*Contribution from the Department of Inorganic Chemistry,
State University, P.O. Box 75, Leyden, The Netherlands*

Complexes with Ligands Containing the S=O Group. X. Metal Solvates with the Ligands 1,3-dithiane Monosulfoxide and 2-phenyl-1,3-dithiane Monosulfoxide

A. H. M. Driessen - Fleur and W. L. Groeneveld

Received July 6, 1972

A number of new solvates containing 1,3-dithiane monosulfoxide (m*DTSO) and 2-phenyl-1,3-dithiane monosulfoxide (P*m*DTSO) as ligand, of the general formula* $M(ligand)_n(anion)_2$ *is reported. In these compounds the metal ions are Mg, Mn, Fe, Co, Ni, Cu, Zn and Cd, the anions are* ClO_4^- *and* BF_4^- *and the value of* n *is 6, except for the* Cu^{II} *compounds where* n *is 4 or 6. The solvates are characterized and identified by chemical analyses and physical measurements.*

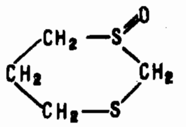
The ligands are shown, by means of infrared spectroscopy to coordinate via *the oxygen atom of the sulfoxide group. In the compounds of both ligands metal-ligand stretching vibrations occur in the region 390-460* cm^{-1}.

The ligand-field spectra, in combination with X-ray powder diagrams indicate the presence of octahedrally surrounded metal ions in the present compounds. The ligand-field parameters are compared with those of other cyclic sulfoxides. In the hexakis Cu^{II} *solvates Jahn-Teller distortions are indicated by the infrared spectra and the paramagnetic resonance measurements.*

Introduction

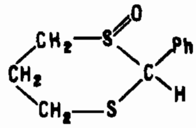
Two preceding papers[1,2] in this series dealt with the properties of 1,4-dithiane monosulfoxide (DTMSO) as a ligand to metal(II) perchlorates and tetrafluoroborates,[1] halides, isothiocyanates and nitrates.[2] In most of these compounds the ligand DTMSO coordinates through the oxygen atom. In case of sulfur coordination, the sulfide S-atom coordinates rather than the sulfoxide S-atom.

It seemed interesting to see whether or not the position of the sulfide atom in the ring influenced the ligand properties. We extended therefore our studies to 1,3- or *meta*-dithiane monosulfoxide (abbreviated *m*DTSO):



1,3-dithiane monosulfoxide

We investigated also the complexformation of 2-phenyl-1,3-dithiane monosulfoxide (abbreviated P*m*-DTSO) to study the influence of a large group adjacent to the donor site.



2-diphenyl-1,3-dithiane monosulfoxide

So, the present paper describes metal(II) solvates with ClO_4^- and BF_4^- as anions containing *m*DTSO and P*mDTSO*. In literature no complexes with these ligands have been reported.

Experimental Section

Starting Materials. 1,3-dithiane was prepared by condensation of 1,3-propanedithiol and methylal in the presence of boron-trifluoride etherate in chloroform.[3] 2-Phenyl-1,3-dithiane was isolated after treating an equimolar solution of 1,3-propanedithiol and benzaldehyde in chloroform with dry hydrogen chloride.[4] Carefull oxidation of the 1,3-dithianes with one equivalent sodium metaperiodate in methanol/water afforded the monosulfoxides.[5]

The hydrated metal(II) perchlorates were commercially available. The hydrated metal(II) tetrafluoroborates were prepared from the corresponding metal carbonates or hydroxides and hydrofluoroboric acid.

Preparation of the Complexes. The hydrated metal salts were dehydrated with triethyl orthoformate in ethanol.[6] The monosulfoxide, dissolved in ethanol was added in a metal salt to ligand ratio of 1:6. Upon standing, crystals separated; in a few cases after the addition of dry diethyl ether. The crystals were wased twice with dry diethyl ether and finally dried *in vacuo* at room temperature. The tetrakis Cu^{II} compounds were prepared with a metal salt to ligand ratio of 1:2, the hexakis Cu^{II} compounds with a metal salt to ligand ratio of 1:9.

---

(1) J. Reedijk, A.H.M. Fleur, and W.L. Groeneveld, *Rec. Trav. Chim.*, *88*, 1115 (1969).
(2) A.H.M. Fleur and W.L. Greneveld, *Rec. Trav. Chim.*, *91*, 317 (1972).
(3) D. Seebach, N.R. Jones, and E.J. Corey, *J. Org. Chem.*, *33*, 300 (1968).
(4) D. Seebach, B.W. Erickson, and G. Singh, *J. Org. Chem.*, *31*, 4303 (1966).
(5) R.M. Carlson and P.M. Helquist, *J. Org. Chem.*, *33*, 2596 (1968).
(6) P.W.N.M. van Leeuwen and W.L. Groeneveld, *Inorg. Nucl. Chem. Lett.*, *3*, 145 (1967)

Table Ia. Analytical data and other properties of coordination compounds containing *m*DTSO.

Compound	% Metal Found	Calc.	Color	M.P. (°C)	X-ray type
Mg(*m*DTSO)$_6$(ClO$_4$)$_2$	2.42	2.34	white	203-204	A
Mn(*m*DTSO)$_6$(ClO$_4$)$_2$	5.21	5.13	white	177-178	B
Mn(*m*DTSO)$_6$(BF$_4$)$_2$	5.21	5.25	white	171-172	B
Fe(*m*DTSO)$_6$(ClO$_4$)$_2$	5.12	5.21	yellow	161-162	A
Fe(*m*DTSO)$_6$(ClO$_4$)$_2$	5.07	5.21	yellow	172-174	C
Fe(*m*DTSO)$_6$(BF$_4$)$_2$	5.47	5.34	yellow	150-152	A
Co(*m*DTSO)$_6$(ClO$_4$)$_2$	5.46	5.48	rose	197-198	C
Co(*m*DTSO)$_6$(BF$_4$)$_2$ [a]	5.56	5.62	rose	187-188	A
Co(*m*DTSO)$_6$(BF$_4$)$_2$ [b]	5.70	5.62	rose	191-193	C
Ni(*m*DTSO)$_6$(ClO$_4$)$_2$	5.46	5.46	green	209-210	C
Ni(*m*DTSO)$_6$(BF$_4$)$_2$	5.74	5.60	green	206-207	A
Cu(*m*DTSO)$_6$(ClO$_4$)$_2$	5.96	5.88	light blue	126-128	C
Cu(*m*DTSO)$_6$(BF$_4$)$_2$	5.99	6.02	light blue	129-130	A
Cu(*m*DTSO)$_4$(ClO$_4$)$_2$	7.65	7.87	light green	157-158	E
Cu(*m*DTSO)$_4$(BF$_4$)$_2$	8.30	8.12	light green	154-155	E
Zn(*m*DTSO)$_6$(ClO$_4$)$_2$	6.20	6.05	white	167-168	C
Zn(*m*DTSO)$_6$(BF$_4$)$_2$	6.09	6.19	white	156-157	A
Cd(*m*DTSO)$_6$(ClO$_4$)$_2$	10.1	9.98	white	130-131	B
Cd(*m*DTSO)$_6$(BF$_4$)$_2$	10.4	10.2	white	128-130	B

[a] % C: 27.22 (calc. 27.45), % H: 4.68 (4.61), % S: 35.20 (36.64). [b] % C: 27.20 (calc. 27.45), % H: 4.60 (4.61), % S: 35.09 (36.64).

Table Ib. Analytical data and other properties of coordination compounds containing P*m*DTSO.

Compound	% Metal Found	Calc.	Color	M.P. (°C)	X-ray type
Mg(P*m*DTSO)$_6$(ClO$_4$)$_2$	1.79	1.62	white	192-194	D
Mn(P*m*DTSO)$_6$(ClO$_4$)$_2$ [a]	3.83	3.60	white	174-175	D
Mn(P*m*DTSO)$_6$(BF$_4$)$_2$	3.86	3.66	white	183-185	D
Fe(P*m*DTSO)$_6$(ClO$_4$)$_2$	3.65	3.65	yellow	167-168	D
Fe(P*m*DTSO)$_6$(BF$_4$)$_2$	3.75	3.71	yellow	176-177	D
Co(P*m*DTSO)$_6$(ClO$_4$)$_2$	3.71	3.85	rose	160-161	D
Co(P*m*DTSO)$_6$(BF$_4$)$_2$ [b]	3.91	3.91	rose	191-192	D
Ni(P*m*DTSO)$_6$(ClO$_4$)$_2$	3.71	3.83	green	175-176	D
Ni(P*m*DTSO)$_6$(BF$_4$)$_2$	4.15	3.90	green	205-207	D
Cu(P*m*DTSO)$_6$(ClO$_4$)$_2$	4.09	4.14	yellow-green	120-121*	D
Cu(P*m*DTSO)$_6$(BF$_4$)$_2$	4.29	4.20	yellow-green	126-127	D
Cu(P*m*DTSO)$_4$(ClO$_4$)$_2$	5.60	5.71	light blue	123*	F
Cu(PmDTSO)$_4$(BF$_4$)$_2$	5.90	5.85	light green	165-167	F
Zn(P*m*DTSO)$_6$)ClO$_4$)$_2$	4.37	4.25	white	175-176	D
Zn(P*m*DTSO)$_6$(BF$_4$)$_2$	4.42	4.32	white	191-192	D
Cd(P*m*DTSO)$_6$(ClO$_4$)$_2$	7.30	7.09	white	173-174	D
Cd(P*m*DTSO)$_6$(BF$_4$)$_2$	7.16	7.21	white	206-207	D

* explodes. [a] % C: 46.93 (calc. 47.17), % H: 4.60 (calc. 4.75), % S: 24.09 (calc. 25.18). [b] % C: 47.41 (calc. 47.83), % H: 4.67 (calc. 4.82), % S: 24.38 (calc. 25.54).

Analyses and Measurements. Analyses and measurements were carried out as described previously;[1,2] in addition EPR measurements were performed on a Varian E-3 apparatus using X-band frequencies. The spectra of the powdered solid compounds were run as the first derivative. Galvanoxyl was used as a reference compound.

Results and Discussion

In Tables Ia and Ib the coordination compounds are listed together with analytical results, colors and melting points. Further in these tables the X-ray types for the several compounds are listed and indicated with A-F. The division into these groups was made according to the X-ray powder diagrams of the compounds which were very similar in *d* values (Å) and intensities for members of the same group. These similarities in X-ray powder patterns strongly suggest isomorphism between the several compounds of the same group. Whereas the solvates of P*m*DTSO are of the same type (D), three different X-ray types are found for the compounds containing *m*DTSO: for solvates with large metal ions (viz. Cd^{II} and Mn^{II}) type B, for the other solvates type A with BF$_4^-$ as the anion and type C with ClO$_4^-$ as the anion (except Mg(*m*DTSO)$_6$(ClO$_4$)$_2$ of type A). Fe(*m*DTSO)$_6$(ClO$_4$)$_2$ and Co(*m*DTSO)$_6$(BF$_4$)$_2$ were isolated either as type A or as type C. The tetrakis Cu^{II} compounds form classes by themselves.

As an obvious extension of the investigation of the influence of large substituents we also studied the ligand 2,2-diphenyl-1,3-dithiane monosulfoxide. This sulfoxide, reported in literature[7,8] was prepared analogously to P*m*DTSO. However, all attempts to prepare metal solvates with this ligand failed, probably because of the steric requirements of two bulky phenyl groups adjacent to the sulfoxide group.

Characterization of the *m*DTSO and P*m*DTSO compounds with the aid of physical measurements is described below.

Infrared Spectra. The coordination site of these ligands can be determined from the nature of the shift of the SO stretching vibration in the solvates compared with the free ligand, as has been stated[1,2] for 1,4-dithiane monosulfoxide complexes. The SO stretching absorptions (listed in Table II) are shifted in all solvates toward lower energy. We conclude therefore that these ligands coordinate *via* the oxygen atom of the sulfoxide group as in the solvates of DTMSO,[1,2] PMSO (pentamethylene sulfoxide) and TMSO (tetramethylene sulfoxide).[9]

For several *m*DTSO solvates (those of X-ray type B and C) the SO stretching vibration occurs as a split band with components separated about 15 cm^{-1}. For all other sulfoxide complexes studied till now, only one SO stretching absorption, often rather sharp, has been found.[1,2,9] This splitting can be caused by several effects: (i) Interactions with other fundamentals, overtones or combination bands of the same symmetry. If the splitting should be due to these kinds of interactions, we would expect the phenomenon to occur in all *m*DTSO solvates. (ii) The presence of two different SO groups in the moiety [M(*m*DTSO)$_6$]$^{2+}$.

In six membered cyclic sulfoxides, having a chair conformation[10,11] the SO group may occupy an axial or equatorial position. For the equatorial group ν_{SO} is found at higher energy than for the axial one.[12,13] In free *m*DTSO two absorptions are found at 1068 and 1052 cm^{-1} (in carbon tetrachloride). In general the conformer bearing the axial oxygen atom has been shown to be the more stable one.[14,15] In *m*DTSO, however, the axial sulfoxide group will be less favored above the equatorial one as a result of the repulsion of the oxygen atom and the *syn*axial lone pair on the sulfide atom at the 3-position. In the *m*DTSO solvates which show split SO stretching absorptions, we therefore assume the presence of both conformers in the moiety [M(*m*DTSO)$_5$]$^{2+}$.

To verify this assumption, a crystal structure determination of Zn(*m*DTSO)$_6$(ClO$_4$)$_2$ is undertaken.[16] The differences in positions and intensities of the other absorption bands in the solvates are found in accordance with their division in X-ray types.

In P*m*DTSO the bulky phenyl group with a preference for an equatorial position, will "anchor" the conformation. We suppose therefore the presence of only one conformer. Indeed the SO stretching vibration is observed as a single band in nearly all P*m*DTSO solvates. Exceptions are, however, the compounds Cu(P*m*DTSO)$_6$(ClO$_4$)$_2$ and Cu(P*m*DTSO)$_6$(BF$_4$)$_2$. In these compounds, just as in the hexakis Cu^{II} solvates of *m*DTSO, the SO stretching vibration occurs as a split band with components at about 1000 and 955 cm^{-1}. This rather large splitting may be caused by a Jahn-Teller distortion of the [Cu(O)$_6$]$^{2+}$ octahedron as has been found in other Cu^{II} solvates.[1,9,17]

In the spectra of the solvates the absence of splittings of the ν_3 and ν_4 anion absorption bands indicates that the anions are not coordinated to the metal ions.[18] In the tetrakis copper(II) compounds the anions are supposed to be, weakly, coordinated to the metal ion (see below). The anion absorptions in these compounds, however, do not split, but only broaden, suggesting square planar coordinated Cu^{III} ions.

For DMSO (dimethyl sulfoxide)[19] and TMSO (tetramethylene sulfoxide)[20,21] strong bands occur in the 400 cm^{-1} region, which can be attributed to metal-ligand stretching. In order to see whether or not such M-L stretching absorptions could be observed in the solvates of *m*DTSO and P*m*DTSO, far-infrared spectra of our solvates were recorded. The spectral data in the 300-460 cm^{-1} region are also given in Table II.

For the P*m*DTSO compounds a strong band is found in the 395-450 cm^{-1} region(due neither to ligand nor to anion absorptions. These bands may be assigned to metal-ligand stretching vibrations (ν_{ML}). This is supported by the following observations: the sequence of the metal ions, as listed in Table II with increasing ν_{ML} frequency, is the same as found for solvates of other ligands as DMSO,[19] TMSO[20,21] and PYNO (pyridine-N-oxide)[17] and corresponds with the well-known *Irving-Williams* stability order for bivalent transition-metal ions.[22] The order of the metal ions goes parallel for ν_{ML} and ν_{SO}, except Mg^{2+} with its largely different mass. Comparison of the M-L stretching frequencies in the P*m*DTSO and TMSO solvates for each metal ion, yields a constant ratio ν_{ML}(TMSO)/ν_{ML}(P*m*DTSO) for all metal ions (0.97-0.98). Comparison of the other ligand absorptions in this region with ν_{ML} (TMSO) does not yield such a constant ratio for all metal ions.

In *m*DTSO a weak ligand absorption is found at 405 cm^{-1}. In the solvates of *m*DTSO, however, a strong band is observed between 412 an 460 cm^{-1} with a behavior similar to the M-L stretch in the P*m*DTSO solvates. The ratios ν_{ML}(TMSO)/ν_{ML}(*m*DTSO) fall in a narrow range for all metal ions (0.92-0.94), while the other ligand absorptions compared with ν_{ML} (TMSO) yield different ratios for the various metal ions. We suppose therefore that these absorption bands may be assigned also to metal-ligand stretching vibrations, which appear to be only slightly coupled with the weak ligand absorption at 405 cm^{-1}.

Ligand-fied spectra. Diffuse reflectance spectra of

---

(7) R. Kuhun and F.A. Neugebauer, *Chem. Ber.*, *94*, 2629 (1968).

(8) W. Otting and F.A. Neugebauer, *Chem. Ber.*, *95*, 540 (1962).

(9) P.W.N.M. van Leeuwen, Thesis, University of Leyden (1967).

(10) H.M.M. Shearer, *J. Chem. Soc.*, *1959*, 1394.

(11) H. Montgomery, *Acta Cryst.*, *13*, 381 (1960).

(12) P.B.D. de la Mare, D.J. Millen, J.G. Tillet, and D. Watson, *J. Chem. Soc.*, *1963*, 1619.

(13) T. Cairns, G. Eglinton, and D.T. Gibson, *Spectrochim. Acta*, *20*, 159 (1964).

(14) C.R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, *86*, 2935 (1964).

(15) N.L. Allinger, J.A. Hirsch, M.A. Miller, and I.J. Tyminsky, *J. Am. Chem. Soc.*, *91*, 337 (1969).

(16) G.C. Verschoor and A.H.M. Driessen-Fleur, to be published.

(17) J. Reedijk, *Rec. Trav. Chim.*, *88*, 499 (1969)

(18) J. Reedijk, *Rec. Trav. Chim.*, *88*, 1451 (1969).

(19) B.F.G. Johnson and R.A. Walton, *Spectrochim. Acta*, *22*, 1853 (1966); C.V. Berney and J.H. Weber, *Inorg. Chem.*, *7*, 283 (1968).

(20) J. Reedijk, P.W.N.M. van Leeuwen, and W.L. Groeneveld, *Rec. Trav. Chim.*, *87*, 1073 (1968).

(21) C.V. Berney and J.H. Weber, *Inorg. Chim. Acta*, *5*, 375 (1971).

(22) H. Irving and R.J.P. Williams, *J. Chem. Soc.*, *1953*, 3192.

Table II. Infrared spectral data of the solvates M(ligand)$_6$(anion)$_2$ in the 1000-950 and 460-300 cm^{-1} region

M	anion	X-ray type	Ligand = *m*DTSO			Ligand = P*m*DTSO		
			ν_{SO}	ν_{M-L}	other bands	ν_{SO}	ν_{M-L}	other bands
–	–		nuiol: 1048vs, 1039vs 1026s CCl$_4$: 1068vs,1052vs		405w,388m,337m,317m	nujol: 1055sh,1046sh 1035vs CCl$_4$: 1060vs,1045vs		375w,371w,362w,340m,320m,
Cd	ClO$_4^-$	B	989vs+971vs	412s	386m,342m,330sh,320m	983vs	397s	374sh,346m,335m,318m
Cd	BF$_4^-$	B	990vs+970vs	413s	387m,343m,331sh,321m	982vs	397s	374sh,368sh,345m,335m,318m
Mn	ClO$_4^-$	B	994vs+976vs	412s	385m,344m,324m	988vs	396s	375sh,345m,334m,318m
Mn	BF$_4^-$	B	994vs+977vs	413s	385m,344m,323m	987vs	398s	375sh,346m,336m,320m
Zn	ClO$_4^-$	C	987vs+976vs	425s	346m,328sh,323m,304m	982vs	400s	376sh,347m,334m,319m
Zn	BF$_4^-$	A	981vs	423s	384m,344m,327m,303m	983vs	400s	374sh,347m,334m,318m
Fe	ClO$_4^-$	A	980vs	423s	383w,345m,328m,305w	980vs	402s	375sh,348m,335m,319m
Fe	ClO$_4^-$	C	984vs+972vs	422s	348m,332sh,325m,303m			
Fe	BF$_4^-$	A	977vs	422s	387m,344w,330sh,321m,305w	978vs	404s	376sh,348m,336m,320m
Co	ClO$_4^-$	C	981vs+970vs	432s	349m,326m,305m	977vs	410s	377sh,350m,336m,320m
Co	BF$_4^-$	A	976vs	428s	384m,346m,329m,303m	976vs	411s	377sh,350m,336m,320m
Co	BF$_4^-$	C	980vs+970vs	432s	349m,326m,304m			
Ni	ClO$_4^-$	C	982vs+972vs	437s	352m,327m,307m	972vs	418s	375sh,352m,336m,321m
Ni	BF$_4^-$	A	978vs	434s	384m,347m,331m,307m	974vs	420s	377vw,353m,336m,320m
Mg	ClO$_4^-$	A	1003vs	435s	384m,355m,332m,305m	1005vs	418s	379sh,353sh,344m,321m
Cu	ClO$_4^-$	C	1000s,965vs+955vs	450m	346m,331w,322w,311w	997s,957vs	437m	380vw,349m,335m,319m
Cu	BF$_4^-$	A	1000s,960vs	452m	425w,383m,350m,331m,310m	1000s,960vs	433m	389w,348s,335m,318m
Cu	ClO$_4^-$*	E	962vs+951vs	460s	408m,390w,381m,337m,307m	945vs	458s	362s,350sh,335w,325w
Cu	BF$_4^-$*	E	960vs+950vs	450s	409m,392w,383w,345m,332sh,310w	948vs	458s	362s,350sh,334w,325w

vs = very strong; s = strong; sh = shoulder; * Cu(ligand)$_4$(anion)$_2$

Table III. Ligand-field spectral data of *m*DTSO and P*m*DTSO complexes; band maxima are in kK, Dq and B in cm^{-1}, Dq/B is a real number.

Compound	X-ray type	Band maxima and assignments				Dq	B	Dq/B
		$^5E_g \leftarrow {}^5T_{2g}$						
Fe(*m*DTSO)$_6$(ClO$_4$)$_2$	A	9.85						
Fe(*m*DTSO)$_6$(ClO$_4$)$_2$	C	10.0						
Fe(*m*DTSO)$_6$(BF$_4$)$_2$	A	9.85						
Fe(P*m*DTSO)$_6$(ClO$_4$)$_2$	D	9.30						
Fe(P*m*DTSO)$_6$(BF$_4$)$_2$	D	9.30						
		$^4T_{2g} \leftarrow {}^4T_{1g}(F)$	$^4A_{2g}$,	$^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$				
Co(*m*DTSO)$_6$(ClO$_4$)$_2$	C	8.05	16.0	19.6		875	840	1.04
Co(*m*DTSO)$_6$(BF$_4$)$_2$	C	8.10	16.0	19.6		880	840	1.05
Co(*m*DTSO)$_6$(BF$_4$)$_2$	A	7.85	15.6	19.4		855	835	1.02
Co(P*m*DTSO)$_6$(ClO$_4$)$_2$	D	7.45	15.9	18.8		810	825	0.98
Co(P*m*DTSO)$_6$(BF$_4$)$_2$	D	7.40	15.9	18.8		810	825	0.98
		$^3T_{2g} \leftarrow {}^3A_{2g}$	$^3T_{1g}(F) \leftarrow {}^3A_{2g}$	$^1E_g \leftarrow {}^3A_{2g}$	$^3T_{1g}(P) \leftarrow {}^3A_{2g}$			
Ni(*m*DTSO)$_6$(ClO$_4$)$_2$	C	8.25	13.4	14.3sh	24.5	825	900	0.92
Ni(*m*DTSO)$_6$(BF$_4$)$_2$	A	8.15	13.2	14.2sh	24.4	815	895	0.91
Ni(P*m*DTSO)$_6$(ClO$_4$)$_2$	D	7.80	12.7	14.1sh	23.6	780	880	0.88^5
Ni(P*m*DTSO)$_6$(BF$_4$)$_2$	D	7.75	12.7	14.1sh	23.6	775	885	0.87^5
		$^2T_{2g} \leftarrow {}^2E_g$						
Cu(*m*DTSO)$_6$(ClO$_4$)$_2$	C	11.8						
Cu(*m*DTSO)$_6$(BF$_4$)$_2$	A	11.8						
Cu(P*m*DTSO)$_6$(ClO$_4$)$_2$	D	8.80sh, 10.4						
Cu(P*m*DTSO)$_6$(BF$_4$)$_2$	D	8.85sh, 10.5						
Cu(*m*DTSO)$_4$(ClO$_4$)$_2$	E	12.9						
Cu(*m*DTSO)$_4$(BF$_4$)$_2$	E	13.1						
Cu(P*m*DTSO)$_4$(ClO$_4$)$_2$	F	12.9						
Cu(P*m*DTSO)$_4$(BF$_4$)$_2$	F	13.1						

sh = shoulder

the solid Fe^{II}, Co^{II}, Ni^{II} and Cu^{II} compounds were recorded in order to compare the ligand-field strengths of *m*DTSO and P*m*DTSO with the other cyclic sulfoxides, such as 1,4-dithiane monosulfoxide and pentamethylene sulfoxide.[9] The band maxima, assignments and ligand-field parameters are given in Table III.

Interpretation of these spectra was possible in terms of octahedral [M(ligand)$_6$]$^{2+}$ groups.

Because of the occurrence of isomorphism with the "uncolored" compounds, all solvates of formula M(ligand)$_6$(anion)$_2$ reported in Tables 1a and 1b, are believed to be octahedrally coordinated. The absorption bands in the tetrakis copper compounds correspond with both octahedral distorted and square planar coordinated Cu^{II} ions, in accordance with the infrared data. The ligand-field parameters Dq and B

(23) J. Reedijk, W.L. Driessen and W.L. Groeneveld, *Rec. Trav. Chim.*, *88*, 1095 (1969).

Table IV. EPR parameters of the Cu^{II} compounds containing *m*DTSO and P*m*DTSO

Compound	Type spectrum	$g_\perp$ or g_{max}	$g_\parallel$	$A_\parallel$ (Gauss)	Bandwidth $g_\perp$* (Gauss)
Cu(*m*DTSO)$_6$(ClO$_4$)$_2$ [a]	symmetric	2.18			150
Cu(*m*DTSO)$_6$(ClO$_4$)$_2$ [b]	asymmetric	2.12	2.24	100	260
Cu(*m*DTSO)$_6$(BF$_4$)$_2$ [a]	asymmetric	2.12	2.38	100	280
Cu(*m*DTSO)$_6$(BF$_4$)$_2$ [b]	asymmetric	2.12	2.38	100	260
Cu(P*m*DTSO)$_6$(ClO$_4$)$_2$ [a]	symmetric	2.21			180
Cu(P*m*DTSO)$_6$(ClO$_4$)$_2$ [b]	nearly symmetric	2.20**			100
Cu(P*m*DTSO)$_6$(BF$_4$)$_2$ [a]	symmetric	2.21			180
Cu(P*m*DTSO)$_6$(BF$_4$)$_2$ [b]	nearly symmetric	2.20			195
Cu(*m*DTSO)$_4$(ClO$_4$)$_2$ [a]	asymmetric	2.08	2.22	[c]	60
Cu(*m*DTSO)$_4$(BF$_4$)$_2$ [a]	asymmetric	2.08	2.23	[c]	120
Cu(P*m*DTSO)$_4$(ClO$_4$)$_2$ [a]	asymmetric	2.07	2.32	140	50

* measured between points of maximum slope. ** shoulder at $g = 2.08$. [a] at room temperature. [b] at low temperature (−196°C). [c] unresolved.

were calculated in accordance to ref. [23] for Co^{II} and ref. [24] for Ni^{II} solvates. The parameters are in the same order of magnitude as those of other sulfoxide complexes[1]. The parameters of the *m*DTSO solvates of X-ray type C deviate only slightly from those of the other *m*DTSO solvates. The presence of both conformers of *m*DTSO, as was suggested by the infrared spectra, is not supposed to influence the ligand-field parameters very much, since these are mainly determined by the six oxygen atoms of the sulfoxide groups around the metal ion.[25] Comparison of the Dq values of the various cyclic sulfoxides yields the spectrochemical series (with increasing Dq), 2-phenyl-1,3-dithiane monosulfoxide < 1,3-dithiane monosulfoxide ≅ 1,4 dithiane monosulfoxide < pentamethylene sulfoxide. Thus P*m*DTSO behaves as a spectrochemically weaker ligand than the other sulfoxides, probably as a result of the presence of the large pheyl group adjacent to the coordinating SO group. The nephelauxetic B for these sulfoxide ligands is nearly the same.

Paramagnetic Resonance Spectra. To obtain more information about the nature of the distortion in the Cu^{II} compounds, suggested by infrared spectroscopy, we recorded the paramagnetic resonance spectra of the solid powdered compounds. The data are listed in Table IV. The spectral parameters of Cu(*m*DTSO)$_6$(BF$_4$)$_2$ with an asymmetric signal at room temperature, are quite normal for a Cu^{II} ion in a distorted octahedral environment caused by a static Jahn-Teller effect.[17,26] For Cu(mDTSO)$_6$(ClO$_4$)$_2$, Cu(P*m*DTSO)$_6$(ClO$_4$)$_2$ and Cu(P*m*DTSO)$_6$(BF$_4$)$_2$ symmetric signals are observed at room temperature. At low temperature (−196°C) the signal of Cu(*m*DTSO)$_6$(ClO$_4$)$_2$ becomes clearly asymmetric. The Jahn-Teller distortion, probably dynamical at room temperature, has become static at low temperature.[17,26] The signals of both P*m*DTSO solvates become only slightly asymmetric at −196°C; probably the transition from the dynamical Jahn-Teller distortion into a static on takes place below this temperature. Further investigations on these transitions and on Cu-doped Zn and Cd compounds are planned for the near future.

The spectra of the tetrakis complexes are in accordance with Cu^{II} ions in tetragonal environments.[27] Two separated signals are observed for $g_\parallel$ and $g_\perp$; with the larger ligand P*m*DTSO the hyperfine components on $g_\parallel$ are resolved.

Conclusions

From the results discussed above, the following conclusions can be drawn: Both 1,3-dithiane monosulfoxide and 2-phenyl-1,3-dithiane monosulfoxide coordinate to bivalent metal ions yielding hexasolvates with ClO$_4^-$ and BF$_4^-$ as the anions. Only with Cu^{II} also tetrakis compounds are formed. Just as in most complexes of other sulfoxides, the oxygen of the sulfoxide group is the donor atom of the ligand. Metal-ligand stretching frequencies occur in the usual range for sulfoxide ligands.

In the spectrochemical series 2-phenyl-1,3-dithiane monosulfoxide behaves as a weaker ligand than the other cyclic sulfoxides, probably as a result of the steric requirements of the phenyl group at the 2-position. 1,3-Dithiane monosulfoxide has the same position at its 1,4 analogue in the series of sulfoxide ligands. Deviations in the infrared spectra of some solvates of 1,3-dithiane monosulfoxide may be due to the presence of conformational isomers in the ligand ring system and are subject of further investigations. The Jahn-Teller distortions, found in the Cu^{II} solvates, are either static or dynamic as shown by their temperature dependence.

Acknowledgement. The authors are indebted to Dr. M.W.G. de Bolster and Dr. J. Reedijk for reading the manuscript, to Mr. A. van der Linden for recording the infrared spectra and to Mr. J.G. Vos for the measurements of the paramagnetic resonance spectra. The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with finacial aid from the Netherlands Organization for Advancement of Pure Research (ZWO).

---

(24) J. Reedijk, P.W.N.M. van Leeuwen, and W.L. Groeneveld, *Rec. Trav. Chim.*, *87*, 129 (1968).

(25) C.K. Jørgensen, Modern Aspects of Ligand Field Theory, North-Holland Publishing Company, Amsterdam, 1971.

(26) J. Reedijk, *Rec. Trav. Chim.*, *88*, 1139 (1969).

(27) J. Reedijk, J.C.A. Windhorst, N.H.M. van Ham, and W.L. Groeneveld, *Rec. Trav. Chim.*, *90*, 234 (1971).