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The Solvolysis of Hexaaquochromium(III) in Dimethyl Sulfoxide

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Although several different workers have reported preparing the hexa(dimethyl sulfoxide)chromium(III) perchlorate, $Cr(DMSO)_6(ClO_4)_3$, no one has reported preparing any compound containing an ion of the series $Cr(H_2O)_n(DMSO)_{6-n}{}^{3+}$, $n = 1$–5.[1] We would like to report the results of a more extensive investigation of the reaction of $Cr(H_2O)_6{}^{3+}$ with DMSO. These results are (1) the position of absorption maxima as a function of the average number of DMSO ligands per chromium and (2) the average number of DMSO ligands per chromium as a function of DMSO concentration in aqueous solution.

Experimental Section

$Cr(H_2O)_6(ClO_4)_3$ was prepared by reducing reagent grade CrO_3 with H_2O_2 in 1 *M* $HClO_4$. The product was recrystallized once from hot water. The ultraviolet spectrum compared favorably with that reported by Plane.[2] $Cr(DMSO)_6(ClO_4)_3$ was prepared by the method reported by Cotton and Francis.[1a] The DMSO was used as received. Three separate preparations of the compound gave products with Cr:DMSO ratios ranging from 1:5.1 to 1:5.8. Recrystallizing the compound from DMSO at 100° gave a product with a Cr:DMSO ratio of 1:5.95. *Anal.* Calcd for $Cr(DMSO)_6(ClO_4)_3$: Cr, 6.35; DMSO, 57.2. Found: Cr, 6.33; DMSO, 56.4. The molar absorptivities at 444 and 634 mμ were 36.3 and 33.5 M^{-1} cm^{-1}, respectively. Drago reported 34.6 and 33.4, and Schläfer reported 31.6 and 30.2 M^{-1} cm^{-1} for the molar absorptivities at 444 and 634 mμ.[1b,c] The compound was analyzed for chromium by oxidizing the chromium to dichromate with peroxydisulfate in the presence of a small amount of $AgNO_3$. A known excess of standard ferrous solution was added and the excess was back-titrated with standard dichromate solution. The compound was analyzed for DMSO as described elsewhere.[3]

The absorption spectrum as a function of the average number of DMSO ligands attached to the chromium was determined in the following manner. A number of 125-ml erlenmeyer flasks, each containing 25 ml of DMSO, were suspended in a constant-temperature bath maintained at 40.0°. A known amount of $Cr(H_2O)_6(ClO_4)_3$, *ca.* 0.25 g, was added to each flask. At time intervals of about 15 min near the start and about 30 min later, flasks were removed and were quenched in a Dry Ice–acetone bath. Later each flask was warmed to room temperature, and a quantity of the solution from each flask was used to determine the absorption spectrum from 400 to 450 mμ and from 575 to 650 mμ using a Beckman DB recording spectrophotometer. Ten milliliters of the solution from each flask was used to charge a cation-exchange column containing Dowex 50-X 8 (100–200 mesh) resin in the H^+ form. Ten bed volumes of cold water were washed through the column to clean it of the solvent DMSO. Blank experiments confirmed that this was sufficient water to wash the resin bed free of solvent DMSO. The Cr(III) species were eluted with 8 *N* H_2SO_4. The effluent was analyzed for DMSO. The concentration of Cr(III) was determined from the initial amount of $Cr(H_2O)_6(ClO_4)_3$ used.

An attempt to isolate various $Cr(H_2O)_n(DMSO)_{6-n}{}^{3+}$ species using cation-exchange resins was made. A jacketed column was constructed from a 50-ml buret and 45-mm glass tubing. Dowex 50-X 8 (100–200 mesh) resin in the H^+ form was used to pack the column. Water at 1° was circulated through the jacket. About 3 mmoles of $Cr(H_2O)_n(DMSO)_{6-n}{}^{3+}$, where *n* averaged 3 as determined from Figure 1, was run into the top of the column and the column was washed with 500 ml of cold water. The column was eluted with 8 *N* H_2SO_4 at a flow rate of 1 ml/hr. No separation of the band was obtained. The absence of a second band also indicates that no appreciable formation of polymeric material had occurred.

In the experiments designed to determine the average number of DMSO ligands per chromium as a function of DMSO concentration in aqueous solution, the following procedure was employed. Solutions containing various amounts of DMSO were made by adding the calculated amount of DMSO to a volumetric flask and diluting to volume with distilled water. About 0.25 g of $Cr(H_2O)_6(ClO_4)_3$ was added to 25 ml of the desired solution and was allowed to come to equilibrium at 40.0°. The spectrum of the solution was determined using a Beckman DB spectrophotometer. The location of the absorption maxima was used along with Figure 1 in estimating the average number of DMSO molecules coordinated.

Results and Discussion

The investigation of Cr(III) in methanol and methanol–water mixtures has been reported by Jayne and King.[4] They showed that methanol could replace water molecules in the coordination sphere; however, methanol does not compete for coordination positions nearly as well as DMSO does. Several investigators[5] have shown that in the series of compounds $Cr(H_2O)_n(NH_3)_{6-n}{}^{3+}$, $n = 0$–6, the absorption maximum shifts to higher energy as *n* decreases. This would be expected when ligands of one crystal field strength are replaced stepwise by ligands of a larger crystal field.

Figure 1 shows the relation between the wavelength of the absorption maximum of the $Cr(H_2O)_n(DMSO)_{6-n}{}^{3+}$ species and the average ligand DMSO:Cr ratio. If one makes the assumption that the stepwise rate constants for the formation of $Cr(DMSO)_6{}^{3+}$ are all of the same order of magnitude, one must conclude that all $Cr(H_2O)_n(DMSO)_{6-n}{}^{3+}$ species exist in appreciable concentration at some time during the solvolysis of $Cr(H_2O)_6{}^{3+}$ in DMSO. This assumption is reasonable in view of the equilibrium constants calculated for the chromium(III)–methanol species.[4] The scatter of the points in Figure 1 is due to the expected poor precision of the analytical method involving ion-exchange separation.

From the results shown in Figure 1 it is obvious that

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[1] (a) F. H. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960); (b) D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962); (c) H. L. Schläfer and H. P. Opitz, *Z. Chem.*, **2**, 216 (1962).

[2] R. A. Plane and J. A. Laswick, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

[3] K. R. Ashley and R. E. Hamm, *Inorg. Chem.*, **5**, 1645 (1966).

[4] J. C. Jayne and E. L. King, *J. Am. Chem. Soc.*, **86**, 3989 (1964).

[5] (a) R. I. Coimar and F. W. Schwartz, *ibid.*, **54**, 3204 (1932); (b) R. Tsuchida, *J. Chem. Soc. Japan*, **13**, 388, 436, 471 (1938); (c) E. Jørgensen and J. Bjerrum, *Acta Chem. Scand.*, **12**, 1047 (1958).

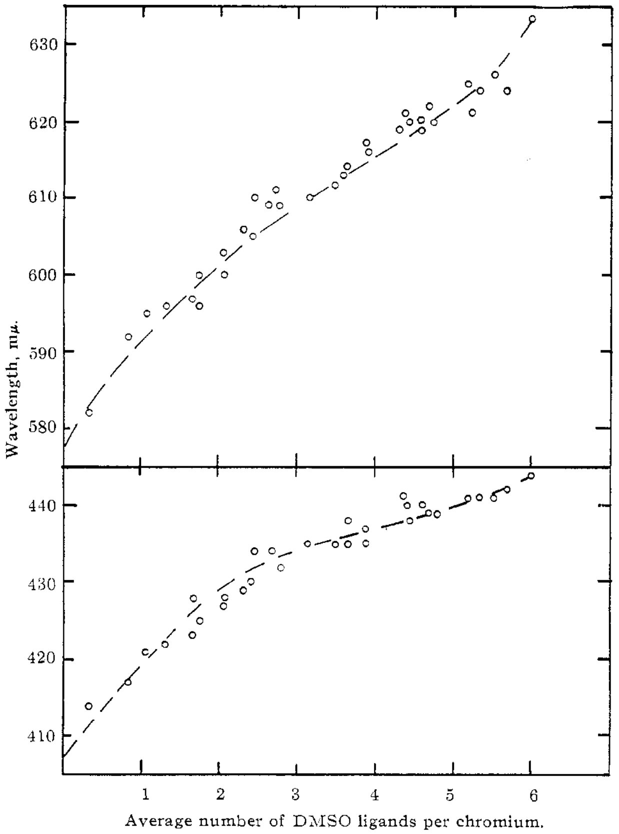

Figure 1.—The position of the absorption maximum as a function of the average number of DMSO ligands in the series of compounds $Cr(H_2O)_n(DMSO)_{6-n}{}^{3+}$.

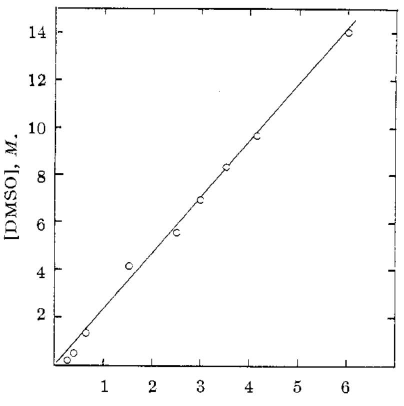

Figure 2.—The average number of DMSO ligands per chromium at equilibrium as a function of the concentration of DMSO in aqueous solution.

one may estimate the average number of DMSO ligands from the wavelengths of the maxima in the absorption spectrum.

Figure 2 shows a plot of the equilibrium ligand DMSO:Cr ratio *vs.* the DMSO concentration at 40.0°. This plot appears to be very nearly linear, with the greatest deviations at low DMSO concentration. This linear relation implies that the stepwise formation constants for $Cr(DMSO)_6{}^{3+}$ are all of the same order of magnitude. If this were not so, a linear relationship would not be observed.

An investigation of the kinetics of aquation of $Cr(DMSO)_6{}^{3+}$ and the solvolysis of $Cr(H_2O)_6{}^{3+}$ in DMSO produced ambiguous results. This was a direct result of the inability to isolate intermediate species and the lack of information concerning the activities of $Cr(H_2O)_n(DMSO)_{6-n}{}^{3+}$, DMSO, and water in the DMSO–water solutions.

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The Pentacyanocobaltate(II) Ion and Acetylenic Compounds

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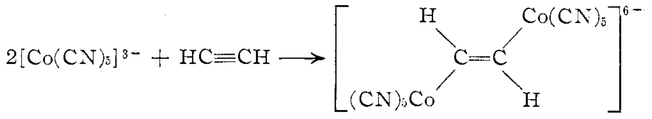
The interaction of pentacyanocobaltate(II) ion in aqueous solution with organic and inorganic compounds has led to some novel complexes with cobalt–carbon[2,3] and cobalt–metal bonds.[4] For example, in 1959 Griffith and Wilkinson[5] reported that acetylene and $[Co(CN)_5]^{3-}$ yield I, a moderately stable adduct with cobalt–carbon bonds



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We wish to report on our studies with $[Co(CN)_5]^{3-}$ and acetylenic systems.

Experimental Section

Materials.—Baker Analyzed reagent chemicals were used throughout. Prepurified nitrogen was passed through a water solution of $[Co(CN)_5]^{3-}$ to remove oxygen. Distilled water was deaerated under vacuum or by bubbling nitrogen through the solvent. Dimethyl acetylenedicarboxylate was obtained from Aldrich Chemical Co. and distilled before use. Dicyanoacetylene was prepared according to Blomquist and Winslow.[6] Methyl propiolate was prepared by oxidation[7] of propargyl alcohol followed by esterification of the resultant acid. Tetracyanoethylene was purchased from Aldrich Chemical Co. and sublimed before use. Diphenylacetylene, 1-phenylpropyne, 1-propyne, perfluorobutyne, and allene were used as received. All of the reactions of $[Co(CN)_5]^{3-}$ were performed in the general manner described below.

Reaction of Pentacyanocobaltate(II) Ion with Dimethyl Acetylenedicarboxylate.—A deaerated aqueous solution (*ca.* 40 ml) which contained 2.38 g (0.01 mole) of $CoCl_2 \cdot 6H_2O$ was added to a magnetically stirred aqueous solution (*ca.* 30 ml) which contained 3.6 g (0.055 mole) of KCN, under nitrogen at 0°. The green solution was stirred for 3 min, whereupon 0.71 g (0.005 mole) of $CH_3CO_2C{\equiv}CCO_2CH_3$ in 2 ml of deaerated methanol was

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[1] NSF undergraduate summer research participant.

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