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Sulfolane as a Ligand. VII. Complexes with Ligands Containing S=O *

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A number of new compounds containing sulfolane as a ligand are reported. The compounds have the general formula $MX_n(\text{sulfolane})_m$, in which $X = Cl^-$, Br^-, $SbCl_6^-$, $InBr_4^-$, $InCl_4^-$, $FeCl_4^-$, $AlCl_4^-$; $n = 2\text{-}5$ and $m = 1\text{-}6$.
The compounds are characterized by chemical analyses, ligand-field spectra, infrared spectra and magnetic susceptibility measurements. Sulfolane appears to coordinate via *the lone-pair orbital of one of the oxygen atoms.*
Ligand-field parameters are determined for the octahedral ions $M(\text{sulfolane})_6^{2+}$, with M = Fe, Co, Ni, and Cu, and compared with those of other $M(\text{ligand})_6^{2+}$ ions.

Introduction

Sulfolane, also called tetramethylene sulfone ($TMSO_2$), is a well-known aprotic solvent frequently used in organic synthetic reactions. Examples are nitrations with $NO_2^+BF_4^-$ and several nucleophilic substitution reactions.[1,2]

The molecule is known to have rather low donor properties to Lewis acids and metal ions, resulting in the fact that only a few coordination compounds containing sulfolane as a ligand are known in the literature.

Langford and Langford[3] reported the preparation of $CoCl_2(TMSO_2)$ and $Co(ClO_4)_2(TMSO_2)_3$ in 1961. Drago and co-workers[4] described the adduct C_6H_5OH-$(TMSO_2)$ and recently Jones[5] prepared the compound $BF_3(TMSO_2)$.

Very recently Henderson, Machin and Thompson[6] described some adducts with $CoCl_2$, $CoBr_2$ and $Co(CNS)_2$. These compounds were prepared from cobalt metal and the corresponding mercury(II) salts in sulfolane at high temperatures. The same investigators found many other metal salts to be dehydrated in sulfolane at high temperatures.[6] However, no solid adducts or solvates could be isolated, with the exception of the cobalt salts described above.

About the molecular configuration of $TMSO_2$, there is a contradiction between dipole moment measurements[7] and vibrational spectra.[8] The former method suggests a planar C_4S ring, whereas the vibrational spectra evidently indicate a non-planar ring. However, very recently the structure of the adduct $C_3H_6N_6O_6(TMSO_2)$ was determined,[9] and the sulfolane ring was demonstrated to be non-planar.

The present paper describes the synthesis and characterization of a number of adducts and complex solvates containing sulfolane as a coordinated ligand.

Experimental Section

As most of the compounds to be investigated were very sensitive to hydrolysis, all operations were carried out in a dried glove-box.

Starting materials. Sulfolane (Shell Chemie, The Hague) was purified by vacuum distillation, after removal of sulfolene with potassium permanganate.

Metal dihalides were available as the hydrates. They were dehydrated by pumping *in vacuo* at high temperature (50-150°C.), by refluxing them with thionyl chloride, or by heating them in a stream of dry HCl or HBr. Metal trihalides were prepared from the elements by standard procedures. Antimony pentachloride (Merck A. G., Darmstadt) was purified by crystallization from sulfolane and than handled as the adduct $SbCl_5(TMSO_2)$.

Preparation of the compounds. Adducts with metal halides were prepared by dissolving the metal halides in an excess of $TMSO_2$ at about 30°C. In some cases stirring was necessary for rapid reactions. When all solid disappeared, dry toluene was added for crystallization of the compounds. The products were filtrated, washed with dry toluene (three times) and dried *in vacuo*.

Solvates of metal ions with sulfolane (*i.e.* compounds in which sulfolane is the only ligand coordinated to the metal ion) containing complex halide anions, were prepared by blending stoichiometric amounts of MX_2 and MX_3 (or MX_5) in excess of sulfo-

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(*) Part VI. J. Reedijk, P. W. N. M. van Leeuwen, and W. L. Groeneveld, *Rec. Trav. Chim.*, *87*, 1073 (1968).
(1) S. J. Kuhn and G. A. Olah, *J. Am. Chem. Soc.*, *83*, 4564 (1961).
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lane. When all solids were dissolved, dry toluene was added where upon the solvates crystallized. After washing with several portions of toluene, the crystals were dried *in vacuo.*

Analyses. Metal(II) and metal(III) determinations were carried out by complexometric titrations as described by Vogel[10] and Schwarzenbach.[11] Antimony was determined iodometrically. Halogens were analyzed by the Volhard procedure.

Infrared spectra. Spectra in the 2000-700 cm^{-1} region were recorded on a Beckman IR 10 and on a Hitachi EPI-G2 grating spectrophotometer. The compounds were measured as nujol mulls sandwiched between sodium chloride plates. Bands are believed to be accurate to ± 2 cm^{-1}. Spectra in the 700-200 cm^{-1} region were taken on a Hitachi EPI-L spectrophotometer, and in the 400-150 cm^{-1} region on a Perkin Elmer 301 spectrophotometer. Instead of NaCl, polythene was used as a window material in this region. Calibration peaks in the high frequency region were taken from polystyrene, whereas water vapour served as a calibrant in the low-frequency region.[12]

Ligand field spectra. Diffuse reflectance spectra were recorded on a Beckman DK-2A ratio recording spectrophotometer, equipped with the standard reflectance set. The samples were protected against moisture in a sample holder as described by Van Leeuwen.[13] The spectra were measured by the double-beam technique, with magnesium oxide as a reference. The crystal-field parameters for the several ions M(TMSO$_2$($_6^{2+}$ were calculated using the weak-field formalism. Procedures for calculation of these parameters from the spectra are given elsewhere.[14,15]

Magnetic measurements. Magnetic susceptibilities were determined with a Gouy balance at room temperature. As a calibrant HgCo(CNS)$_4$ was used.[16] Magnetic moments were calculated with the relation $\mu = \sqrt{8.T.\chi_{\text{corr.}}}$, in which $\chi_{\text{corr.}} = \chi_{\text{mol.}} - \chi_{\text{dia.}} - \chi_{\text{TIP}}$.

Results and Discussion

General. In Table I some sulfolane adducts with metal halides are reported, together with analytical results, colours and melting points.

No solid adducts could be obtained for FeCl$_2$, NiCl$_2$, SnCl$_2$, AlCl$_3$, CrBr$_3$, CrCl$_3$, FeBr$_3$, FeCl$_3$, InBr$_3$, and InCl$_3$.

The compound CoCl$_2$(TMSO$_2$) reported by Langford and Langford[3] could not be prepared. The formula of our compound CoCl$_2$(TMSO$_2$)$_{1\frac{1}{2}}$, corresponds to the molecular weight of about 300 found by Langford and Langford.[3]

In the case of larger anions than chloride and bromide, it was even possible to obtain sulfolane solvates containing six molecules of TMSO$_2$ per metal ion. These compounds are listed in Table II. Together with analytical data, colours and melting points.

The preparation of these latter compounds was only possible by means of the so-called chloride-ion transfer process, which introduces very large anions (*e.g.* SbCl$_6^-$ or InCl$_4^-$) allowing the formation of the large cations M(TMSO$_2$)$_6^{2+}$. General information about this chloride or bromide-ion transfer was given previously.[17,18]

When smaller anions than these chloro- or bromo-anions are used (*e.g.* the ClO$_4^-$ ion), no hexasolvates of sulfolane can be obtained as shown by the compound Co(TMSO$_2$)$_3$(ClO$_4$)$_2$ reported by Langford and Langford.[3]

Ligand-field spectra. Evidence for octahedrally coordinated ions M(TMSO$_2$)$_6^{2+}$ was obtained from ligand-field spectra for the compounds with M = Fe, Co, Ni and Cu. The adduct CoCl$_2$(TMSO$_2$)$_{1\frac{1}{2}}$ showed a spectrum typical for tetrahedral Co$^{\text{II}}$, whereas CuCl$_2$(TMSO$_2$)$_{4/3}$ appeared to be octahedral. For the other adducts and solvates with sulfolane described in Tables I and II, no conclusions about metal-ion environment could be drawn from these spectra, because of the absence of ligand-field bands.

Some spectra for octahedral ions M(TMSO$_2$)$_6^{2+}$ are shown in Figures 1-4. Band maxima, assignments and ligand-field parameters are given in Table III. It should be noticed that the rather weak, but sharp absorptions at 1200 and 1750 nm are infrared overtones due to TMSO$_2$.

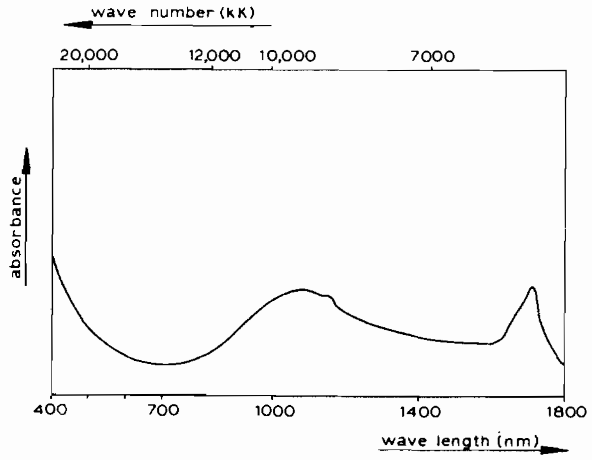

Figure 1. Ligand-field spectrum of Fe(TMSO$_2$)$_6$(SbCl$_6$)$_2$.

As can be seen from the figures and the Table, the observed Dq values are rather low, indicating the weak ligand properties of TMSO$_2$.

In Table IV a comparison is made with some other ligands, and TMSO$_2$ can be placed in the spectrochemical and nephelauxetic series.

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Table I. Metal-halide adducts of sulfolane; analyses colours and melting points

Adduct	% Metal		% Halogen		Colour	Melting point (°C.)
	Found	Calcd.	Found	Calcd.		
$MgCl_2(TMSO_2)_3$	5.40	30.6	16.1	15.6	white	148-150
$MnCl_2(TMSO_2)_{4/3}$	19.4	19.2	24.6	24.8	rose	>250
$CoCl_2(TMSO_2)_{3/2}$	19.4	19.0	23.8	23.0	blue	>250
$CuCl_2(TMSO_2)_{4/3}$	22.3	21.7	25.8	24.2	brown	>250
$ZnCl_2(TMSO_2)_2$	17.4	17.4	18.5	18.9	white	70-75
$CdCl_2(TMSO_2)_{4/3}$	30.7	30.6	21.4	21.7	white	>250
$CdBr_2(TMSO_2)$	41.3	40.7	29.1	28.6	white	>250
$SnCl_4(TMSO_2)_2$	23.8	23.7	28.2	28.4	white	65-69
$SbCl_5(TMSO_2)$	29.3	29.9	42.3	42.3	white	155-158
$HgCl_2(TMSO_2)$	50.7	51.2			white	87-91
$HgCl_2(TMSO_2)_2$	39.2	39.3			white	96-98
$HgBr_2(TMSO_2)_2$	42.6	41.7			white	128-133
$TlCl_3(TMSO_2)_2$	36.7	36.9			white	68-71

Table II. Metal(II) solvates of sulfolane; analyses, colours and melting points

Compound	% Halogen		% Metal(II)		% M(III or V)		Colour	Melting point (°C.)
	Found	Calcd.	Found	Calcd.	Found	Calcd.		
$Mg(TMSO_2)_6(InCl_4)_2$	22.8	22.6	1.99	1.93	18.4	18.2	white	250 d.
$Mg(TMSO_2)_6(SbCl_6)_2$	29.8	30.1	1.66	1.72	17.1	17.2	white	250 d.
$Ca(TMSO_2)_6(SbCl_6)_2$	29.7	29.8	2.84	2.80	18.1	17.0	white	250 d.
$Mn(TMSO_2)_6(AlCl_4)_2$	24.2	25.5	5.02	4.93			white	155-160
$Mn(TMSO_2)_6(InCl_4)_2$	21.4	21.9	4.21	4.26	18.0	17.8	white	215-217
$Mn(TMSO_2)_6(SbCl_6)_2$	29.2	29.5	3.79	3.80	17.1	16.9	white	238-239
$Fe(TMSO_2)_6(FeCl_4)_2$	23.5	24.2	4.89	4.76	9.67	9.53	yellow	220-223
$Fe(TMSO_2)_6(InCl_4)_2$	22.9	22.0	4.73	4.33	18.2	17.8	yellow	169-172
$Fe(TMSO_2)_6(SbCl_6)_2$	28.7	29.4	4.01	3.86	18.8	16.8	pale yellow	117-121
$Co(TMSO_2)_6(FeCl_4)_2$	22.8	24.1	5.11	5.01	10.5	9.50	brown	198-206
$Co(TMSO_2)_6(InCl_4)_2$	22.3	22.0	4.50	4.56	18.1	17.8	pink	197-201
$Co(TMSO_2)_6(InBr_4)_2$	39.4	38.8	3.67	3.57	14.3	13.9	pink	240-245
$Co(TMSO_2)_6(SbCl_6)_2$	28.9	29.4	4.04	4.07	16.8	16.8	pink	240-241
$Ni(TMSO_2)_6(InCl_4)_2$	22.6	22.0	4.59	4.53	18.1	17.8	yellow green	136-140
$Ni(TMSO_2)_6(InBr_4)_2$	38.6	38.8	3.51	3.54	14.0	13.9	yellow green	150-160
$Ni(TMSO_2)_6(SbCl_6)_2$	29.1	29.4	4.30	4.05	17.1	16.8	yellow green	214-218
$Cu(TMSO_2)_6(SbCl_6)_2$	29.1	29.2	4.41	4.37			pale yellow	154-155
$Zn(TMSO_2)_6(SbCl_6)_2$	28.3	29.2	4.43	4.49	16.8	16.7	white	195-198
$Cd(TMSO_2)_6(SbCl_6)_2$	27.6	28.3	7.51	7.49	15.9	16.2	white	195-199

d = decomposes

Table III. Electronic spectra of sulfolane compounds. Assignments and calculations according to references 13-15

Compound	Band maxima (kK) and assignments								
	$^5E_g \leftarrow ^5T_{2g}$				anion bands			Dq(cm^{-1})	B(cm^{-1})
$Fe(TMSO_2)_6(SbCl_6)_2$	9.30							930	—
$Fe(TMSO_2)_6(InCl_4)_2$	9.35							935	—
$Fe(TMSO_2)_6(FeCl_4)_2$	9.30				14.6	16.4	18.7	930	—
	$^4T_{2g} \leftarrow ^4T_{1g}$	$^4A_{2g} \leftarrow ^4T_{1g}$	$^4T_{1g}(P) \leftarrow ^4T_{1g}$		anion bands				
$Co(TMSO_2)_6(SbCl_6)_2$	6.90	13.9	18.5	29.6 sh				740	840
$Co(TMSO_2)_6(InBr_4)_2$	7.05	14.3	18.6	20.6 sh				755	835
$Co(TMSO_2)_6(InCl_4)_2$	7.06	14.7	18.6	20.6 sh				760	835
$Co(TMSO_2)_6(FeCl_4)_2$	7.05	14.6	18.7		14.6	16.4	18.7	760	ca.835
	$^3T_{2g} \leftarrow ^3A_{2g}$	$^3T_{1g}(F) \leftarrow ^3A_{2g}$	$^1E_g \leftarrow ^3A_{2g}$	$^3T_{1g}(P) \leftarrow ^3A_{2g}$					
$Ni(TMSO_2)_6(SbCl_6)_2$	7.45	12.4	14.5	23.3				745	895
$Ni(TMSO_2)_6(InBr_4)_2$	7.45	12.4	14.3	23.3				745	895
$Ni(TMSO_2)_6(InCl_4)_2$	7.50	12.5	14.2	23.2				750	890
	$^2T_{2g} \leftarrow ^2E_g$								
$Cu(TMSO_2)_6(SbCl_6)_2$	10.5							1050	—

Table IV. Comparison of spectral parameters for some octahedral complexes $M(ligand)_6^{2+}$; values for other ligands than $TMSO_2$ from ref. 13-15

Metal ion	Fe	Co			Ni			Cu
Ligand	Dq	Dq	B	Dq/B	Dq	B	Dq/B	Dq
$POCl_3$	—	725	865	0.840	720	910	0.79	1220
$TMSO_2$	930	755	835	0.900	745	895	0.83	1050
TMSO	1005	875	820	1.065	825	890	0.93	1220
H_2O	1040	925	850	1.065	885	920	0.96	1250
C_5H_5NO	930	885	780	1.140	820	840	0.98	1220

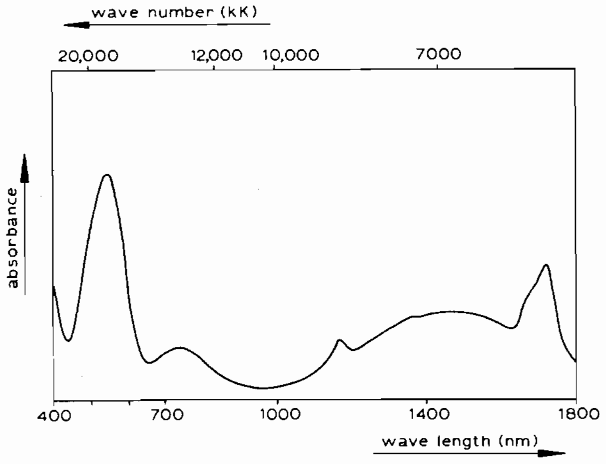

Figure 2. Ligand-field spectrum of $Co(TMSO_2)_6(SbCl_6)_2$.

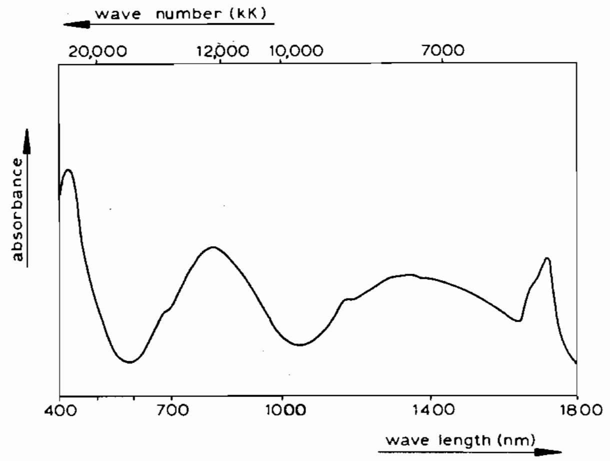

Figure 3. Ligand-field spectrum of $Ni(TMSO_2)_6(SbCl_6)_2$.

According to this Table the spectrochemical series for the ligands mentioned is: $POCl_3 < TMSO_2 < C_5H_5NO < TMSO < H_2O$. With reference to Fe^{II} and Cu^{II} the sequence is not certain, because our Dq value was taken from the band maximum, and this maximum also depends upon the distortion of the octahedron.[19]. The nephelauxetic series for the above ligands is: $POCl_3 \approx H_2O < TMSO_2 < TMSO < C_5H_5NO$. Finally the series of Dq/B is: $POCl_3 < TMSO_2 < TMSO < H_2O < C_5H_5NO$. This latter series can be used as a measure for the stability[14] of the complex ions $M(ligand)_6^{2+}$.

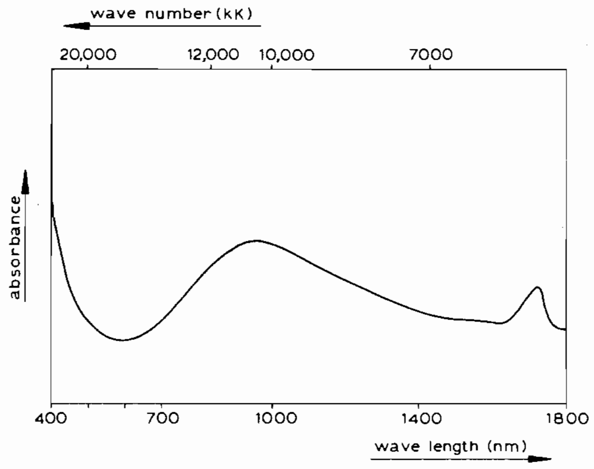

Figure 4. Ligand-field spectrum of $Cu(TMSO_2)_6(SbCl_6)_2$.

The ligand-field spectra of the compounds $M(TMSO_2)_6(FeCl_4)_2$, with M = Fe^{II} and Co^{II}, which were also reported in Table III, appeared to be simple additions of both the absorbing species $M(TMSO_2)_6^{2+}$ and $FeCl_4^-$. The spectrum of the latter ion is well known in literature.[20,21]

Infrared spectra. To obtain further insight into the nature of the coordinate bond between sulfolane and the metal ion, infrared spectra were recorded. The infrared spectrum of the free ligand has been reported by Katon and Feairheller,[8] together with tentative assignments of the vibrational modes.

When coordinated to Lewis acids (*e.g.* metal ions), alterations in the infrared spectrum are expected to occur. This is well known for many other ligands like sulfoxides,[13,22,23] nitriles[24-26] and *N*-oxides.[26-28] Indeed also sulfolane demonstrated band shifts in the i.r. absorptions upon coordination, although the magnitude of the shifts is rather small. The most important absorption bands of sulfolane below 1333 cm^{-1}

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Table V. Infrared spectra of sulfolane compounds below 1333 cm^{-1}

Frequency^a of the liquid[8]	Frequency of the solid (this work)	Description[8]	Shift range upon coordination
1313 vs, sh	1313 vs, sh	CH$_2$ wagging	1313-1309 s, sh
1301 vvs	1302 vvs	antisymm. OSO stretch	1300-1275 vvs
1275 vs	1275 vs	CH$_2$ wagging	1280-1270 s, sh
1259 vs	1260 vs	CH$_2$ twisting	1260-1245 s
1199 w	1200 w	CH$_2$ twisting	1208-1200 w
1147 vvs	1148 vs	symm. OSO stretch	1148-1138 vs
1110 vvs	1110 vs	CH$_2$ twist or wagging	1110-1099 vs
1085 s, sh	1085 s, sh	CH$_2$ twisting CH$_2$ twisting	1100-1080 s 1087-1065 vs
1032 m	1032 m	C—C stretching	1032-1025 m
903 vs	906 s	CH$_2$ rocking	909-906 s
733 vs	735 vs	antisymm. CSC stretch	738-725 vs
670 m	670 m	symm. CSC stretch	670-660 w
567 s	566 s	SO$_2$ scissor	568-562 s
520 m	519 m	SO$_2$ wagging	521-514 s 517-512 m (sh) 469-452 m, sh
440 s	441 s	SO$_2$ twisting	457-430 s 442-430 m (sh)
	400 m, sh		420-405 m
385 m	388 m	C—S—C deformation	394-384 m 375-367 m
310 w	—	—	

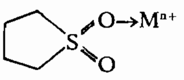
^{a}v = very; w = weak; m = medium; s = strong; sh = shoulder

are listed in Table V, together with the assignments according to Katon and Feairheller[8] and the observed band shifts in our compounds.

As can be seen from the Table, most absorption bands shift towards lower frequencies upon coordination. A few bands show clear splittings in some of the solvates, in other cases the splittings are not resolved and shoulders are observed on the main bands of the compounds. So, in most complexes the free ligand pair at 1110 and 1085 cm^{-1}, appears as a triple absorption. Further the absorption in the 520 cm^{-1} region occurs as a doublet in many compounds, whereas the free-ligand bands at 440 and 388 cm^{-1} even split into three components in many of our solvates.

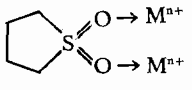
Before discussing the reasons for the splittings of the bands upon coordination, first the magnitude of the band shifts will be considered.

Regarding the molecular shape of sulfolane with neglection of the configuration within the C$_4$S ring, the following coordination possibilities should be considered:



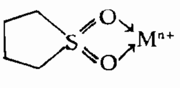
I

monodentate ligand



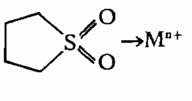
II

bidentate bridging ligand



III

bidentate chelating ligand



IV

monodentate « chelating » ligand

No *a priori* decision about one of the possible coordination forms could be made. However, according to the stoichiometry of the compounds MX$_n$(TMSO$_2$)$_m$ and especially M(TMSO$_2$)$_6$(anion)$_2$ the bidentate forms II and III can be eliminated. Only for a few compounds, *i.e.* HgCl$_2$(TMSO$_2$), CdBr$_2$(TMSO$_2$) and Co(ClO$_4$)$_2$(TMSO$_2$)$_3$, one of the forms II or III may be possible, although not necessary.

So it seems reasonable to make our choice between I and IV. When form I is considered, it would be expected that both the symmetrical and the antisymmetrical OSO stretching frequency shift towards lower values upon coordination. This decrease is well known for many sulfoxides coordinated *via* the oxygen lone pair[13,22,23] and interpreted as a decrease in the π-bond between the sulfur and the oxygen.

In the case of coordination form IV, both oxygen atoms must occupy the same coordination site of the metal ion. This is known to be the case for NO$_3^-$ ligands in Co(NO$_3$)$_4^{2-}$ and Ce(NO$_3$)$_6^{2-}$, in which the metal ions have four (resp. six) coordination and eight (resp. twelve) nearest oxygen neighbours.[29] In this coordination form the angle between the coordinating NO bonds is reduced from the free-ion value, because of the small O—M—O angle of about 50-55°.[29]

The same arguments are expected to hold for the sulfolane coordination, and so form IV is expected to decrease the O—S—O angle strongly, altering the vibrational modes of the sulfolane molecule also, since for instance the coupling between the symmetrical and the antisymmetrical OSO vibrations mainly depends upon the O—S—O angle.[30]

Regarding Table V again, it is seen that none of the frequencies is shifted significantly with respect to the free ligand, indicating only small changes in the nor-

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(29) J. G. Bergman and F. A. Cotton, *Inorg. Chem.*, 5, 1208 (1966).
(30) L. J. Bellamy, Advances in Infrared Group Frequencies, Methuen, Bungay (1968).
(31) J. Reedijk, to be published.

mal modes of $TMSO_2$ upon coordination. Since the small shifts can be understood with form I completely, we believe that, in expectation of X-ray analysis, sulfolane coordinates to metal ions *via* one oxygen atom.

Compared with sulfoxides, however, which have shifts[13,23] in the SO stretch of 0-80 cm^{-1}, the magnitude of the shifts in the SO_2 stretches are rather small. This can be explained by taking into account the much smaller metal-ligand bonds in sulfolane complexes (see ligand-field spectra), and by the influence of the other, uncoordinated oxygen on the vibrational modes.

Despite the small shifts, it was possible with the aid of precise measurements of the SO_2 stretches, to make a rather rough sequence of Lewis acids, according to their SO_2 stretches compared to the free ligand. This sequence is: $Ca^{2+} < Mn^{2+}, Cd^{2+}, Zn^{2+} < Fe^{2+} < Co^{2+}, Ni^{2+} < Cu^{2+} < SnCl_4, HgCl_2 < SbCl_5 < HgBr_2$.

The following point to study, is the occurrence of some split bands in a number of compounds $M(TMSO_2)_6(anion)_2$. On going from the simple molecule $TMSO_2$ to the octahedrally coordinated group $M(TMSO_2)_6$, the symmetry of the resulting species must be lower than O_h, because of the non-linearity of $TMSO_2$ itself. Assuming non-puckered sulfolane rings, the symmetry must be lowered to — at least — S_6, but according to molecular models, ligand-ligand repulsions must again lower the symmetry to D_{3d}, or possibly D_3 or C_{3v}.

From simple group-theoretical considerations it is easily seen that only single bands (triple degenerate) can be observed for O_h symmetry in the infrared. Reduction of symmetry to S_6 introduces some new bands, together with splitting of all the absorption bands. Further decrease in symmetry again introduces new bands, whereas many bands will be split even into three components. Although it is not possible to make conclusions about the point-group of the complexes, the occurrence of double and triple split infrared absorption bands, clearly demonstrates a symmetry lower than D_{3d} or S_6 for the whole molecule.

This was again confirmed by the metal-ligand vibrations of these complexes. For most of the metal ions studied, these vibrations appeared as broad or split bands in the region 280-150 cm^{-1}. The complete results of a metal-ligand vibrational study will be published in a future paper[31]. Some preliminary results are given in Table VI.

Table VI. Infrared spectra in the 350-150 cm^{-1} region for some solvates $M(TMSO_2)_6(anion)_2$

Anion	Metal ion	Bands due to the M—L stretch	Bands due to the anion
$SbCl_6^-$	Mg	287, 275, 242 sh	340, 178
$InCl_4^-$	Mn	191 br	330
$FeCl_4^-$	Fe	194 br	
$InCl_4^-$	Fe	193 br	330
$FeCl_4^-$	Co	205 sh, 193	
$InCl_4^-$	Co	205, 193	330
$SbCl_6^-$	Co	205, 198	340, 178
$InBr_4^-$	Co	205 sh, 190	235
$TlCl_4^-$	Co [a]	206, 195	300 sh, 280
$SbCl_6^-$	Ni	218, 205	340, 178
$SbCl_6^-$	Cu	271 sh, 221	340, 178
$TlCl_4^-$	Zn [a]	199, 184 sh	300 sh, 280

[a] Synthesis to be published[31]

This Table clearly demonstrates the split nature of most M–L stretches due to the low symmetry of the species $M(ligand)_6^{2+}$. These split M–L vibrations occur rather seldom in hexakis transition-metal compounds, because in these vibrations the donor atoms are the only moving particles, and the first coordination sphere seldom deviates from octahedral.

Magnetic susceptibility measurements. Another source of information about coordination around transition metal ions comes from the magnetic susceptibility.

To make use of this method, we determined the susceptibility of the paramagnetic solvates of formula $M(TMSO_2)_6(SbCl_6)_2$, and calculated their magnetic moments. The results are given in Table VII.

The results given in the Table are in complete agreement with those obtained from the chemical analyses, infrared spectra and ligand-field spectra. All magnetic moments fall in the range usually observed for octahedrally coordinated transition metal ions.[33]

Conclusion

Regarding the results given above, the following conclusions can be drawn:

1. Sulfolane appears to be a very weak ligand to Lewis acids, although it is able to yield coordination compounds of sufficent stability with many inorganic compounds.

Table VII. Magnetic data for some sulfolane solvates

Compound	$\chi_{mol.}$ cgs × 10^6	$-\chi_{dia.}$ [a]	$\chi_{TIP.}$ [b]	$\chi_{corr.}$	T (°K)	μ (B.M.)	$\mu_{exp.}$ [c] (B.M.)	Ground state
$Mn(TMSO_2)_6(SbCl_6)_2$	14250	750	0	15000	293	5.94	5.92	$^6A_{1g}$
$Fe(TMSO_2)_6(SbCl_6)_2$	11800	750	ignored	12550	298	5.47	4.90	$^5T_{2g}$
$Co(TMSO_2)_6(SbCl_6)_2$	10280	750	ignored	11030	297	5.12	3.88	$^4T_{1g}$
$Ni(TMSO_2)_6(SbCl_6)_2$	4310	750	280	4780	293	3.34	2.83	$^3A_{2g}$
$Cu(TMSO_2)_6(SbCl_6)_2$	1080	750	100	1730	293	2.01	1.73	^2E_g

[a] Diamagnetic corrections are from standard tables;[32] [b] The TIP values from Figgis' formulae,[33] with 10Dq values from Table III; [c] $\mu_{exp.}$ are the spin-only values from the relation $\mu\ \sqrt{n(n+2)}$, with n = the number of unpaired electrons.

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(32) Handbook of Chemistry and Physics, 44th Edn., Chemical Rubber, Cleveland.

(33) B. N. Figgis, Introduction to Ligand Fields, Interscience, New York, (1966), chapter IX.

2. Adducts can be isolated with a large number of metal halides. Solvates containing six molecules of $TMSO_2$ can be prepared with large chloro- or bromo- anions (*e.g.* $SbCl_6^-$).

3. The molecule appears to coordinate *via* the lone pair of one of the SO_2 oxygen atoms, based on the lowering of the SO_2 stretching frequencies.

4. According to their infrared spectra, some ions $M(TMSO_2)_6^{2+}$ have distorted octahedral symmetry, although this distortion is too small for observation in the ligand-field spectra.

5. The low position of $TMSO_2$ in the series of Dq and Dq/B agrees with the low stability of its complexes relative to other ligands.

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