TABLE II

MAGNETIC DATA FOR COMPLEXES OF THE TYPE $(RNC)_2CoX_2$

I			II	III Apparent μ^b for CoX_4^{-2} with μ of $[Co(RNC)_4]^{+2}$ = 1.70 B.M.	IV Apparent μ^b for CoX_4^{-2} with diamagnetic $[Co_2(RNC)_8]^{+2}$	V Literature value of μ for CoX_4^{-2} c
R	X	μ(B.M.)^{a,b}		B.M.	(RNC)₈]$^{+2}$	
CH₃	Cl	3.26 (293)		4.29	4.61	4.76 ± 0.05¹
CH₃	Br	3.31 (293)		4.36	4.68	4.79 ± .05¹
CH₃	NCS	3.02 (293)		3.92	4.27	4.46 ± .04²
C₆H₅	Br	4.53 (293)		..	..	....
C₂H₅	Cl	3.33 (300)		4.39	4.74	4.76 ± .05¹
C₂H₅	Br	3.41 (301)		4.52	4.82	4.79 ± .05¹

^{a} Temperature, °K., in parentheses; assuming the formula $(RNC)_2CoX_2$. ^{b} Diamagnetic corrections estimated by present authors. ^{c} The values are those which would be calculated from the susceptibilities at ~300°K. using the Curie law, since those in column IV are calculated from the Curie law (i.e., taking θ to be zero); moments are corrected for diamagnetism.

paired $[(RNC)_4Co]^{+2}$ ions,[34] the correlations of Figgis and Nyholm would lead us to expect a moment considerably greater than 1.7 B.M. in which case the calculated apparent moments of the $[CoX_4]^{-2}$ ions would be still lower than the figures in column III. Hence we feel that the structure described for these compounds by Malatesta is unacceptable.

We wish to offer the hypothesis that these five compounds consist of diamagnetic $[Co(RNC)_4]_n^{2n+}$ cations (n must be even and perhaps most likely 2) and $[CoX_4]^{-2}$ anions. On this basis we calculate the apparent moments for the $[CoX_4]^{-2}$ anions given in column IV which compare rather satisfactorily with the authentic values given in column V. The result for $(CH_3NC)_2Co(NCS)_2$ is not really

(34) It has been pointed out[1,2] that tetrahedral Co(II) complexes cannot be spin-paired unless the field is so strong as to change the electronic configuration from d^7 to d^8s or d^6p which seems improbable and is, at any rate, so far without precedent.

satisfactory but we reserve judgement until this and all of the compounds not measured by us have been checked. It would be premature to speculate upon the structure of the suggested $[(RNC)_4Co]_n^{2n+}$ ion, but experimental studies in progress may provide useful information.

Experimental

Preparation of Compounds. Bis-(p-toluidine)-Co(NCS)₂. —Absolute ethanol solutions of p-toluidine and anhydrous $Co(NCS)_2$ in stoichiometric proportions were mixed. A pink crystalline precipitate quickly formed and was washed with absolute ethanol and ether and dried in a desiccator.

Anal. Calcd. for $Co(C_7H_9N)_2(NCS)_2$: Co, 15.14; C, 49.35; H, 4.66; N, 14.39. Found: Co, 14.9; C, 48.97; H, 4.67; N, 14.68.

$(C_2H_5NC)_2CoCl_2$. —Prepared according to Hofmann and Bugge[33] by adding 3 g. of C_2H_5NC (obtained by the method of Jackson and McKusick[35]) to a solution of 3 g. of anhydrous $CoCl_2$ in 50 ml. of methanol. The volume of the solution was reduced by a pump until a microcrystalline green product precipitated. The solution was cooled in ice-salt and filtered. The product was washed with ether-methanol and dried *in vacuo* under continual pumping to remove excess isocyanide.

Anal. Calcd. for $Co(C_2H_5NC)_2Cl_2$: Co, 24.56; C, 30.03; H, 4.70; N, 11.67; Cl, 29.54. Found: Co, 24.5; C, 29.56; H, 4.47; N, 11.97; Cl, 29.17.

$(C_2H_5NC)_2CoBr_2$. —Prepared in the same manner as the chloride compound: 5.5 g. of anhydrous $CoBr_2$ dissolved in 50 ml. of methanol and 3 g. of C_2H_5NC added slowly with stirring. A fine olive-green precipitate separated. The solution was reduced in volume, cooled and filtered. The product was washed with alcohol and ether to remove a dark brown contaminant, blotted dry between filter papers and dried under continual pumping.

Anal. Calcd. for $Co(C_2H_5NC)_2Br_2$: Co, 17.92; C, 21.91; H, 3.06; N, 8.52; Br, 48.59. Found: Co, 17.9; C, 21.67; H, 3.27; N, 8.63; Br, 48.30.

Magnetic Measurements. —Measurements were made by the Gouy method as previously described.[1,2] The molar diamagnetic correction for ethyl isocyanide was taken to be -34×10^{-6}.

(35) H. L. Jackson and B. C. McKusick, *Org. Syn.*, **35**, 62 (1957).

Sulfoxides as Ligands. I. A Preliminary Survey of Methyl Sulfoxide Complexes

BY F. A. COTTON AND R. FRANCIS

The preparation of a large number of complexes of dimethyl sulfoxide is reported. The structures of some of them have been elucidated on the basis of infrared and visible spectra, magnetic measurements and steric considerations. It appears that oxygen is the donor atom in all cases reported except toward Pd(II) in $[(CH_3)_2SO]_2PdCl_2$ where infrared evidence suggests Pd←S bonding. Some of the complexes, such as $[(CH_3)_2SO]_2SnCl_4$ and $[(CH_3)_2SO]_2FeCl_3$, have great thermal stability. $NiCl_2 \cdot 3[(CH_3)_2SO]$, $CoCl_2 \cdot 3[(CH_3)_2SO]$ and $CoBr_2 \cdot 3[(CH_3)_2SO]$ are shown to contain, respectively, the tetrahedral anions $NiCl_4^{-2}$, $CoCl_4^{-2}$ and $CoBr_4^{-2}$.

Several years ago we commenced an investigation of the ability of the sulfur-oxygen grouping in sulfoxides (RR'SO) to function as an electron donor. Positive results soon were obtained and several preliminary reports have been made.[1] Recent attention in trade literature to the com-

(1) F. A. Cotton, Annual Reports of USAEC Contract AT(30-1)-1965, No. NYO-8653 for period 9/15/57–9/14/58 and No. NYO-2246 for period 9/15/58–9/14/59.

mercial availability and unusually favorable solvent properties of dimethyl sulfoxide (DMSO) has prompted us to issue a preliminary survey of the complexes we have prepared with this sulfoxide. Most of them have been or are being investigated in more detail, especially in respect to their spectral and magnetic properties and the light such properties shed upon the structures of

the compounds. More detailed reports on these studies will appear in due course.

The original impetus for this work came from the consideration that, superficially at least, sulfoxides resemble phosphine oxides and the latter are known to form coördination compounds with Lewis acids[2] and with metal ions.[3-6] It is also known that certain phosphine oxides are excellent extracting agents, either alone or synergistically with trialkyl phosphates, for heavy metal ions such as Fe(III), Ti(IV) and U(VI)O$_2^{+2}$.[7] Since sulfoxides might be similarly useful, we have also begun an investigation of their potentialities as extractants.

It was recognized at the outset, however, that too much stress should not necessarily be laid on the analogy of sulfoxides and phosphine oxides, since the former are potentially capable of more complicated behavior. It should be recalled that the sulfoxides are pyramidal molecules with unshared pairs on both sulfur and oxygen, and one point of importance in considering the structures of the adducts of sulfoxides is the identification of the donor atom. It also seems prudent to consider the possibility that widely different acceptors might bond to different donor atoms. Thus while we might expect with some confidence that oxygen is the donor toward BF$_3$, it does not seem certain that we may discount the possibility of sulfur being the donor with an acceptor such as Pt(II), Pd(II), or Au(III). The latter metals form some of their most important and stable complexes with donor atoms which have vacant d orbitals, as sulfur does but oxygen does not. In this connection we may note the observations of Addison and Sheldon[8] that while N$_2$O$_4$ formed 1:1 adducts with several alkyl sulfoxides, no adducts were obtained with sulfones. They suggested that this might be due to the fact that sulfur is the donor atom in the sulfoxide complexes whereas it cannot so function in the sulfones. While this suggestion may be correct for the adducts of N$_2$O$_4$—the Lewis acidity of which is, incidentally, not thoroughly understood—we have noted in some limited studies that sulfones do not appear to form complexes with transition metals very readily, if at all, whereas (*vide infra*) there is evidence suggesting that dimethyl sulfoxide coördinates to the same metal ions through oxygen.

There are various ways in which it should be possible, with varying degrees of certainty, to ascertain whether coördination is *via* sulfur or oxygen. (1) Obviously, this can always be done by performing a complete X-ray structure determination. Several of the compounds reported here are under study by Prof. K. Eriks, Boston University, *viz.*, CoCl$_2$·3DMSO, DMSOBF$_3$, and PdCl$_2$·2DMSO. There are also the three following indirect, and therefore less certain, methods which are, however,

more feasible for routine use; (2) infrared studies, particularly of the effect of complex formation upon the S–O stretching frequency. If, as has been concluded from theoretical[10] and experimental[9,11] studies, the S–O bond has at least partial double bond character, which may be considered to result from the superposition of pπ→dπ bonding from O to S upon the S→O sigma bonding, then attachment of oxygen to a positive atom, or any draining of electrons from oxygen, should lessen the pπ-dπ back bonding and hence lower the S–O bond order and the S–O stretching frequency. The same kind of effect would be expected in phosphine oxide complexes and has been observed.[12] Conversely, attachment of sulfur to a positive center would be expected to increase the pπ-dπ back bonding and thus raise the S–O stretching frequency. Results in hand indicate that the S–O stretching frequency of coördinated DMSO does decrease. A detailed report of the infrared data will be given later. (3) For complexes with transition metal ions, the visible spectra are determined by the symmetry and strength of the ligand field. Since oxygen and sulfur may be expected to differ in the strength of field they will provide, comparison of spectra of sulfoxide complexes with spectra of comparable complexes containing sulfur and oxygen as ligand atoms could suggest which is the ligand atom in the sulfoxide complexes. However, due to the paucity of useful reference compounds with sulfur ligands, use of this method has thus far been limited to comparing spectra of analogous aquo and DMSO compounds. (4) Steric considerations can provide fairly cogent support for one possibility or the other under conditions where they indicate that the one is *easily possible* while the other seems *strongly* disfavored. It is probably a safe criterion only when the situation appears extreme in both cases. A good example among the compounds described here is an ion of the type [M(DMSO)$_6$]$^{+n}$. Inspection of good scale models indicates that six DMSO molecules cannot fit around the metal ion if the sulfur atoms are coördinated because of intermolecular interference of CH$_3$– and –O groups, whereas if the oxygens are coördinated the –S(CH$_3$)$_2$ tails need not collide.

The compounds reported and discussed here, and in fact the vast majority of all those we have prepared to date, contain DMSO. Two lines of evidence suggest that, aside from the steric effects in sulfoxides having bulkier groups on the sulfur, the behavior of DMSO may be regarded as fairly typical for sulfoxides in general. First, in those cases where the preparation of analogs to the DMSO compounds has been attempted, analogous compounds with other sulfoxides have been obtained. Secondly, we have measured the dipole moment of DMSO (which, curiously, has never before been reported), and it is quite comparable

(2) A. B. Burg and W. E. McKee, THIS JOURNAL, **73**, 4590 (1951).

(3) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **89**, 262 (1906).

(4) J. C. Sheldon and S. Y. Tyree, THIS JOURNAL, **80**, 4775 (1958).

(5) F. A. Cotton, R. Bannister, R. Barnes and R. H. Holm, *Proc. Chem. Soc.*, 158 (1959).

(6) F. A. Cotton and E. Bannister, *J. Chem. Soc.*, in press.

(7) Blake, Brown and Coleman, ORNL-1964, August 26, 1955 (Unclassified).

(8) C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 2705 (1956).

(9) C. W. N. Crumper and S. Walker, *Trans. Faraday Soc.*, **52**, 193 (1956).

(10) (a) W. Moffitt, *Proc. Roy. Soc.* (*London*), **A200**, 509 (1950); (b) H. P. Koch and W. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951); (c) H. P. Koch, *J. Chem. Soc.*, 408 (1949).

(11) G. M. Phillips, J. S. Hunter, L. E. Sutton, *ibid.*, 146 (1945).

(12) F. A. Cotton, R. Barnes and E. Bannister, *ibid.*, in press.

<div style="text-align:center">TABLE I</div>

FORMULAE, COLORS AND ANALYTICAL DATA FOR REPRESENTATIVE COMPLEXES OF DIMETHYLSULFOXIDE(DMSO)

Compound	Color	Carbon[a] Theory	Carbon[a] Found	Hydrogen[a] Theory	Hydrogen[a] Found	Element	Other Theory	Other Found	Notes
BF₃·DMSO	White	16.46	16.42	4.15	4.26	F	39.05	35.8	b,c
AlCl₃·6DMSO	White	23.89	22.85	6.02	5.71	Al	4.63	4.63	
						Cl	17.64	17.72	
Al(NO₃)₃·6DMSO	White	21.14	20.77	5.32	5.31	Al	3.96	3.90	
SnCl₄·2DMSO	White	11.53	11.75	2.90	2.78	Sn	28.48	28.51	c
						Cl	34.03	33.75	
[Mn(DMSO)](ClO₄)₂	Pale pink					Mn	7.60	7.46	
[Fe(DMSO)₆](ClO₄)₃·DMSO	Yellow-green	18.66	18 43	4.70	4.65	Fe	6.20	6.21	
[Co(DMSO)₆](ClO₄)₂	Pink	19.83	20.02	4.99	4.88	Co	8.11	8.08	
[Ni(DMSO)₆](ClO₄)₂	Pale green	19.84	19.97	5.00	4.83	Ni	8.08	8.00	
[Zn(DMSO)₆](ClO₄)₂	White	19.66	19.83	4.95	4.96	Zn	8.92	8.85	
[Cu(DMSO)₄](ClO₄)₂	Pale blue	16.71	16.61	4.21	4.11	Cu	11.05	11.17	
[Cr(DMSO)₆](ClO₄)₃	Deep green	17.59	17.48	4.43	4.37				
CoCl₂·3DMSO	Deep blue	19.78	19.94	4.98	5.04	Co	16.18	16.19	
						Cl	19.47	19.16	
CoBr₂·3DMSO	Deep blue	15.90	16.06	4.00	4.03	Co	13.01	12.87	
CoI₂·6DMSO	Red	18.35	18.46	4.62	4.69	Co	7.48	7.27	
NiCl₂·3DMSO	Green-blue	19.80	19.60	4.98	5.10	Ni	16.21	16.0	
						Cl	19.48	19.22	
MnCl₂·3DMSO	Pale yellow	20.00	19.37	5.04	4.78	Mn	15.25	15.11	
						Cl	19.68	19.72	
MnBr₂·2DMSO	Pale yellow	12.94	12.50	3.26	3.39	Mn	14.80	14.91	
						Br	43.08	43.00	
MnI₂·4DMSO	Pink	15.46	15.51	3.89	4.16	Mn	8.84	8.41	
						I	40.85	40.51	
FeCl₃·2DMSO	Yellow	15.08	15.13	3.80	3.84	Fe	17.53	17.30	c
						Cl	33.38	32.80	
FeBr₃·6DMSO	Red-brown	18.85	17.65	4.75	4.60	Fe	7.31	7.23	
						Br	31.36	31.76	
CrCl₃·3DMSO	Lilac	18.35	18.36	4.62	4.51	Cl	27.08	26.58	
CuCl₂·2DMSO	Emerald green	16.52	16.59	4.16	4.21	Cu	21.86	21.81	
						Cl	24.39	24.38	
CuBr₂·3DMSO	Lime	15.74	16.11	3.96	3.95	Cu	13.88	13.63	
						Br	34.91	34.72	
CuBr₂·2DMSO	Yellow-brown	12.65	12.62	3.16	3.09	Cu	16.74	16.79	
Cu(NO₃)₂·2DMSO	Blue	13.97	14.49	3.52	3.71	Cu	18.48	18.24	
CuSO₄·2DMSO	Green	15.21	15.05	3.83	3.98	Cu	20.12	19.35	
PdCl₂·2DMSO	Orange	14.39	14.88	3.62	3.99	Pd	31.96	31.03	
						Cl	21.24	21.34	
Zn(NO₃)₂·2DMSO	White	13.90	14.16	3.50	3.42	Zn	18.91	18.83	
ZnCl₂·2DMSO	White	16.42	16.58	4.14	4.28	Zn	22.35	22.44	d
ZnBr₂·DMSO	White	12.59	12.36	3.17	2.98	Zn	17.14	16.86	
						Br	41.90	41.72	
CdCl₂·DMSO	White	9.17	9.03	2.31	3.01	Cl	27.12	26.80	
UO₂(NO₃)₂·2DMSO	Yellow	8.73	9.01	2.26	2.20	U	43.27	42.75	
Th(NO₃)₄·6DMSO	White	15.19	14.71	3.82	3.67				
Mn(ClO₄)₂·3DMSO·4H₂O	White	12.86	12.95	4.69	4.80	Mn	9.80	9.60	
MnBr₂·3DMSO·6H₂O	Pale pink	12.93	13.03	5.43	5.20	Mn	9.84	9.54	
						Br	28.68	28.58	

[a] Carbon and hydrogen microanalyses by Dr. S. Nagy, M.I.T., and Schwartzkopf, Microanalytical Laboratory, Long Island, New York. [b] We are informed that determination of fluorine in presence of sulfur is difficult, which presumably accounts for the low fluorine analysis. [c] Sublimes. [d] Analytically pure sample obtained after recrystallization from chloroform.

to those of other sulfoxides,[3] *viz.*, DMSO, 3.9, Et₂SO, 3.85, Ph₂SO, 3.90, (*i*-C₄H₉)₂SO, 3.92 D. Since the total moments of all these compounds are due predominantly to the >SO grouping, which is also the seat of their Lewis basicity, it may be expected that they will differ little in this characteristic.

The interaction of sulfoxides with a variety of partner types has been studied. These partners may conveniently be placed in the following three categories: (1) compounds of non-transitional metals; (2) salts of transitional metals; (3) metal carbonyls.

1. Adducts with Compounds of Non-transitional Elements.—Compounds of this kind are listed in Table I. They will be described rather completely here since no further work on those obtained thus far is planned in the near future.

The DMSO·BF$_3$ adduct forms easily on passing BF$_3$ into a chloroform solution of DMSO. It is quite hygroscopic and insoluble in solvents suitable for infrared work; thus attempts to obtain satisfactory infrared spectra so far have failed. It melts sharply at 53° and may be purified by sublimation. It is not known to what extent the vapor may be dissociated. This compound is decomposed by water.

All attempts to characterize a BCl$_3$ adduct of DMSO have failed. The work described in the Experimental section suggests that an unstable 1:1 or 2:1 compound may exist but it is clearly too unstable to be of much use or interest.

Aluminum nitrate gives the compound Al(NO$_3$)$_3$·6DMSO, which is white and salt-like in its properties. It is interesting that aluminum chloride shows analogous behavior giving AlCl$_3$·6DMSO, instead of behaving as a molecular Lewis acid to give AlCl$_3$·DMSO. It seems reasonable to suppose that both of these aluminum compounds contain the [Al(DMSO)$_6$]$^{+3}$ ion as do a number of similar compounds of the transition metal salts.

The adduct with tin(IV)chloride is a compound of surprising stability. In order to preclude the hydrolysis of Sn–Cl bonds, Dr. E. Bannister carried out the preparation under strictly anhydrous conditions. This was done by mixing chloroform solutions of SnCl$_4$ and DMSO, with the latter in mole ratio of 2:1 to the former, in a vacuum line. A vigorous reaction occurred immediately with the formation of a white precipitate which was washed with chloroform and pumped dry. Analysis showed it to be SnCl$_4$·2DMSO. It then was found that this substance possesses great thermal stability and can be sublimed without decomposition at 180°. The sublimate also gave excellent analyses for SnCl$_4$·2DMSO. Parallel with this work, the reaction of SnCl$_4$ and DMSO in aqueous solution was examined and it was found that the same compound is obtained. Thus not only is the hydrophobic SnCl$_4$·2DMSO stable toward hydrolysis, but SnCl$_4$ in the presence of DMSO is precipitated as the very stable SnCl$_4$·2DMSO instead of being hydrolyzed, at least to a large extent.

2. Adducts with Salts of Transition Metals.— The majority of the complexes listed in Table I are with salts of transition metals, and it is complexes of this class which have been most extensively studied to date. The first group listed are those of the type [M(DMSO)$_{4 \text{ or } 6}$](ClO$_4$)$_{2 \text{ or } 3}$. These compounds stand in direct stoichiometric analogy to the corresponding aquo compounds and might be presumed to contain the [M(DMSO)$_6$]$^{+n}$ and [M(DMSO)$_4$]$^{+2}$ cations indicated. We have spectral and magnetic evidence to support this view which will be presented in detail in later reports. As mentioned above, steric considerations provide a very strong suggestion that in the [M(DMSO)$_6$]$^{+n}$ species coördination must be via oxygen.

The complexes of the cobaltous halides are a particularly interesting series. The chloride and bromide complexes have the formulas CoX$_2$·3DMSO and are deep blue. Spectral and magnetic evi-

dence show that these compounds should be formulated [Co(DMSO)$_6$]$^{+2}$[CoX$_4$]$^{-2}$. The magnetic moment of the Co(II) in [Co(DMSO)$_6$](ClO$_4$)$_2$ was found to be 5.01 ± 0.05 B.M., while the moment of Co(II) in CoCl$_2$·3DMSO was found to be 4.83 ± 0.05 B.M. Both of these figures are computed from the susceptibilities at 297–298°K. using the Curie law. The moment of Co(II) in the CoCl$_4$$^{-2}$ ion at 295 ± 1°K. calculated from susceptibility data[13] in the same way is 4.62 ± 0.05 in Cs$_3$CoCl$_5$, 4.73 ± 0.05 in [C$_6$H$_5$]$_3$AsCH$_3$]$_2$CoCl$_4$ and 4.71 ± 0.05 in (C$_9$H$_8$N)$_2$CoCl$_4$, for an average of 4.69 ± 0.05. If the proposed structure be correct the observed moment per formula unit, CoCl$_2$·3DMSO, should be the root-mean-square of 5.01 and 4.69, which has the value 4.85 ± 0.05. Thus this necessary but not sufficient test of the correctness of the formulation is adequately met. Conclusive proof of the assigned structure is obtained by comparison of the spectra of [Co(DMSO)$_6$](ClO$_4$)$_2$, (C$_9$H$_8$N)$_2$(CoCl$_4$) and CoCl$_2$·3DMSO, as shown in Fig. 1. Allowance must be made for the fact that
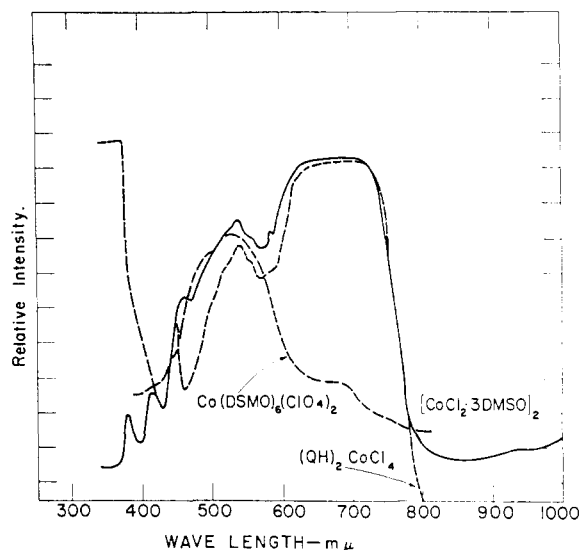

Fig. 1.—Reflectance spectra of [Co(DMSO)$_6$](ClO$_4$)$_2$, (C$_9$H$_8$N)$_2$CoCl$_4$ and CoCl$_2$·3DMSO.

intensities are not intercomparable between separate spectra obtained by the reflectance technique. It can be seen that the spectrum of CoCl$_2$·3DMSO is a superposition of the spectra of the [Co(DMSO)$_6$]$^{+2}$ and [CoCl$_4$]$^{-2}$ ions. The compound CoBr$_2$·3DMSO has not yet been investigated spectroscopically or magnetically, but its stoichiometry and deep blue color leave little doubt that it is correctly formulated as [Co(DMSO)$_6$][CoBr$_4$]. Cobaltous iodide has given a complex of stoichiometry CoI$_2$·6DMSO, which, judging by its color, may be formulated [Co(DMSO)$_6$]I$_2$.

Investigation of the complexes formed by the nickel(II) halides is not complete, except for the compound NiCl$_2$·3DMSO. The greenish-blue color immediately led us to consider the formula [Ni(DMSO)$_6$]$^{+2}$[NiCl$_4$]$^{-2}$ with a tetrahedral anion for this compound and spectral and magnetic data prove conclusively that this is the correct formula.

(13) R. H. Holm and F. A. Cotton, J. Chem. Phys., 31, 788 (1959).

The moment per formula unit, NiCl$_2$·3DMSO, calculated from the susceptibility at 300°K. using the Curie law is 3.65 ± 0.05 B.M. The moment of the octahedrally coördinated Ni(II) ion in [Ni(DMSO)]$_6$(ClO$_4$)$_2$ has been found to be 3.36 ± 0.05 B.M. From these data we calculate a moment 3.92 ± 0.05 B.M. for Ni(II) in the postulated [NiCl$_4$]$^{-2}$ ion. This is in excellent agreement with the value recently reported[14] for this ion (3.89 B.M.) in [(C$_6$H$_5$)$_3$AsCH$_3$]$_2$[NiCl$_4$]. Moreover, as in the case of CoCl$_2$·3DMSO, a comparison of the spectrum of NiCl$_2$·3DMSO with the spectra of [Ni(DMSO)$_6$](ClO$_4$)$_2$ and (C$_9$H$_8$N)$_2$(NiCl$_4$) provides excellent evidence for the [Ni(DMSO)$_6$]-[NiCl$_4$] structure as shown in Fig. 2.
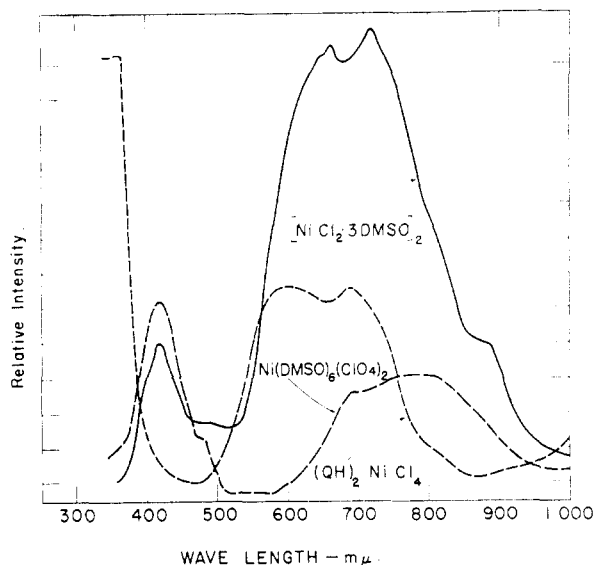
Fig. 2.—Reflectance spectra of [Ni(DMSO)$_6$](ClO$_4$)$_2$, (C$_9$H$_8$)$_2$NiCl$_4$ and NiCl$_2$·3DMSO.

The structures of the complexes of the manganous and iron halides are as yet unknown.

Cupric salts seem characteristically to form complexes containing two DMSO's. In CuBr$_2$·3DMSO, one DMSO is held very weakly and is readily lost when the crystals merely stand in air. The infrared spectrum of this compound shows two distinct strong bands in the S–O stretching region, the upper one disappearing on conversion to Cu Br$_2$·2DMSO. This suggests that one DMSO is not coördinated but only held loosely in the lattice.

The complex of palladous chloride is of especial interest since its infrared spectrum has a band presumably assignable to S–O stretching at 1120 cm.$^{-1}$, i.e., ∼60 cm.$^{-1}$ higher than the S–O stretching band in free DMSO. On the basis of arguments given above about the effect of complexation upon the S–O stretching frequency, we tentatively conclude that in PdCl$_2$·2DMSO coördination is via sulfur. We have not so far found any other complex in which this appears to be the case.

The structures of the zinc, cadmium, uranyl and thorium compounds are unknown. Mercuric salts do not yield any well defined compounds. The chloride and bromide give white crystalline sub-

stances which, after drying at 65° in vacuum, have carbon and hydrogen analyses corresponding roughly to (HgCl$_2$)$_2$·DMSO and (HgBr$_2$)$_3$·2DMSO. Mercuric iodide crystallizes from DMSO in beautiful crystals containing no DMSO. The two manganese compounds, Mn(ClO$_4$)$_2$·3DMSO·4H$_2$O and MnBr$_2$·3DMSO·6H$_2$O, are cited as examples of the sort of compounds which are often obtained from a mixture of DMSO and water which is relatively rich (30–50%) in water.

3. Reactions of DMSO with Metal Carbonyls.—No metal carbonyl compounds containing DMSO as a substituent have as yet been isolated and characterized, but preliminary studies indicate that such compounds probably exist and further work in this direction is being undertaken. On refluxing Mo(CO)$_6$ and DMSO in inert solvents (e.g. hexane), there is some gas evolution and the infrared spectra of the solutions show CO stretching bands in the 1900–2000 cm.$^{-1}$ range indicative of substitution of CO by a ligand which is a poorer back-acceptor.

Fe(CO)$_5$ and DMSO are immiscible at room temperature, but on heating to about 80° a homogeneous intensely black-red solution forms and there appears to be some gas evolution. On adding petrol to the cooled solution a red-black powder precipitates. This apparently decomposes fairly rapidly on handling in air and satisfactory analyses have not been obtained as yet. It is most likely a product of disproportionation of Fe(CO)$_5$ such as [Fe(DMSO)$_6$] [Fe$_3$(CO)$_{13}$] rather than a substitution compound.

Experimental

Preparation (general).—Except as noted specifically elsewhere in the paper, all compounds reported here were prepared simply by adding the appropriate metal salt (hydrated or unhydrated according to convenience) to DMSO (nearly anhydrous, m.p., ∼16°) and then removing the excess DMSO under vacuum. In many cases the materials so obtained are oily in appearance and further pumping at temperatures of 50–60° is required to obtain analytically pure compounds. In some cases concentrated aqueous solutions of the metal salts can be used, but this is of uncertain reliability; often the compounds obtained contain water as well as DMSO. Apparently water and DMSO compete fairly evenly for places in the coördination sphere and it is necessary only that the concentration of water be low rather than nil in order for it to be excluded.

BCl$_3$–DMSO Reaction[15].—The reaction between boron trichloride and dry dimethyl sulfoxide (twice distilled in vacuo from freshly crushed BaO) was first studied by allowing the reactants at −20° to mix in a sealed Faraday tube in vacuo, using chloroform (dried with P$_2$O$_5$) as a solvent and reaction moderator. On warming, a vigorous reaction ensued with the deposition of a flocculent white precipitate, which was filtered and washed with fresh chloroform in a vacuum line, prior to pumping for 24 hr. before analysis. The solid was then transferred to a dry stoppered bottle and placed in a desiccator. After a short while the compound became yellowish and after four days brown, looking like burnt sugar and having a repugnant odor. Analyses for carbon, hydrogen and chlorine on the partially decomposed product were suggestive of a 1:1 complex although the chlorine analysis was nearer to a 2:1 complex.

		C	H	Cl
Calcd. for	BCl$_3$·Me$_2$SO	12.29	3.10	54.46
Calcd. for	2BCl$_3$·Me$_2$SO	7.68	1.94	68.07
	Found	10.96	2.87	64.9

The analyses are not reliable as the compound smelled strongly and was difficult to weigh out accurately due to a continuous change in weight.

(14) N. S. Gill, R. S. Nyholm and P. Pauling, Nature, **182**, 168 (1958).

(15) By Dr. E. Bannister.

WAVE LENGTH — mμ

Further samples were prepared so that the gaseous decomposition products could be investigated. The white precipitate once formed was kept *in vacuo* and any gases liberated condensed out in a bulb surrounded by liquid nitrogen. The vapor density and infrared spectrum of the gas were obtained.

Assuming that 1 g. mole of gas would occupy 22.4 l. at N.T.P., the vapor density measurements gave an average mol. wt. of 40.8.

The infrared spectrum of this sample showed that hydrogen chloride was present along with other unidentified products. The hydrogen chloride was removed by condensing the gases at $-78°$ and pumping the hydrogen chloride (b.p. $-83.7°$) away. The infrared spectrum of the remaining gaseous product showed absorption bands at 1715–1090 (m), 1305–1275 (w), 1225 (m. sharp), 1050^{-}–1030(s), 770 (s. sharp) and 710–690 cm. $^{-1}$(w).

From these figures it is impossible to say with certainty what, other than hydrogen chloride, had been formed, but methylene chloride, thionyl chloride and sulfur dioxide may be present.

The infrared spectra of the gaseous products were found to vary from one run to another.

Preparation of SnCl$_4$·2DMSO *in Vacuo.*[15]—To a solution of SnCl$_4$ in chloroform was added a slight excess of DMSO. A vigorous exothermic reaction occurred with the formation of a white precipitate which was filtered, washed with chloroform and pumped under high vacuum for several hours. The material was then removed from the vacuum system and a portion of it sublimed at 180° in high vacuum.

Anal. Calcd. for SnCl$_4$·2(CH$_3$)$_2$SO: C, 11.53; H, 2.90; Cl, 34.03. Found for unsublimed material: C, 11.48; H, 2.94; Cl, 33.03. Found for sublimate: C, 11.51; H, 2.95; Cl, 33.83.

Preparation of SnCl$_4$·2DMSO in Aqueous Solution.—Twenty-five ml. of SnCl$_4$ was added to 100 ml. of water to give a clear, colorless solution; 10 ml. of DMSO was then added until precipitation occurred in a very exothermic reaction. The precipitate was filtered, dried in vacuum at 55° and analyzed (data quoted in Table I).

Preparation of FeCl$_3$·2DMSO *in Vacuo.*[15]—Anhydrous ferric chloride (twice sublimed *in vacuo*) was covered with chloroform and then DMSO was added. The solution first turned yellow and then a yellow solid precipitated. This was filtered and pumped in high vacuum for 2 hr. The material was removed from the vacuum line and a portion analyzed; the rest was sublimed in vacuum at 190°. The magnetic susceptibility of the sublimate was measured at room temperature and a portion of this then analyzed.

Anal. Calcd. for FeCl$_3$·2(CH$_3$)$_2$SO: C, 15.08; H, 3.80; Fe, 17.53; Cl, 33.38. Found for unsublimed material: C, 15.96; H, 3.93; Fe, 17.02; Cl, 34.62. Found for sublimate: C, 14.96; H, 3.74; Fe, 17.28; Cl, 33.70. Analyses quoted in Table I are on material prepared on the bench with no precautions to exclude water.

Preparation of Chromium Complexes.—Because of the kinetic inertness often encountered with chromic complexes, the procedure used in preparing those reported here is summarized. CrCl$_3$·3DMSO was prepared by adding chromium metal to DMSO kept saturated with HCl. The resulting green solution was filtered to remove excess metal and then taken to dryness in vacuum at 10°, affording a red-lilac powder. Cr(ClO$_4$)$_3$·6DMSO was prepared by adding DMSO to a very concentrated solution of Cr(ClO$_4$)$_3$, prepared by treating excess Cr(OH)$_3$ with 71% HClO$_4$. On concentrating the DMSO solution at 100° in vacuum emerald green needles separated. They were separated by filtration and dried in vacuum at 65°.

Dipole Moment Measurement.—The dipole moment of dimethylsulfoxide was measured by the heterodyne beat method using apparatus kindly placed at our disposal by Mr. William Westphal. The results were calculated by standard methods.[16] The data are given in Table II.

TABLE II

EXPERIMENTAL DATA FOR DIPOLE MOMENT OF (CH$_3$)$_2$SO

	N_1	N_2	ϵ	d	$_TP^{(DMSO)}$
Benzene	1.000	0.000	2.2741	0.87388	...
1	0.89679	.10321	4.6883	.90009	231.7
2	.92477	.07523	3.9421	.88069	256.1
3	.94653	.05347	3.4345	.88726	265.7
4	.96817	.03183	2.9402	.88145	282.6

$_\infty P = 315 \pm 10$.

$_E P = 19.98$ (n^{25}D of DMSO = 1.4740).

$\mu = 0.0128 \sqrt{(_T P - _E P)T} = 3.9 \pm 0.1 D$.

$_T P$ of benzene = 26.66.

Magnetic Measurements.—These were made by the Gouy method; tubes were calibrated with Mohr's salt. The data for moments quoted in the text are as shown, where we list the compound, its corrected molar susceptibility, the diamagnetic correction and the temperature in degrees Kelvin: (1) [Ni(DMSO)$_6$](ClO$_4$)$_2$, 4652 $\times$ 10^{-6}, $-347 \times$ 10^{-6}, 301°; NiCl$_2$·3DMSO, 5478 $\times$ 10^{-6}, $-198 \times$ 10^{-6}, 300°; [Co(DMSO)$_6$](ClO$_4$)$_2$, 10,462 $\times$ 10^{-6}, $-347 \times$ 10^{-6}, 298°; CoCl$_2$·3DMSO, 9753 $\times$ 10^{-6}, $-198 \times$ 10^{-6}, 297°; CuCl$_2$·2DMSO, 1742 $\times$ 10^{-6}, $-152 \times$ 10^{-6}, 299°; FeCl$_3$·2DMSO, (aqueous prep., unsublimed) 14,536 $\times$ 10^{-6}, $-176 \times$ 10^{-6}, 296°; FeCl$_3$·2DMSO, (anhydrous prep., sublimed) 14,000 $\times$ 10^{-6}, $-176 \times$ 10^{-6}, 301°. The corrected susceptibilities are believed to be accurate to within $\pm 1\%$.

Reflectance Spectra.—These were obtained using a Beckman DU Spectrophotometer with standard Beckman reflectance attachment and MgCO$_3$ as the blank material.

(16) See, for example, R. J. W. LeFevre, "Dipole Moments," Methuen and Co., London, 1953.