Solvation of Chromium(III) Ion in Acidic Water–Dimethyl Sulfoxide Solutions[1]

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Abstract: The solvation of chromium(III) ion in acidic water–dimethyl sulfoxide solutions has been studied using ion-exchange procedures to separate the differently solvated species $(Cr(OH_2)_{6-n}(OS(CH_3)_2)_n{}^{3+}$, n = 0–6 inclusive) from one another. The equilibrium relative concentrations at 60° of each of these species, including isomeric species with n = 2, 3, and 4, were determined over the solvent composition range, $Z = 0.00365$ to 0.819 (Z = mole fraction of dimethyl sulfoxide). Equilibrium quotients for each of the stepwise replacement reactions in which water in the first coordination shell around chromium(III) is replaced by dimethyl sulfoxide decrease with increasing concentration of dimethyl sulfoxide in the solvent. This may be caused by outer-sphere association of dimethyl sulfoxide with solvated chromium(III) ions. Extrapolated to pure water, the equilibrium quotient for the first stepwise reaction is $Q_1 = [Cr(OH_2)_5(OS(CH_3)_2)^{3+}]a_{H_2O}/\{[Cr(OH_2)_6{}^{3+}]a_{(CH_3)_2SO}\} = 220$; this value is based upon pure water and pure dimethyl sulfoxide as the standard states. Values of the equilibrium quotients for formation of each of the other species from hexaaquochromium(III) ion show a mild increase with increasing n after appropriate correction for the statistical factor. The more easily eluted species for each of the compositions where isomerism is possible (n = 2, 3, and 4) is the *cis* isomer. Kinetic studies have been made on the reaction involving formation of the species with n = 1.

Dimethyl sulfoxide is a polar aprotic solvent[3] with two electron-rich sites for coordination to metal ions. There is abundant evidence for such interaction in liquid solution[4,5] and in the solid phase. A number of crystalline coordination compounds of dimethyl sulfoxide and transition metal ions, including chromium(III) ion, have been prepared and characterized.[6–9] On the basis of the infrared frequency due to sulfur–oxygen stretching, the bonding between chromium(III) and dimethyl sulfoxide in $(Cr(OS(CH_3)_2)_6)(ClO_4)_3$ is believed to involve oxygen, not sulfur.[10] Recently, Berney and Weber observed the chromium(III)–oxygen stretching band in the infrared spectrum of this compound.[11]

In its coordination with chromium(III), dimethyl sulfoxide exhibits a smaller ligand field strength than water (~1580 cm^{-1} compared to ~1740 cm^{-1} for water[8,9]); nevertheless chromium(III) forms solvated species containing zero to six coordinated dimethyl sulfoxide molecules $(Cr(OH_2)_{6-n}(OS(CH_3)_2)_n{}^{3+}$, n = 0–6 inclusive) in aqueous dimethyl sulfoxide solutions.[12] The present paper reports a detailed study of the equilibria existing in acidic aqueous dimethyl sulfoxide solutions of chromium(III) at 35 and 60°. The inertness of chromium(III) allows the use of ion-exchange procedures both for evaluation of $\bar{n}$, the average number of bound dimethyl sulfoxide molecules per chromium(III) ($\bar{n}$ = moles of bound dimethyl sulfoxide/total moles of chromium(III)), and for separation of the individual differently solvated chromium(III) species. The ion-exchange procedures were patterned after those used in earlier studies on solvation of chromium(III) in water–methanol solution,[13] water–ethanol solution,[14] and water–pyridine N-oxide solution.[15] As in the last of these studies,[15] separation of isomeric species containing two, three, and four ligands of one kind has been accomplished. In addition to equilibrium studies, the rates of formation and aquation of pentaaquo (dimethyl sulfoxide) chromium(III) ion have been determined at 60°.

Experimental Details and Results

Reagents. Chromium(III) perchlorate was prepared by reduction of reagent grade chromium(VI) oxide with hydrogen peroxide in perchloric acid solution. The solid chromium(III) perchlorate hydrate obtained in this way was recrystallized once or twice from aqueous perchloric acid (1–5 *M*). Stock aqueous solutions were prepared from the recrystallized material; in all such solutions the concentration of perchloric acid was greater than 1 *M*. An inappreciable amount of polymeric chromium(III) species was present in the solutions as judged by the ratio of absorbance values at 260 and 230 mμ; $A_{230}/A_{260} \leqslant 0.3$.[16] Reagent grade acids were used without additional purification. Water was doubly distilled, with the second distillation being from an all-Pyrex still. Between the two distillations, the water was passed through an ion-exchange demineralizer. For most experiments, reagent grade dimethyl sulfoxide (Matheson Coleman and Bell) was used without further purification; some batches were purified

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by vacuum distillation from calcium hydride. No evidence was obtained to suggest that the unpurified material was inadequate. Reagent grade Dowex 50W ion-exchange resins were used in the hydrogen ion form. (Resin with different degrees of cross-linking was used in different experiments; the degree of cross-linking will be specified for each type of experiment.) The resin was treated in a manner similar to that employed in earlier studies.[14,15]

Analytical Procedures. Analysis for chromium was made by conversion to chromate ion with alkaline hydrogen peroxide. The concentration of chromate ion was determined from its light absorption at 372 nm ($a = 4820$ l. mole^{-1} cm^{-1}).[17] Dimethyl sulfoxide was analyzed by reaction with excess permanganate ion.[18] Before analysis for dimethyl sulfoxide bound to chromium(III) ion, the effluent solutions were heated at 75–80° for 1–2 days to cause aquation of the chromium(III) species. (It was not proved, however, that this step is necessary.) Chromium(III) does not interfere with the analysis for dimethyl sulfoxide.

Solutions for Equilibration. Solutions for equilibration were prepared using weighed portions of dimethyl sulfoxide, measured volumes of stock perchloric acid–chromium(III) perchlorate solution of known density, and water to give a particular volume of solution, the density of which then was measured. The solvent composition will be described in terms of Z, the mole fraction of dimethyl sulfoxide, calculated with only water and dimethyl sulfoxide taken into account (Z = (moles of dimethyl sulfoxide)/(moles of dimethyl sulfoxide + moles of water)).

Evaluation of $\bar{n}$. The values of $\bar{n}$ were determined over a range of solvent composition at 35 and 60°. Solutions with 0.073–0.155 M perchloric acid and 0.0058–0.0120 M chromium(III) perchlorate (with $[H^+]/[Cr^{III}]$ between 7 and 13) were equlibrated for 50–100 days at 35° and 3–14 days at 60°. Rough kinetic experiments showed these times to be ~10 times the half-time for establishment of equilibrium. A chilled portion of equilibrated solution containing 0.2–0.4 mmole of chromium(III) was added to a jacketed column containing Dowex 50W-X8 (100–200 mesh) resin. (Solutions with a high concentration of dimethyl sulfoxide ($Z > 0.08$) were diluted with cold 0.1 M perchloric acid before being added to the column.) In solutions containing an appreciable amount of hexakis(dimethyl sulfoxide)chromium(III) ion (solutions with $Z > 0.20$), the perchlorate salt of this cation was precipitated by this procedure. If this occurred, the precipitate was transferred with the solution to the ion-exchange column. The free solvent dimethyl sulfoxide was rinsed from the column with cold (~0°) 0.1 M perchloric acid. Elution of all chromium(III) species except hexakis(dimethyl sulfoxide)chromium(III) ion was accomplished with cold (5–15°) 3 M perchloric acid. To remove the hexakis(dimethyl sulfoxide)chromium(III) ion, the column temperature was raised by passing steam through the jacket; removal of the remaining chromium then was possible with 3 M perchloric acid. The chromium recovery was good, being greater than 99% in all but a few experiments. Analysis of the eluent for chromium and dimethyl sulfoxide by the procedures already described allowed evaluation of $\bar{n}$. For 35° these values are (given as $r_Z = (Z/(1 - Z))$, $\bar{n}$): 0.0091, 0.18; 0.0181, 0.36; 0.0194, 0.37; 0.0300, 0.58; 0.0406, 0.80; 0.0428, 0.85; 0.0555, 1.18; 0.0661, 1.35; 0.0893, 1.78; 0.0992, 1.92; 0.110, 2.13; 0.113, 2.34; 0.168, 2.72 (three experiments); 0.225, 3.17; 0.245, 3.29; 0.344, 3.73; 0.351, 3.73; 0.406, 3.90; 0.565, 4.17; 0.531, 4.20; 0.728, 4.45; 0.794, 4.58; 1.29, 5.07; 1.72, 5.25; 2.24, 5.22; 3.43, 5.62; and 3.47, 5.47. For 60° these values are 0.0060, 0.14; 0.0118, 0.30; 0.0203, 0.51; 0.0304, 0.78 (two experiments); 0.0312, 0.80; 0.0323, 0.84; 0.0410, 1.06; 0.0472, 1.21; 0.0748, 1.78; 0.0787, 1.91; 0.0872, 2.03; 0.0922, 2.07 (two experiments); 0.104, 2.28; 0.138, 2.65; 0.192, 3.10; 0.202, 3.24; 0.281, 3.66; 0.292, 3.65; 0.422, 4.07; 0.562, 4.25; 0.752, 4.64; 0.816, 4.82; 1.035, 4.82 (two experiments); 1.32, 5.04; 1.96, 5.30; 2.00, 5.33; 2.18, 5.31; and 3.96, 5.70. (These data are presented without specification of the solute concentrations. There were no trends of $\bar{n}$ with changes of concentration of perchloric acid or chromium(III) perchlorate.) These data for 60° and values of $\bar{n}$ calculated from the experimentally determined relative concentrations of the individual chromium(III) species are presented in Figure 1. The figure also includes values of $\bar{n}$ for aluminum(III) ion in the same solvent system at 35° obtained from nuclear magnetic resonance data.[19]

Evaluation of the Relative Concentration of Hexakis(dimethyl sulfoxide)chromium(III) Ion in the $\bar{n}$ Experiments. The procedures just outlined allowed evaluation of the relative concentration of hexakis(dimethyl sulfoxide)chromium(III) ion since this species was not removed in the initial effluent. The values of α_6 (the fraction of chromium(III) present as $Cr(OS(CH_3)_2)_6{}^{3+}$) as a function of solvent composition at 35° are (given as $r_Z = (Z/(1 - Z))$, α_6): 0.351, 0.036; 0.406, 0.040; 0.531, 0.071; 0.565, 0.093; 0.728, 0.138; 0.794, 0.158; 0.946, 0.200; 1.291, 0.302; 1.72, 0.423; 2.24, 0.500; 3.43, 0.648; and 3.47, 0.661. For 60°, the corresponding data are: 0.202, 0.021; 0.281, 0.043; 0.292, 0.034; 0.422, 0.070; 0.562, 0.109; 0.752, 0.196; 0.816, 0.224; 1.03, 0.293; 1.04, 0.280; 1.32, 0.377; 1.96, 0.541; 2.00, 0.490; 2.18, 0.566; and 3.96, 0.743. These values are based, of course, upon the assumption that no hexakis(dimethyl sulfoxide)chromium(III) ion was eluted with cold 3 M perchloric acid.

Ion-Exchange Separation of Differently Solvated Species. Ion-exchange procedures have allowed separation of differently solvated species $Cr(OH_2)_{6-n}(OS(CH_3)_2)_n{}^{3+}$ (n = 0–6 inclusive, with two species each for n = 2, 3, and 4). Gradient elution with sulfuric acid as eluting agent was used in these experiments. The concentration of sulfuric acid ranged between a low of 1–3 M and a high of 6 M. The initial concentration was made higher in experiments on solutions with a higher concentration of dimethyl sulfoxide. Dowex 50W-X12 or Dowex 50W-X4 ion-exchange resin was used. The separations were better using the X-4 resin. The column dimensions were 1.5 cm (i.d.) × 150 cm, flow rates were ~10 ml/hr, and the temperature was maintained at $-1 \pm 2°$ by circulating chilled water–ethylene glycol solution through the column jacket. Free dimethyl sulfoxide was rinsed from the resin with 0.01 M per-

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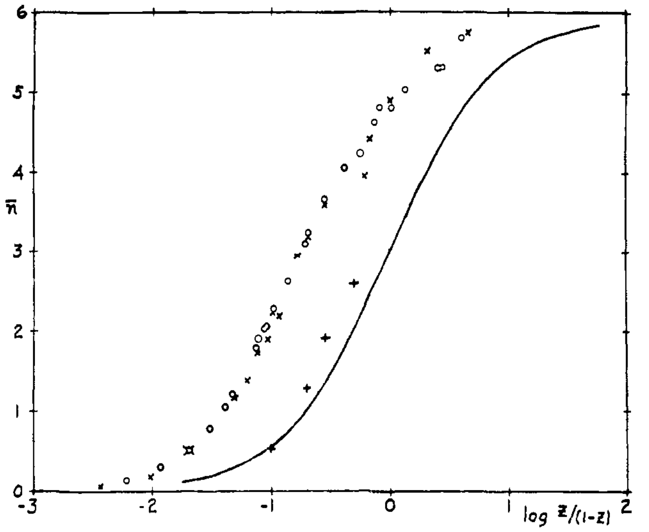

Figure 1. The average number of dimethyl sulfoxide molecules bound per chromium(III) ion, $\bar{n}$, as a function of solvent composition, Z (Z = mole fraction of dimethyl sulfoxide) at 60°: (○) $\bar{n}$-type experiment; (×) $\bar{n}$ calculated from the relative concentration of several species (see Table I); (+) $\bar{n}$ values for aluminum(III) ion (data from ref 19). The solid line gives $\bar{n}$ values expected on the basis of random solvation (*i.e.*, $\bar{n}/(6 - \bar{n}) = z/(1 - z)$).

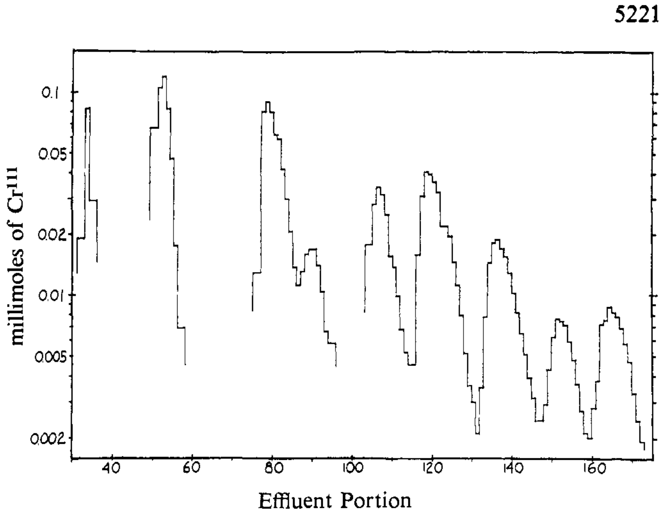

Figure 2. Elution separation of species $Cr(OH_2)_{6-n}(OS(CH_3)_2)_n{}^{3+}$, Z = 0.095. The values of $\bar{n}$ determined for certain combined portions of effluent (volume of each effluent portion was ~7 ml) are: 33 (single portion), 0.00; 51–55, 1.00; 77–81, 2.03; 88–91; 2.08; 105–108, 2.97; 118–121, 2.96; 135–138, 3.88; 150–155, 4.87; and 162–167, 3.93. Gradient elution: 1.5–6 *M* H_2SO_4; Dowex 50W-X4 (200–400 mesh).

chloric acid before elution was started. Figure 2 shows an elution profile of an equilibrated solution with Z = 0.095. The indicated portions were analyzed for both dimethyl sulfoxide and chromium, and the values of $\bar{n}$ (given in the figure caption) indicate the elution order in this experiment to be $Cr(OH_2)_6{}^{3+}$, $Cr(OH_2)_5(OS(CH_3)_2)^{3+}$, $Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}$ (two different species which will be designed α, the more easily eluted, and β, the less easily eluted), $Cr(OH_2)_3(OS(CH_3)_2)_3{}^{3+}$ (two different species), $Cr(OH_2)_2(OS(CH_3)_2)_4{}^{3+}$, $Cr(OH_2)(OS(CH_3)_2)_5{}^{3+}$, and finally another species, $Cr(OH_2)_2(OS(CH_3)_2)_4{}^{3+}$, containing four dimethyl sulfoxide molecules. On the basis of the elution pattern observed in the separation of species in solutions with $Z < 0.08$, it was anticipated that the various species would be eluted strictly in the order of increasing value of n (in $Cr(OH_2)_{6-n}(OS(CH_3)_n{}^{3+})$. For solutions in which there was an appreciable amount of species with $n = 5$, the pattern differed as is seen in Figure 2. If hexakis(dimethyl sulfoxide)chromium(III) ion was present, it was eluted in a band which overlapped the band due to the more easily eluted of the species containing four bound dimethyl sulfoxide molecules. Resolution of the relative amounts of the two species was based on one of two possible procedures. The measured value of $\bar{n}$ for the band can be used to calculate the relative amounts of the two species. Parallel elution experiments can be done; one is a regular elution and the other involves an equilibrated solution from which hexakis(dimethyl sulfoxide)chromium(III) ion is precipitated as the perchlorate with 1.5 *M* perchloric acid.

Twenty-four equilibrated solutions with Z between 3.65×10^{-3} and 0.819 were analyzed in this way for the concentrations of the differently solvated chromium(III) species. The results are presented in Table I. Comparison of the three series of experiments at $Z \cong 0.047$ shows that variations of the concentrations of chromium(III) perchlorate and perchloric acid have no appreciable effect on the relative concentrations of the several species.

Activities of the Solvent Components. The Distribution of Dimethyl Sulfoxide between Aqueous Solution and Organic Solvents. The interpretation of the relative concentrations of the differently solvated chromium(III) species in terms of equilibrium quotients for the stepwise solvation exchange reactions requires the ratio of activities of the solvent components. Values of the activities of each solvent component at 35 and 60° can be obtained from excess free-energy values at 25 and 70° based upon heats of mixing at 25° and vapor pressure data at 70°.[20] Excess free-energy values were interpolated to the temperatures of interest and fit at each of these temperatures to an equation

$$G^{ex} = 2.3RT\{Z(1 - Z)(A + B(2Z - 1) + C(2Z - 1^2)\}$$

by the method of least squares. The values of A, B, and C obtained in this way are at 35° −0.817, 0.320, and −0.107, respectively, and at 60° −0.682, 0.229, −0.084, respectively. With values of these parameters, the activity coefficients of each solvent component can be calculated. For 60°, the values so calculated are (given as Z, γ_{DMSO}, γ_{H_2O}): 0, 0.101, 1.00; 0.050, 0.149, 0.990; 0.100, 0.207, 0.965; 0.200, 0.353, 0.881; 0.300, 0.504, 0.779; 0.400, 0.649, 0.680; 0.500, 0.771, 0.592; 0.600, 0.862, 0.518; 0.700, 0.925, 0.453; 0.800, 0.966, 0.400; 0.900, 0.991, 0.345; and 1.000, 1.00, and 0.290. Because use of these activity coefficient values gave values of equilibrium quotients which showed an appreciable dependence on solvent composition, it seemed appropriate to check the activity coefficient for dimethyl sulfoxide in dilute aqueous solution in an independent study. This was done by measurement of its distribution between aqueous solution and two different organic solvents, benzene and *sym*-tetrachloroethane. These experiments were carried out at 60°, and each phase was analyzed for dimethyl sulfoxide. Values of the distribution coefficient are probably accurate to

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Table I. Amount of Chromium(III) Present as $Cr(OH_2)_{6-n}(OS(CH_3)_2)_n{}^{3+}$ at 60°[a]

100 × Z	0.365	0.954[b]	1.99	4.70[c]	4.73[b,c]	4.74[e]	5.98[b]	7.1[f]	8.7	9.5	10.4	14.1	17.4	21.6	29.2	40.0	58.2	67.0	81.9
% Cr^{III} as species n																			
n = 0	89.4	78.	58.4	28.0	27.8	29.5	20.4	12.5	8.3	6.6	4.7	1.8	(0.9)[d]	(0.3)[d]	...	...	...		
1	7.4	17.2	27.6	33.2	33.3	35.0	32.1	28.8	21.2	19.4	15.7	9.0	5.1	2.5	(0.7)[d]	...	...		
2α			6.2[i]	18.7	18.2	19.0	22.5	22.2	24.0	24.4	22.6	19.2	14.3	9.8	4.3	...	...		
2β				4.1	(5.4)[d]	(6.6)[h]	(10.2)[h]	4.6	(13.2)[h]	5.6	(14.3)[h]	4.6	3.4	2.6	1.4	...	...		
3α			2.4[i]	3.8	3.7			6.7		9.6		11.9	12.7	10.2	7.0	4.3	(1.6)[d,i]		
3β				5.3	6.4	6.9	10.6	16.2	16.6	15.5	29.4	19.2	19.5	17.7	14.9	8.3			
4α							(1.0)[d,i]	2.3[i]	4.7	7.5	6.3[i]	13.8[g]	17.0[g]	20.9[g]	21.8[g]	22.9	17.0	5.9	1.6
4β										3.7		8.0	8.7	12.6	14.1	10.3	6.9	3.1	(0.4)[d]
5										2.8		8.0	11.1	17.0	24.7	31.9	40.7	24.6	18.2
6												(1.1)[d,g]	(0.)9[d,g]	2.7[g]	3.3	8.7	28.0	58.2	77.2
% Cr recovery	97	95	95	93	95	97	97	93	88	95	93	96	94	96	92	86	94	92	97

[a] 0.098 M $HClO_4$, 0.0100 M $Cr(ClO_4)_3$, unless noted otherwise. [b] 2.5 × 10^{-3} M $Cr(ClO_4)_3$, 5.0 × 10^{-2} M $HClO_4$. [c] Average of three experiments. [d] Uncertain value. [e] 5.0 × 10^{-4} M $Cr(ClO_4)_3$, 2.0 × 10^{-2} M $HClO_4$. [f] Average of two experiments. [g] Resolution of 4α and 6 from average n. [h] Resolution of 2β and 3α peaks not achieved. [i] Isomer not separated.

±10%. The results are presented in Table II, which includes values for the distribution coefficients expected on the basis of the activity coefficient values cited above and assumed conformity of dimethyl sulfoxide to Henry's law in the organic phase. Within experimental error these distribution data are consistent with the activity coefficient values obtained from vapor pressure data. Since the aqueous phase in each of these experiments contained electrolyte (including chromium(III) species in some cases) which had no appreciable effect upon the distribution coefficient, use of the activity coefficient data obtained for electrolyte-free binary solvent mixtures is appropriate for calculations pertaining to the electrolyte-containing solutions studied. The concentrations of dimethyl sulfoxide in the two different organic phases (in equilibrium with a particular aqueous phase) differed by a factor of approximately 30. The agreement of the two sets of extraction data supports, therefore, the assumption of obedience to Henry's law in each organic solvent.

Preparation of Isomeric Bis(dimethyl sulfoxide)chromium(III) Ion by Other Methods. Nonequilibrium mixtures of dimethyl sulfoxide–chromium(III) species were prepared by two different methods: the solvolysis of pentaaquoiodochromium(III) ion in an aqueous dimethyl sulfoxide solution, and the reaction of *trans*-tetraaquodichlorochromium(III) ion with mercury(II) in a similar solvent.

On the basis of the study by Moore, Basolo, and Pearson,[21] it was anticipated that the *trans* isomer of bis(dimethyl sulfoxide)chromium(III) would be formed in greater amounts than the corresponding *cis* isomer in the solvolysis of pentaaquoiodochromium(III) ion. Iodochromium(III) ion was prepared by the reaction of chromium(II) ion and triiodide ion,[22] and was purified from excess triiodide ion, iodide ion, and hexaaquochromium(III) ion by ion-exchange separation. Elution with aqueous 1 M perchloric acid directly into pure dimethyl sulfoxide gave a solution with a final composition of $Z \cong 0.05$. This solution was allowed to stand at ~5° for 2 days, and it was then processed by the ion-exchange procedure already outlined. The ratio $[\alpha\text{-}Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}]/[\beta\text{-}Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}]$ was 0.53 and the fraction of chromium recovered as bis(dimethyl sulfoxide) species was ~20%.

Although there is little basis for assuming that the stereospecific reaction

$$trans\text{-}Cr(OH_2)_4Cl_2{}^{+} + 2Hg^{2+} + 2(CH_3)_2SO = trans\text{-}Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+} + 2HgCl^{+}$$

occurs exclusively in the reaction of mercury(II) ion and *trans*-dichlorochromium(III) ion, it was assumed that the *trans* isomer of the bis(dimethyl sulfoxide)chromium(III) species would be produced in a larger amount than the corresponding *cis* isomer. Green hydrated chromium(III) chloride was the source of *trans*-dichlorochromium(III) ion.[23] A solution of this chromium(III) species in aqueous perchloric acid was added to a freshly prepared acidic aqueous dimethyl sulfoxide solution ($Z \cong 0.8$) of mercury(II) perchlorate. A color

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Table II. The Distribution of Dimethyl Sulfoxide between Aqueous Solution and an Immiscible Organic Phase, $D = [(CH_3)_2SO]_{org}/[(CH_3)_2SO]_{aq}$[e]

		Extractant: Benzene[d]			
Z(aq)	10^3D (exptl)	10^3D (calcd)[a]	Z(aq)	10^3D (exptl)	10^3D (calcd)[a]
0.0095	4.6	4.3	0.0713	7.0	7.0
0.0185	4.6	4.6	0.1295	10.8	9.8
0.0413	5.1	5.6			
		Extractant: *sym*-Tetrachloroethane[d]			
Z(aq)	$10D$ (exptl)	$10D$ (calcd)[b]	Z(aq)	$10D$ (exptl)	$10D$ (calcd)[b]
0.0005	1.3[c]	1.2	0.0157	1.3	1.3
0.0016	1.3[c]	1.2	0.0315	1.6	1.6
0.0053	1.2[c]	1.2	0.0580	1.7	1.9
0.0113	1.2[c]	1.3	0.0983	2.2	2.4

[a] Calculated from $10^3D = 4.0\gamma/\gamma_0$ (γ_0 is activity coefficient of dimethyl sulfoxide in infinitely dilute aqueous solution). [b] Calculated from $10D = 1.2\gamma/\gamma_0$. [c] 0.010 M $Cr(ClO_4)_3$ in aqueous phase. [d] At 60°, 0.10 M $HClO_4$. [e] Ratio of molarities in two phases.

change (between two different shades of green) occurred upon mixing. Ion exchange was used to separate the chromium(III) species produced. The ratio $[\alpha\text{-}Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}]/[\beta\text{-}Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}]$ was 0.49, and the fraction of chromium(III) recovered as bis(methyl sulfoxide) species was 42%. In neither of these experiments was the bis(dimethyl sulfoxide)–chromium(III) product exclusively one isomer. In each, however, the same isomer was produced in larger amounts, and this information is a partial basis for assignment of the *trans* configuration to the less easily eluted bis species.

Spectra of the Differently Solvated Chromium(III) Ions. Spectra, over the region 350–700 nm, were measured for two to four different effluent portions containing predominantly single chromium(III) species. These measurements were made promptly after each species was eluted, and the spectra did not change with time over periods long compared to the times required for the elution and spectral measurement. (This observation is relevant since sulfatochromium(III) species[24] would be expected to form in the effluent media.) In the spectral range studied, effects due to ion-pairing of sulfate ion and the chromium(III) cations were not detected; this was shown by measurement of the spectra after dilution of an effluent portion with water. Table III summarizes the peak positions for each species.

Table III. Peak Positions in the Visible Spectra[a] of Species $Cr(OH_2)_{6-n}(OS(CH_3)_2)_n{}^{3+}$

n	λ, nm (a, l. mole^{-1} cm^{-1})	n	λ, nm (a, l. mole^{-1} cm^{-1})
0[b]	574 (13.4), 408 (15.6)	4α	615 (26.4), 434 (27.6)
1	586 (18.1), 415 (20.3)	4β	615 (26.7), 433 (29.7)
2α	595 (20.4), 422 (22.8)	5	620 (26.6), 438 (28.5)
2β	595 (23.1), 422 (25.7)	6[c]	634 (33.5), 444 (36.3)
3α	603 (22.6), 427 (25.3)		
3β	603 (24.3), 427 (25.6)		

[a] Measured in sulfuric acid solutions. The approximate molarity of acid in the solution with each value of n is (given as n, concn): 1, 2.5; 2α, 3.0; 2β, 3.2; 3α, 3.3; 3β, 3.5; 4α, 3.7; 4β, 4.0; and 5, 3.9. [b] J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959). [c] From ref 12. The same peak positions are reported in ref 9, but the values of a (the molar absorbancy index) differ slightly.

Kinetic Experiments. Studies of the rate of the reaction

$$Cr(OH_2)_6{}^{3+} + (CH_3)_2SO = Cr(OH_2)_5(OS(CH_3)_2)^{3+} + H_2O$$

have been made at 60° over a range of concentration conditions. In experiments in which equilibrium was approached from the left, the $\bar{n}$ value of the chromium(III) species was followed as a function of time using the ion-exchange separation and the analytical methods already described. Six to eight samples were analyzed in the time interval during which the reaction was proceeding ~90% to equilibrium. An "infinity" sample was determined after the reaction had gone >99.8% to equilibrium. In each experiment, the approach to equilibrium was nicely first order. The results of these experiments are reported in Table IV.

Table IV. The Rate of Approach to Equilibrium in the Reaction[a] $Cr(OH_2)_6{}^{3+} + (CH_3)_2SO = Cr(OH_2)_5(OS(CH_3)_2)^{3+} + H_2O$

10^2Z	$\bar{n}_\infty$[b]	$[H^+]$[c]	10^5k, sec^{-1} [d]	10^5k_f, sec^{-1}	10^5k_r, sec^{-1}
0[e]	~0	0.93	1.3	...	1.3
0.125	0.030	0.24	1.8	0.054	1.8
0.494	0.119	0.23	1.9	0.23	1.7
0.494	0.128	0.59	1.5	0.19	1.3
0.82[e]	0.256	0.90	1.6	0.41	1.2
0.97	0.250	0.23	1.8	0.45	1.35
0.97	0.283	0.94	1.4	0.40	1.0
0.98	0.264	0.59	1.3	0.34	1.0
1.30	0.387	0.94	1.2	0.46	0.74
1.58[e]	0.418	0.84	2.0	0.84	1.2

[a] At 60°, $C_{Cr} = 0.018$ M. [b] $\bar{n}$ evaluated in kinetic experiments. [c] Perchloric acid; ionic strength approximately equal to $[H^+]$. [d] $k = 0.69/t_{1/2}$, where $t_{1/2}$ is the half-time for approach to equilibrium. [e] Experiment starting with mono(dimethyl sulfoxide)-chromium(III) ion ($C_{Cr} \cong 0.010$ M).

Experiments in which equilibrium was approached from the right were run using mono(dimethyl sulfoxide)-chromium(III) ion which had been separated from other chromium(III) species by column ion-exchange procedures. In the preparation, mono(dimethyl sulfoxide)-chromium(III) ion was eluted with 3 M perchloric acid after hexaaquochromium(III) ion had been eluted with 1.5 M sulfuric acid. Rinsing the column with 0.1 M perchloric acid removed sulfate ion before elution of mono(dimethyl sulfoxide)chromium(III) ion. In experiments of this type, the concentration of hexaaquochromium(III) was followed as a function of time; the hexaaquochromium(III) ion produced was analyzed after being separated from the reaction mixture by column ion-exchange procedures using 1.5 M sul-

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(24) N. Fogel, J. M. J. Tai, and J. Yarborough, *J. Am. Chem. Soc.*, **84**, 1145 (1962).

furic acid as eluting agent. The results of these experiments also are summarized in Table IV. Values of the pseudo-first-order rate constants for the forward and reverse reactions are calculated using the relationships[13b] $k_f = \bar{n}_{eq}k$ and $k_r = k - k_f$.

Derived Quantities

Equilibrium Quotient Values Determined from the Concentrations of Individual Differently Solvated Species $\mathbf{Cr(OH_2)_{6-n}(OS(CH_3)_2)_n^{3+}}$ (n = 1–5). The data in Table I allow calculation of equilibrium quotient values for the stepwise reactions

$$Cr(OH_2)_{7-n}(OS(CH_3)_2)_{n-1}^{3+} + (CH_3)_2SO = Cr(OH_2)_{6-n}(OS(CH_3)_2)_n^{3+} + H_2O$$

$$Q_n = \frac{[Cr(OH_2)_{6-n}(OS(CH_3)_2)_n^{3+}]}{[Cr(OH_2)_{7-n}(OS(CH_3)_2)_{n-1}^{3+}]r_a}$$

in which $r_a = a_{DMSO}/a_{H_2O}$. These equilibrium quotients differ, therefore, from thermodynamic equilibrium constants in omitting the ratio of activity coefficients of the product and reactant chromium(III) species. If this ratio of activity coefficients were independent of solvent composition, Q_n would also be independent of solvent composition. This ratio of activity coefficients for chromium(III) species involved in the reaction with n = 1 depends, however, upon solvent composition; values of Q_1 as a function of Z are (given as Z,Q_1)[25]: 0.0037, 220; 0.0095, 210; 0.020, 195; 0.0471, 164 (the average of seven experiments); 0.060, 156; 0.0713, 155 (the average of two experiments); 0.0870, 136; 0.0955, 135; 0.104, 133; and 0.141, 110.

Equilibrium quotients for the stepwise formation of other species in the series also decrease with increasing dimethyl sulfoxide in the solvent. A simple empirical correlation of the solvent dependence for the experimental values of each equilibrium quotient (n = 1–5, inclusive) of the form

$$\log Q_n = \log Q_n^0 - a_nZ$$

is reasonably successful. For each value of n, the values of Q_n^0 and a_n are: n = 1, 220, 2.3; n = 2 (α), 94, 2.2; n = 2 (β), 17, 1,3; n = 3 (3α formed from 2α), 38, 3.0; n = 3 (3β formed from 2α), 70, 3.0; n = 4 (4α formed from 3β), 50, 3.0; n = 4 (4β formed from 3β), 20, 2.6; and n = 5 (formed from 4α), 33, 3.0 (two solutions with $Z \geq 0.58$ omitted). The average values of differences of log Q_n calculated with each of these equations and observed values correspond to the following percentage differences in Q_n: n = 1, 3%; n = 2 (α), 1%, n = 2 (β), 3%; n = 3 (3α formed from 2α), 4%; n = 3 (3β formed from 2α), 20%; n = 4 (4α formed from 3β), 13%; n = 4 (4β formed from 3β), 6%; and n = 5 (formed from 4α), 5%. (For stepwise reactions in which isomeric reactants are possible, the dominant isomer has been chosen as reactant; no implications regarding mechanism are intended.) The average of the values of a_n is 2.6, which corresponds to an approximately 35% change in Q for a change in Z of 0.05.

The Evaluation of Q_6. Values of Q_6 can be derived from some of the experiments reported in Table I and also from the α_6 data. In the latter calculation

$$Q_6 = \frac{\alpha_6}{1 - \alpha_6}\left\{\frac{1}{r_a} + \frac{1}{Q_5r_a^2} + \frac{1}{Q_4Q_5r_a^3} + \ldots\right\}$$

values of Q_n ($n \leqslant 5$) are needed, and values appropriate for the medium in question were used. The values of Q_6 so calculated show appreciable scatter, but a mild medium dependence of the type already mentioned is apparent. At $Z \cong 0.8$, $Q_6 \cong 0.35$; and at $Z = 0.5$, $Q_6 \cong 0.75$. These interpolated values correspond to $a_6 \cong 1.1$ and $Q_6^0 \cong 2.6$, but extrapolation to obtain a value of Q_6 appropriate for pure water seems very uncertain. A correlation given in Figure 3 (to be discussed) corresponds to $Q_6^0 \cong 19$. The medium effects appear to be less dramatic at higher values of Z; experimental values of Q_5 (reactant is 4α species) are 1.08 and 1.06 at Z = 0.582 and 0.67, respectively. If instead of $a_6 = 1.1$ one uses $a_6 = 2.6$ (the average a_n which correlated the medium dependence of the other Q_n values) and $Q_6 = 0.75$ at $Z = 0.5$, one obtains $Q_6^0 \cong 15$, which agrees more closely with the value obtained in the correlation shown in Figure 3.

Calculation of ΔH_1 from $\bar{n}$ Data. Since $\bar{n}$ data were obtained at two different temperatures, they are a potential source of values of ΔH for the reactions being studied. The evaluation of equilibrium quotients for the stepwise reactions from $\bar{n}$ data depends, however, upon absence of medium effects,[14] a condition which does not exist for the present study. Although not as simple for computational purposes as the equation used (log Q_n = log $Q_n^0 - a_nZ$), an equation of the form $Q_n = Q_n^0(1 + b_nr_a + c_nr_a^2 + \ldots)$ will fit the medium dependence of each Q_n. A consequence of this is the correct identification as Q_1^0 of the parameter Q_1 in the equation correlating $\bar{n}$.[14] The values of Q_1^0 so obtained from the $\bar{n}$ data are Q_1^0 = 380 at 35° and = 240 at 60°. This value of Q_1^0 obtained from $\bar{n}$ data at 60° agrees reasonably well with the value obtained from the measured concentrations of species extrapolated to Z = 0. This agreement gives confidence that the value of Q_1 obtained from $\bar{n}$ data at 35° also is approximately correct. Values of the equilibrium quotients for $\bar{n} \geqslant 2$ derived from the $\bar{n}$ data are not reported, however, because they cannot be accepted as correct since they include contributions from medium effects.[14]

From the values of Q_1 extrapolated to pure water as solvent at 35 and 60° (the values obtained from the $\bar{n}$ data), one can calculate $\Delta H_1° = -3.7$ kcal mole^{-1}, and $\Delta S_1° = -0.3$ cal mole^{-1}deg^{-1}. These values correspond to the reaction

$$Cr(OH_2)_6^{3+}(aq) + (CH_3)_2SO(l) = Cr(OH_2)_5(OS(CH_3)_2)^{3+}(aq) + H_2O(l)$$

If the standard state for dimethyl sulfoxide is the hypothetical ideal 1 M solution with properties extrapolated from very dilute aqueous solution, the values for these thermodynamic quantities become: $\Delta H° = +0.8$ kcal mole, and $\Delta S° = +1.3$ cal mole^{-1} deg^{-1}. (The heat of solution of dimethyl sulfoxide in water to form an infinitely dilute solution is -4.5 kcal mole^{-1}.)[20]

Rate Constants Derived from Kinetic Data. The kinetic data (first-order rate constants for the establishment of equilibrium) have been resolved to yield values of the

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(25) These equilibrium quotient values are based on each of the pure liquid components as the standard state for that component. To convert these values to equilibrium quotients based upon pure liquid water and the hypothetical ideal liquid dimethyl sulfoxide with properties extrapolated from dilutea queous solutions of dimethyl sulfoxide, they should be multiplied by 0.101, the activity coefficient of dimethyl sulfoxide in infinitely dilute aqueous solution at 60°.

pseudo-first-order rate constants for the forward and reverse reactions for formation of the mono(dimethyl sulfoxide) species. The values of k_f are approximately proportional to the concentration of dimethyl sulfoxide indicating a first-order dependence upon this reagent. Values of the quotient $10^6k_f\,(\text{sec}^{-1})/a_{(\text{CH}_3)_2\text{SO}}$ for the nine experiments of Table IV which allow such a calculation are (preceded by the value of Z): 0.00125, 4.3; 0.00494, 4.5, 3.7 (two values); 0.0082, 4.7; 0.0097, 4.3, 3.8 (two values); 0.0098, 3.2; 0.0130, 3.2; and 0.0158, 4.2. (In this calculation, values of the activity coefficient of dimethyl sulfoxide which were used measure deviations from Henry's law. The mole fraction concentration scale was used.) Experimental error disguises any trend in values of this ratio. (The value of Q_1, the equilibrium quotient for this reaction, shows a medium dependence, but over the solvent composition range of the kinetic studies this dependence is small ($\sim$10%).) The data are consistent with the relationship $k = k_f' \cdot a_{(\text{CH}_3)_2\text{SO}} + k_r'a_{\text{H}_2\text{O}}$, with $k_f' = 4.0 \times 10^{-6}$ sec^{-1}, and $k_r' = 1.3 \times 10^{-5}$ sec^{-1}. The ratio of these quantities k_f'/k_r' with incorporation of the limiting value of the activity coefficient of dimethyl sulfoxide to allow a direct comparison[26] gives an independent value of Q_1^0; the value so obtained is 300 $[4.0 \times 10^{-6}/(1.3 \times 10^{-5})(0.101)]$. The agreement with 220 (based on the relative concentrations of species) and 240 (based on $\bar{n}$ data) is not completely satisfactory. The scatter of values of k_f' and k_r' allows an uncertainty of $\sim$10% in k_f' and 20–30% in k_r' which would rationalize the discrepancy.

Discussion

The principal basis for assignment of configuration to the isomers is their relative stability. Whether one considers the original data (Table I) or the equilibrium quotient values extrapolated to $Z = 0$, the relative concentrations of isomers for the compositions $n = 2$, 3, and 4 support the assignment of *cis* configuration to the more easily eluted isomer in each case. Values of concentration ratio [α isomer]/[β isomer] extrapolated to $Z = 0$ are $n = 2$, 5.5; $n = 3$, 0.54; and $n = 4$, 2.5. The values expected for this ratio if the α isomer has *cis* configuration in each case are $n = 2$, 4.0; $n = 3$, 0.67; and $n = 4$, 4.0. The assignment of *cis* configuration to the more easily eluted bis(dimethyl sulfoxide)chromium(III) species suggested by this comparison is supported also by the smaller relative concentration of this species produced in the reported experiments which were expected to give the *trans* isomer. Although steric or electronic effects might change the relative stabilities of the isomeric species from the statistically expected values, the deviations due to steric effects (*cis* interactions) or electronic effects (*trans* interactions?) would be approximately the same for each composition. In conversion of each *cis* isomer to the corresponding *trans* isomer (for $n = 2$, 3, and 4), one *cis* dimethyl sulfoxide–dimethyl sulfoxide interaction plus one *cis* water–water interaction give two *cis* water–dimethyl sulfoxide interactions. This same conversion (for $n = 2$, 3, and 4) results also in conversion of two *trans* dimethyl sulfoxide–water interactions into one *trans* water–water interaction plus one *trans* dimethyl sulfoxide–dimethyl sulfoxide interaction.

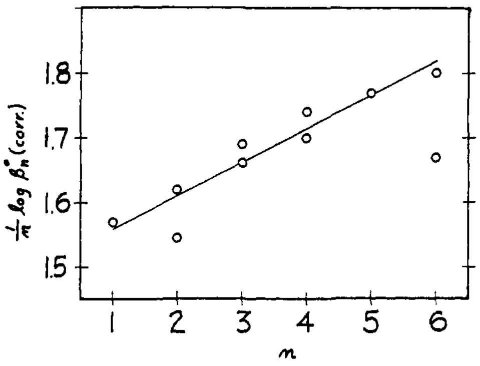

Figure 3. Values of $(1/n)\log(\beta_n^0(\text{cor}))$ *vs.* n, where $(\beta_n^0)^{1/n}$ is the equilibrium quotient for the reaction $(1/n)\text{Cr(OH}_2)_6{}^{3+} + (\text{CH}_3)_2\text{SO} = (1/n)\text{Cr(OH}_2)_{6-n}(\text{OS(CH}_3)_2)_n{}^{3+} + \text{H}_2\text{O}$, extrapolated to water as solvent. The values are corrected for the statistical factor ($\beta_n^0(\text{cor}) = \beta_n^0(\text{exptl}) \times (\sigma_P/\sigma_R)$, where σ_P and σ_R are the symmetry members of the product and reactant complex ions). For $n = 2$, 3, and 4, the two points are for the two isomers. For $n = 6$ the two points are for the two uncertain extrapolations discussed in the text.

Conclusions regarding trends in stability of the species $\text{Cr(OH}_2)_{6-n}(\text{OS(CH}_3)_2)_n{}^{3+}$ with increasing n are particularly direct if made on the basis of a series of reactions in each of which hexaaquochromium(III) ion is the reactant with 1 mole of dimethyl sulfoxide replacing 1 mole of water in the first coordination shell around chromium(III).[15]

$$\frac{1}{n}\text{Cr(OH}_2)_6{}^{3+} + (\text{CH}_3)_2\text{SO} = \frac{1}{n}\text{Cr(OH}_2)_{6-n}(\text{OS(CH}_3)_2)_n{}^{3+} + \text{H}_2\text{O}$$

After correction of the equilibrium quotient $(\beta_n^{1/n})$ for the statistical factor (multiplication by the nth root of the appropriate ratio of symmetry numbers[27]), the values (extrapolated to $Z = 0$) are $n = 1$, 37; $n = 2$ (*cis*), 41.5; $n = 2$ (*trans*), 35; $n = 3$ (*cis*), 46; $n = 3$ (*trans*), 49; $n = 4$ (*cis*), 50; $n = 4$ (*trans*), 55; and $n = 5$, 59. Figure 3, a plot of $\log(\beta_n)^{1/n}$ *vs.* n, shows a mild trend of increasing stability with increasing number of coordinated dimethyl sulfoxide molecules. Extrapolation to $n = 6$ gives $\sqrt[6]{\beta_6} \cong 66$. The trend is small, corresponding to a difference of less than 400 cal in $\Delta G°$ values for the reaction with $n = 1$ and $n = 6$. The qualitative conclusion that there are no large differences of stability of the species in this series has already been suggested by Ashley, Hamm, and Magnuson.[12,28] The $\bar{n}$ data for aluminum(III) ion[19] presented in Figure 1 show an apparent increase in the tendency for aluminum(III) to bind dimethyl sulfoxide with increasing concentration of dimethyl sulfoxide: values of $(\bar{n}/(6 - \bar{n}))/(Z/(1 - Z))$ are 0.9, 1.3, 1.6, and 1.7 (in order of increasing Z) for the four points. Since each of these solutions contained 3 M chloride ion, the trend may be due in part to the preferential solvation of chloride ion by water.[3,4,29]

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(26) Equilibrium quotient values are based upon pure liquid water and pure liquid dimethyl sulfoxide as the standard states. The standard state for dimethyl sulfoxide in the rate constant k_f' is the hypothetical pure liquid dimethyl sulfoxide with properties extrapolated from the infinitely dilute aqueous solution.

(27) S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

(28) The work of these authors is based, however, on incorrect assignments of average spectral peak positions as a function of $\bar{n}$. The solutions used in their assignment (shown in their Figure 1) did not contain equilibrium distributions of the differently solvated chromium(III) species. Since these solutions had high values of Z (but were not heated sufficiently long to come to equilibrium), the distribution should favor species containing more bound dimethyl sulfoxide. This conclusion is supported by a comparison of our equilibrium $\bar{n}$ data with the data in their Figure 2.

(29) See also R. F. Rodewald, K. Mahendran, J. L. Bear, and R. Fuchs, *J. Am. Chem. Soc.*, **90**, 6698 (1968).

This suggestion is supported by the observed[19] increased tendency for aluminum(III) to coordinate dimethyl sulfoxide with increasing concentration of aluminum(III) chloride in a solvent of a particular stoichiometric composition.

Chromium(III) ion discriminates in favor of dimethyl sulfoxide over water to a significantly greater extent than does aluminum(III) ion. (On a mole fraction basis, there is little discrimination by aluminum(III) ion for water or dimethyl sulfoxide in its first coordination shell.) Like chromium(III) ion, hydrogen ion discriminates in favor of dimethyl sulfoxide over water.[30]

The assignment of *cis* configuration to the more easily eluted isomer in the present system is the same as the assignment in the system of aquopyridine N-oxide–chromium(III) species.[15] The relationship of this assignment and the ease of elution of the isomeric species is the opposite of that used, and in some cases proved, for isomeric species containing four water or ammonia molecules and two anionic ligands bound to chromium(III) or cobalt(III). A significant difference between these two types of systems is the net ionic charge and the consequent difference in the electrolyte concentration needed for elution. In the present study the reagent for elution of species with $n = 2$, 3, and 4 ranged from 2.8 to 4.2 M sulfuric acid. In separation of isomeric tetraaquodichlorochromium(III) ions, 0.1 M perchloric acid was used.[23a] Perhaps the relative tendency for the *cis* isomer to be in the aqueous electrolyte phase compared to the resin phase increases as the electrolyte concentration increases. The assignment of configuration to the species with $n = 2$ and $n = 4$ is also opposite of that based upon the light absorption.[31] The species to which we assign *cis* configuration have smaller total light absorption in the region of d–d transitions, as was the case also for chromium(III)–pyridine N-oxide species.[15]

If one does not consider specific outer-sphere interaction, the decrease of each equilibrium quotient for the stepwise replacement of water by dimethyl sulfoxide in the coordination shell around chromium(III) is due, *by definition*, to a solvent dependence upon the ratio of activity coefficients of the two differently solvated chromium(III) species. (The lack of dependence of the relative concentrations of the several species upon electrolyte concentration rules out an explanation based solely upon differences between the solvent activity coefficients due to the presence of electrolyte.) The decrease of Q_1 with an increase in Z indicates that the activity coefficient of hexaaquochromium(III) ion is decreased to a greater extent than is the activity coefficient of pentaaquo(dimethyl sulfoxide)chromium(III) ion. One can interpret this trend, however, in terms of outer-sphere association of the solvated chromium(III) ions and dimethyl sulfoxide. If this is done, association equilibrium quotients for the reactions

$$\mathrm{Cr(OH_2)_{6-\mathit{n}}(OS(CH_3)_2)_{\mathit{n}}{}^{3+} + (CH_3)_2SO \rightleftharpoons Cr(OH_2)_{6-\mathit{n}}(OS(CH_3)_{2\mathit{n}}{}^{3+}\cdot(CH_3)_2SO}$$

with $n = 0$ and $n = 1$ are 12.6 and 5.1, respectively. These values are based upon the mole fraction concentration scale for dimethyl sulfoxide and activity coefficients for dimethyl sulfoxide which correlate its nonideality relative to Henry's law. To convert these quantities to more familiar molar concentration units, they should be multiplied by 0.0183, giving 0.23 and 0.093 l. mole^{-1}, respectively. Outer-sphere association is an attractive postulate since hydrogen-bonding between dimethyl sulfoxide and the hydrogen of coordinated water molecules seems reasonable.[32] If this is the basis for the interaction, it would be expected to be greatest for hexaaquochromium(III) ion. The magnitudes of the derived outer-sphere association equilibrium quotients are so low, however, that it does not seem worthwhile to employ this postulate in a quantitative treatment of the medium dependence of each of the equilibrium quotients. It should be noted that the observed lack of dependence of the distribution coefficient of dimethyl sulfoxide between an acidic aqueous phase and an immiscible organic phase upon the presence of 0.10 M hexaaquochromium(III) ion (Table II) is not inconsistent with the outer-sphere association just considered. With an association equilibrium quotient of 0.23 l. mole^{-1}, only 2.3% of dimethyl sulfoxide would be associated in a solution containing 0.10 M hexaaquochromium(III) ion. (To alter the distribution coefficient by a factor of 2, the concentration of hexaaquochromium(III) would have to be ~4.3 M; it is not practical, therefore, to explore the outer-sphere interaction by a study of the effect of hexaaquochromium(III) ion on the activity of dimethyl sulfoxide.)

The observed value of k_r' at 60° (1.3×10^{-5} sec^{-1}) is the basis for an estimate of its value at 25°. Extrapolation using $\Delta H^{\ddagger} = 24.0$ and 27.0 kcal mole^{-1} (which are reasonable limits) gives values 1.7×10^{-7} and 1.0×10^{-7} sec^{-1}, respectively. This range of values can be compared with those tabulated elsewhere.[14] The rate constant for aquation of pentaaquo(dimethyl sulfoxide)chromium(III) is lower than that for analogous species containing bound methanol, ethanol, chloride, bromide, and iodide;[14] it is lower also than that for the nitratochromium(III) ion;[33] it is larger, however, than that for pentaaquoisothiocyanatochromium(III) ion[34] (~9.1×10^{-9} sec^{-1} at 25°). The comparison of rate constants for the methanol and dimethyl sulfoxide containing species indicates that the greater thermodynamic stability of the dimethyl sulfoxide containing species is correlated with its lower rate of dissociation.

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(30) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *J. Am. Chem. Soc.*, 90, 23 (1968).

(31) F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955); see, however, C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 186.

(32) B. M. Fung, *J. Am. Chem. Soc.*, **89**, 5788 (1967); W. R. Fitzgerald, A. J. Parker, and D. W. Watts, *ibid.*, 90, 5744 (1968).

(33) T. W. Swaddle, *ibid.*, **89**, 4338 (1967); M. Ardon and N. Sutin, *Inorg. Chem.*, **6**, 2268 (1967).

(34) C. Postmus and E. L. King, *J. Phys., Chem.*, **59**, 1216 (1955).