show, we believe, the power of the technique in answering certain questions and also provide, even in the present state of rudimentary development of the technique, unique information on the ground electronic states of these compounds. We consider our most striking results to be the demonstration of two kinds of nitrogen in porphine free base, the demonstration of the similarity of the two kinds of nitrogen in metal phthalocyanines and the suggestion that the Fe in oxidized and reduced iron porphyrins differs in charge by about 0.44 electron. The good agreement between our results and the calculations of Gouterman and coworkers gives us hope that a combination of X-ray photoelectron spectroscopy and theory will prove fruitful in attacking the structure of complex systems.

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Solvolysis of Iodopentaaquochromium(III) Ion in Acidic Aqueous Dimethyl Sulfoxide[1,2]

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Abstract: The kinetics and stereochemical course of reactions of $Cr(OH_2)_5I^{2+}$, *cis*- and *trans*-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$, and *cis*- and *trans*-$Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}$ in acidic aqueous dimethyl sulfoxide have been studied. The solvolysis of $Cr(OH_2)_5I^{2+}$ in this solvent gives *trans*-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$ confirming a suggestion of Moore, Basolo, and Pearson. This species then loses iodide to give both isomeric species of the composition $Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}$. Both isomers of $Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$ are produced when chromium(II) is oxidized with triiodide ion in acidic aqueous dimethyl sulfoxide. Identification of isomeric species was accomplished by consideration of their reactivity patterns and by comparison of their relative abundances with the statistically expected values. The earlier identification of *cis*-$Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}$ as the more easily eluted bis(dimethyl sulfoxide)chromium(III) species has been confirmed.

Of the halopentaaquochromium(III) ions, that involving iodide ion as ligand is the least stable in both a thermodynamic[3] and a kinetic[4] sense. Coordinated iodide also labilizes other ligands bonded to chromium(III).[5,6] Moore, Basolo, and Pearson[5] assumed that this labilization is localized at the site trans to the bound iodide ion, but this was not proved. The situation is more complicated than implied in their paper; both isomeric tetraaquobis(dimethyl sulfoxide)chromium(III) species are produced when iodopentaaquochromium(III) ion solvolyzes in aqueous dimethyl sulfoxide.[7,8]

The present study deals with the solvolysis of iodopentaaquochromium(III) ion[9] in mixed water–dimethyl sulfoxide solvent with a mole fraction of dimethyl sulfoxide (Z) of 0.705.[10] One objective was detection of the iodo(dimethyl sulfoxide)chromium(III) ion intermediate, which would be present in the solvolysis of iodochromium(III) ion in aqueous dimethyl sulfoxide if the labilization by iodide occurs as suggested.[5] Identification of the geometry of this intermediate also was an important objective. Because of the extraordinary inertness of (dimethyl sulfoxide)chromium(III) species[7] and the separability of the isomeric species with two, three, and four molecules of dimethyl sulfoxide coordinated to chromium(III),[7] study of this system was expected to be particularly informative with respect to these objectives as well as others. Regrettably the study does not shed much additional light on the question of whether the loss of coordinated iodide by chromium(III) ion generates a pentacoordinated intermediate.[6,11]

A number of reactions interconverting species of the type $Cr(OH_2)_{6-d-i}(OS(CH_3)_2)_dI_i{}^{(3-i)+}$ have been studied in the mixed solvent in the course of this work. These reactions are indicated in Scheme I in which each species is represented by the notation (d,i). In addition the loss of iodide by cis (1,1) and trans (1,1) was studied in acidic aqueous solution.

Experimental Section

Reagents. Doubly distilled water was used in the preparation

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(1) Taken in part from the Ph.D. Thesis of Dennis B. Vanderheiden, University of Colorado, 1972.

(2) This work was supported by National Science Foundation Grant, GP 7185-X.

(3) T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, 7, 1915 (1968).

(4) T. W. Swaddle and E. L. King, *Inorg. Chem.*, 4, 532 (1965).

(5) P. Moore, F. Basolo, and R. Pearson, *Inorg. Chem.*, 5, 223 (1966).

(6) S. P. Ferraris and E. L. King, *J. Amer. Chem. Soc.*, 92, 1215 (1970).

(7) L. P. Scott, T. J. Weeks, Jr., D. E. Bracken, and E. L. King, *J. Amer. Chem. Soc.*, 91, 5219 (1969).

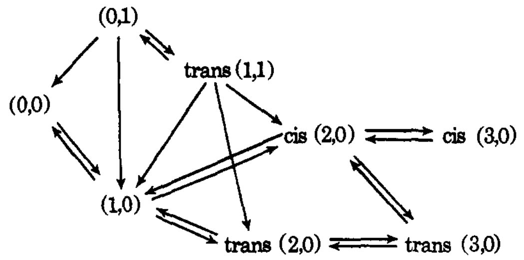
(8) This observation was the result of a single experiment in which an aqueous solution of iodopentaaquochromium(III) ion was added to pure dimethyl sulfoxide. The solvent composition changed, therefore, as addition proceeded.

(9) Hereafter this species will be called iodochromium(III) ion. In general for chromium(III) species with coordination number six, all ligands other than water will be given in a name. For postulated unstable pentacoordinated species, all ligands including water will be specified in the name.

(10) In calculation of the composition of the mixed solvent, only the solvent components are considered.

(11) M. Ardon, *Inorg. Chem.*, 4, 372 (1965).

Scheme I



of all solutions. Reagent grade dimethyl sulfoxide (0.05% water) (Matheson Coleman and Bell or Fisher Scientific) was used without further purification. Dowex 50W cation-exchange resin (J. T. Baker Analyzed Reagent Grade) was used in column ion-exchange procedures, X4(200–400 mesh) was used in long column (185 cm) elution experiments, and X-8(100–200 mesh) was used in preparative work and in short column (40 cm) elution experiments. Ion-exchange resin was rinsed with distilled water and treated alternately with 2 M hydrochloric acid and alkaline ($\sim$2 M sodium hydroxide) peroxide solution before use. It was finally rinsed with 0.1 M perchloric acid and was used in the hydrogen ion form. Chromium(II) perchlorate solutions were prepared by dissolving 99.999% pure chromium metal (United Mineral and Chemical Corp.) in deoxygenated 1 M perchloric acid.[12] (The chromium pellets were cleaned with concentrated hydrochloric acid and rinsed before being dissolved.) Some chloride (less than 2% based upon total chromium) is formed in this procedure. Iodochromium(III) ion in acidic solution was produced by reaction of chromium(II) with triiodide ion.[13] The solution so prepared was frozen until used, at which time the excess triiodide ion was reduced with hydrogen sulfite ion, and the iodochromium(III) ion (and a small amount of chlorochromium(III) ion) was separated from other species by a cation column ion-exchange procedure.[4] All other chemicals were reagent grade quality.

Analyses. Analysis of chromium(III) species for coordinated iodide was carried out by an indirect Volhard procedure. Dimethyl sulfoxide was analyzed by its reaction with permanganate ion to give dimethyl sulfone.[14] If the aqueous solution containing dimethyl sulfoxide coordinated to chromium(III) was not heated to cause aquation prior to analysis, the permanganate oxidation was allowed to proceed for 30–60 min to ensure complete oxidation of bound dimethyl sulfoxide. If the solution to be analyzed for dimethyl sulfoxide had been analyzed previously for iodide, blank solutions were used which duplicated conditions of a previous iodide analysis. Chromium was analyzed spectrophotometrically as chromate(VI) ion in alkaline solution;[15] conversion of each chromium(III) species to chromate(VI) ion was brought about in alkaline hydrogen peroxide.

Column Ion-Exchange Procedures. All column ion-exchange procedures were carried out using jacketed columns with cooled ($\sim$0°) ethylene glycol-water solution circulating through the annular space. Short columns with an i.d. of 1 cm were used with $\sim$12 ml of wet resin for purification procedures and in analysis of reaction mixtures from certain kinetic experiments. Long columns with an i.d. of 1.2 cm were used with 190–200 ml of wet resin for separations of mixtures of species resulting from reaction of iodochromium(III) ion in aqueous dimethyl sulfoxide. If a complete profile was needed, the column effluent was collected in 6.5-ml portions using a fraction collector; in some cases superior evaluation of the resolution of adjacent elution peaks was achieved by collecting 2- or 3-ml fractions.

Spectral Studies. Spectra of several unstable iodide-containing chromium(III) species were determined promptly after elution. The time at which collection of the sample started was the time to which extrapolation of the observations was made if the spectrum changed at an appreciable rate. If there was to be delay in measuring a spectrum, the column effluent was frozen by collection in a flask chilled to −78°; such a sample was kept at −78° for up to 24 hr before being thawed and diluted with 1 M perchloric acid before measurement. The peak positions and molar absorptivity values in the spectra of previously uncharacterized species are (given as λ, nm (ϵ, l. mol^{-1} cm^{-1})): *cis*-$\mathrm{Cr(OH_2)_4(OS(CH_3)_2)I^{2+}}$ 654 (39), 477 (34), 306 (sh) (2200), and 261 (5700); *trans*-$\mathrm{Cr(OH_2)_4(OS(CH_3)_2)I^{2+}}$ 652 (53), 475 (39), 306 (sh) (3200), and 267 (8700); $\mathrm{Cr(OH_2)_3(OS(CH_3)_2)_2I^{2+}}$ (presumably with one dimethyl sulfoxide molecule cis to iodide and one trans to iodide) 660 (40), 479 (33), 306 (sh) (2400), and 264 (6200).

Rate of Equilibration of Chromium(III) in a Mixed Solvent with Z = 0.705. In a solution with $Z = 0.705$, $\bar{n}_D \simeq 5.5$[7,16] at equilibrium. Even though a sequence of six (or more) reactions must occur to bring to equilibrium a system consisting initially of aquochromium(III) ion in this solvent, a plot of ln ($\bar{n}_{D\infty} - \bar{n}_D$) *vs.* time for experiments with $[\mathrm{Cr^{III}}] = 0.016\ M$ and $[\mathrm{H^+}] = 0.04\ M$ is approximately linear. The values of $\bar{n}_D$ in the effluent were obtained from a short column ion-exchange procedure in which solvent dimethyl sulfoxide in a portion of reaction mixture was separated from solvated chromium(III) ion by rinsing with 0.1 M perchloric acid. Elution with 3–6 M sulfuric acid, followed by analysis, gave values of $\bar{n}_D$. The data are (given as time (hr), $\bar{n}_D$) at 45°: 1.0, 0.28; 4.0, 0.94; 17.5, 2.64; 21.5, 2.92; 25.0, 3.35; 42.0, 4.03; 90.5, 5.45; 180, 5.50 (∞, 5.50), and at 60°: 0.25, 0.59; 4.5, 3.91; 6.0, 4.26; 16.0, 5.42; 24.0, 5.47 (∞, 5.50). From these data one calculates the half-time for establishment of equilibrium to be 19.5 hr at 45° and 2.64 hr at 60°. These values correspond to an activation energy of 28 kcal mol^{-1} and allow extrapolation to values of the half-time for equilibration of 276, 376, and 2820 hr at 27, 25, and 0°, respectively.

Short-time experiments in which mono(dimethyl sulfoxide)-chromium(III) ion was the starting material also were performed in this solvent. At $[\mathrm{H^+}] = 0.0377\ M$ and 27°, 1.1% of this reactant is converted to the isomeric bis(dimethyl sulfoxide)chromium(III) species per hour. The ratio of isomeric bis(dimethyl sulfoxide)-chromium(III) species formed in an experiment of this type in which less than 5% of the reactant was converted to the bis products was [*cis*-$\mathrm{Cr(OS(CH_3)_2)_2^{3+}}$]/[*trans*-$\mathrm{Cr(OS(CH_3)_2)_2^{3+}}$] = 3.2 ± 0.1.

Addition of Dimethyl Sulfoxide to Isomeric Bis(dimethyl sulfoxide)chromium(III) Ions. The distribution of isomeric tris(dimethyl sulfoxide)chromium(III) species resulting from the reaction of each of the pure isomeric bis species with dimethyl sulfoxide (reaction (2,0) → (3,0)) was determined to allow identification of the isomers. Each purified bis isomer[7] was allowed to react at 27° for 13.5 hr in a solution with $Z = 0.705$ and $[\mathrm{H^+}] = 0.04\ M$. A column ion-exchange procedure applied to the reaction mixture[7] allowed separation of the five species containing one, two, and three coordinated dimethyl sulfoxide molecules per chromium(III) ion. In the experiment involving the more easily eluted bis isomer, 9.5% of the chromium was present as tris species, with the ratio of tris products being (more easily eluted tris isomer)/(less easily eluted tris isomer) = 0.73. In the experiment involving the less easily eluted bis isomer, 10.0% of the chromium was present as tris species, with the ratio of the tris products being (more easily eluted tris isomer)/(less easily eluted tris isomer) = 0.026.

Preparation of Isomeric Iodo(dimethyl sulfoxide)chromium(III) Ions. Since the oxidation of chromium(II) by iodine (or triiodide ion) gives iodochromium(III) ion,[13] it was assumed that the corresponding reaction in a mixed solvent would produce a variety of iodo–aquo–(dimethyl sulfoxide)chromium(III) species including both isomers of the complex containing one iodide ion and one dimethyl sulfoxide molecule per chromium(III) ion. This proved to be the case. In an experiment with $Z \cong 0.025$ and $[\mathrm{H^+}] \cong 0.03\ M$, 8.7% of the product chromium(III) was present as iodo(dimethyl sulfoxide)chromium(III) ion. A column cation-exchange procedure accomplished the clean separation of two species with this composition. The more easily eluted species (analyzed to have 1.18 mol of iodide and 0.94 mol of dimethyl sulfoxide per mole of chromium(III)) had a spectrum with the features reported earlier in this paper for *trans*-$\mathrm{Cr(OH_2)_4(OS(CH_3)_2)I^{2+}}$. A less easily eluted species (analyzed to have 0.95 mol of iodide and 1.01 mol of dimethyl sulfoxide/mol of chromium(III)) had a spectrum with the features reported earlier in this paper for *cis*-$\mathrm{Cr(OH_2)_4(OS(CH_3)_2)I^{2+}}$. The relative amount of the isomers produced in the reaction was [more easily eluted $\mathrm{Cr(OS(CH_3)_2)I^{2+}}$]/[less easily eluted $\mathrm{Cr(OS(CH_3)_2)I^{2+}}$] = 0.3.

Solvolysis of Iodochromium(III) Ion in a Solution with Z = 0.705. Iodochromium(III) ion was allowed to solvolyze at 27° in a mixed solvent with $Z = 0.705$ for varying periods of time. Portions of reaction mixture were quenched in mixtures of ice and dilute aqueous perchloric acid resulting in cold solutions (t < 5°)

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[12] J. P. Fackler, Jr., and D. G. Holah, *Inorg. Chem.*, **4**, 954 (1965).

[13] H. Taube and H. Myers, *J. Amer. Chem. Soc.*, **76**, 2103 (1954).

[14] T. B. Douglas, *J. Amer. Chem. Soc.*, **68**, 1072 (1946).

[15] G. W. Haupt, *J. Res. Nat. Bur. Stand.*, **48**, 414 (1952).

[16] The average number of bound dimethyl sulfoxide molecules per chromium(III) is represented as $\bar{n}_D$; the corresponding quantity for bound iodide is $\bar{n}_I$.

Table I. Percentage Yields of Products in Solvolysis of Iodochromium(III) Ion as a Function of Time[a]

Species	% yield at reaction time (hr) 0.5	1.0	1.5	2.25	3.0	3.75	9.0	10.5	12.0	15.0
$CrCl^{2+}$	0.95		0.15		1.77	2.23	0.54	1.20	1.08	0.31
CrI^{2+}	25.50	14.34	6.11	2.96	1.35	0.59	0.36			
Cr^{3+}	21.72	17.23	18.17	17.84	15.73	16.26	7.81	14.85	14.31	12.32
trans-$Cr(OS(CH_3)_2)I^{2+}$	6.36	16.00	9.89	8.59	8.08	7.55	1.81	(3.70)	0.87	0.31
$CrOS(CH_3)_2{}^{3+}$	40.26	45.57	57.35	57.75	57.30	55.61	53.34	50.68	49.07	51.22
cis-$Cr(OS(CH_3)_2)_2{}^{3+}$	0.81	2.03	3.85	5.40	6.84	8.58	12.79	↑	13.85	16.84
trans-$Cr(OS(CH_3)_2)_2{}^{3+}$	0.59	1.57	3.04	4.47	5.64	6.68	11.86	28.06[b]	11.64	12.59
Total $Cr(OS(CH_3)_2)_3{}^{3+}$						0.38	1.77	↓	1.94	3.20
% recovery	96.2	96.7	98.6	96.6	96.8	97.9	90.7	98.5	93.9	98.0

[a] $Z = 0.705$; $[CrI^{2+}]_0 = 3–5 \times 10^{-3}$ *M*; $[H^+] = 0.028–0.037$ *M*; I = 0.042–0.046 *M*; $T = 27°$. [b] This is the sum of all bis- and tris(dimethyl sulfoxide)chromium (III) species.

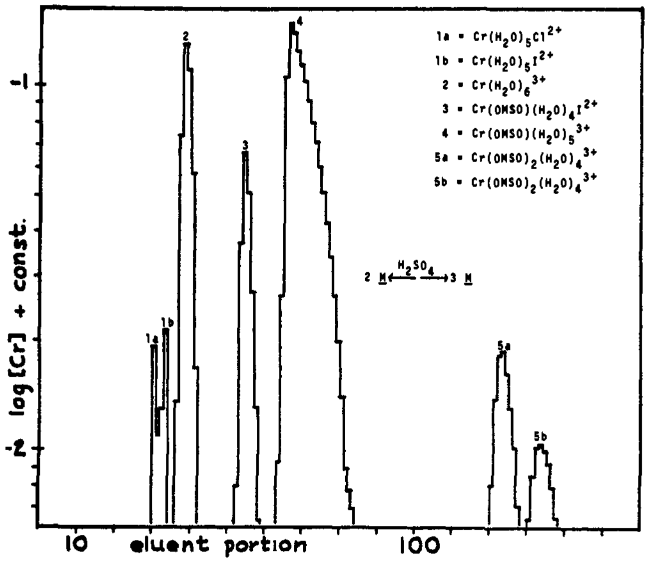

Figure 1. Elution profile for species present in reaction mixture: $Z = 0.705$, $[H^+] \cong 0.032$ *M*, $[CrI^{2+}]_0 = 0.0040$ *M*, and reaction time 3 hr at 27°. Elutent portion volumes were 6.5 ml. Eluting agent was 2 *M* H_2SO_4 to portion 100 then 3 *M* H_2SO_4 after portion 100.

with $[H^+] = 0.026–0.030$ *M*. All chromium(III) species in the reaction mixture were absorbed into a slight excess of Dowex 50 W resin. After being rinsed free of dimethyl sulfoxide with cold 0.1 *M* perchloric acid, the chromium(III)-containing resin was transferred to the top of a long column of resin for elution. Figure 1 shows an elution curve from one experiment. The analyzed values of iodide/chromium ($\bar{n}_I$) and dimethyl sulfoxide/chromium ($\bar{n}_D$) for species in the elution peaks are first 0, 0.007; second 0.96, 0.014; third 0.024, 0.013; fourth 1.00, 1.03; fifth 0.009, 1.01; sixth 0.028, 2.06; and seventh 0.028, 1.99. In experiments lasting 4 hr or more, eighth and ninth elution peaks were recovered. These had $\bar{n}_I = 0.028$, $\bar{n}_D = 3.02$ and $\bar{n}_I = 0$ (negative qualitative test for iodide), $\bar{n}_D = 3.05$, respectively. (The chlorochromium(III) ion, ranging from 0 to 2%, results from the small amount of chloride ion in the solution of chromium(II) ion used in preparation of iodochromium(III) ion.) Using the notation developed earlier, the reactions occurring in this mixtue are: (0,1) → (0,0), (1,0), and trans (1,1); trans (1,1) → (1,0) and both cis and trans (2,0); cis (2,0) → cis and trans (3,0); and trans (2,0) → trans (3,0). A summary of the yields of each product (and unreacted reactant) as a function of time in experiments at $[H^+] = 0.028–0.037$ *M* and I = 0.042–0.046 *M* is given in Table I. Limited studies also were made of the relative yields of *cis*- and *trans*-bis(dimethyl sulfoxide)chromium(III) ion as a function of the concentrations of hydrogen ion and perchlorate ion. These data are presented in Table II.

The elution order obtained with 2 *M* sulfuric acid shown in Figure 1, $CrCl^{2+}$, CrI^{2+}, Cr^{3+}, *trans*-$CrI(OS(CH_3)_2)^{2+}$, $Cr(OS(CH_3)_2)^{3+}$, *cis*-$Cr(OS(CH_3)_2)_2{}^{3+}$, *trans*-$Cr(OS(CH_3)_2)_2{}^{3+}$, has an unexpected feature, the elution of an ion of charge 3+ (aquochromium(III) ion) before one of charge 2+ (iodo(dimethyl sulfoxide)chromium(III) ion). If the eluting agent is perchloric acid (1-3 *M*), iodo(dimethyl sulfoxide)chromium(III) ion is eluted before aquochromium(III) ion, and this also is the elution order if 1 *M* sulfuric acid is used.

Table II. The Relative Yields of Isomeric $Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}$ in Solvolysis of Iodochromium(III) Ion[a]

$[H^+]$, *M*	I,[b] *M*	Reaction time, hr	[*cis*-$Cr(OS(CH_3)_2)_2{}^{3+}$]/[*trans*-$Cr(OS(CH_3)_2)_2{}^{3+}$][d]
0.030	0.045	3.0[c]	1.17 ± 0.03
0.034	0.043	3.0[c]	1.26 ± 0.05
0.034	0.136	3.0	0.97 ± 0.04
0.040	0.539	3.0	0.82 ± 0.02
0.067	0.537	2.5	0.64 ± 0.03
0.098	0.537	4.0	0.52 ± 0.02
0.188	0.537	4.5	0.39 ± 0.02
0.520	0.537	5.5	0.27 ± 0.01

[a] $Z = 0.705$, $T = 25°$, $[CrI^{2+}]_0 = 0.0032–0.0055$ *M*. [b] Perchlorate ion is predominant anion present. [c] $T = 27°$. [d] These are uncorrected values. The formation of isomeric $Cr(OS(CH_3)_2)_2{}^{3+}$ from $Cr(OS(CH_3)_2)^{3+}$ was not studied under these conditions of acidity and perchlorate ion concentration.

Identification of the iodo(dimethyl sulfoxide)chromium(III) ion produced in the solvolysis as the trans isomer is based upon comparison of its spectrum with those of the separated isomers. The positions of spectral peaks are 650, 474, and 267 nm. This species has an apparent light absorption 90 ± 1% of that determined for the more easily eluted isomer of composition ($Cr(OS(CH_3)_2)I^{2+}$); this is appreciably greater (1.04–1.37-fold) than that for the less easily eluted isomer. That the light absorption is less than observed for the species produced in the triiodide–chromium(II) reaction is due to the longer duration of the long column ion-exchange separation of the products of solvolysis. During this procedure some decomposition of *trans*-iodo(dimethyl sulfoxide)chromium(III) ion occurred.

Rate of Solvolysis of Iodochromium(III) Ion in a Solution with $Z = 0.705$. The rates of disappearance of iodochromium(III) ion and appearance of iodo(dimethyl sulfoxide)chromium(III) ion (reaction (0,1) → trans (1,1)) were measured at 25° in solutions of four different acidities at I = 0.53–0.54 *M*; the initial concentration of iodochromium(III) ion was 4.5×10^{-3} *M*. A column ion-exchange procedure allowed separation of three fractions: unreacted iodochromium(III) ion, iodo(dimethyl sulfoxide)chromium(III) ion, and the less easily eluted species of charge 3+. The disappearance of iodochromium(III) was nicely first order in experiments followed 80% to completion. The first-order rate constants $-d \ln [CrI^{2+}]/dt = k$ are (given as $[H^+]$, 10^4k (sec^{-1})): 0.0400, 1.97; 0.102, 1.62; 0.280, 1.43; and 0.515, 1.40. (The hydrogen ion dependence of these rate constants is correlated with the rate constants given in Table IV with an average difference of 0.8% between the observed and calculated values.) Late in a run the loss of iodide by *trans*-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$ (reactions trans (1,1) → (1,0) and (2,0) (both isomers)) becomes appreciable; early in a run calculation of the ratios of species produced is rendered uncertain by some uncertainty in the amounts of product species present at zero time. For these reasons data from the middle range of extent of reaction (20–65%) were weighted most heavily in arriving at the values of [*trans*-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$]/[all products]. This quantity has the values 0.65, 0.68, and 0.74 at $[H^+] = 0.102, 0.280$, and 0.515 *M*, respecitvely. The product of these values and the observed first-order rate constants is $(1.02 \pm 0.03) \times 10^{-4}$ sec^{-1}.

Rate of Solvolysis of *trans*-Iodo(dimethyl sulfoxide)chromium(III) Ion. The loss of iodide by the more easily eluted isomer of iodo(dimethyl sulfoxide)chromium(III) ion (identified in the Discussion as the trans isomer) (reaction trans (1,1) → trans (2,0) and cis (2,0)) was followed spectrophotometrically at 320 nm, where the light absorption by species containing no iodide is very small ($a_{00} \cong 0.4$ l. mol^{-1} cm^{-1}, $a_{10} \cong 1$ l. mol^{-1} cm^{-1}).[17] At this wavelength molar absorbancy indices of the several iodide-containing species are comparable ($a_{01} = 1.9 \times 10^3$, $a_{11t} = 2.62 \times 10^3$, $a_{11c} = 1.95 \times 10^3$ l. mol^{-1} cm^{-1}), and the light absorption by iodine(0) also is high. Since iodide ion produced in solvolysis can be oxidized at an appreciable rate by dimethyl sulfoxide,[18] this complicated the observations at long times in experiments run in aqueous dimethyl sulfoxide ($Z = 0.705$), particularly at high acidity. To minimize the effect of this complication, values of the apparent first-order rate constant were derived from points obtained during approximately the first half-time. This procedure also minimizes complications due to the formation of iodochromium(III) ion (reaction trans (1,1) → (0,1)) in the reaction mixture. These values for experiments at $I = 0.53$ *M*, $Z = 0.705$ (given as $[H^+]$, $-d \ln [trans\text{-}Cr(OS(CH_3)_2)I^{2+}]/dt$ (sec^{-1})) are: 0.0453, 2.62×10^{-5}; 0.102, 1.64×10^{-5}; 0.166, 1.46×10^{-5}; and 0.227, 1.27×10^{-5}. (The hydrogen ion dependence of these rate constants is correlated with the rate constants given in Table IV with an average difference of 2.4% between the observed and calculated values.)

This reaction also was studied in aqueous solution; the spectrophotometric procedure employed was ill-suited, however, because production of iodochromium(III) ion was more important in aqueous solution than in a solvent with $Z = 0.705$. (In an experiment with $[H^+] = 0.335$ *M* and $I = 0.73$ *M*, the ratio $[Cr^{3+}]/[Cr(OS(CH_3)_2)^{3+}]$ was 0.21 after 99% of *trans*-iodo(dimethyl sulfoxide)chromium(III) had solvolyzed.) Plots of ln *A* *vs.* time showed curvature; the rate constants were derived from points early in each experiment. These rate constants ($k = -d \ln [trans\text{-}Cr(OH_2)_4(OS(CH_3)_2)I^{2+}]/dt$) as a function of the concentration of hydrogen ion in solutions of $I = 0.56$–0.61 *M* are (given as $[H^+]$, 10^4k (sec^{-1})): 0.093, 4.2; 0.188, 3.2; 0.340, 2.6; and 0.541, 1.90. (The hydrogen ion dependence of these rate constants is correlated with the rate constants given in Table IV with an average difference of ~7% between the observed and calculated values.)

Rate of Solvolysis of *cis*-Iodo(dimethyl sulfoxide)chromium(III) in Aqueous Solution. The side reaction producing iodochromium(III) ion and eventually aquochromium(III) ion is less important in solvolysis of the cis isomer of iodo(dimethyl sulfoxide)chromium(III) (reaction cis (1,1) → (1,0)) compared to the trans isomer. The decrease in light absorption at 320 nm indicated the reaction to be nicely first order. Values of the rate constants for the aquation of this species ($k = -d \ln [cis\text{-}Cr(OH_2)_4(OS(CH_3)_2)I^{2+}]/dt$) at 25° as a function of acidity in solutions with $I = 0.56$ *M* are (given as $[H^+]$, 10^4k (sec^{-1})): 0.0887, 10.0; 0.0904, 7.74; 0.138, 6.37; 0.186, 5.03; 0.239, 4.17; and 0.539, 2.55. (The hydrogen ion dependence of these rate constants is correlated with the rate constants given in Table IV with an average difference of 4% between the observed and calculated values. Only the points at the two lowest acidities deviate appreciably.)

Derived Results and Discussion

The exponential approach of $\bar{n}_D$ to its equilibrium value in the series of reactions $(0,0) \rightleftarrows (1,0) \rightleftarrows (2,0) \rightleftarrows$ etc., indicates that the various rate constants have relative values close to those expected on a statistical basis. It is well known that the titration curve for a polybasic acid has exactly the same form as that of a monobasic acid if the stepwise acid dissociation constants for the acid are related to one another by the statistical factor.[19] Related to this is the more complicated case of light absorption by a series of species $MA_{N-n}B_n$ for which $\log (I_0/I)$ *vs.* [B]/[A] has the same form for $N = 2$, $n = 0$, 1, and 2 as it has for $N = 1$, $n = 0$ and 1 if both the equilibrium constants and the individual molar absorbance indices are related statistically.[20] It seems likely, therefore, that the rate of approach of $\bar{n}_D$ to its equilibrium value has the same form as that for a simple one-step reversible first-order reaction if all of the rate constants are related statistically and if the concentrations make each step a pseudo-first-order reaction. This can be shown for the two-step example

$$M(OH_2)_2 + X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M(OH_2)X + H_2O$$

$$M(OH_2)X + X \underset{k_4}{\overset{k_3}{\rightleftharpoons}} MX_2 + H_2O$$

If k_f and k_r are the intrinsic rate constants for the forward and reverse reactions, the rate constants in this example become $k_1 = 2k_f$, $k_2 = k_r$, $k_3 = k_f$, and $k_4 = 2k_r$, and $\bar{n}$ approaches its equilibrium value $(2k_f[X]/(k_f[X] + k_r))$ exponentially; for $\bar{n}_0 = 0$[21]

$$\bar{n}/\bar{n}_{eq} = 1 - e^{-(k_f[X] + k_r)t}$$

It is certain that the same result arises for a six site example ($N = 6$), and therefore, the extrapolated half-time of 276 hr for approach to solvation equilibrium at 27° and $Z = 0.705$ is interpreted to be related to the corresponding sum of intrinsic pseudo-first-order rate constants for the reactions in this system $(k_fa_D + k_ra_W)$

$$276 \text{ hr} \times 3600 \text{ sec hr}^{-1} = \frac{0.69}{(k_fa_D + k_ra_W)}$$

$$k_fa_D + k_ra_W = 6.95 \times 10^{-7} \text{ sec}^{-1}$$

The pseudo-first-order rate constants (k_fa_D) and (k_ra_W) are the products of intrinsic rate constants and the activity of the reacting solvent component.[22] The quotient k_f/k_r is equal to the statistically corrected equilibrium constant for replacement of coordinated water by dimethyl sulfoxide. With $k_fa_D + k_ra_W = 6.95 \times 10^{-7}$ sec^{-1} and $k_fa_D/k_ra_W \cong 6.8$,[23] one obtains $k_fa_D \cong 6 \times 10^{-7}$ and $k_ra_W \cong 9 \times 10^{-8}$ sec^{-1} at 27° in a solvent of $Z = 0.705$. A value $k_fa_D = 6 \times 10^{-7}$ sec^{-1} corresponds to an initial change of 1.1% per hour for the transformation of $Cr(OS(CH_3)_2)^{3+}$ to $Cr(OS)(CH_3)_2)_2^{3+}$ (both isomers) in agreement with the value observed directly.

The assignment of configuration to the isomeric bis- and tris(dimethyl sulfoxide)chromium(III) species is an important result of this study. An earlier assignment was based on the close agreement between the relative concentrations at equilibrium and the statistically

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[17] The subscripts to a_{di} define the number of coordinated dimethyl sulfoxide molecules, *d*, and iodide ions, *i*.

[18] J. H. Krueger, *Inorg. Chem.*, **5**, 132 (1966).

[19] E. Q. Adams, *J. Amer. Chem. Soc.*, **38**, 1503 (1916).

[20] R. F. Kruh, *J. Amer. Chem. Soc.*, **76**, 4865 (1954).

[21] The integrated rate equations for this sequence of two reactions can be found in A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, pp 175–176. The above equation results from the indicated substitution.

[22] For the dependence of the rate of the process $Cr(OH_2)_6^{3+} + (CH_3)_2SO \rightarrow Cr(OH_2)_5(OS(CH_3)_2) + H_2O$ upon the concentration o dimethyl sulfoxide to be given by $6k_f[Cr(OH_2)_6^{3+}]a_D$, the quotient of the activity coefficients of the reactant $Cr(OH_2)_6^{3+}$ and the transition-state $\{Cr(OH_2)_6^{3+} \cdot (CH_3)_2SO\}^{\ddagger}$ must be independent of solvent composition. For the present situation in which a particular composition of solvent is used, the quotient of activity coefficients must have the same value for each reaction ($n = 0$–6) for the simplifications given in the text to be valid.

[23] The value 6.8 for k_fa_D/k_ra_W was obtained from the relative concentrations of $Cr(OH_2)(OS(CH_3)_2)_5^{3+}$ and $Cr(OH_2)_2(OS(CH_3)_2)_4^{3+}$ (both isomers) at 60° in a solvent with $Z = 0.67$ given in ref 7.

expected values.[7] The basis for identification in the present study is the comparison of the observed yield of tris products under kinetic control with the statistically expected yield if reaction of bis reactants involves no rearrangements. In this comparison, presented in Table III, the more easily eluted isomer is identified as the cis isomer for each composition, an identification the same as that already proposed.[7] If the deviations of the observed ratios of tris products are the result of starting with impure bis reactants, the cis reactant contained 16% trans and the trans reactant contained 5% cis.

Table III. Yields of Isomeric $Cr(OH_2)_3(OS(CH_3)_2)_3{}^{3+}$ from Each Isomeric $Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}$

Reactant[a]	Ratio[a] $[A\text{-}Cr(OS(CH_3)_2)_3{}^{3+}]/[B\text{-}Cr(OS(CH_3)_2)_3{}^{3+}]$				
		Expected on statistical basis[c]			
	Obsd[b]	I	II	III	IV
$A\text{-}Cr(OS(CH_3)_2)_2{}^{3+}$	0.73	1	1	0	∞
$B\text{-}Cr(OS(CH_3)_2)_2{}^{3+}$	0.026	0	∞	1	1

[a] A isomer is more easily eluted isomer. [b] 13.5-hr reaction period; $Z = 0.705$; $[H^+] = 0.04$ *M*. [c] (I) $A\text{-}Cr(OS(CH_3)_2)_2{}^{3+}$ = cis, $A\text{-}Cr(OS(CH_3)_2)_3{}^{3+}$ = cis; (II) $A\text{-}Cr(OS(CH_3)_2)_2{}^{3+}$ = cis, $A\text{-}Cr(OS(CH_3)_2)_3{}^{3+}$ = trans; (III) $A\text{-}Cr(OS(CH_3)_2)_2{}^{3+}$ = trans, $A\text{-}Cr(OS(CH_3)_2)_3{}^{3+}$ = cis; (IV) $A\text{-}Cr(OS(CH_3)_2)_2{}^{3+}$ = trans, $A\text{-}Cr(OS(CH_3)_2)_3{}^{3+}$ = trans.

With both isomers of iodo(dimethyl sulfoxide)chromium(III) ion prepared, the question of assignment of configuration arises here also. In the preparation from chromium(II) and triiodide ion, the relative concentrations of the isomers were [more easily eluted isomer]/[less easily eluted isomer] = 0.3. This suggests that the more easily eluted isomer is the trans isomer; production of the isomers in the statistically expected relative amounts would have given a ratio of 0.25 with this assignment of configuration. The products of reaction of dimethyl sulfoxide with each of the isomers support this assignment. The more easily eluted isomer produces no species containing one iodide ion and two dimethyl sulfoxide molecules per chromium(III). The less easily eluted isomer of iodo(dimethyl sulfoxide)chromium(III) ion gives a major amount of iodobis(dimethyl sulfoxide)chromium(III) ion as a product. These observations are consistent with iodide being a trans labilizing group and with the isomer identification proposed.

It should be noted that the isomer of iodo(dimethyl sulfoxide)chromium(III) identified as trans has light absorption greater than that identified as cis, a relationship not expected on the basis of simple theory.[24] The isomeric bis(dimethyl sulfoxide)chromium(III) ions[7] and bis(pyridine *N*-oxide)chromium(III) ions[25] also have spectra with relative light absorption contrary to simple theory.

Certain observations in this study regarding the relative ease of elution of related species deserve mention. Greater ion pairing of the more highly charged ion in 2 *M* sulfuric acid is believed to cause the elution of species of charge 3+ ($Cr(OH_2)_6{}^{3+}$) ahead of a species of charge 2+ ($Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$). In media with a smaller potential for ion pairing (1 *M* sulfuric acid or 1–3 *M* perchloric acid), the elution order is the normal one. The relative ease of elution of isomeric octahedral complex ions is not the same for species of all compositions and charges; the charge (and therefore the concentration of eluting agent) is a variable with which a correlation exists. For species of charge 1+ (*e.g.*, $Co(NH_3)_4(NO_2)_2{}^+$ [26] and $Cr(OH_2)_4Cl_2{}^+$),[27] the trans isomer is more easily eluted, but for species of charge 3+ (*e.g.*, $Cr(OH_2)_4(OS(CH_3)_2)_2{}^{3+}$)[7] the cis isomer is more easily eluted. For the species of charge 2+ studied here ($Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$), the trans isomer is the more easily eluted although the eluting agent (2 *M* sulfuric acid) is closer to that typically used for the elution of 3+ ions than it is to that used for 1+ ions (0.1 *M* acid). The substituton of water by dimethyl sulfoxide in the first coordination shell results in a lower elution rate. For the elution with 2 *M* sulfuric acid pictured in Figure 1, this substution results in approximately the same reduction in elution rate whether the species has charge 3+ ($Cr(OH_2)_5(OS(CH_3)_2)^{3+}$ compared to $Cr(OH_2)_6{}^{3+}$) or 2+ (*trans*-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$ compared to $Cr(OH_2)_5I^{2+}$); the elution peak for the first listed of each pair occurs with a volume of eluting agent 1.74 ± 0.02 times the volume required for the peak elution of the second listed member of each pair. This is not, however, a general phenomenon; isomeric species have different elution rates.

The kinetics of several reactions have been studied as a function of the acidity. In each case the pseudo-first-order rate constant can be correlated with the concentration of hydrogen ion by an equation of the form

$$k = k_0 + k_{-1}[H^+]^{-1}$$

Table IV summarizes values for k_0 and k_{-1} for each reaction studied kinetically; also included are data from the literature[4] for related reactions.

The reaction of iodochromium(III) ion to give *trans*-iodo(dimethyl sulfoxide)chromium(III) ion does not exhibit the inverse hydrogen ion dependence (at $[H^+] > 0.1$) shown by the other reactions. Although the labilizing effect of coordinated hydroxide upon chromium(III) ion has been shown not to be exclusively a trans effect,[28,29] it would appear that the trans labilizing effect of coordinated iodide has a dominant effect in the acidity range studied. At still lower acidities where the labilizing effect of a cis hydroxide and a trans iodide were both operative, an inverse hydrogen ion dependence would be observed.

The magnitude of the labilizing effect of a trans iodide can be judged from the first two entries in Table

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(24) 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, New York, N. Y., 1962, p 186.

(25) T. J. Weeks, Jr., and E. L. King, *J. Amer. Chem. Soc.*, **90**, 2545 (1968).

(26) E. L. King and R. R. Walters, *J. Amer. Chem. Soc.*, **74**, 4471 (1952).

(27) E. L. King, M. J. M. Woods, and H. S. Gates, *J. Amer. Chem. Soc.*, **80**, 5015 (1958); for confirmation of configuration, see I. G. Dance and H. C. Freeman, *Inorg. Chem.*, **4**, 1555 (1965); B. Morosin, *Acta Crystallogr.*, **21**, 280 (1966).

(28) D. W. Carlyle and E. L. King, *Inorg. Chem.*, **9**, 2333 (1970).

(29) A comparison analogous to that presented in ref 28 for the isomeric bisisothiocyanatochromium(III) ions can be made for the isomeric iodo(dimethyl sulfoxide)chromium(III) ions using rate constants given in Table IV. For the loss of iodide by pathway with rates independent of the concentration of hydrogen ion, $k(\text{cis})/k(\text{trans}) \cong 0.7$; for pathways with rates inversely dependent upon the concentration of hydrogen ion, $k(\text{cis})/k(\text{trans}) \cong 2.3$. As pointed out, however, the values of k for reaction of the trans isomer are very uncertain.

Table IV. Summary of Rate Constants

Reactant	Charge on transition state	Solvent Z	Product	k (25°)[a]
$Cr(OH_2)_6^{3+}$	3+	0.705	$Cr(OH_2)_5(OS(CH_3)_2)^{3+}$	4.1×10^{-6}
$Cr(OH_2)_5I^{2+}$	2+	0.705	*trans*-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$	1.02×10^{-4}
$Cr(OH_2)_5I^{2+}$	2+	0.705	$Cr(OH_2)_6^{3+} + Cr(OH_2)_5(OS(CH_3)_2)^{3+}$	0.33×10^{-4}
$Cr(OH_2)_5I^{2+}$	1+	0.705	$Cr(OH_2)_6^{3+} + Cr(OH_2)_5(OS(CH_3)_2)^{3+}$	0.026×10^{-4}
trans-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$	2+	0.705	$Cr(OH_2)_5(OS(CH_3)_2)^{3+}$	0.095×10^{-4}
trans-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$	1+	0.705	$Cr(OH_2)_5(OS(CH_3)_2)^{3+}$	7.6×10^{-7}
$Cr(OH_2)_5I^{2+}$	2+	0	$Cr(OH_2)_6^{3+}$	0.84×10^{-4} [b]
$Cr(OH_2)_5I^{2+}$	1+	0	$Cr(OH_2)_6^{3+}$	0.34×10^{-4} [b]
cis-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$	2+	0	$Cr(OH_2)_5(OS(CH_3)_2)^{3+}$	1.25×10^{-4}
cis-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$	1+	0	$Cr(OH_2)_5(OS(CH_3)_2)^{3+}$	7.0×10^{-5}
trans-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$	2+	0	$Cr(OH_2)_5(OS(CH_3)_2)^{3+}$	1.7×10^{-4} [c]
trans-$Cr(OH_2)_4(OS(CH_3)_2)I^{2+}$	1+	0	$Cr(OH_2)_5(OS(CH_3)_2)^{3+}$	2.6×10^{-5} [c]

[a] All rate constants have dimensions sec^{-1}; if a second-order rate law is involved, the mole fraction concentration scale was used for the reactant solvent component. [b] From ref 4. [c] Uncertain value.

IV. After correction for the statistical factor in the reaction of aquochromium(III) ion with dimethyl sulfoxide, the comparison is $1.02 \times 10^{-4}/(^1/_6 \times 4.1 \times 10^{-6}) \cong 1.5 \times 10^2$. Moore, Basolo, and Pearson[5] found that the rate of exchange of ^{18}O between solvent water and iodopentaaquochromium(III) ion (presumably the trans site) is governed by a rate constant $1.2 \times 10^{-3}\ sec^{-1} > k > 2.7 \times 10^{-4}\ sec^{-1}$. Since the rate constant for ^{18}O exchange of hexaaquochromium(III) ion is $3 \times 10^{-6}\ sec^{-1}$, the corresponding comparison is (using the geometric mean of the extreme values): $5.7 \times 10^{-4}/(^1/_6 \times 3 \times 10^{-6}) \cong 1.1 \times 10^3$. Coordinated iodide is seen to have a labilizing effect which is larger than that due to coordinated hydroxide ion,[28] comparable to that due to coordinated sulfite ion,[28] and smaller than that due to a coordinated chloromethyl group.[30]

The effect of changing the solvent upon the rate of loss of iodide by iodochromium(III) ion is that expected; the greater solvating ability of water for anions[31] is manifested by larger rates in purely aqueous media. This is particularly striking for the transition state of involving a coordinated hydroxide ion. In this transition state, the iodide ion would be released to a greater extent (compared to the transition state involving coordinated water instead of hydroxide), and the anion solvating ability of the solvent would, therefore, be more important.

The present study confirms the suggestion by Moore, Basolo, and Pearson[5] that coordinated iodide is a trans labilizing group; based upon the present study, however, it seems likely that the ultimate product in their study was not solely *trans*-$Cr(OH_2)_4(^{18}OH_2)_2^{3+}$. Whether loss of iodide by iodo(dimethyl sulfoxide)chromium(III) produces a pentacoordinated intermediate ($Cr(OH_2)_4(OS(CH_3)_2)^{3+}$) is not proved by the observation that both isomers of bis(dimethyl sulfoxide)chromium(III) ion are produced in the solvolysis reaction. If solvolysis goes *via* a pentacoordinated intermediate, a number of geometries in addition to the initially produced intermediate of C_{4v} symmetry are possible. (Still more geometries are possible if one includes the hydroxide ion containing intermediate $Cr(OH_2)_3(OH)(OS(CH_3)_2)^{2+}$.) If only a single intermediate was producing both products or if several intermediates were in constant relative amounts, the relative yields of the two isomeric products would not depend upon the extent of reaction. In the experiments reported in Table I, appreciable amounts of isomeric bis(dimethyl sulfoxide)chromium(III) ions are produced in the reactions

$$Cr(OH_2)_5(OS(CH_3)_2)^{3+} + (CH_3)_2SO = \textit{cis- and trans-}Cr(OH_2)_4(OS(CH_3)_2)_2^{3+} + H_2O$$

Correction of the data for these reactions has been made by assuming that $(1/4.2) \times 1.1\% = 0.26\%$ of $Cr(OH_2)_5(OS(CH_3)_2)^{3+}$ gives *trans*-$Cr(OH_2)_4(OS(CH_3)_2)_2^{3+}$ per hour and $(3.2/4.2) \times 1.1\% = 0.84\%$ of *cis*-$Cr(OH_2)_4(OS(CH_3)_2)_2^{3+}$ per hour. The concentration of $Cr(OH_2)_5(OS(CH_3)_2)^{3+}$ is approximately constant (50 ± 5% of the total) between 1 and 15 hr (see Table I), and this value has been assumed in all calculations in which the concentrations at a particular time are compared with those existing at 1 hr. The corrected values of the ratio [*cis*-$Cr(OS(CH_3)_2)_2^{3+}$]/[*trans*-$Cr(OS(CH_3)_2)_2^{3+}$] are not constant but decrease from ~1.2 at 1.5 hr to ~0.8 at 12 hr. Some uncertainty is introduced into the later points by the reaction of isomeric bis(dimethyl sulfoxide)chromium(III) ions to give the isomeric tris species, and if only the data at 1.5, 2.25, 3.00, and 3.75 hr are considered the ratio is approximately constant, 1.10 ± 0.05. Clearly the important question of whether or not there are several intermediates present in varying amounts as reaction occurs remains unsettled. Better data will be attainable in experiments in which the starting material is purified *trans*-iodo(dimethyl sulfoxide)chromium(III) ion.

If the production of isomeric bis(dimethyl sulfoxide)chromium(III) ions from iodo(dimethyl sulfoxide)chromium(III) ion occurred by direct reaction without formation of pentacoordinated intermediates, the ratio of the products would be independent of the extent of reaction. The possibility that thermal loss of iodide does not give a pentacoordinated intermediate is raised by the recent work of Guastalla and Swaddle,[32] in which the effect of pressure upon the rates of aquation of halopentaamminechromium(III) ions suggests an associative (I_a) mechanism. The iodoamminechromium(III) species may react differently than the iodoaquochromium(III) species. This is suggested by the retention of configuration during loss of iodide by *cis*- and *trans*-iodoaquotetraamminechromium(III)

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[30] J. H. Espenson and W. R. Bushey (private communication) have found a rate enhancement of ~10^5 for anation by thiocyanate of $Cr(OH_2)_5CH_2Cl^{2+}$ compared to $Cr(OH_2)_6^{3+}$.

[31] A. J. Parker, *Quart. Rev., Chem. Soc.*, **16**, 163 (1962).

[32] G. Guastalla and T. W. Swaddle, *Can. J. Chem.*, **51**, 821 (1973).

ions,[33] a result which contrasts with observations in the present study.

Another question which remains unsettled is the following. Do the pathways for solvolysis of *trans*-$(H_2O)_4Cr(OS(CH_3)_2)I^{2+}$ with transition states of net charge 2+ and 1+ yield intermediates which are in rapid equibrium with one another? Regrettably the form of the equation giving the hydrogen ion dependence of the ratio of the isomeric $(H_2O)_4Cr(OS(CH_3)_2)_2{}^{3+}$ products is the same whether independent intermediates are produced or a rapidly established proton dissociation–association equilibrium of the intermediates exists, giving a common pool of intermediates which go on to yield bis(dimethyl sulfoxide)chromium(III) products regardless of the pathway by which the intermediates are formed. The equation relating [*cis*-$Cr(OS(CH_3)_2)_2{}^{3+}$]/[*trans*-$Cr(OS(CH_3)_2)_2{}^{3+}$] to $[H^+]$ has the form

$$\frac{[cis\text{-}Cr(OS(CH_3)_2)_2{}^{3+}]}{[trans\text{-}Cr(OS(CH_3)_2)_2{}^{3+}]} = \frac{A[H^+] + B}{C[H^+] + 1}$$

The uncorrected data presented in Table II are correlated with this equation with the parameters A = 10.1 l. mol^{-1}, B = 2.0, and C = 48 l. mol^{-1}. The parameter B (2.0) can be compared with A/C (0.21). Each of these is the ratio of rate constants for formation of the cis isomer compared to the trans isomer; B is the ratio for the case where the precursor contains hydroxide ion, and A/C is the ratio for the case where the precursor does not contain hydroxide ion. The cis product is formed more readily from the precursor containing hydroxide. (This qualitative conclusion would not be altered by use of corrected values of the product ratio.)

The limited data (Table II) showing an appreciable dependence of the relative yields of the isomeric bis(dimethyl sulfoxide)chromium(III) products upon the ionic strength reveal additional complexity in this system. Perchlorate ion appears to play a role in the reaction. Presumably this is due to an intermediate containing perchlorate ion, either iodoperchloratochromium(III) or perchlorato(dimethyl sulfoxide)chromium(III) ion,[34] which produces relatively more trans bis product.

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Reactions of Bis(trifluoromethyl) Trioxide[1]

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Abstract: Reactions of bis(trifluoromethyl) trioxide, CF_3OOOCF_3, with a variety of inorganic compounds are described. The trioxide is shown to be a convenient source of compounds containing CF_3O– and CF_3OO– groups. Improved syntheses of the previously reported CF_3ONF_2, CF_3OOSO_2F, and $(CF_3O)_2SF_4$ are described, and the new compounds $CF_3OOSO_2OCF_3$, *cis*-$CF_3OOSF_4OCF_3$, and $CF_3OOC(O)OCF_3$ are reported.

Perfluoroalkyl trioxides are the only catenated oxygen compounds of the type sufficiently stable for isolation and study in the pure state under ambient conditions. The four known examples are CF_3OOOCF_3,[2,3] $CF_3OOOC_2F_5$,[3] $C_2F_5OOOC_2F_5$,[4] and $CF_3OOOCF_2OOCF_3$.[5] Based on the chemistry of peroxides, trioxides are expected to behave similarly with facile cleavage of the O–O bonds forming $R_fO\cdot$ and $R_fOO\cdot$ radicals. Because of its symmetry, availability, and the decreasing stability of higher perfluoroalkoxy radicals, CF_3OOOCF_3 is the most suitable trioxide for study in order to provide information on the chemistry of these novel materials. In this paper reactions of CF_3OOOCF_3 with a variety of inorganic substrates are reported. Convenient syntheses of the previously known CF_3ONF_2,[6,7] CF_3OOSO_2F,[8] and $(CF_3O)SF_4$[9,10] are given and the new compounds $CF_3OOSO_2OCF_3$, $CF_3OOSF_4OCF_3$, and $CF_3OOC(O)OCF_3$ are reported.

Results and Discussion

Bis(trifluoromethyl) trioxide is a convenient chemical source of both CF_3O– and CF_3OO– moieties; its reactions with $S_2O_6F_2$, N_2F_4, and SO_3 yield CF_3O– derivatives exclusively, while reactions with SF_4, SO_2,

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