via the –O–P–O– bridges is plausible. In fact, an analogous case is that of copper(II) formate tetrahydrate, the subnormal moment of which has been primarily attributed to superexchange through a π pathway set up by using 3d orbitals of the Cu(II) ion and $2p\pi$ orbitals of bridging $HCOO^-$ radicals.[31] Magnetic exchange to a small extent between adjacent polymeric molecules is also possible.[30] Such an interaction would account for the decreased demagnetization with increasing bulkiness of the ligand.

In conclusion a number of Ti(III), V(III), and Cr(III) crystalline complexes of monoacidic phosphates and phosphonates were prepared and characterized. The properties of these compounds are in favor of polymeric configurations, probably involving eight-membered phosphato or phosphonato bridges. The Ti(III), V(III), and Cr(III) complexes of EEP, IMP, BBP, or DBP are almost isostructural, but the MMP and DMP analogs exhibit different X-ray pattens. Apparently in the case of the bulkier ligand complexes the arrangement of the substituent groups in space is the factor determining the stereochemistry of the polymeric molecule as well as that of the ligand-field symmetry of each metal ion. However, in the complexes of the less bulky methyl-substituted ligands the central metal ion influences the degree of distortion from pure O_h symmetry and the overall structure of the crystalline polymers.

Acknowledgment.—The support of U. S. Army Edgewood Arsenal, Md., under Contract No. DAAA 15-67-C-0644 is gratefully acknowledged.

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Electron-Transfer Reactions between Hexaaquochromium(II) Cation and Chlorodiaquotriamminechromium(III), Chlorotriaquodiamminechromium(III), and Chlorotetraaquoamminechromium(III) Cations[1]

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In an attempt to isolate factors contributing to the overall activation energy, particularly nonbridging ligand effects, for electron-transfer reactions between Cr_{aq}^{2+} and Cr(III) complexes of the type $Cr(NH_3)_n(OH_2)_{5-n}X^{2+}$, the kinetic parameters for electron exchange between Cr_{aq}^{2+} and three recently synthesized complexes were measured by spectrophotometrically observing their Cr_{aq}^{2+}-catalyzed ammine aquation in 1.5 *F* $HClO_4$ at 20–30°. These complexes, $Cr(NH_3)_3(OH_2)_2Cl^{2+}$, $Cr(NH_3)_2(OH_2)_3Cl^{2+}$, and $Cr(NH_3)(OH_2)_4Cl^{2+}$, are all thought to have the chloro and an aquo ligand in *trans* positions, and with *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ they give four examples where the only variable may be considered to be a change in ligand field strength in positions *cis* to the chloro ligand. These complexes were all shown to undergo electron transfer by an inner-sphere mechanism (*i.e.*, the chloro ligand is transferred *via* a Cl-bridged activated complex to the oxidized product, $Cr(OH_2)_5Cl^{2+}$). Kinetic parameters were also remeasured for $Cr(NH_3)_5Cl^{2+}$, *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$, and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$. The activation energies for this series of six complexes are discussed as a function of changing ligand field strength in terms of a simple model for the activated complex. For $Cr(NH_3)_3(OH_2)_2Cl^{2+}$, $Cr(NH_3)_2(OH_2)_3Cl^{2+}$, and $Cr(NH_3)(OH_2)_4Cl^{2+}$, respectively, at 25° values of k from the rate law $R = k[Cr^{2+}][\text{complex}]$ are 2.19 ± 0.25, 6.94 ± 0.80, and 19.1 ± 1.9 $M^{-1}\ sec^{-1}$; E_a: 9.9 ± 0.4, 9.1 ± 0.4, 8.4 ± 0.3 kcal mol^{-1}; log $PZ(M^{-1}\ sec^{-1})$: 7.59 ± 0.29, 7.50 ± 0.29, 7.44 ± 0.22.

Introduction

The $Cr(OH_2)_6^{2+}$-catalyzed aquation of a number of Cr(III) complexes has been studied, and in every case where a hydroxo or halo ligand is present in the Cr(III) coordination sphere the rate of aquation appears to be controlled by the rate of the electron-transfer reaction between Cr(II) and Cr(III) *via* a bridged activated complex or transition state. Meaningful correlations of reaction rates for earlier data with changes in the nature of the Cr(III) complex are complicated by unknown acid dissociation constants in the case of hydroxo complexes and by the limited data for series of reactions where only one feature of the Cr(III) complex is systematically changed. With the determination of electron-transfer rates between Cr_{aq}^{2+} and $Cr(NH_3)_3(OH_2)_2Cl^{2+}$, $Cr(NH_3)_2(OH_2)_3Cl^{2+}$, and $Cr(NH_3)(OH_2)_4Cl^{2+}$, we have extended the data for complexes of the type $Cr(NH_3)_n(OH_2)_{5-n}Cl^{2+}$ to six examples having their geometry with respect to the chloro ligand known reasonably well. This permits a discussion of the effects of changing the nonbridging ligands in positions *cis* and *trans* to the bridge in the activated complex, as well as of overall effects. The available data have also been treated semiempirically, using the approach of Marcus (*i.e.*, the activation energy is given by the sum

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of individual contributions from a proposed model for the activation process).[2]

Since the experimental procedures are somewhat different from those used by earlier workers, the rates for catalyzed aquation by Cr_{aq}^{2+} were also remeasured for $Cr(NH_3)_5Cl^{2+}$ [3] and *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ [4] in order to check the method and possibly to give better data for comparison purposes.

Experimental Section

Chloropentaamminechromium(III) Chloride.—This red compound was prepared as described earlier.[5] *Anal.* Calcd for $[Cr(NH_3)_5Cl]Cl_2$: Cr, 21.3; Cl, 43.7; NH_3, 34.8. Found: Cr, 21.0; Cl, 44.4; NH_3, 34.0. Aqueous solutions of the solid had visible absorption bands at 512 (ϵ 36.6) and 376 nm (ϵ 35.0), in good agreement with the reported[6] values, namely, 512 (ϵ 36.9) and 376 nm (ϵ 37.5).

***cis*-Chloroaquotetraamminechromium(III) Chloride.**—Preparation of this pink solid by a reported procedure[7] gave the expected compound as indicated by chemical analysis and the agreement of its visible absorption bands, 517 (ϵ 39.3) and 383 nm (ϵ 33.6), with the reported maxima, 518 (ϵ 40.4) and 384 nm (ϵ 33.3).[8] *Anal.* Calcd for $[Cr(NH_3)_4(OH_2)Cl]Cl_2$: Cr, 21.2; Cl, 43.5, NH_3, 27.8. Found: Cr, 20.9; Cl, 43.6; NH_3, 28.2.

***trans*-Chloroaquotetraamminechromium(III) Cation.**—This complex was prepared by a series of reactions involving a hydroxo-bridged intermediate leading to the *trans*-chloroaquo structure.[9] *Anal.* Calcd for $[Cr(NH_3)_4(OH_2)Cl]Cl_2$: Cr, 21.2; Cl, 43.5; NH_3, 27.8. Found: Cr, 21.0; Cl, 43.6; NH_3, 27.6. Although analysis of the magenta chloride salt suggested that the compound was pure, the visible absorption spectrum of an acidic solution of the solid did not give the amount of additional splitting in the low-energy transition that was reported.[8] For this reason the complex was further purified, using ion-exchange chromatography. A solution of the solid in 0.1 *F* $HClO_4$ was charged onto a 20-cm column of H^+ Dowex AG50W-X8 resin (100–200 mesh) at 2° and the complex was slowly eluted with 1.5 *F* $HClO_4$. The first *ca.* 60% of the band eluted (no visible separation) was collected and its spectrum had bands at 550 (ϵ 19.7), 470 (ϵ 17.1), and 383 nm (ϵ 39.5), more closely agreeing with the reported values, namely, 555 (ϵ 20.0), 468 (ϵ 18.2), and 383 nm (ϵ 39.2).[8]

Chlorodiaquotriamminechromium(III) Cation.—Pale green-blue $[Cr(NH_3)_3(OH_2)Cl_2]Cl$ was prepared as suggested.[7] About 0.1 g of the solid was then dissolved in 50 ml of 0.3 *F* $HClO_4$, heated to 60°, and let stand for 5–10 min. The resulting violet solution was charged onto a 10-cm exchange column (as described above) and the column was washed with *ca.* 80 ml of 0.3 *F* $HClO_4$, completely eluting a faint green band. The desired species of 2+ charge was then completely eluted with *ca.* 100 ml of 1.5 *F* $HClO_4$ (no visible trace of higher charged species); analyses gave mole ratios of Cl:Cr = 1.04 and NH_3:Cr = 3.10. The visible absorption spectrum of this species gave bands at 537 (ϵ 25.0) and 394 nm (ϵ 33.1) for repeated chromatographic separations, the molar absorptivities being somewhat higher than the values reported earlier[10] for the triammine complex, namely, 539 (ϵ 20.3) and 396 nm (ϵ 29.5). For reasons discussed previously[10] this complex is believed to have the chloro ligand *trans* to one of the water ligands (1-chloro-2,6-diaquo-3,4,5-triammine configuration).

Chlorotriaquodiamminechromium(III) Cation.—For this complex, the green salt $[Cr(NH_3)_2(OH)_2Cl_2]Cl$ was first prepared as previously described[11] from Eastman White Label Reinecke's salt. The dichloro species was then aquated and chromatographed as described for the triammine species. The violet solution of the complex (2+ charge from chromatographic behavior) gave mole ratios of Cl:Cr = 1.07 and NH_3:Cr = 2.09 in good agreement with the formula of the expected species, $Cr(NH_3)_2(OH_2)_3Cl^{2+}$. The observed absorbance maxima were at 551 (ϵ 24.8) and 403 nm (ϵ 30.2), showing the expected increase in wavelength relative to the bands of the triammine species. Since Reinecke's salt has been shown to have the ammine ligands *trans* to each other,[12] the species obtained would have the chloro ligand *trans* to one of the water ligands (1-chloro-2,4,6-triaquo-3,5-diammine configuration) assuming retention of configuration in both aquation steps.

Chlorotetraaquoamminechromium(III) Cation.—The synthesis and characterization of this complex (tentatively assigned the *cis*-chloroammine configuration) are described elsewhere.[13]

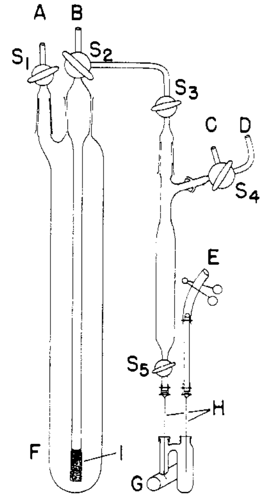

Figure 1.—Apparatus (not to scale) used for preparing solutions for kinetic runs: A, vacuum inlet; B, inlet for N_2 or $HClO_4$; C, N_2 inlet; D, vacuum inlet; E, outlet to atmosphere regulated by pinch clamp on Tygon tubing; F, vessel for preparation and storage of Cr^{2+} stock solutions; G, special spectral cell with side compartment, equipped with rubber serum caps; H, hypodermic injection needles; I, gas dispersion tube.

Stock Hexaaquochromium(II) Solutions.—Using the apparatus shown in Figure 1, solutions of Cr_{aq}^{2+} could be prepared and diluted under N_2, with the oxidation of less than *ca.* 10% of the Cr(II) to $Cr(OH_2)_6^{3+}$ or a higher charged dinuclear species.[14] For the preparation of Cr^{2+} stock solutions, 25 ml of 3.0 *F* HCl was added to vessel F and scrubbed with N_2 added through inlet B while heating the acid to *ca.* 70°. When all air was displaced from the vessel, the joint bearing stopcock S_1 was removed and electrolytic Cr metal (99.999% pure, United Mineral & Chemical Corp., New York, N. Y.) was added with a vigorous N_2 flow to exclude air, then stopcock S_1 was reattached and connected *via* tubing and trap to a vacuum pump. While the metal was dissolving with continued heating, stopcock S_2 was closed and the pressure inside vessel F was regulated by opening stopcock S_1 when necessary (H_2 given off in reaction). When the Cr had dissolved, full vacuum was applied *via* stopcock S_1 and the solution was taken to dryness with only mild heating, yielding mainly $CrCl_2$. Solvent, 1.5 *F* $HClO_4$, which had been scrubbed

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(2) R. A. Marcus, *Ann. Rev. Phys. Chem.*, **15**, 155 (1964).

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(4) M. J. DeChant and J. B. Hunt, *ibid.*, **90**, 3695 (1968).

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(12) Y. Takeuchi and Y. Saito, *Bull. Chem. Soc. Jap.*, **30**, 319 (1957), and earlier references therein.

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(14) M. Ardon and R. A. Plane, *J. Amer. Chem. Soc.*, **81**, 3197 (1959).

with N_2 in a second vessel (not shown), was then added to vessel F through inlet B under a positive pressure of N_2. After removing some of the Cr^{2+} solution through stopcocks S_2 and S_3 for use, the solution remaining in vessel F could be diluted by addition of more 1.5 *F* $HClO_4$ *via* inlet B.

Other Chemicals.—Other chemicals included reagent grade $HClO_4$ and HCl. All water was doubly distilled and run through a mixed-bed anion–cation-exchange resin column. The $Cr(OH_2)_5Cl^{2+}$ used to obtain the infinite-time spectrum for the electron-transfer reaction product was prepared by dissolution of reagent grade $CrCl_3 \cdot 6H_2O$ (containing only $Cr(OH_2)_4Cl_2^{+}$[15]), aquation by heating, and chromatographic separation (as described above for $Cr(NH_3)_3(OH_2)_2Cl^{2+}$) of the three possible complexes present, $Cr(OH_2)_4Cl_2^{+}$, $Cr(OH_2)_5Cl^{2+}$, and $Cr(OH_2)_6^{3+}$; purity of the $Cr(OH_2)_5Cl^{2+}$ fraction was confirmed by its absorption spectrum. The $[Co(NH_3)_5Cl]Cl_2$ used in the Cr^{2+} analysis was prepared as described,[7] and its purity was checked by spectral comparisons.

Analytical Methods.—The procedures used for analysis of Cr, Cl, and NH_3 have been given.[13] Analysis for Cr^{2+} in the reaction mixture was done by withdrawing an aliquot (*ca.* 2 ml) from the spectral cell, using a syringe which had been previously flushed with N_2, and then quickly discharging the aliquot into a solution containing excess $Co(NH_3)_5Cl^{2+}$. The aliquot volume was accurately determined by weighing. To 5.00 ml of this mixture 45.0 ml of 12 *F* HCl was added. After standing overnight at *ca.* 5°, the solution was decanted from the precipitated excess $[Co(NH_3)_5Cl]Cl_2$ for spectral absorbance measurement at 690 nm. From this the concentration of Co^{2+} formed quantitatively from the Cr^{2+} reduction was found ($CoCl_2 \cdot 6H_2O$ standard solutions gave a linear Beer's law plot) and related, after correction for a small extent of oxidation of the Cr^{2+}, to the initial Cr^{2+} concentration of the reaction mixture by known dilutions. Spectral measurements for analysis were done using a Beckman DU spectrophotometer and matched 1- or 10-cm cylindrical capped silica cells. For species identification and kinetic runs, a Cary Model 15 spectrophotometer was used with matched 10-cm silica cells or the special cell (G) shown in Figure 1.

Kinetic Run Procedure.—An $HClO_4$ solution of the Cr(III) complex was pipetted into the side compartment of a special silica cell assembly (G, Figure 1), which was then attached to the rest of the apparatus of Figure 1 and flushed with N_2. Then by using the N_2 (C) and vacuum (D) inlets, an aliquot of Cr^{2+} solution (*ca.* 27 ml; volume determined accurately by weighing) was withdrawn from vessel F and delivered into the spectral cell (G) under N_2. The cell assembly was then submerged in the spectrophotometer's circulating constant-temperature bath for 10 min, quickly dried, and then placed in the spectrophotometer cell compartment. The spectrum of the Cr^{2+} stock solution was recorded, and the two solutions in the cell assembly were mixed by tipping it back and forth and quickly returning it to the cell compartment. Although only the cell portion of the cell assembly was contained in the cell compartment temperature block, tests showed that a temperature constant to ±0.1° and within ±0.3° of the bath temperature was maintained in the cell. Where necessary, the absorbance measurements for the kinetic run could be begun within *ca.* 15 sec of mixing. For slow reactions scans (700–340 nm) were taken as a function of time, while for faster reactions the spectrophotometer was set at a constant wavelength and the recorder was run at a constant chart speed. After spectral measurements for a kinetic run were made, an aliquot of the solution was removed for Cr^{2+} analysis.

Infinite-time absorbance values, A_∞, were calculated for the slow reactions by applying the known dilution to the absorbance of the Cr^{2+} stock solution and adding this to an absorbance calculated from the Cr(III) complex concentration and the measured molar absorptivities for the reaction product $Cr(OH_2)_5Cl^{2+}$. For faster reactions the infinite-time absorbance was measured after *ca.* 10 reaction half-lives. Since the Cr^{2+} concentration remained constant (no spectral change observed for Cr^{2+} solutions for at least 2 hr), these data can be used to calculate a pseudo-first-order rate constant, k_0, according to the relation

$$k_0 t = 2.303 \log [(A - A_\infty)/(A_0 - A_\infty)] \qquad (1)$$

Because the catalyzed aquation reactions obey a second-order rate law, rate $= k[Cr^{2+}][\text{complex}]$, the second-order rate constant k can be calculated from $k_0 = k[Cr^{2+}]$.

Results

TABLE I

SECOND-ORDER RATE CONSTANTS FOR THE Cr^{2+}-CATALYZED AQUATION OF SOME MONOCHLOROCHROMIUM(III)–AMMINE COMPLEXES IN 1.50 *F* $HClO_4$

Complex	Temp, °C	C_0,[a] m*M*	$[Cr^{2+}]$,[b] m*M*	k,[c] M^{-1} sec^{-1}
$Cr(NH_3)_5Cl^{2+}$	20.32	2.56	11.6	0.0642 ± 0.0046
(520 nm)	20.32	2.56	11.6	0.0595 ± 0.0056[d]
	23.58	2.51	11.6	0.0813 ± 0.0062
	30.70	2.51	12.5	0.128 ± 0.010
cis-$Cr(NH_3)_4(OH_2)Cl^{2+}$	20.10	2.67	4.62	0.0963 ± 0.0078
(520 nm)	20.10	2.67	4.62	0.0941 ± 0.0075[d]
	23.62	2.65	4.66	0.128 ± 0.008
	27.20	2.68	5.47	0.153 ± 0.012
	30.08	2.73	5.50	0.184 ± 0.015
	29.82	2.06	0.940	0.203 ± 0.020
	29.75	2.04[e]	0.956	0.212 ± 0.020
trans-$Cr(NH_3)_4(OH_2)Cl^{2+}$	20.50	4.65	1.97	1.00 ± 0.08
(380 nm)	20.50	4.65	1.97	0.90 ± 0.11[g]
	23.40	4.69	1.93	1.16 ± 0.08
	26.25	4.66	1.89	1.37 ± 0.12
	30.30	4.65	1.90	1.68 ± 0.12
trans-$Cr(NH_3)_3(OH_2)_2Cl^{2+}$ [f]	20.58	3.63	0.924	1.72 ± 0.19
(540 nm)	20.58	3.63	0.924	2.00 ± 0 25[h]
	26.45	3.61	1.09	2.39 ± 0.21
	29.70	3.60	1.04	2.71 ± 0.23
trans-$Cr(NH_3)_2(OH_2)_3Cl^{2+}$ [f]	20.80	5.61	0.989	5.54 ± 0.62
(560 nm)	20.80	5.61	0.989	5.85 ± 0.60[h]
	23.55	5.57	0.959	6.52 ± 0.76
	26.67	5.55	1.03	7.60 ± 0.88
	29.65	5.59	1.03	8.68 ± 1.04
trans-$Cr(NH_3)(OH_2)_5Cl^{2+}$ [f]	20.20	3.82	0.612	15.3 ± 1.5
(570 nm)	23.75	3.87	0.604	18.0 ± 1.7
	27.30	3.84	0.675	21.4 ± 2.0
	30.60	3.86	0.617	24.9 ± 2.4

[a] Initial concentration of complex. [b] Error ±5% (see Results). [c] Calculated from $k = k_0/[Cr^{2+}]$, where k_0 is the first-order rate constant determined experimentally from spectral change at the wavelength given inside parentheses under the substrate formula, except as noted for other wavelengths; errors given are standard errors estimated as stated in Results. [d] At 380 nm. [e] Concentration of oxidized Cr tripled above normal value (see Results). [f] Isomeric assignment not certain; the Cl ligand is believed to be *trans* to one of the OH_2 ligands. [g] At 540 nm. [h] At 400 nm.

The rate constants determined for various experimental conditions are given in Table I. For each complex listed, at least one experimentally determined set of isosbestic points was determined where the reactions were slow enough to allow wavelength scanning. These points were well defined for times up to at least 2 half-lives and closely agreed (±2 nm) with wavelengths predicted by plots of wavelength *vs.* molar absorptivity for spectra of the isolated Cr(III) complex ion and the product of the reaction, $Cr(OH_2)_5Cl^{2+}$. The molar absorptivities of the isosbestic points, after correction for absorbance of the Cr^{2+} (and any Cr(III) species formed by oxidation in the stock solution), agreed with those predicted within *ca.* 10%. Where infinite-time spectra were taken (namely, for the faster reactions, which were slowed as much as conveniently possible by making the concentration of Cr^{2+} smaller),

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[15] J. H. Espenson and S. G. Slocum, *Inorg. Chem.*, **6**, 906 (1967).

TABLE II

KINETIC PARAMETERS FOR ELECTRON-TRANSFER REACTIONS BETWEEN $Cr(OH_2)_6^{2+}$ AND MONOHALOCHROMIUM(III)–AMMINE COMPLEXES, *trans*-CrY_4LX^{2+}, IN 1.5 *F* $HClO_4$ AT 25°[a]

Species no.	Ligands on Cr(III)			k,[b] M^{-1} sec^{-1}	E_a,[c] kcal mol^{-1}	$\Delta S^{\ddagger}_{298}$,[c] cal deg^{-1} mol^{-1}	$10^3/\lambda_{max}$,[d] cm^{-1}
	L	Y_4	X				
1	NH_3	$(NH_3)_4$	F	0.00027[e]	14.0[e]	−30[e]	20.0[f]
2	NH_3	$(NH_3)_4$	N_3	0.021[g]	11.3 ± 0.1[g]	−30 ± 1[g]	20.1[f]
3	NH_3	$(NH_3)_4$	Cl	0.088[h]	11.7 ± 0.4[h]	−26 ± 2[h]	19.6[h]
3	NH_3	$(NH_3)_4$	Cl	0.051[e]	11.7[e]	−27[e]	19.6[h]
4	NH_3	$(NH_3)_4$	Br	0.32[e]	9.1[e]	−33[e]	19.1[f]
5	NH_3	$(NH_3)_4$	I	5.5[e]	...	...	18.5[f]
6	NH_3	$(NH_3)_3OH_2$	Cl	0.134[h]	11.0 ± 0.3[h]	−28 ± 2[h]	19.3[h]
6	NH_3	$(NH_3)_3OH_2$	Cl	0.120[i]	11.2 ± 0.5[i]	...	19.3[h]
7	OH_2	$(NH_3)_4$	Cl	1.27[h]	9.8 ± 0.3[h]	−28 ± 1[h]	18.4[h]
7	OH_2	$(NH_3)_4$	Cl	1.20[i]	10.3 ± 0.5[i]	...	18.4[h]
8	OH_2	$(NH_3)_3OH_2$	Cl	2.19[h]	9.9 ± 0.4[h]	−26 ± 1[h]	18.7[h]
9	OH_2	$(NH_3)_2(OH_2)_2$	Cl	6.94[h]	9.1 ± 0.4[h]	−27 ± 2[h]	18.2[h]
10	OH_2	$(NH_3)(OH_2)_3$	Cl	19.1[h]	8.4 ± 0.3[h]	−27 ± 1[h]	17.4[h]

[a] The *trans* designation refers to the L and X ligands (in some cases the configuration is not fully certain); where two sets of kinetic parameters are presented for a given species, the first set given has been used in the calculations found in the Discussion section. [b] Second-order rate constant in rate law rate = $k[Cr^{2+}]$[complex]. [c] Errors are estimated standard errors. [d] Lowest energy spectral transition ($A_{1g} \rightarrow T_{2g}$) for Cr(III) complex. [e] Reference 3; 1 *F* $HClO_4$. [f] Reference 6. [g] R. Fisher, I. F. Gearon, and J. B. Hunt, private communication, 1969; ~1 *F* $HClO_4$. [h] This research. [i] Reference 4.

these agreed with the spectrum of $Cr(OH_2)_5Cl^{2+}$ when corrected as indicated. The method of rate measurement was also checked, using *cis*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ as an example, by varying the Cr^{2+} concentration greatly to show that the rate constants conform to the expected second-order rate law and by increasing the amount of oxidation products of Cr^{2+} in the reaction solution to confirm that their presence has a negligible effect on the rate. The errors given in Table I were obtained by allotting a ±10% error to the calculated A_∞ (±5% where A_∞ was directly measured), as indicated by the isosbestic point agreement, and a ±5% error to the analyzed Cr^{2+} concentrations; the combined error should be a liberal estimate of a standard error for the second-order rate constants. The second-order rate constants gave linear Arrhenius plots well within the errors quoted in Table I. The calculated activation parameters and the extrapolated values for rate constants at 25° are given in Table II, along with values for related complexes.

Discussion

Kinetic Studies.—The mechanism for catalyzed ammine aquation by Cr_{aq}^{2+} is thought to be directly related to the electron-transfer rate between Cr_{aq}^{2+} and the kind of Cr(III) complexes studied in this work (*i.e.*, the rate-determining step for catalyzed aquation is the formation of the bridged activated complex in which electron transfer occurs).[16] For this reason these reactions will be referred to as electron-transfer reactions in the following discussion.

For reactions previously studied (species **1**–**7** in Table II) the mechanism for the reactions has been shown to be inner sphere by the transfer of the bridging halo ligand X from the Cr(III) reactant to the Cr(II) atom which becomes the Cr(III) product, $Cr(OH_2)_5X^{2+}$. The isosbestic points and infinite-time spectra for the new reactions studied (species **8**–**10**) show that the product of these reactions is $Cr(OH_2)_5Cl^{2+}$, demonstrating that these complexes also undergo electron transfer by an inner-sphere mechanism. The agreement of the experimental isosbestic points with the theoretical values also shows that other reactions (*e.g.*, spontaneous aquation, isomerization, or electron transfer with other than chloro bridging) are much slower than the chloro-bridged electron-transfer reaction and do not interfere with the rate measurements. The effect of the small amount of free Cl^- originating from the initial $CrCl_2$ salt was not studied, but other work[3,4] indicates that for $[Cl^-] < 0.1$ *M* the rate constants are not increased by more than *ca.* 10% in the presence of Cl^- ($[Cl^-] < 0.02$ *M* in our runs).

As shown in Table II, the remeasurement of rate constants for species **3**, **6**, and **7** is generally in agreement with previously reported values, except for $Cr(NH_3)_5Cl^{2+}$, for which our k value is significantly higher than that previously reported (the activation energy is the same within experimental error, however).

Qualitative Observations.—A qualitative survey of the data given in Table II reveals some interesting trends. For the same bridging ligand (in this case Cl) a comparison of the rate constants for species **3** and **7** and **6** and **8** shows an increase by a factor of *ca.* 15 when NH_3 is substituted by OH_2 in a position *trans* to the bridging ligand. However, for NH_3 being substituted by OH_2 in positions *cis* to the bridging ligand (*i.e.*, for species **3** and **6**, **7** and **8**, **8** and **9**, and **9** and **10**) the rate constants are increased by only a factor of 1.5–3.2 where either NH_3 or OH_2 is in the *trans* position. Since the activation entropies are constant within experimental error, the differences in activation energies are responsible for these rate variations. With perhaps the exception of X = N_3 as bridging ligand, the rate increases with decreased ligand field strength (according to the spectrochemical series). For this reason the rate constants (except for a minor reversal for species **7**) and activation energies correlate well with the $1/\lambda_{max}$ values given in Table II for the

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[16] N. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).

same bridging ligand, Cl. Where only the bridging ligand is changed (*i.e.*, species **1–5**) the k and E_a values follow the same trend as the spectral transitional energies (except for a minor reversal of species **1** and **2**).

The importance of the ligand *trans* to the bridging ligand has been recently discussed,[17] and the rate has been previously related to the ligand field strength of the ligand in that position.[18] The activation energy has been postulated to be partially the result of bond length changes in matching electronic states, as required by Franck–Condon restrictions, for the two metal ions.[2] Recent studies of ^{18}O isotope fractionation for the *cis*- and *trans*-$Cr(NH_3)_4(OH_2)Cl^{2+}$ [4] have shown that this is evidently a requirement in the formation of the activated complex in the electron-transfer reactions between Cr_{aq}^{2+} and the type of Cr(III) complex being discussed. The kinetic fractionation factor f (defined as $([^{18}O]/[^{16}O])$ in complex/$([^{18}O]/[^{16}O])$ in solvent water) was found to be 1.072 for OH_2 *trans* to Cl and 1.007 for OH_2 *cis* to Cl, in good agreement with the importance of the *trans* ligand for the rate comparisons in the preceding discussion.

Semiempirical Treatment.—The qualitative correlation of activation energy with the spectral splitting ($1/\lambda_{max}$ in Table II) may be rationalized by the following semiempirical treatment. It has been limited to the electron-transfer reactions of the analogous Cr(III) complexes given in Table II since the multiplicity changes possible in Co(III) systems have been neglected and the treatment is partially based on the similarity of complexes in a series of reactions being considered.

With reference to the Marcus theory of electron-transfer reactions,[2] the activation energy is made up of a number of contributions

$$E_a = E_c^{\ddagger} + E_o^{\ddagger} + E_{ir}^{\ddagger} + E_{io}^{\ddagger} - E_r^{\ddagger} \qquad (2)$$

where the terms correspond to the energies for overcoming coulombic repulsions ($E_c^{\ddagger}$), rearrangement of solvent molecules and ion atmosphere ($E_o^{\ddagger}$), internal rearrangement of the coordination sphere of the reductant ($E_{ir}^{\ddagger}$), and internal rearrangement of the bond lengths of the oxidant ($E_{io}^{\ddagger}$). The resonance energy term, $E_r^{\ddagger}$, is considered negligible in the Marcus theory, but this may not be true for bridged mechanisms and the term is included to account for energy gained through metal-to-bridge π overlap or processes such as a "superexchange" mechanism.[19] The value of the series of reactions given in Table II is that their similarity permits the assumption that some of the terms in eq 2 remain constant as the coordination sphere of the Cr(III) complex is changed. The value for $(E_c^{\ddagger} + E_o^{\ddagger})$ should be the same for all reactants in Table II provided the relative differences in internal rearrangement do not cause significant differences in $E_o^{\ddagger}$, and the term $(E_{ir}^{\ddagger} - E_r^{\ddagger})$ should be approximately constant, given the same bridging ligand X and a similar geometry for the activated complex. The activation energy is then given by eq 3, where C is the approximately

$$E_a = E_{io}^{\ddagger} + C \qquad (3)$$

constant sum of the terms $E_c^{\ddagger}$, $E_o^{\ddagger}$, $E_{ir}^{\ddagger}$, and $-E_r^{\ddagger}$.

A simple model for internal rearrangement after bridge formation involves compression of Cr(II) bonds to distances equivalent to those of $Cr(OH_2)_5Cl^{2+}$, followed by changes on the Cr(III) metal center to account for differences in the ligand field strength around the two ions in the bridged transition state matching their electronic states, as is required by Franck–Condon restrictions (*i.e.*, during the electron exchange the free-ion terms for the two ions are presumably matched at some point and a similar ligand field potential should facilitate the matching of the electronic states). To simplify the model only the ligand *trans* to the bridge will be moved from a distance r to r', holding those *cis* to the bridge at their initial distance. The change in ligand field potential for the *trans* ligand L is given by eq 4, where Q_L may be thought of as the product of some

$$\Delta Dq_L = (Q_L/r') - (Q_L/r) \qquad (4)$$

effective point charge for the ligand electron distribution and an effective point charge corresponding to the electron being exchanged in the electronic state required for the electron transfer. The energy required for this displacement, which according to the model used represents the total internal rearrangement energy of the oxidant, $E_{io}^{\ddagger}$, is given by eq 5, where k_L is the force constant of the

$$E_{io}^{\ddagger} = k_L(r' - r)^2/2 \qquad (5)$$

Cr(III)–L bond. Solving for r' in eq 4 and substituting into eq 5 gives

$$E_{io}^{\ddagger} = (k_L/2)[r^2\Delta Dq_L/(Q_L - r\Delta Dq_L)]^2 \qquad (6)$$

which, upon substituting into eq 3 and making the approximation that $\Delta Dq_L \ll Q_L/r$,[20] gives

$$E_a = [(k_L/2)r^4(\Delta Dq_L)^2/Q_L^2] + C \qquad (7)$$

The evaluation of the ligand field change for the *trans* ligand L is most simply done by assuming that the octahedral case approximates the less symmetrical complexes given in Table II (*i.e.*, the overall ligand field strength, an average of the octahedral values for the individual ligands, is given by a tenth of the splitting for the low-energy transition). Taking the splitting E ($1/\lambda_{max}$ from Table II) for the Cr(III) complex and the low-energy transition, E', for the corresponding $Cr(OH_2)_5X^{2+}$ complex, the change in potential for the ligand L is given by $\Delta Dq_L = (6/10)$

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[17] D. E. Pennington and A. Haim, *Inorg. Chem.*, **5**, 1887 (1966).

[18] L. Orgel, Report of the Tenth Solvay Conference, Brussels, 1956, p 289.

[19] J. Halpern and L. E. Orgel, *Discuss. Faraday Soc.*, **29**, 32 (1960).

[20] A value for Q_L/r may be roughly estimated by considering the interaction of the sp^3 orbital of nitrogen or oxygen (containing two electrons) and the d_{z^2} Cr(III) orbital (containing one electron after electron transfer). Using a separation of 2.0 Å and charges of 0.30e for sp^3 and 1.00e for d_{z^2} (e is the electronic charge in statcoulombs) reported for Cr–N in $[Cr(NH_3)_6][CuCl_5]$ by K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968), and Cr–N = 2.08 Å and Cr–O = 2.05 Å, bond lengths found in the *trans*-dichloro compound $[Cr(en)(OH_2)_2Cl_2]Cl$ by R. Stomberg and I. Larking, *Acta Chem. Scand.*, **23**, 343 (1969), $Q_L/r \approx 50$ kcal mol^{-1}. The maximum ΔDq_L used by us is 5.5 kcal mol^{-1}.

$(E' - E)$.[21] An alternate method is to use the results of Perumareddi's calculations,[6] which show that the low-energy transition for Cr(III) complexes of the form $Cr(OH_2)_5X^{2+}$ is given by $E' = (15/2)Dq_{OH_2} + (5/2)Dq_X$ and for complexes of the general formula *trans*-MX_4Y_2 the lowest energy transition is given by $E = 5Dq_X + 5Dq_Y$, using octahedral Dq values. Using this method the octahedral Dq values for ligands on and off the bridging axis are averaged individually (*i.e.*, for $Cr(NH_3)_n(OH_2)_{4-n}LX^{2+}$ (L and X *trans*) the low-energy transition is $E = 5[(nDq_{NH_3} + (4 - n) \cdot Dq_{OH_2})/4] + 5[(Dq_L + Dq_X)/2]$). Then changing Dq_L to Dq'_L so that $E = E'$, $Dq'_L = [(2 + n)/2]Dq_{OH_2} - (n/2)Dq_{NH_3}$ and $\Delta Dq_L = Dq'_L - Dq_L$.

Plots of E_a *vs.* $(\Delta Dq_L)^2$ (suggested by the mathematical form of eq 7) for the octahedral symmetry approximation and the lower symmetry treatment are shown as (a) and (b) respectively of Figure 2. Both plots appear to be linear within the error limits. The intercepts of the plots, C, are about the same, 8.4 ± 0.2 kcal mol^{-1}; however, the slopes differ by a factor of *ca.* 2. If the model is correct, the internal energies, $E_{io}^{\neq}$, for rearrangement of the chromium(III)-chloro complexes given in Table II are in the range 0–3.3 kcal mol^{-1} and should be essentially independent of the nature of the bridging ligand X. Although the slope of the plots could be considered as only an empirical constant, the proposed expression for the slope, $(k_L/2) \cdot r^4/Q_L^2$, yields a value of $(0.9\text{–}2.1) \times 10^{-20}$ statcoulomb^2 for Q_L (*i.e.*, of the order of the product of some fractions of electronic charge) using $r = 2.0$ Å,[20] $k_L = (1\text{–}5) \times 10^5$ dyn cm^{-1},[22,23] and a slope of 7.4 mol kcal^{-1}, the average of the slopes of the two plots in Figure 2.

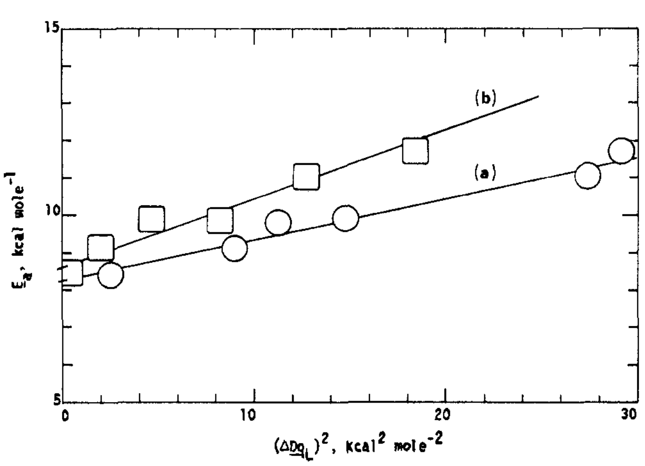

Figure 2.—Plot of activation energy *vs.* $(\Delta Dq_L)^2$ (see text, eq 7) for electron-transfer reactions between Cr_{aq}^{2+} and $Cr(NH_3)_n(OH_2)_{5-n}Cl^{2+}$ (n = 1–5); plots a and b result from two different models discussed in the semiempirical treatment section, with the dimensions of the squares and circles approximating the standard errors in the parameters.

Considering changes in activation energy with changing bridging ligand X, two further approximations can be made. At high ionic strength the coulombic repulsion term, $E_c^{\neq}$, is small (for $\mu = 1.5\,M$, $r = 4$ Å, $E_c^{\neq}$ is estimated to be ~0.8 kcal mol^{-1} [24]). The outer-sphere rearrangement energy, $E_o^{\neq}$, may also be small since it depends on the difference in charge between the two reactants (both are formally 2+). If we neglect these two terms and calculate an average value for $E_{io}^{\neq}$ at the proper $(\Delta Dq_L)^2$ from Figure 2, the energies associated with $E_{ir}^{\neq} - E_r^{\neq}$ are 10.9, 8.7, 8.1, and 6.4 kcal mol^{-1}, respectively, for X = F, Cl, N_3, and Br. Again according to the model used, this difference must be the result of either Cr(II)–X bond length changes or a change in the amount of resonance energy gained in the activated complex. The trend exhibited accommodates both ideas since the Cr(II)–F bond should have the highest force constant while the more polarizable Br ligand should give the most electron delocalization. The differences could be formally accounted for by changes in force constants in the range $(1\text{–}3) \times 10^5$ dyn cm^{-1} for the Cr(II)–X bonds, requiring 2.8–8.4 kcal mol^{-1} for a bond shortening of 0.2 Å (that suggested for the difference between radii for $Cr(OH_2)_6^{2+}$ and $Cr(OH_2)_6^{3+}$ [22]).

Conclusions

While the data indicate a strong correlation between the activation energies and the ligand field strength of the Cr(III) oxidant, the model used to rationalize this correlation is, of course, open to question. The use of $Cr(OH_2)_5X^{2+}$ as a model for the contracted Cr(II) coordination sphere is approximate at best, but it has the advantage of giving accessible ligand field strength estimates. Fractionation studies with ^{18}O show an isotope effect for products of the $Cr(en)_2^{2+}$–$Co(NH_3)_5Cl^{2+}$ electron-transfer reaction which suggests that bond shortening does occur on the Cr(II) reductant.[25] The $Cr(OH_2)_5X^{2+}$ model may give only an approximate upper limit for these bond-length changes. Our calculations also assume that the reactions studied are adiabatic and there is a high probability of electron transfer in the proposed activated complex (if this commonly made assumption were not valid here, the experimental E_a would include an unknown term for the enthalpy of formation of the bridged activated complex).

Depending on the validity of the model and the approximations made, the preceding treatment supports the applicability of the Marcus theory for electron transfer using bridged mechanisms, as well as Orgel's proposal that the internal rearrangement to form the activated compex may occur primarily along the bridge axis, at least for these reactions. In any case, the value $(\Delta Dq_L)^2$, as described, empirically correlates well with changes in activation energy as only nonbridging Cr(III) ligands are changed. The importance of the ligand *trans* to the bridge, as noted in the qualitative observations, is apparently the result of the more

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(21) Using octahedral values of Dq for the ligands Y_4LX, $E/10 = (\Sigma Dq_{Y_i} + Dq_X + Dq_L)/6$ and $E'/10 = (\Sigma Dq_{Y_i} + Dq_X + Dq'_L)/6$. Therefore, $\Delta Dq_L = (Dq'_L - Dq_L) = (6/10)(E' - E)$.

(22) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962).

(23) The values given are for Fe(II) and Fe(III) hexaaquo ions, but should give correct order of magnitude k_L values for the Cr(III) complexes.

(24) W. L. Reynolds and R. W. Lumry, "Mechanisms of Electron Transfer," Ronald Press, New York, N. Y., 1966, p 123.

(25) M. J. DeChant and J. B. Hunt, private communication, 1970.

direct influence of this ligand on the electronic state used for electron transfer. A comparison of data[17] for electron-transfer reactions between Cr_{aq}^{2+} and *cis*- and *trans*-$Cr(en)_2(OH_2)Cl^{2+}$ (en = ethylenediamine) with the plots in Figure 2 gives good agreement for the *cis*-chloroaquo complex; however, the *trans* complex results are significantly different from that expected, suggesting that chelation brings in still another factor which must be considered in a calculation of E_a. Although isotopic fractionation studies[4,26] suggest that ligand motion on the oxidant is more important for Cr(III) than for Co(III) in the formation of the activated complex, the range of calculated $E_{io}^{\ddagger}$ values (0–3.3 kcal mol^{-1}) indicates that this term makes a small but sometimes significant contribution to the overall activation energy for Cr(II)–Cr(III) electron-transfer reactions.

[26] M. Green, K. Schug, and H. Taube, *Inorg. Chem.*, **4**, 1184 (1965).

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Electron Paramagnetic Resonance of *trans*-Disubstituted Bis(ethylenediamine)chromium(III) Complexes in Frozen Solutions[1a]

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Electron paramagnetic resonance (epr) spectra are reported for low-temperature glassy solutions of the *trans*-dichloro-, -diaquo-, -dihydroxo-, and -dithiocyanatobis(ethylenediamine)chromium(III) complexes. Spin-Hamiltonian parameters are determined from the spectra by a method applicable to other transition metal ion systems with zero-field splittings large in comparison to $h\nu$. It is shown that the absolute magnitude of the experimentally determined spin-Hamiltonian parameter E for these *trans*-$Cr(en)_2A_2^{n+}$ complexes is proportional to the ligand field strength of the A ligands as deduced from the visible absorption spectra of the corresponding $CrA_6^{3\pm}$ complexes.

Introduction

The *trans*-$Cr(en)_2A_2^{n+}$ complexes make up a well-characterized series and have been the subjects of a number of visible absorption spectral investigations.[2-4] A single-crystal epr study has been carried out only for the dichloro complex,[5] at least partially because of the difficulty involved in growing suitable single crystals. However, even when magnetically dilute single crystals cannot be prepared, all magnetic resonance information except the orientation of the symmetry axes can be obtained from epr spectra of low-temperature glassy solutions. Spectra and spin-Hamiltonian parameters for the quartet ground-state *trans*-$Cr(en)_2A_2^{n+}$ complexes with A = SCN^-, Cl^-, H_2O, and OH^- are reported in this paper.

The method used to analyze the epr spectra of these quartet ground-state ions involves techniques which are similar to those recently described by Dowsing and coworkers in the interpretation of epr spectra of randomly oriented sextet ground-state ions.[6-10] Relevant discussions of techniques are given by Dowsing and Gibson[9] and by Aasa, Falk, and Reyes.[11] Because of the greater simplicity of the experimental systems, analysis of these quartet ground-state spectra can be carried further than was possible for the sextet ground-state spectra. The analyses are more quantitative than those previously reported for chromium(III) systems in glasses[12-16] with results comparable to those for magnetically dilute powders.[11,17-19]

Experimental Procedures

Epr spectra of frozen solutions were recorded at approximately −120° on a Varian X-band spectrometer, Model 4502. Field strengths were obtained using the Fieldial. The compounds were prepared by established procedures as indicated and their visible absorption spectra in solution agree with those of Baker and Phillips[2a] and of Woldbye.[20]

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