH_3)_4(OH_2)Br^{2+}$ formed in the first aquation step. From the similarity of the spectrum of the solution of product complexes to that of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, we may conclude further that the product of the replacement of Br^- in *trans*-$Cr(NH_3)_4BrCl^+$ by H_2O is primarily (>95%) *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$.

First-order rate constants for the aquation reactions of the various halotetraammine complexes are recorded in Table I. The rate constants tabulated for the *trans*-$Cr(NH_3)_4BrCl^+$ and *trans*-$Cr(NH_3)_4Cl_2^+$ ions are for the replacement of the first halide ion. The observed rate constant for the bromochloro complex is a composite rate constant for (at least) two parallel reactions

$$H_2O + trans\text{-}Cr(NH_3)_4BrCl^+ \longrightarrow trans\text{-}Cr(NH_3)_4(OH_2)Cl^{2+} + Br^- \quad (1)$$

$$H_2O + trans\text{-}Cr(NH_3)_4BrCl^+ \longrightarrow trans\text{-}Cr(NH_3)_4(OH_2)Br^{2+} + Cl^- \quad (2)$$

Since we have set a lower limit of 87% on the contribution of reaction 1 to the observed net change, we may likewise set a lower limit of 87% on the contribution of reaction 1 to the observed first-order rate constant. We estimate therefore that the first-order rate constant for reaction 1 is at least 8.4×10^{-4} sec^{-1} at 35°, 1.5×10^{-3} sec^{-1} at 40°, and 2.3×10^{-3} sec^{-1} at 45°.

Of the complexes studied here only the *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ ion has been the subject of a previous kinetic investigation. Nazarenko and Bratushko[14] followed the loss of Cl^- from the *cis*-chloroaquo complex at 30° by a conductometric technique. They found that the rate of loss of chloride became greater as the acidity was lowered, suggesting that *cis*-$Cr(NH_3)_4(OH)Cl^+$ lost Cl^- more readily than did *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$. They reported that the first-order rate constant at 30° and in 0.001 *N* HCl is 8.9×10^{-5} sec^{-1}. From our own data at higher temperatures we estimate that $k = 1.3 \times 10^{-5}$ sec^{-1} at 30°. The discrepancy between the numbers may indicate that *cis*-$Cr(NH_3)_4(OH)Cl^+$ is kinetically important even at $[H^+] = 10^{-3}$ *M*. However, the data of Table I show that base hydrolysis does not contribute significantly to the loss of chloride from *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ in the strongly acidic solutions (0.1–1 *M* H^+) used in this study, the aquation rate being independent of acidity over the range studied. The aquation rates of *trans*-$Cr(NH_3)_4BrCl^+$ and *trans*-$Cr(NH_3)_4Cl_2^+$ are also independent of acidity over the range studied.

It is seen from Table I that the aquation rate of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ increases substantially as the hydrogen ion concentration decreases, even at acidi-

(13) The spectrum of *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ exhibits maxima at 556 mμ (ε 19.3), 465 mμ (ε 17.2), and 383 mμ (ε 39.9). Minima occur at 500 mμ (ε 14.9) and 435 mμ (ε 13.6). The most sensitive test for the presence of *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ is the absorbance at 500 mμ (ε 35.1) for the *cis* isomer.

(14) Y. P. Nazarenko and Y. I. Bratushko, *Ukr. Khim. Zh.*, **28**, 17 (1962).

ties as high as 0.1–1 *M* H^+. The variation of the first-order rate constant, *k*, with hydrogen ion concentration is expressed fairly well by eq 3. At 70° the acid-de-

$$k = k_1 + \frac{k_2}{[H^+]} \quad (3)$$

pendent term, k_2, contributes less than 10% to the first-order rate constant at $[H^+] = 1.0$ *M*. It is likely that the acid-dependent term corresponds to a path involving *trans*-$Cr(NH_3)_4(OH)Cl^+$ as the active species. We have observed that the base hydrolysis reactions of both *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ are complete within a few minutes at room temperature, these reactions being the basis of the preparations of the diaquotetraammine complexes. A direct study of the aquation kinetics of *cis*- and *trans*-$Cr(NH_3)_4(OH)Cl^+$ is in progress and will be the subject of a separate report.

The trends in the relative rates of the reactions of Table I are the same as Garner and coworkers[2-4] have reported for the analogous ethylenediamine complexes. The change from Cl to Br as the leaving ligand increases the rate of aquation, the dihalo complexes aquate much more rapidly than the haloaquo complexes, and the *cis* isomer of $Cr(NH_3)_4(OH_2)Cl^{2+}$ aquates more rapidly than does the *trans* isomer. Specifically, Br^- is lost at least 8.7 times as rapidly as Cl^- from *trans*-$Cr(NH_3)_4BrCl^+$, and the loss of Br^- from the bromochloro ion is about 10 times as rapid as the loss of Cl^- from *trans*-$Cr(NH_3)_4Cl_2^+$, when the aquation rate constant for the latter complex is corrected for the statistical factor. The difference in aquation rates between *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ is smaller than reported[4] for the analogous ethylenediamine complexes. This smaller effect of geometry may be due to the ability of the nitrogen ligands of the ammonia complexes to move independently of each other, whereas the two nitrogen atoms of ethylenediamine molecule must act in concert. As was noted earlier, the reactions studied here occur with essentially complete retention of configuration, which is again similar to the behavior of the analogous ethylenediamine complexes.

Since the data of Table I show that *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ aquates more rapidly than *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, a possible reaction mechanism for the aquation of the *trans*-chloroaquo ion would seem to be isomerization to the *cis*-chloroquo ion, followed by aquation. This proposal may be rejected on the basis of reaction stoichiometry. The *cis* isomer aquates to give *ca.* 100% *cis*-$Cr(NH_3)_4(OH_2)_2^{3+}$, whereas the *trans* isomer yields largely the *trans*-$Cr(NH_3)_4(OH_2)_2^{3+}$ ion.

Arrhenius activation energies, calculated from the data of Table I, are 24 ± 1 kcal mol^{-1} for *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, 22.0 ± 0.5 kcal mol^{-1} for *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, 21.6 ± 0.3 kcal mol^{-1} for *trans*-$Cr(NH_3)_4Cl_2^+$, and 20.8 ± 0.3 kcal mol^{-1} for *trans*-$Cr(NH_3)_4BrCl^+$. The activation energy for *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ was calculated from the data for $[H^+] = 1.0$ *M*.

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Physicochemical and Spectral Properties of Octahedral Dioxomolybdenum(VI) Complexes

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Complexes of the type MoO_2L_2 (where L = acetylacetonate, benzoylacetonate, $(C_6H_5CO)_2CH^-$, oxinate, $(CH_2)_4NCS_2^-$, and $R_2NCS_2^-$, where R = CH_3, C_2H_5, *n*-C_3H_7, or *n*-C_4H_9) were examined to determine whether they contained *cis*-MoO_2 groups. The infrared spectra of these complexes all show two strong Mo═O stretching modes in the 900-cm^{-1} region as expected for a *cis*-MoO_2 group. These complexes were found to be undissociated by conductivity measurements in CH_3NO_2 and $HCON(CH_3)_2$. The large values of the dipole moments of $MoO_2[(C_2H_5)_2NCS_2]_2$ (9.51 D), $MoO_2[(n\text{-}C_3H_7)_2NCS_2]_2$ (8.05 D), and $MoO_2[(n\text{-}C_4H_9)_2NCS_2]_2$ (7.60 D) confirm the presence of bent MoO_2 groups in these complexes. The presence of *cis*-MoO_2 groups for $MoO_2(C_5H_7O_2)_2$ and $MoO_2[(C_6H_5CO)_2CH]_2$ was indicated by their nmr spectra. It was concluded that all octahedral dioxomolybdenum(VI) complexes prepared to date contain *cis*-MoO_2 groups. The electronic spectra of the β-diketonates possess a charge-transfer band due to the molybdenyl group near 52,000 cm^{-1}, and a similar band occurs in the dithiocarbamate complexes above 53,000 cm^{-1}. The molybdenum(V) complex, $[(C_5H_7O_2)_2Mo{=}O]_2O$, also possesses a charge-transfer band assignable to a O→Mo(V) transition above 53,000 cm^{-1}. Peaks assignable to charge transfer from the ligand donor atoms to molybdenum(VI) were located in the 26,000–31,000 cm^{-1} region.

Introduction

In a previous study[1] of dioxomolybdenum(VI) dialkyldithiocarbamate complexes, $MoO_2(R_2NCS_2)_2$, it was concluded from infrared spectral evidence that these complexes and analogous complexes contain *cis* (bent) dioxomolybdenum groups. The presence of a *cis*-MoO_2 group in $MoO_2[(CH_3)_2NCS_2]_2$ was recently pro-

(1) F. W. Moore and M. L. Larson, *Inorg. Chem.*, **6**, 998 (1967).