form only 1:1 adducts even in the presence of large excesses of base.[3,4,12] This constitutes an interesting body of chemical information which is now understood and can be interpreted in terms of acid–base concepts with relatively little considerations from lattice effects.

Recent X-ray analyses have elucidated the structure of the 1:1 adducts.[17,36] The new adducts prepared in this work are probably analogous, having a square-pyramidal geometry about the copper atom. The structures of the dipyridine adducts of Co(acac)$_2$[37] and Ni(acac)$_2$[38] involve a *trans*-octahedral configuration, and the 2:1 adducts of the copper(II) β-diketonates are probably the same.

Acknowledgment.—This investigation was supported in part by the National Science Foundation, Grant No. GP 5498.

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The Synthesis and Aquation Kinetics of *cis*- and *trans*-Dichlorotriaquoamminechromium(III) and Blue-Violet Chlorotetraaquoamminechromium(III) Cations[1a,b]

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The new complexes *cis*- and *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ have been synthesized, and spectrophotometric and chromatographic evidence has been obtained supporting the isomeric assignments (the location of the NH_3 ligand is uncertain in the *cis* isomer). The aquation of both isomers was studied at 30–45° by spectrophotometry and by Cl^- release. For both isomers the same product, previously unreported blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$ (tentatively assigned as the *cis*-chloroammine isomer), is formed. In 0.3–1 F $HClO_4$ ($\mu = 1\ M$, $NaClO_4$) at 25° (by extrapolation) the first-order rate constant for *cis*-$Cr(NH_3)(OH_2)_3Cl_2^+$ is $k_{1c} = 2.8 \times 10^{-5}\ sec^{-1}$, with $E_a = 23.1 \pm 0.5$ kcal mol^{-1} and log PZ (sec^{-1}) $= 12.47 \pm 0.31$, and for *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ the first-order rate constant is $k_{1t} = 4.8 \times 10^{-5}\ sec^{-1}$, with $E_a = 20.2 \pm 0.2$ kcal mol^{-1} and log PZ (sec^{-1}) $= 10.38 \pm 0.13$. The aquation of blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$ to $Cr(NH_3)(OH_2)_5^{3+}$ was studied spectrophotometrically and by Cl^- release in 0.25–1.5 F $HClO_4$ ($\mu = 0.25$–$1.5\ M$, $NaClO_4$) at 45–70° For $\mu = 1.5\ M$, the observed hydrolysis rate constant, $k_{2,obsd}$ has the form $k_{2,obsd} = k_2 + (k_2'/[H^+])$, where k_2 is the first-order constant for the aquation of blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$ and k_2' has been interpreted as $k_{2h}K_a$, with k_{2h} being the first-order rate constant for aquation of $Cr(NH_3)(OH_2)_3(OH)Cl^+$ and K_a the first acid dissociation constant of blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$. At 45° $k_2 = 7 \times 10^{-6}\ sec^{-1}$, with $E_a = 25.0 \pm 0.7$ kcal mol^{-1} and log PZ (sec^{-1}) $= 11.94 \pm 0.48$, and $k_2' = 8 \times 10^{-7}\ M\ sec^{-1}$. There is little or no aquation of these complexes *via* Cr–N bond rupture. The visible absorption spectra of the new complexes are reported.

Introduction

Only ten monoamine complexes of chromium(III) have been reported, in sharp contrast with the numerous chromium(III)–amine complexes with two, three, and four Cr–N bonds; of the reported monoamine complexes, only two are halo complexes and they have pyridine as the amine ligand.

We report here the synthesis of three new monoamine complexes of chromium(III), namely, *cis*- and *trans*-dichlorotriaquoamminechromium(III) cations, $Cr(NH_3)(OH_2)_3Cl_2^+$, and a blue-violet isomer of chlorotetraaquoamminechromium(III) cation, $Cr(NH_3)(OH_2)_4Cl^{2+}$. We also report our studies of the kinetics of aquation of the dichloro complexes to form the monochloro complex and aquation of the latter to pentaaquoamminechromium(III) cation, $Cr(NH_3)(OH_2)_5^{3+}$. These chloro complexes are of especial interest for comparison of their aquation rates with those of certain related dichloro and monochloro complexes of chromium(III), since these new complexes serve as links between the numerous chloroamine complexes with more than one amine ligand and the chloroaquo complexes of chromium(III) without amine ligands. Moreover, these aquation studies provide another opportunity to examine the possibility of Cr–N bond rupture in competition with Cr–Cl bond rupture, a phenomenon which has been reported in a variety of chromium(III)–amine complexes.

Experimental Section

Pentaaquoamminechromium(III) Cation.—The method of Ardon and Mayer,[2] modified as follows, was used to give a solution of this complex in *ca.* 6 F HCl. Electrolytic Cr metal (*ca.* 0.5 g) was added under N_2 to 25 ml of 3 F HCl which had been freed of dissolved O_2 by scrubbing with N_2, and the Cr was dissolved by heating at *ca.* 80°. Enough 0.1 F NaN_3 was added dropwise to the vigorously stirred Cr(II) solution at *ca.* 20° to give a Cr:N_3^- mole ratio of 2, producing $Cr(NH_3)(OH_2)_5^{3+}$ and

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(1) (a) Work partly supported under Contract AT(11-1)-34, Project No. 170, between the U. S. Atomic Energy Commission and the University of California. This paper constitutes Report No. UCLA-34P170-5 to the AEC. (b) Abbreviations used: en, ethylenediamine; dien, diethylenetriamine; trien, triethylenetetramine.

(2) M. Ardon and B. E. Mayer, *J. Chem. Soc.*, 2816 (1962).

$Cr(OH_2)_5Cl^{2+}$ in equimolar amounts. The mixture was charged onto a 20-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh), and the $Cr(OH_2)_5Cl^{2+}$ was completely eluted with 200–300 ml of 0.5 *F* HCl. The $Cr(NH_3)(OH_2)_5^{3+}$ was then eluted with 35–40 ml of 6 *F* HCl.

Green *cis*-Dichlorotriaquoamminechromium(III) Cation.—A combination of Cl^- anation of $Cr(NH_3)(OH_2)_5^{3+}$ and thermal dehydration of the products was used in attempts to prepare chloroaquoammine complexes of Cr(III), from which $Cr(NH_3)(OH_2)_3Cl_2^+$ could possibly be chromatographically isolated. The above magenta solution of $Cr(NH_3)(OH_2)_5^{3+}$ in 6 *F* HCl was evaporated under vacuum at *ca.* 20° to less than 5% of its original volume, giving in 15–20 hr a dark purple syrupy liquid. This was converted to a green solid by heating at 70–80° under vacuum for 20–30 min.[3] The solid was cooled to 0° and dissolved in *ca.* 50 ml of 0.01 *F* $HClO_4$ at 0°, and the solution (containing *ca.* 5 mg-atoms of complexed Cr) was quickly charged onto an 18-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 (100–200 mesh) resin jacketed at 0–2°. A green species (*ca.* 50% of the total Cr put on the column), which passed through the column during the charging, was completely washed out with an additional 20–30 ml of 0.01 *F* $HClO_4$, indicating that the species was neutral or anionic; failure of this species to adsorb on Cl^- Dowex AG1-X8 (100–200 mesh) anion-exchange resin showed the species was uncharged. This green complex exhibited a rapid change in the visible absorption spectrum, markedly slowly after only 10 min at *ca.* 20° (extrapolated zero-time absorption bands at *ca.* 450 and 630 nm). Since it was found to aquate rapidly to *cis*-$Cr(NH_3)(OH_2)_3Cl_2^+$ and to be uncharged, it is presumably $Cr(NH_3)(OH_2)_2Cl_3$, probably the 1,2,3-trichloro isomer. The complex was not further characterized because of its lability and the difficulty of obtaining a meaningful Cl:Cr atom ratio determination (the large excess of free Cl^- could not be quantitatively removed). A 0.01 *F* $HClO_4$ solution of this green complex was aged for 1 hr at *ca.* 20° in the dark and then rechromatographed on a 15-cm cation-exchange column (same kind as above) at 0–2°, washing with *ca.* 80 ml of 0.01 *F* $HClO_4$ to remove any unreacted trichloro complex (none observed), and then eluting the remaining green band with 100–150 ml of 0.1 *F* or 50–75 ml of 0.3 *F* $HClO_4$ (small amounts of higher charged species were left on the column). Analyses of this effluent (*ca.* 2–5 m*F* in complex) showed that the green complex had mole ratios of NH_3:Cr = 1.05 and Cl:Cr = 2.00, in good agreement with the formula $Cr(NH_3)(OH_2)_3Cl_2^+$. Further characterization, described in the Results, indicates that this complex has a *cis*-dichloro configuration.

Green *trans*-Dichlorotriaquoamminechromium(III) Cation.—After the green uncharged species was chromatographically separated from the initial mixture of complexes in the above procedure, any residual uncharged species was washed out with *ca.* 150 ml of 0.01 *F* $HClO_4$, leaving *ca.* 30% of the total Cr put on the column as a green band, which was eluted with 100–150 ml of 0.1 *F* or 50–75 ml of 0.3 *F* $HClO_4$ to give a green solution *ca.* 4–6 m*F* in $Cr(NH_3)(OH_2)_3Cl_2^+$. Analyses of this effluent showed the complex had mole ratios of NH_3:Cr = 0.99 and Cl:Cr = 1.93, in satisfactory agreement with the formula. The visible absorption spectrum is different from that of the green *cis*-dichloro complex, as is its aquation rate, and the complex appears to be the *trans*-dichloro isomer (see Results). About 20% of the Cr put on the column remained at the top of the column as two bands, a magenta band (probably $Cr(NH_3)(OH_2)_5^{3+}$) and a violet band ($Cr(NH_3)(OH_2)_4Cl^{2+}$) immediately below.

Blue-Violet Chlorotetraaquoamminechromium(III) Cation.—Solutions of *cis-* or *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ in 0.3 *F* $HClO_4$ were aged for 2.5–3.0 hr at 45° (4–5 half-times) in the dark and then charged onto a H^+ Dowex AG50W-X8 (100–200 mesh) resin column operated at 0–2°, and the column was washed with an extra 80 ml of 0.3 *F* $HClO_4$ to remove unreacted dichloro complex. A violet band left on the column was eluted with 0.5–1.5 *F* $HClO_4$ (*ca.* 200 ml of 0.5 to *ca.* 100 ml of 1.5 *F*), depending on the acid concentration desired for kinetic runs. Analyses of the effluent (*ca.* 4–8 m*F* in complex) gave mole ratios of NH_3:Cr = 1.05 and Cl:Cr = 1.04, in acceptable agreement with the formula $Cr(NH_3)(OH_2)_4Cl^{2+}$.

Other Chemicals.—All other chemicals used have been described previously.[4]

Analytical Methods.—Near-ultraviolet and visible absorption spectra were obtained with a Cary Model 15 recording spectrophotometer and matched 10-cm silica cells. The methods for Cr and Cl analyses have been described earlier;[5] NH_3 was analyzed by a standard micro Kjeldahl procedure without H_2SO_4 digestion.

Kinetic Runs.—The spectral kinetic runs for the dichloro species were done as previously described.[6] For $Cr(NH_3)(OH_2)_4Cl^{2+}$ higher temperatures were used, and the reactions were followed by removing aliquots at convenient time intervals from tightly sealed Pyrex flasks placed in constant-temperature baths (±0.05°) and quenching the reaction by rapid cooling to 0°. The spectrum of each aliquot was then measured at *ca.* 20°. The Cl^- release rates were measured as previously described.[4] The method of calculation of rate constants from experimental data was essentially the same as that given earlier.[6]

Results

Characterization of *cis-* and *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ and $Cr(NH_3)(OH_2)_4Cl^{2+}$.—The characterization of the green dichloro complexes as isomers of $Cr(NH_3)(OH_2)_3Cl_2^+$ follows from determinations of their NH_3:Cr (1.05 and 0.99) and Cl:Cr (2.00 and 1.93) mole ratios, their chromatographic behavior (characteristic of a 1+ charge for complexes of this general type and size), and their complete aquation to $Cr(NH_3)(OH_2)_4Cl^{2+}$. The visible absorption spectra of these dichloro isomers are shown in Figure 1 and are similar to the spectra of *cis-* and *trans*-$Cr(OH_2)_4Cl_2^+$,[7,8] with the $Cr(NH_3)(OH_2)_3Cl_2^+$ bands shifted 15–34 nm toward shorter wavelengths, presumably because of the greater ligand field strength of NH_3 relative to H_2O. The absorption bands of *cis*-$Cr(OH_2)_4Cl_2^+$ are at 450 (ϵ 28.8) and 640 nm (ϵ 19.6) and the bands of *trans*-$Cr(OH_2)_4Cl_2^+$ are at 450 (ϵ 21.7) and 640 nm (ϵ 24.4), for which $\epsilon_{640}/\epsilon_{450}$ is 0.68 for the *cis* isomer and 1.1 for the *trans* isomer. The new green dichloro complexes, with bands at 435 (ϵ 32.4) and 604 nm (ϵ 27.4) and at 434 (ϵ 26.9) and 609 nm (ϵ 32.3), have similar molar absorptivity ratios of 0.85 and 1.2, thus suggesting that these $Cr(NH_3)(OH_2)_3Cl_2^+$ isomers have, respectively, *cis*-dichloro and *trans*-dichloro configurations. In support of this assignment, the complex so characterized as *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ has its absorption bands and intensity ratio intermediate to those of *trans*-$Cr(OH_2)_4Cl_2^+$ and blue $Cr(en)(OH_2)_2Cl_2^+$,[4] with bands at 420 (ϵ 22.7) and 580 nm (ϵ 39.1) giving an intensity ratio of 1.7 (the latter complex has been shown[9] by X-ray crystallography to have the *trans*-dichloro configura-

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[3] Longer heating times generate highly charged green species which are presumably polymeric; appreciable amounts are formed in 1 hr, and in 24 hr nearly 100% of the Cr is in this form. Still longer times finally give a violet solid which immediately converts to the green polymer on dissolution in water.

[4] D. M. Tully-Smith, R. K. Kurimoto, D. A. House, and C. S. Garner, *Inorg. Chem.*, **6**, 1524 (1967).

[5] D. A. House, R. G. Hughes, and C. S. Garner, *ibid.*, **6**, 1077 (1967).

[6] T. J. Williams and C. S. Garner, *ibid.*, **8**, 1639 (1969).

[7] E. L. King, M. J. M. Woods, and H. S. Gates, *J. Am. Chem. Soc.*, **80**, 5015 (1958).

[8] J. D. Salzman and E. L. King, *Inorg. Chem.*, **6**, 426 (1967).

[9] R. Stromberg and I. Larking, *Acta Chem. Scand.*, **23**, 343 (1969).

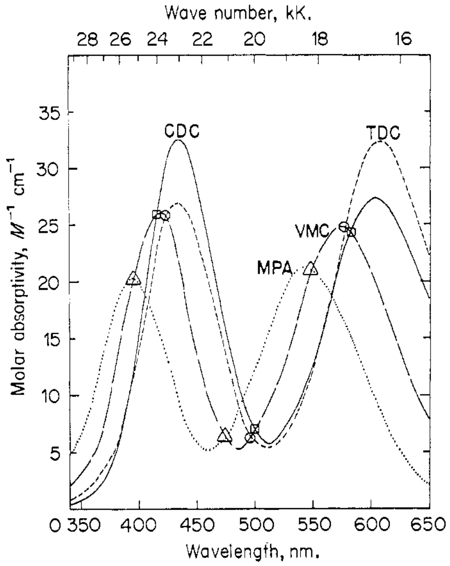

Figure 1.—Visible absorption spectra of some chromatographically isolated chromium(III)-monoammine complexes at 20–25°: CDC, *cis*-$Cr(NH_3)(OH_2)_3Cl_2^+$ in 0.3 *F* $HClO_4$; TDC, *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ in 0.3 *F* $HClO_4$; VMC, blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$ in 1.5 *F* $HClO_4$; MPA, magenta $Cr(NH_3)(OH_2)_5^{3+}$ in 3 *F* $HClO_4$. The molar absorptivity or molar extinction coefficient ϵ is defined by the relation $\log (I_0/I) = A = \epsilon cl$, where *c* is the molarity of the absorbing complex and *l* is the optical path length in centimeters.

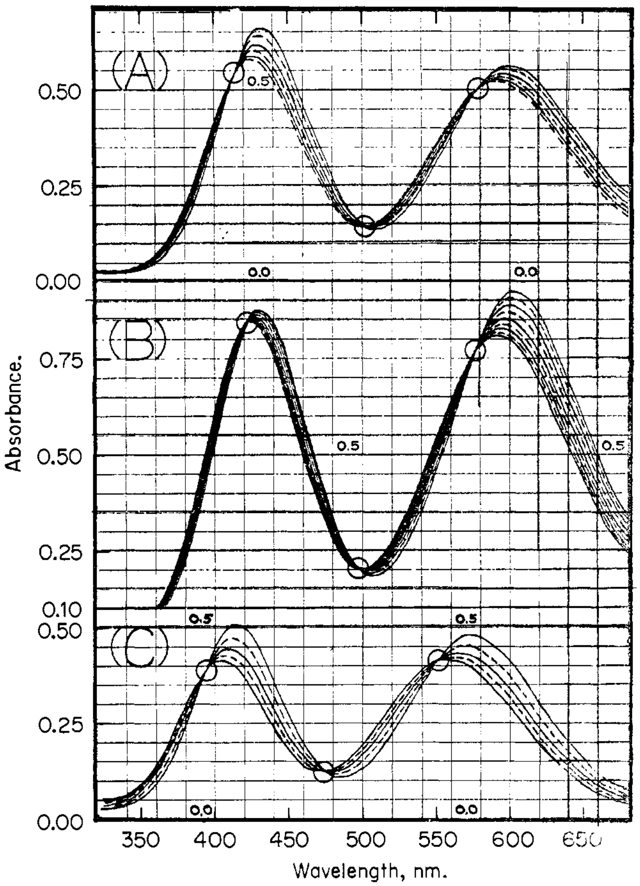

Figure 2.—Change in absorption spectra during hydrolysis: A, *cis*-$Cr(NH_3)(OH_2)_3Cl_2^+$ (C_0 = 2.12 m*F*) in 1 *F* $HClO_4$ (μ = 1 *M*) at 36.30°; reading downward at 620 nm the reaction time is 0, 20, 40, 60, 80, 100 min; B, *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ (C_0 = 3.19 m*F*) in 1 *F* $HClO_4$ (μ = 1 *M*) at 36.33°; reading downward at 620 nm the reaction time is 0, 10, 20, 30, 40, 50, 60, 70, 80 min; C, blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$ (C_0 = 1.96 m*F*) in 0.25 *F* $HClO_4$ (μ = 1.5 *M*) at 60.05°; reading downward at 580 nm the reaction time is 0, 65, 132, 191, 264 min; alternate curves are dashed for convenience in reading.

tion). Further support for our assignment has come from an attempt to separate the green dichloro complexes chromatographically. An equimolar mixture of *cis*- and *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ in 0.02 *F* $HClO_4$ was adsorbed on a 20-cm × 1-cm diameter column of H^+ Dowex AG50W-X8 resin (100–200 mesh) operated at 0–2°, and the band was spread with 220 ml of 0.01 *F* $HClO_4$ and then slowly eluted with 0.1 *F* $HClO_4$. The first several per cent of complex eluted had bands at 435 and 608 nm, with an intensity ratio of 1.2, essentially identical with the spectrum of the species characterized above as *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$. The last several per cent of complex eluted had bands at 434 and 604 nm, with an intensity ratio of 1.0, indicating that it is a mixture of the *cis* and *trans* isomers. Although the separation was not complete, it does show that the species we have tentatively characterized as *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ elutes more readily than the *cis* isomer, in accord with the general observation that *trans* complexes normally elute more easily than their *cis* isomers.

The position of the NH_3 ligand in *cis*-$Cr(NH_3)(OH_2)_3Cl_2^+$ is uncertain. As shown below, both dichloro isomers aquate to a spectrally identical $Cr(NH_3)(OH_2)_4Cl^{2+}$ product. Assuming retention of geometric configuration (always observed so far in aquation of *cis*-diacidoamine complexes of Cr(III); the *trans* isomers usually have been found to aquate with little or no stereochemical change), *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ would generate the 1-chloro-2,3,4,6-tetraaquo-5-amminechromium(III) cation, *i.e.*, the *cis*-chloroammine. Either of the possible isomers of *cis*-$Cr(NH_3)(OH_2)_3Cl_2^+$, *i.e.*, either the isomer with both Cl ligands *cis* to the NH_3 ligand or the isomer with one Cl ligand *trans* to the NH_3 ligand, can generate the above monochloro isomer; the latter dichloro isomer would be expected to generate this monochloro isomer exclusively, however, only if the NH_3 ligand labilizes (relative to H_2O ligand) the Cl ligand *trans* to it. Inasmuch as aquation data on *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ [10] can be interpreted in terms of such *trans* labilization, either or both *cis*-$Cr(NH_3)(OH_2)_3Cl_2^+$ isomers would be compatible with the observed product. The relatively sharp isosbestic points observed in aquation of *cis*-$Cr(NH_3)(OH_2)_3Cl_2^+$ to blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$ (see Figure 2 and below) require that if the *cis*-dichloro complex is an isomeric mixture the two isomers must aquate at essentially the same rate or have essentially the same molar absorptivities at the wavelengths of the observed isosbestic points (a third alternative of isomerization to an equilibrium mixture at a rate rapid relative to aquation seems improbable because of the generally found low rates of

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[10] D. W. Hoppenjans, J. B. Hunt, and C. R. Gregoire, *Inorg. Chem.*, **7**, 2506 (1968).

TABLE I

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF *cis*-$Cr(NH_3)(OH_2)_3Cl_2^+$ [a]

Temp, °C	$[HClO_4]$, *F*	C_0, m*F*[b]	μ, *M*[c]	10^5k_{1c}, sec^{-1} [d]
29.97	0.30	2.50	1.0	4.90 ± 0.10
36.30	0.30	2.12	1.0	11.3 ± 0.4
36.30	1.0	2.12	1.0	11.1 ± 0.3
45.08	0.30	1.53	1.0	30.4 ± 1.2
45.08	0.30	1.52	0.30	33.0 ± 1.5
45.08	0.30	1.52	0.30	32.1 ± 1.6[e]
44.90	0.30	4.56	0.30	35.0 ± 1.1[f]

[a] Determined from spectral change at 440 nm unless otherwise indicated; exposed to light only during spectral scans. [b] Initial concentration of substrate. [c] Ionic strength, adjusted with $NaClO_4$. [d] Errors are standard deviations; for the spectral scans these were estimated from the major source of error, the uncertainty in A_∞. [e] At 620 nm. [f] Found from titrating free Cl^- as a function of time.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ [a]

Temp, °C	$[HClO_4]$, *F*	C_0, m*F*[b]	μ, *M*[c]	10^5k_{1t}, sec^{-1} [d]
30.02	1.0	3.19	1.0	7.32 ± 0.11
29.97	0.30	3.22	1.0	7.40 ± 0.11
30.02	0.30	3.22	0.30	7.55 ± 0.11
36.33	1.0	3.19	1.0	13.9 ± 0.3
45.08	1.0	3.18	1.0	33.5 ± 0.9
45.08	1.0	3.18	1.0	31.4 ± 1.4[e]
44.90	1.0	4.50	1.0	31.5 ± 1.3[f]

[a] Determined from spectral change at 620 nm unless otherwise indicated; exposed to light only during spectral scans. [b] See footnote *b*, Table I. [c] See footnote *c*, Table I. [d] See footnote *d*, Table I. [e] At 440 nm. [f] See footnote *f*, Table I.

TABLE III

OBSERVED FIRST-ORDER RATE CONSTANTS FOR HYDROLYSIS OF BLUE-VIOLET $Cr(NH_3)(OH_2)_4Cl^{2+}$ [a]

Temp, °C	$[HClO_4]$, *F*	C_0, m*F*[b]	μ, *M*[c]	$10^5k_{2,obsd}$, sec^{-1} [d]
44.90	1.5	1.93	1.5	0.70 ± 0.03
44.90	0.75	3.88	1.5	0.76 ± 0.02
44.90	0.25	2.24	1.5	0.98 ± 0.03
60.05	1.5	1.22	1.5	3.67 ± 0.24
60.05	0.75	1.93	1.5	4.34 ± 0.18
60.05	0.25	1.96	1.5	5.84 ± 0.25
60.05	0.25	1.40	0.25	7.00 ± 0.42
70.38	1.5	2.36	1.5	14.1 ± 0.6
70.38	0.75	3.60	1.5	15.0 ± 0.3
70.38	0.75	3.60	1.5	15.2 ± 0.3[e]
70.38	0.75	3.60	1.5	15.7 ± 0.7[f]
70.38	0.25	1.95	1.5	19.0 ± 0.8

[a] Determined from spectral change at 580 nm unless otherwise indicated; exposed to light only during spectral scans. [b] See footnote *b*, Table I. [c] See footnote *c*, Table I. [d] See footnote *d*, Table I. [e] At 420 nm. [f] See footnote *f*, Table I.

isomerization of related chromium(III)–amine complexes).

The characterization of blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$ is based on determination of its NH_3:Cr and Cl:Cr mole ratios (1.05 and 1.04), its chromatographic behavior (compatible with a 2+ charge), its production by aquation of *cis*- and *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$, and its aquation to $Cr(NH_3)(OH_2)_5^{3+}$. As expected, its d–d absorption spectrum (bands at 420 and 575 nm, with ϵ values 26.9 and 24.8; see Figure 1) is similar to that of $Cr(OH_2)_5Cl^{2+}$ (bands at 430 and 605 nm, with ϵ values of 21.6 and 17.8),[11] except for the expected shift to shorter wavelengths. As discussed above, the *cis*-chloroammine configuration is tentatively assigned. This assignment is supported by the aquation rate observed for the blue-violet complex (see Discussion).

Aquation Kinetics.—Tables I–III present the observed first-order rate constants k_n defined by

$$-dC_n/dt = k_nC_n \tag{1}$$

where C_n is the molar concentration of the given substrate complex. First-order rate plots were linear as far as followed (*ca.* 75% reaction in the spectral runs and 50% reaction in the Cl^- release runs). In the spectral runs, values of the "infinite-time" absorbance A_∞ were calculated from the spectrum of blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$ in the *cis*- and *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ runs and from the spectrum (measured in our laboratory) of $Cr(NH_3)(OH_2)_5^{3+}$ in the $Cr(NH_3)(OH_2)_4Cl^{2+}$ runs. No kinetic overlap was observed. The loss of NH_3 in $Cr(NH_3)(OH_2)_5^{3+}$ aquation has been briefly studied[12] in 0.5–1.5 *F* $HClO_4$ ($\mu = 2$ *M*, $LiClO_4$), and the aquation rate constant found to be $<6 \times 10^{-8}$ sec^{-1} at 45°, so aquation of $Cr(NH_3)(OH_2)_5^{3+}$ formed during aquation of blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$ is negligible.

Discussion

Aquation of *cis*- and *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$.—The spectral plots in Figure 1 of the isolated species *cis*-$Cr(NH_3)(OH_2)_3Cl_2^+$ and blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$ predict isosbestic points at 581 (ϵ 24.3), 500 (ϵ 6.9), and 415 nm (ϵ 25.9) for the reaction

$$cis\text{-}Cr(NH_3)(OH_2)_3Cl_2^+ + H_2O \xrightarrow{k_{1c}} \text{blue-violet } Cr(NH_3)(OH_2)_4Cl^{2+} + Cl^- \tag{2}$$

Experimentally, three well-defined isosbestic points were observed in each run (see Figure 2 for a typical run) with their averages being 580 ± 2 (ϵ 24.0 ± 0.6), 501 ± 2 (ϵ 6.9 ± 0.3), and 414 ± 1 nm (ϵ 25.6 ± 0.4), in good agreement with reaction 2. Within experimental error, the values of k_{1c} at 45° in 0.3 *F* $HClO_4$ (see Table I) are the same within experimental error whether based on analysis of spectral changes assuming reaction 2 or on titration of released Cl^-, further indicating that the path

$$cis\text{-}Cr(NH_3)(OH_2)_3Cl_2^+ + H_2O \longrightarrow cis\text{- or } trans\text{-}Cr(OH_2)_4Cl_2^+ + NH_3 \tag{3}$$

competes little or not at all with reaction 2. Moreover, calculations show that a 15% contribution from reaction 3 would shift the observed isosbestic points beyond their experimental errors. Table I shows k_{1c} is essentially independent of acid concentration in the range 0.3–1.0 *F* $HClO_4$ ($\mu = 1$ *M*) at 36°; at 45° in 0.3 *F* $HClO_4$ there is only a small change in k_{1c} on tripling the ionic strength from 0.3 to 1 *M*. An Arrhenius plot of

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(11) P. J. Elving and B. Zemel, *J. Am. Chem. Soc.*, **79**, 1281 (1957).

(12) J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966).

TABLE IV

RATE CONSTANTS (10^5k, SEC^{-1}) FOR THE PRIMARY AQUATION OF SOME *cis*- AND *trans*-DICHLORO COMPLEXES OF Cr(III) AT 35°

Complex	Medium	*cis*	*trans*
$Cr(OH_2)_4Cl_2^+$ [a]	0.2 *F* $HClO_4$	8.3	18
$Cr(NH_3)(OH_2)_3Cl_2^+$ [b]	1.0 *F* $HClO_4$	9.3	12.8
$Cr(en)(OH_2)_2Cl_2^+$ [c]	1.5 *F* $HClO_4$	...	13.8
$Cr(NH_3)_3(OH_2)Cl_2^+$ [d]	0.6 *F* $HClO_4$	...	~14[e]
$Cr(dien)(OH_2)Cl_2^+$ [f]	0.6 *F* $HClO_4$	~100[e]	...
$Cr(NH_3)_4Cl_2^+$ [g]	1.0 *F* $HClO_4$	...	16[h]
$Cr(en)_2Cl_2^+$ [i]	0.1 *F* HNO_3	100	8.0
$Cr(trien)Cl_2^+$ [j]	2.0 *F* $HClO_4$	42	...

[a] Reference 8. [b] This research. [c] Reference 4. [d] Reference 13; the blue isomer, tentatively assigned a *trans*-dichloro configuration. [e] Estimated by multiplying 25° roughly determined *k* by 3.5. [f] Reference 14; the blue isomer, tentatively assigned the 1,2-dichloro-3-aquo configuration. [g] Reference 10. [h] Calculated from 45° *k* and E_a of reference 10. [i] Reference 15; *k* given is for Cl^- release path only (*trans* isomer also aquates with loss of en). [j] Reference 16; the *cis*-α isomer.

the temperature-dependence data (0.3 *F* $HClO_4$, $\mu = 1$ *M*) is linear, giving an extrapolated value at 25° of $k_{1c} = 2.78 \times 10^{-5}$ sec^{-1}. Least-squares activation parameters are $E_a = 23.1 \pm 0.5$ kcal mol^{-1}, log *PZ* (sec^{-1}) = 12.47 ± 0.31, and $\Delta S^*_{298} = -11 \pm 3$ cal deg^{-1} mol^{-1}.

The reaction

$$trans\text{-}Cr(NH_3)(OH_2)_3Cl_2^+ + H_2O \xrightarrow{k_{1t}} \text{blue-violet } Cr(NH_3)(OH_2)_4Cl^{2+} + Cl^- \quad (4)$$

predicts, from the spectra of the isolated species in Figure 1, isosbestic points during aquation of *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ at 578 (ε 24.8), 497 (ε 6.3), and 423 nm (ε 25.8). Sharp isosbestic points were observed, as shown in Figure 2, with the experimental values being 577 ± 1 (ε 24.4 ± 0.6), 495 ± 3 (ε 6.5 ± 0.4), and 422 ± 3 nm (ε 26.4 ± 0.6), in good agreement with the predicted values. Agreement of spectral and Cl^- release values of k_{1t} (see Table II) and calculations showing that a 10% contribution from an aquation path involving NH_3 release would be detectable in a shift of isosbestic points indicate that the aquation of *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ occurs almost exclusively by Cr–Cl bond rupture. Table II shows that at 30° k_{1t} is independent within experimental error of acid concentration in the range 0.3–1.0 *F* $HClO_4$ ($\mu = 1$ *M*) and of ionic strength in the range 0.3–1 *M* (0.3 *F* $HClO_4$). Least-squares activation parameters from a linear Arrhenius plot of the data in 1 *F* $HClO_4$ are $E_a = 20.2 \pm 0.2$ kcal mol^{-1}, log *PZ* (sec^{-1}) = 10.38 ± 0.13, and $\Delta S^*_{298} = -13 \pm 1$ cal deg^{-1} mol^{-1}, giving an extrapolated value at 25° of $k_{1t} = 4.84 \times 10^{-5}$ sec^{-1}.

Table IV compares the aquation rate constants of *cis*- and *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ with those found for related dichloro complexes[4,8,13–16] at 35°. Despite the differences in medium (which are known for complexes 2, 3, 6, 7, and 8 of Table IV to have little or no effect on *k* in the range involved in Table IV), the aquation rates of the *trans*-dichloro complexes are seen to be remarkably similar, whereas there is more than a tenfold range of *k* values for those complexes in which the leaving Cl ligand is *trans* to an H_2O or amine N ligand. A second point of interest is that *trans*-$Cr(NH_3)(OH_2)_3Cl_2^+$ aquates more rapidly at 30–35° than the *cis* isomer, as is the case for *trans*- and *cis*-$Cr(OH_2)_4Cl_2^+$, although the rate ratio is smaller for the ammine species. This is the reverse of the situation with $Cr(en)_2Cl_2^+$, where the *cis* isomer aquates much faster than the *trans* isomer, and indeed for various diacidobis(ethylenediamine) complexes of Cr(III) and Co(III) the *cis* isomer generally aquates more rapidly than the *trans* isomer, as has been discussed[17] in terms of π bonding and the probable need of the *trans* isomer for rearrangement to a trigonal-bipyrimidal structure in forming the transition state. Thus, these monoammine complexes are transitional in their kinetic behavior between the chloroamine complexes with more than one Cr–N bond and the chloroaquo complexes without amine ligands. Unlike the $Cr(OH_2)_4Cl_2^+$ isomers, which isomerize at 35° with rates comparable to their aquation rates,[8] isomerization of the $Cr(NH_3)(OH_2)_3Cl_2^+$ isomers appears to be negligible (there is enough difference in aquation rates and in predicted isosbestic points to have resulted in loss of well-defined isosbestic points in the observed aquation reactions if isomerization were important). Since the aquation rates of $Cr(NH_3)(OH_2)_3Cl_2^+$ and $Cr(OH_2)_4Cl_2^+$ do not differ greatly, the relative unimportance of isomerization for the ammine species may be associated with inhibition of isomerization in the presence of one or more amine ligands, causing chromium(III)–amine complexes in general to isomerize more slowly than they aquate.

Aquation of Blue-Violet $Cr(NH_3)(OH_2)_4Cl^{2+}$.—The isosbestic points predicted from Figure 1, namely, 550 (ε 20.9), 474 (ε 6.2), and 394 nm (ε 20.3), for the reaction

$$\text{blue-violet } Cr(NH_3)(OH_2)_4Cl^{2+} + H_2O \xrightarrow{k_2} Cr(NH_3)(OH_2)_5^{3+} + Cl^- \quad (5)$$

agree with the experimentally observed isosbestic points (Figure 2) for the aquation of the monochloro species, namely, 551 ± 1 (ε 21.0 ± 0.5), 473 ± 1 (ε 6.3 ± 0.2), and 393 ± 2 nm (ε 19.8 ± 0.6). This agreement, together with the agreement of the Cl^- release and spectral values of $k_{2,\text{obsd}}$ (see Table III), indicates that aquation with loss of NH_3 contributes little if any to the aquation reaction. The rate constants given in Table III indicate only a small dependence on ionic strength but a large dependence on the hydrogen ion concentration, with the observed first-order rate constant, $k_{2,\text{obsd}}$, from the $\mu = 1.5$ *M* data fitting the expression

$$k_{2,\text{obsd}} = k_2 + (k_2'/[H^+]) \quad (6)$$

where $[H^+]$ is taken equal to the $HClO_4$ formality. The rate constants, k_2 and k_2', were found both by

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[13] S. H. Caldwell and D. A. House, *Inorg. Chem.*, **8**, 151 (1969).

[14] S. H. Caldwell and D. A. House, *J. Inorg. Nucl. Chem.*, **31**, 811 (1969).

[15] D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 4152 (1961).

[16] C. Y. Hsu and C. S. Garner, *Inorg. Chim. Acta*, **1**, 17 (1967).

[17] See, *e.g.*, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 258.

TABLE V

RATE CONSTANTS FOR HYDROLYSIS OF BLUE-VIOLET $Cr(NH_3)(OH_2)_4Cl^{2+}$ ($\mu = 1.5\ M$)[a]

Temp, °C	10^5k_2, sec^{-1}	$10^6k_2'$, M sec^{-1}
44.90	0.65 ± 0.03	0.84 ± 0.01
60.05	3.36 ± 0.12	6.26 ± 0.06
70.38	14.8 ± 0.6	14.8 ± 0.3

[a] Constants calculated from $k_{2,\mathrm{obsd}}$ (Table III) using $k_{2,\mathrm{obsd}} = k_2 + (k_2'/[H^+])$; standard errors estimated from deviation from linearity of plots of $k_{2,\mathrm{obsd}}$ *vs.* $1/[H^+]$.

plotting $k_{2,\mathrm{obsd}}$ *vs.* $1/[H^+]$ and by a least-squares analysis. The results are presented in Table V. The activation parameters calculated from the temperature dependence of k_2 are $E_a = 25.0 \pm 0.7$ kcal mol^{-1}, log PZ (sec^{-1}) = 11.94 ± 0.48, and $\Delta S^*_{298} = -6 \pm 2$ cal deg^{-1} mol^{-1}. Although both k_2 and k_2' gave linear Arrhenius plots, the activation parameters for k_2' were not calculated since their values would include unknown contributions from other thermodynamic parameters, as is discussed below.

The acid-dependence behavior is similar to that observed in the aquation of magenta $Cr(en)(OH_2)_3Br^{2+}$ [18] and magenta $Cr(en)(NH_3)(OH_2)_2Br^{2+}$ [6] and, as discussed earlier,[6,18] seems best rationalized in terms of contributions of eq 5 (acid independent, with rate constant k_2) and the acid-dependent path

$$Cr(NH_3)(OH_2)_4Cl^{2+} \overset{K_a}{\rightleftharpoons} Cr(NH_3)(OH_2)_3(OH)Cl^{+} + H^{+} \quad \text{(fast equilibrium, far to left)} \qquad (7a)$$

$$Cr(NH_3)(OH_2)_3(OH)Cl^{+} + H_2O \xrightarrow{k_{2h}} Cr(NH_3)(OH_2)_4OH^{2+} + Cl^{-} \qquad (7b)$$

$$Cr(NH_3)(OH_2)_4OH^{2+} + H^{+} \longrightarrow Cr(NH_3)(OH_2)_5^{3+} \text{ (fast)} \qquad (7c)$$

for which $k_2' = K_a k_{2h}$, with K_a being the unknown first acid dissociation constant of blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$.

A comparison of the aquation rate of blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$ with aquation rates of related chloroaquo complexes is shown in Table VI. As in the case of the dichloro complexes of Table IV, where the range of aquation rates is small for the *trans*-dichloro complexes and large for the *cis*-dichloro complexes, the chloroaquo complexes of Table VI aquate at similar rates if the leaving Cl ligand is *trans* to an H_2O ligand but at greater and more variable rates if this is not the case. This similarity of rates for the known *trans*-chloroaquo complexes supports but does not prove the tentative assignment, made earlier in this article, of the *cis*-chloroammine (*i.e.*, *trans*-chloroaquo) configuration for blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$.

Assuming that these chloro complexes all aquate *via* a dissociative mechanism, the observed lower rate of aquation of blue-violet $Cr(NH_3)(OH_2)_4Cl^{2+}$ relative to aquation rates of *cis*- and *trans*-$Cr(NH_3)(OH_2)_3Cl_2^{+}$ is expected on the basis of the higher positive charge of the monochloro substrate. At 35° the rate ratio is 47 for the *cis*-dichloro and 64 for the *trans*-dichloro complex, in the normal range for chromium(III)–amine complexes.

TABLE VI

RATE CONSTANTS (10^6k, SEC^{-1}) FOR AQUATION OF SOME *cis*- AND *trans*-CHLOROAQUO COMPLEXES OF Cr(III) AT 35°

Complex	Medium	*cis*	*trans*[a]
$Cr(OH_2)_5Cl^{2+}$ [b]	1 F $HClO_4$	...	1.3
$Cr(NH_3)(OH_2)_4Cl^{2+}$ [c]	0.3–1.5 F $HClO_4$ ($\mu = 1.5\ M$)	...	2.0[a]
$Cr(en)(OH_2)_3Cl^{2+}$ [e]	1.5 F $HClO_4$	...	<9[f]
$Cr(NH_3)_4(OH_2)Cl^{2+}$ [g]	1 F $HClO_4$	24[h]	3[i]
$Cr(en)_2(OH_2)Cl^{2+}$ [j]	0.1 F $HClO_4$	92	2.8
$Cr(trien)(OH_2)Cl^{2+}$ [k]	2 F $HClO_4$	~230	...

[a] In the complexes labeled "*trans*" one of the H_2O ligands is *trans* to the leaving Cl ligand. [b] T. W. Swaddle and E. L. King, *Inorg. Chem.*, **4**, 532 (1965). [c] This research; blue-violet isomer. [d] Calculated from 45° k and E_a. [e] Reference 4; the magenta isomer, tentatively characterized as the *trans*-chloroaquo isomer. [f] Calculated from 50° k and E_a of ref 4; value given is an upper limit since it is uncorrected for a small contribution from an acid-dependent path. [g] Reference 10. [h] Calculated from 60° k and E_a of ref 10. [i] Calculated from 65° k and E_a of ref 10. [j] D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, **1**, 20 (1962); k given is for Cl^- release path only (*trans* isomer also aquates with loss of en). [k] Reference 16; the *cis*-β or *cis*-β′ isomer.

The rupture of Cr–N bonds in competition with Cr–X (X = halogen or pseudohalogen) bond rupture has been reported in the aquation of a variety of chromium(III)–amine complexes.[19] This phenomenon has not been observed with the three new complexes of this article.

Synthesis of Chloro Complexes.—The method of synthesis used here to prepare *cis*- and *trans*-$Cr(NH_3)(OH_2)_3Cl_2^{+}$ would seem to be applicable to other chromium(III)–amine complexes where the aquoamine species is obtainable in concentrated solutions of volatile halogen acids. The halide salts may possibly serve as well, since failure of the HCl solution of $Cr(NH_3)(OH_2)_5^{3+}$ in the vacuum evaporation at 20° (see Experimental Section) to turn green implies that spontaneous Cl^- anation under these conditions is not extensive, the formation of the dihalo species apparently requiring the dehydration in the presence of Cl^- under heat and vacuum.

Although the kinetic data and characterization work indicate that the *cis*- and *trans*-dichloro complexes synthesized were reasonably isomerically pure, it is not clear from the method of synthesis why the trichloro species formed should have an apparently predominantly 1,2,3 (or *cis*) configuration, whereas the dichloro species produced in the same synthesis is the *trans* isomer. One possible explanation may be that the 1,2,6-trichloro complex may be unstable in the solid state relative to the 1,2,3 isomer. Another explanation may be that both 1,2,6- and 1,2,3-trichloro isomers are produced in the synthesis and that on dissolution of the solid in 0.01 F $HClO_4$ at 0° the 1,2,6 isomer may aquate rapidly to generate the observed *trans*-dichloro product, with the 1,2,3 isomer (here assumed to aquate more slowly than the 1,2,6 isomer) largely unaquated. Other explanations may exist, and it does not seem fruitful to speculate further on the origin of the observed isomers.

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(18) R. G. Hughes and C. S. Garner, *Inorg. Chem.*, **7**, 1988 (1968).

(19) See ref 4 and 6–11 in ref 18.