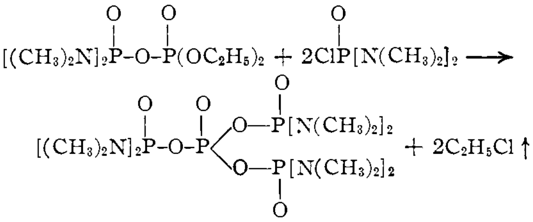
quite closely. This means that factors other than charge difference between building units can play an important role in determining the values of the structural-unit-reorganization equilibria. As will be indicated in the discussion of Paper XI in this series, change in the degree of π-bonding when going from one building unit to another[20] may well be the cause of $K_1 = 5 \times 10^{-4}$ and $K_2 = 2.5 \times 10^{-2}$ instead of $K_1 = K_2 = 0.333$.

In this system, branches are not present in appreciable amounts until $R < 1.2$. This means that the region corresponding to $1.2 < R < 1.4$ is free of branches and of the ortho species so that all of the phosphorus must be present only in the form of chain and ring compounds. The highest average chain length in this region is $\bar{n} = 10 \pm 1$, with rings disregarded. For higher average chain lengths, the amount of chain branching and cross linking due to the presence of branch structural units must increase gradually.

Structures from Reaction Data.—Previous descriptions in the literature[8] of the tripoly, tetrapoly and isotetrapoly molecules are in error in that they refer to the reorganization-equilibrium mixtures and not to pure species as alleged. This is most obvious in the case of the isotetrapoly structure which Tolkmith believed was formed in the reaction



$$[(\mathrm{CH_3})_2\mathrm{N}]_2\overset{\overset{\mathrm{O}}{|}}{\mathrm{P}}\text{–O–}\overset{\overset{\mathrm{O}}{|}}{\mathrm{P}}(\mathrm{OC_2H_5})_2 + 2\mathrm{Cl}\overset{\overset{\mathrm{O}}{|}}{\mathrm{P}}[\mathrm{N(CH_3)_2}]_2 \longrightarrow [(\mathrm{CH_3})_2\mathrm{N}]_2\overset{\overset{\mathrm{O}}{|}}{\mathrm{P}}\text{–O–}\overset{\overset{\mathrm{O}}{|}}{\mathrm{P}}\left\langle\begin{matrix}\mathrm{O}\text{—}\overset{\overset{\mathrm{O}}{|}}{\mathrm{P}}[\mathrm{N(CH_3)_2}]_2\\ \mathrm{O}\text{—}\underset{\underset{\mathrm{O}}{|}}{\mathrm{P}}[\mathrm{N(CH_3)_2}]_2\end{matrix}\right. + 2\mathrm{C_2H_5Cl}\uparrow \quad (6)$$

If the reaction proceeded as written, 75% of the phosphorus would have been present as end groups and 25% as branches. Instead, n.m.r. showed that the reaction product consists of the reorganization-equilibrium mixture of 1% ortho, 48% ends and 51% middles with no branches being observed, when the reaction was carried out exactly as reported.[8] This is an example of the fact that reorganization often occurs during a reaction and that structure proofs acceptable in organic chemistry generally do not apply to inorganic chemistry or to the organic derivatives of elements in the second row or below in the Periodic Table!

Although use of hydrolysis to investigate inorganic structures often leads to false conclusions,[5] the predominately unbranched polyphosphoryldimethylamides appear to represent the unusual case in which the structure of the reaction products of hydrolysis carried out under optimum conditions can be related approximately to the structure of the unhydrolyzed substance. In other words, the data indicate that all dimethylamido groups can be converted to dimethylammonium ions of the corresponding phosphates without rearrangements involving the P–O–P linkages, when branching groups are absent or present in only small amounts. This is probably attributable to a combination of a slow rate of P–N scission with a considerably slower rate of P–O–P scission in water at room temperature or below.

The reorganization in carbon tetrachloride to form rings without concomitant molecular degradation indicates that rings are favored when the reorganizing molecules are separated by molecules of an inert solvent. This is in accord with the theory of ring formation developed by organic chemists. It, therefore, appears that the production of rings during the hydrolysis of long-chain phosphates is a phenomenon which is separable from the degradation process. In other words, the first step in path 3 in the hydrolysis scheme presented by McCullough, Van Wazer and Griffith[17] is probably a simple structural reorganization step not involving reaction with the water molecules.

Acknowledgment.—We wish to thank Dr. L. C. D. Groenweghe for equations 4 and 5 of this paper and the ideas underlying them.

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[20] J. R. Van Wazer, This Journal, **78**, 5709 (1956). Also see H. H. Jaffé, *J. Inorg. Nuclear Chem.*, **4**, 372 (1957).

[Contribution from the W. A. Noyes Laboratory, University of Illinois, Urbana, Illinois]

Transition Metal Ion Complexes of Dimethyl Sulfoxide

By Devon W. Meek, Darel K. Straub and Russell S. Drago[1]

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The preparation and characterization of transition metal ion complexes of dimethylsulfoxide have been described. The complexes have the general formula $\{M[OS(CH_3)_2]_n\}[MX_4]$, where $n = 4$ or 6 and X is a halogen. Shifts of the infrared stretching frequency of the S–O bond in the direction of lower energy have been attributed to coördination through the oxygen. Using dimethylsulfoxide as the solvent and cobalt(II) as the metallic ion, it appears that chloride is more, and iodide less, strongly coördinated than the sulfoxide. Equilibria existing in solution are discussed.

Introduction

In the course of our research program in the area of nonaqueous solvents we have observed that several inorganic salts have appreciable solubility in dimethylsulfoxide (DMSO). Precipitation of some of these materials from the solvent is often accompanied by dramatic color changes leading one to suspect coördination by sulfoxide.

Very little has been reported on the ability of dimethylsulfoxide to coördinate. Carbonyl complexes of the type $Mo(CO)_3(DMSO)_3$[2] and [Fe-

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[1] Author to whom correspondence regarding this article should be addressed.

[2] W. Hieber, K. Englert and K. Rieger, *Z. anorg. allg. Chem.*, **300**, 295 (1959).

$(DMSO)_6][Fe_4(CO)_{13}]$[3] have been reported. The molecular addition compounds $SiF_4 \cdot 2DMSO$,[4] $SbCl_5 \cdot DMSO$[5] and $MF_4 \cdot DMSO$[6] can also be prepared. In all of these compounds coördination is reported to occur through the oxygen.

It was of interest to determine the nature of the species obtained from dimethylsulfoxide solutions of various metal ions. The infrared spectra of the complexes were investigated in nitromethane solutions and on Nujol mulls of the solids. Coördination of dimethylsulfoxide occurs through the oxygen on all of the complexes we prepared. Elemental analyses, metathetical reactions and the visible spectra of nitromethane solutions support the formulation of these materials as $[M(DMSO)_n][MX_4]$ type complexes where $n = 4$ or 6 and X is a halogen. Evidence for the existence of more complex equilibria in solution is presented.

Experimental

Reagents.—Commercial dimethyl sulfoxide (Crown Zellerbach Chemical Co.) is purified by drying over calcium or barium oxide with occasional shaking for several days followed by fractional distillation under reduced pressure. The fraction with a b.p. of 54–55° was used. Addition of glass wool to the flask helped minimize the vigorous bumping encountered when dimethylsulfoxide is distilled.

Methylene chloride and nitromethane were fractionally distilled. All other solvents were reagent grade and were used without special purification.

Reagent grade anhydrous cupric bromide and mercuric chloride were obtained commercially. Mercuric thiocyanate was prepared from mercuric nitrate and potassium thiocyanate. Anhydrous nickel chloride, cobalt chloride, cupric chloride and manganous chloride are obtained by dehydrating the corresponding reagent grade hydrated salts at 110–120° for 48 hr.

The infrared spectra were obtained using a Perkin-Elmer, Model 21, infrared spectrometer with sodium chloride optics. The instrument was frequency calibrated. Visible spectra were obtained with a Model 14*M*, recording Cary spectrophotometer.[7]

Hexakis-(dimethylsulfoxide)-nickel(II) Tetrachloronickelate (II).—Twenty grams of anhydrous nickel chloride was dissolved in 150 ml. of dimethylsulfoxide, the solution filtered, and an equal volume of benzene was added. The initial light green solution turned intensely blue in about three to five minutes and blue crystals precipitated. The crystals were removed by filtration, washed with benzene and dried over phosphorus pentoxide. Care was taken to exclude atmospheric moisture, as the compound is extremely deliquescent. The yield was 97%.

Anal. Calcd. for $\{Ni[OS(CH_3)_2]_6\}[NiCl_4]$: C, 19.80; H, 4.98. Found: C, 19.85; H, 4.96.

Acetone and ethyl ether precipitate the same compound when used in place of benzene.

When the dimethylsulfoxide solution of nickel chloride is heated to about 50°, the color changes from light green to intense blue. This color change is completely reversible upon heating and cooling. Maintenance of the temperature at 50° for 6 hr. resulted in the deposition of large blue crystals, which were filtered, washed with acetone and dried over phosphorus pentoxide.

Anal. Calcd. for $\{Ni[OS(CH_3)_2]_6\}[NiCl_4]$: C, 19.80; H, 4.98. Found: C, 19.60; H, 4.96.

Trimethylphenylammonium Tetrachloronickelate (II).—In order to establish the formula as written for the above compound, metathesis reactions were performed. Trimethylphenylammonium nitrate (0.014 moles) in 50 ml. of absolute ethanol was mixed with an ethanolic solution containing 0.007 moles of $[Ni(DMSO)_6]$ $[NiCl_4]$. A blue powder precipitated upon vacuum removal of three-fourths of the ethanol. Two recrystallizations from absolute ethanol produced the pure product.

Anal. Calcd. for $(C_9H_{14}N)_2NiCl_4$: C, 45.71; H, 5.97; N, 5.92. Found: C, 45.52; H, 5.97; N, 6.16.

Hexakis-(dimethylsulfoxide)-nickel(II) Tetraphenylborate.—One gram of $[Ni(OS(CH_3)_2)_6]$ $[NiCl_4]$ was dissolved in absolute ethanol and added to an ethanolic solution of sodium tetraphenylborate.

After the addition of excess ether the green precipitate which forms was filtered off and recrystallized three times from absolute ethanol. The resultant light green needles are slightly hygroscopic.

Anal. Calcd. for $\{Ni[OS(CH_3)_2]_6\}[B(C_6H_5)_4]_2$: C, 61.80; H, 6.57. Found: C, 62.13; H, 6.82.

Hexakis-(dimethylsulfoxide)-cobalt(II) Tetrachlorocobaltate (II).—Twenty grams of anhydrous cobalt(II) chloride was dissolved in 125 ml. of dimethylsulfoxide by warming the solution to 50°. After stirring the solution for 10 hr. with a magnetic stirrer, a hygroscopic blue powder precipitated upon the addition of 300 ml. of ethyl acetate. Washing with anhydrous ethyl ether and drying over phosphorus pentoxide gave a 96% yield of product. The product was recrystallized twice from a 50% nitromethane–ethyl acetate mixture.

Anal. Calcd. for $\{Co[OS(CH_3)_2]_6\}[CoCl_4]$: C, 19.78; H, 4.98. Found: C, 19.25; H, 5.22.

Trimethylphenylammonium Tetrachlorocobaltate(II).—This compound was produced from $[Co(DMSO)_6][CoCl_4]$ in 97% yield by a procedure similar to that described for the corresponding nickel complex.

Anal. Calcd. for $(C_9H_{14}N)_2CoCl_4$: C, 45.69; H, 5.96; N, 5.92. Found: C, 45.73; H, 5.95; N, 5.86.

Hexakis-(dimethylsulfoxide)-cobalt(II) Iodide.—A solution of 13 g. of anhydrous cobalt chloride in 75 ml. of absolute ethanol was added, with stirring, to a solution of 30 g. of sodium iodide in 130 ml. of absolute ethanol; the solution was filtered from the precipitated sodium chloride. To the blue solution 100 g. of dimethylsulfoxide was added with stirring. Upon the addition of 300 ml. of ether a coarsely crystalline precipitate forms immediately. This material was filtered and air-dried (weight 75 g.). The crude compound was purified by three recrystallizations from hot methylene chloride. The pink crystals obtained are only slightly deliquescent.

Anal. Calcd. for $\{Co[OS(CH_3)_2]_6\}I_2$: C, 18.44; H, 4.61. Found: C, 18.43; H, 4.80.

Hexakis-(dimethylsulfoxide)-cobalt(II) Tetraiodocobaltate (II).—This compound was prepared by a method identical to the one used for hexakis(dimethylsulfoxide)-cobalt(II) iodide, except 25 g. of dimethylsulfoxide was added instead of 100 g. Upon addition of ether, the compound separates as an oil, which quickly crystallizes with further stirring. The yield was 76% of deep green deliquescent crystals. This product was recrystallized from hot absolute ethanol.

Anal. Calcd. for $\{Co[OS(CH_3)_2]_6\}[CoI_4]$: C, 13.16; H, 3.29. Found: C, 12.88; H, 3.37.

Tetrakis-(dimethylsulfoxide)-copper(II) Tetrachlorocuprate (II).—A dark brown solution was obtained by dissolving 6 g. of cupric chloride in 35 ml. of dimethylsulfoxide. After stirring for twenty minutes a light green slurry formed. The slurry was stirred for 2 hr., benzene added to complete precipitation, the solid was filtered and washed with anhydrous ether. The product was dissolved in warm ethanol and precipitated by adding petroleum ether and cooling to − 5°. Light green flakes are obtained in 91% yield.

Anal. Calcd. for $\{Cu[OS(CH_3)_2]_4\}[CuCl_4]$: C, 16.52; H, 4.16. Found: C, 16.51; H, 4.12.

Tetrakis-(dimethylsulfoxide)-copper(II) Tetrabromocuprate (II).—A very dark colored solution is obtained when 10 g. of cupric bromide is dissolved in 100 ml. of dimethylsulfoxide. The solution was filtered and excess benzene was added. After vigorous stirring for two minutes yellow crystals precipitated. The product obtained in 90% yield was filtered, washed with ether and dried. The product is slightly hygroscopic and was recrystallized from ethanol.

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(3) W. Hieber and A. Lipp, *Chem. Ber.*, **92**, 2085 (1959).

(4) V. Gutmann and K. Utvary, *Monatsh. Chem.*, **90**, 706 (1959).

(5) I. Lindqvist and P. Einarsson, *Acta Chem. Scand.*, **13**, 420 (1959).

(6) E. L. Muetterties, THIS JOURNAL, **82**, 1082 (1960).

(7) NOTE ADDED IN PROOF.—Subsequent to the acceptance of this paper an article by F. A. Cotton and R. Francis, THIS JOURNAL, **82**, 2986 (1960), on the preparation and properties of some of these compounds has appeared.

Anal. Calcd. for $\{Cu[OS(CH_3)_2]_4\}[CuBr_4]$: C, 12.65; H, 3.19. Found: C, 12.74; H, 3.11.

Hexakis-(dimethylsulfoxide)-manganese(II) Tetrachloromanganate (II).—Dimethylsulfoxide was saturated with anhydrous manganese (II) chloride at 60–70°, filtered, and an equal volume of absolute ethanol was added. The solution deposited large tan-brown crystals after standing for several hours at room temperature. These were removed by filtration, washed with a 1:4 ethanol–ether mixture and dried *in vacuo*. Special care was taken throughout to exclude moisture, since the compound is extremely deliquescent.

Anal. Calcd. for $\{Mn[OS(CH_3)_2]_6\}[MnCl_4]$: C, 20.00; H, 5.00. Found: C, 20.18; H, 5.14.

Mercuric Thiocyanate-dimethyl Sulfoxide Complex.—Dimethylsulfoxide was saturated with mercuric thiocyanate at 70–80°. The filtered solution was allowed to stand several hours, whereupon large colorless crystals are deposited. These were removed and dried.

Anal. Calcd. for $Hg(SCN)_2 \cdot 2(CH_3)_2SO$: C, 15.22; H, 2.54; N, 5.92. Found: C, 15.39; H, 2.53; N, 5.89.

Though the stoichiometry is well established the structure of this complex is yet unknown.

TABLE I

SPECTRA OF COMPLEXES IN VISIBLE REGION IN NITROMETHANE SOLUTION

Complex ion	λ_{max}	ϵ_{max}	Molarity of CH_3NO_2 solution
$\{Mn[OS(CH_3)_2]_6\}[MnCl_4]$	442	3.10	0.08
	428	3.91	
	371	12.35	
$\{Co[OS(CH_3)_2]_6\}[CoCl_4]$	668	859	.0009
	586	482	
$[(CH_3)_3NC_6H_5]_2[CoCl_4]$	693	767	.0005
	666	659	
	635	468	
$\{Co[OS(CH_3)_2]_6\}I_2$	708	707	.0005
	670	818	
	655	826	
	620	723	
	371	3473	
$\{Co[OS(CH_3)_2]_6\}[CoI_4]$	665	538	.0003
	371	2423	
$\{Cu[OS(CH_3)_2]_4\}[CuCl_4]$	466	1164	.0007
	370	1520	
$\{Cu[OS(CH_3)_2]_4\}[CuBr_4]$	642	993	.0008
	371	2640	
$\{Ni[OS(CH_3)_2]_6\}[B(C_6H_5)_4]_2$	660	2.10	.05
	370	10.5	

Discussion

When the metal halides employed in this research are dissolved in the solvent dimethylsulfoxide, interaction between the solvent and metal ion occur. Solid compounds containing coördinated dimethylsulfoxide and the tetrahalometalate anion are obtained when the metals are precipitated from solution. These structures are supported by elemental analyses and examination of the visible spectra of the compounds in solution. In addition, metathesis reactions were carried out to further support the assigned structure. Trimethylphenylammonium tetrachloronickelate (II) and hexakis-(dimethylsulfoxide)-nickel(II) tetraphenylborate were obtained from the $NiCl_2$-dimethylsulfoxide complex. Trimethylphenylammonium tetrachlorocobaltate-(II) was obtained in 97% yield from the corresponding cobalt complex.

TABLE II

INFRARED SPECTRA OF THE COMPLEXES IN NITROMETHANE SOLUTION[a]

Complex	S=O stretch, cm.$^{-1}$
$(CH_3)_2SO$	1045 i,s
$\{Mn[OS(CH_3)_2]_6\}[MnCl_4]$	1004 i,s
$\{Co[OS(CH_3)_2]_6\}[CoCl_4]$	994 i,m
$\{Co[OS(CH_3)_2]_6\}I_2$	1045 i,m
	1001 i,m[b]
$\{Co[OS(CH_3)_2]_6\}[CoI_4]$	987 i,s
$\{Ni[OS(CH_3)_2]_6\}[NiCl_4]$	1037 m,br
	1000 i,s
$\{Cu[OS(CH_3)_2]_4\}[CuCl_4]$	1042 m,br
	1014 m,br
	(Poorly defined)
	987 i,s
$\{Cu[OS(CH_3)_2]_4\}[CuBr_4]$	1030–1037 (shoulder)
	989 i,s

[a] The first symbol refers to the band intensity: i, intense; m, medium; The second symbol refers to band width: s, sharp; m, medium; br, broad; v, very. [b] Frequency not accurate because of overlap.

TABLE III

INFRARED SPECTRA OF THE COMPLEXES IN NUJOL MULL[a]

Complex	S=O stretch, cm.$^{-1}$
$\{Co[OS(CH_3)_2]_6\}[CoCl_4]$	1002 i,s
$\{Co(OS(CH_3)_2]_6\}I_2$	992 i,s
$\{Co[OS(CH_3)_2]_6\}[CoI_4]$	987 i,s
$\{Ni[OS(CH_3)_2]_6\}[NiCl_4]$	992 i,m
$\{Ni[OS(CH_3)_2]_6\}[B(C_6H_5)_4]_2$	1000 i,s
$\{Cu[OS(CH_3)_2]_4\}[CuCl_4]$	1028 i,vs
	995 i,vs
	985 m,vs
$\{Cu[OS(CH_3)_2]_4\}[CuBr_4]$	1027 i,vs
	992 i,vs
	982 m,vs
$Hg(SCN)_2 \cdot 2(CH_3)_2SO$	1027 i,s

[a] The first symbol refers to the band intensity: i, intense; m, medium; The second symbol refers to band width; s, sharp; m, medium; br, broad; v, very.

The complexes are decomposed immediately when placed in water. The complexes of $NiCl_2$, $CoCl_2$, $HgCl_2$ and $MnCl_2$ are very hygroscopic, while the $CuCl_2$ complex is not affected on standing in air for three to four days.

The nature of the species in solution is more complex. It appears that sulfoxide and chloride have coördinating abilities that enable competition between the two species; chloride being a slightly better coördinator under the conditions studied. This leads to equilibria which are demonstrated by nickel(II) chloride solutions. The color of $[Ni(DMSO)_6]^{++}$ cation is a pale green as demonstrated by the color of its tetraphenylborate salt. The color of the alkyl ammonium tetrachloronickelates (II) are an intense blue. When nickel chloride is dissolved in dimethylsulfoxide a light green solution is obtained. When the temperature is raised or a low dielectric constant solvent is added, an intense blue color develops. This suggests the equilibria

$$\begin{tikzcd}[\mathrm{Ni(DMSO)_6}]^{++} + y\mathrm{Cl^-(solv)} \arrow[r, shift left] & \arrow[l, shift left] [\mathrm{Ni(DMSO)}_x\mathrm{Cly}]^{2-y} + (6-x)\mathrm{DMSO} \arrow[d, shift right, "+\mathrm{Cl^-}"'] \\ & [\mathrm{NiCl_4}]^{=} + x\,\mathrm{DMSO} \arrow[u, shift right, "-\mathrm{Cl^-}"'] \end{tikzcd} \qquad (1)$$

A dilution of sulfoxide, or a decrease in the dielectric constant of the solvent, shifts the above equilibria to the right. The change in color with temperature is reversible. The formation of $NiCl_4^=$ at elevated temperatures may be due to decreased solvation of chloride ion or to a difference in the heat and entropy of formation of the chloro and sulfoxide complexes such that a plot of log K_f *vs.* $1/T$ for the chloro tetrahedral complex crosses that of the octahedral sulfoxide complex. It is not necessary that the curves actually cross, for in view of the high ϵ_{max} for $NiCl_4^=$ they need only approach each other.

The visible and infrared spectra of solutions of these complexes gives additional support to the proposed equilibria in solution. The visible spectra are similar in shape to those reported by Gill and Nyholm[8] for the corresponding alkylammonium tetrahalometalates. However, the λ_{max} and ϵ_{max} values are different and the peaks are often not as well resolved. These differences cannot be attributed to absorptions by the six-coordinate cations which are present in our compounds but not in the ammonium salts, for in general the ϵ_{max} values for octahedral ions are very small[8] as demonstrated by our result with $[Ni(DMSO)_6][B(C_6H_5)_4]_2$. The spectra must arise from the presence of other four-coördinate species of the general formula $M[B_{4-x}Cl_x]^{+2-x}$ where B = solvent or dimethylsulfoxide. There is evidence that such equilibria exist in the tetrahalo complexes reported by Gill and Nyholm. Even with halide–metal ion ratios of four to one these authors often observed a change in the spectra upon the addition of excess halide. In solutions of $[Co(DMSO)_6][CoCl_4]$ a similar change occurs upon the addition of chloride ion. The absorption becomes more intense and the peaks are more clearly resolved. The λ_{max} and ϵ_{max} values calculated for $CoCl_4^=$ in this solution containing 4 moles of added chloride ion per mole of complex are identical with those of $[C_6H_5N(CH_3)_3]_2[CoCl_4]$. Thus all of the cobalt is converted to tetrachlorocobaltate and the dimethylsulfoxide is displaced. A similar result is obtained when excess chloride or bromide is added to solutions of the dimethylsulfoxide complexes of copper.

The infrared spectra of nitromethane solutions of our complexes supports the proposed equilibria and furnishes evidence that sulfoxide coördinates through the oxygen. In free dimethylsulfoxide, the S–O stretching frequency occurs at 1045 cm.$^{-1}$. In all of the complexes studied in this research, this absorption is shifted to lower frequency indicating coördination through oxygen. The infrared spectrum of $[Co(DMSO)_6][CoCl_4]$ indicates no free dimethylsulfoxide in nitromethane solution. However, when chloride is added, free dimethylsulfoxide is observed, consistent with the conversion of all of the cobalt to $CoCl_4^=$.

The above equilibrium between halide and dimethylsulfoxide is nicely demonstrated by the iodo and tetraiodocobaltate complexes of hexakis-(dimethylsulfoxide) cobalt(II). Iodide is a poorer coördinating agent than chloride, and in the presence of a large excess of sulfoxide all of the cobalt is coördinated by sulfoxide. When sulfoxide is not present in excess, the iodide competes effectively with sulfoxide, and the hexakis-(dimethylsulfoxide)-cobalt(II) tetraiodocobaltate(II) is formed along with the iodide. Stoichiometric amounts of sulfoxide results in the formation of $[Co(DMSO)_6][CoI_4]$. The infrared spectrum of a Nujol mull of $[Co(DMSO)_6]I_2$ indicates all the sulfoxide is coördinated. When the infrared spectrum of this complex is examined in nitromethane solution, an uncomplexed sulfoxide peak is observed, and the presence of tetraiodocobaltate is indicated by the visible spectrum, supporting an equilibrium of the type

$$2[Co(DMSO)_6]I_2 \rightleftarrows [Co(DMSO)_6][CoI_4] + 6DMSO \quad (2)$$

The dissolution of $[Co(DMSO)_6]I_2$ in nitromethane is accompanied by a visual change in color from pink to the characteristic blue-green color of the tetraiodocobaltate ion.

The frequency shift of the sulfoxide upon coördination should be proportional to the strength of the metal–oxygen bond. It thus appears from an examination of the spectra in nitromethane solution that cobalt and copper are roughly comparable in their coördinating ability toward sulfoxide, while manganese and nickel may be weaker and mercury the weakest.

The colors of the solid complexes of copper are surprising in that they are different from the colors of the corresponding alkylammonium tetrahalocuprates. Though there is definite evidence for the existence of $CuX_4^=$ in solution, the structure of the solid is not known with certainty. The structure of the mercury complex is also in doubt because the insolubility of this substance and lack of color made investigation difficult.

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(8) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).