

Transition Metal Complexes of 1,3-Bis(methylsulfinyl)propane, 1,4-Bis(methylsulfinyl)butane and 1,2-Bis(ethylsulfinyl)ethane¹

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The title bidentate sulfoxides have been synthesized and employed as ligands toward Mn⁺², Co⁺², Ni⁺², Cu⁺² and Zn⁺². The resulting complexes were characterized by analyses, magnetic measurements and visible and infrared spectra. All metal ions are bound to the ligands via the oxygens of the sulfoxide groups and are 6-coordinate with the exception of Cu⁺², which is 4-coordinate. Crystal field calculations for the Ni⁺² species indicate a slight decrease in field strength with an increase in the number of CH₂ groups between the sulfoxide functions and also with increasing size of the substituent attached to the sulfur.

Introduction

Transition metal complexes of sulfoxide-containing ligands have been investigated extensively in recent years. Most of these investigations have dealt with sulfoxides of the type RS(O)R', in which R and R' were varied, although two reports of the coordination behavior of bidentate species of the type RS(O)(CH₂)₂S(O)R [2, 3] have also appeared. These latter compounds introduce the possibility of varying the length of the chain between the sulfoxide moieties as well as the substituent R. Since relatively few studies appear to have been carried out on the effect of chelate ring size on the donor properties of bidentate ligands, we have synthesized and studied the title compounds; 1,3-bis(methylsulfinyl)propane, (MSP), and 1,4-bis(methylsulfinyl)butane, (MSB), and their complexes. We have also prepared the related compound 1,2-bis(ethylsulfinyl)ethane (ESE) along with a number of its complexes in order to examine the effect of the larger R group on the behavior of this ligand toward metal ions.

Experimental

Synthesis of Ligands and Complexes

The three disulfoxides used in this study were prepared by the HCl-catalyzed oxidation of the

parent dithia compounds (Wateree Chemical Lugoff S.C.) with DMSO. In a typical synthesis, 40 ml of 2,7-dithiaoctane (0.267 mol), 80 ml of DMSO, 36 drops of 12M HCl, and 5 ml of benzene were heated to 100 °C for 1.5 hour. Five ml of benzene were added and the solution was allowed to cool overnight. The white crystals which separated were filtered, washed several times with benzene, and dried *in vacuo* (yield 53%). Elemental analyses (Strauss Micro-analytical Laboratory, Oxford, England) of all compounds were in good agreement with theory and their narrow melting point ranges (MSP 150–152°, MSB 121–122°, and ESE 142–145 °C) indicate that only a single product was obtained from each reaction. Previous studies [2, 4] have indicated that the sole product obtained from the DMSO oxidation is the high melting isomer, now identified as the racemic mixture of the *d* and *l* forms.

All complexes were prepared by mixing ethanolic solutions of the appropriate ligand (0.009 mol) and a hydrated metal perchlorate (0.003 mol). In those instances when the product did not form immediately, solutions were reduced in volume and cooled to induce precipitation. All compounds were washed with ethanol and ether and stored *in vacuo*.

Physical Measurements

Infra-red spectra were obtained as Nujol mulls in the 4000–300 cm⁻¹ region using a Beckman IR-12 spectrophotometer. Electronic spectra in the visible and near infra-red regions were measured on a Cary 14 spectrophotometer by spreading Nujol mull suspensions of the compounds on filter paper. Crystal field parameters were calculated by the method of Lever [6] employing the two higher energy bands for Ni(II), because of the difficulty encountered in fixing λ_{\max} of the very broad lowest energy absorbance. Magnetic moments were determined with a Faraday balance which had been calibrated with mercury(II) tetrathiocyanatocobaltate(II) [7].

Molar susceptibilities were corrected for diamagnetic contributions [8] and magnetic moments were calculated with the equation $\mu_{\text{eff}} = 2.84 \sqrt{\chi_{\text{M}}^{\text{corr}}} T$.

TABLE I. Analytical and Magnetic Data.

	% C		% H		% ClO ₄		10 ⁶ χ _M ^{corr}	μ _{eff} B.M.
	Calcd.	Found	Calcd.	Found	Calcd.	Found		
L = MSP								
MnL ₃ (ClO ₄) ₂	23.75	23.66	4.78	4.80	26.22	26.60	13959	5.80
CoL ₃ (ClO ₄) ₂	23.62	23.90	4.76	4.95	26.08	26.18	10630	4.97
NiL ₃ (ClO ₄) ₂	23.63	23.81	4.76	4.79	26.08	25.56	4665	3.35
CuL ₂ (ClO ₄) ₂	20.05	20.59	4.04	4.33	33.20	33.02	2198	2.29
ZnL ₃ (ClO ₄) ₂	23.42	23.69	4.72	4.87	25.86	26.12		
L = MSB								
CoL ₃ (ClO ₄) ₂	26.87	27.14	5.26	5.05	24.71	24.49	9935	4.89
NiL ₃ (ClO ₄) ₂	26.87	27.12	5.26	5.46	24.72	24.22	4351	3.24
CuL ₂ (ClO ₄) ₂	22.99	22.18	4.50	5.09	31.72	31.93	1961	2.17
ZnL ₃ (ClO ₄) ₂	26.65	27.02	5.22	5.33	24.52	24.98		
L = ESE								
MnL ₃ (ClO ₄) ₂	26.99	27.54	5.29	5.47	24.87	24.73	14210	5.85
CoL ₃ (ClO ₄) ₂	26.89	26.19	5.26	5.16	24.74	24.06	9903	4.88
NiL ₃ (ClO ₄) ₂	26.87	27.36	5.26	5.47	24.75	23.75	3940	2.91
CuL ₂ (ClO ₄) ₂	23.03	23.89	4.50	4.40	31.74	31.54	1421	1.85
ZnL ₃ (ClO ₄) ₂	26.65	26.54	5.22	5.50	24.55	24.87		

Discussion

The analytical data (Table I) clearly indicate the formulations ML₃ for M ≠ Cu, and CuL₂. The spectral behavior of the NiL₃ and CoL₃ species suggest octahedral environments although the low solubilities of all compounds precluded the determination of molecular weights and it is unclear at this time whether these species are monomeric or polymeric, with some of disulfoxides bridging two metal ions. Four-coordinate copper complexes have also been reported for dibenzyl sulfoxide [9], as well as tetramethylene and pentamethylene sulfoxides [10], whereas the copper complexes of other bidentate sulfoxides have been found to be six-coordinate [2, 3].

The magnetic moments found for the various compounds (Table I) are in the range expected for high-spin octahedral complexes of manganese(II), cobalt(II), and nickel(II) with the respective ligands. The deviations from spin only values of 5.92 B.M. (Mn), 2.83 B.M. (Ni), and 3.87 B.M. (Co) which do occur can be attributed to orbital contributions from other electronic states. The cobalt compounds show the greatest difference from the spin only value (~1.0 B.M.) but are consistent with the values found for cobalt(II) complexes with dimethylsulfoxide [12] tetramethylene sulfoxide [13] and bis(methylsulfinyl)ethane [2]. The moments for the copper(II) complexes lie in the range expected for four-coordinate copper species (D_{4h}-1.91 B.M. and Td-

2.2 B.M.) [14] but structural assignments cannot be made on this basis alone.

Infra-red Spectra

The principal features of the infra-red spectra are shown in Figure 1 and presented in Table II. The bands found at 1100 cm⁻¹ and 622 cm⁻¹ have been attributed to the antisymmetric stretching and bending vibrations of the perchlorate ion [15], and the fact that neither of these bands is split indicates that this ion is not coordinated [16].

Of the remaining vibrations which are common to the ligand and complexes, only the strong band near 1000 cm⁻¹ will be considered in detail since this band, which is due to the S-O stretching frequency

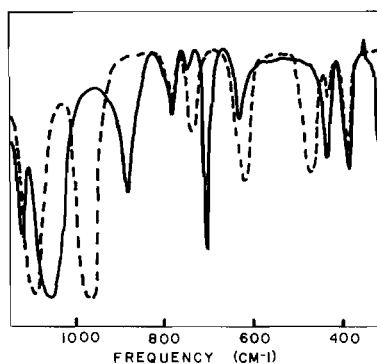


Figure 1. Typical infra-red spectra of MSB (—) and Co(MSB)₃(ClO₄)₂ (---).

TABLE II. Infra-red Data.

L = MSP	1280s, 1145s, 1040s, 780m, 538m, 528m, 495m
MnL ₃ (ClO ₄) ₂	1100s, 1000s, 622s, 422m
CoL ₃ (ClO ₄) ₂	1100s, 987s, 622s, 435m
NiL ₃ (ClO ₄) ₂	1100s, 970s, 622s, 450m
CuL ₂ (ClO ₄) ₂	1100s, 972s, 950s, 622s, 530m
ZnL ₂ (ClO ₄) ₂	1100s, 990s, 622s, 430m
L = MSB	1120s, 1025s, 880m, 772m, 697s, 638m, 412m, 380m
CoL ₃ (ClO ₄) ₂	1090s, 978s, 622s, 450m
NiL ₃ (ClO ₄) ₂	1090s, 985s, 622s, 448m
CuL ₂ (ClO ₄) ₂	1100s, 958s, 622s, 490m
ZnL ₃ (ClO ₄) ₂	1100s, 985s, 622s, 440m
L = ESE	1130s, 1020s, 797m, 740m, 682m, 650m, 495m, 405m, 390m
MnL ₃ (ClO ₄) ₂	1100s, 1000s, 622s, 480m
CoL ₃ (ClO ₄) ₂	1100s, 980s, 622s, 482m
NiL ₃ (ClO ₄) ₂	1100s, 980s, 622s, 482m
CuL ₂ (ClO ₄) ₂	1097s, 948s, 624s, 494m
ZnL ₃ (ClO ₄) ₂	1100s, 986s, 622s, 478m

[17], can be used to determine the mode of coordination of the sulfoxide. The fact that this band shifts to lower frequencies in all instances is evidence that the ligands are bonded to the metal via the oxygen atoms [18]. This assignment is further supported by the appearance of a new band near 500 cm⁻¹ in the complexes which can be attributed to a metal-oxygen bond, in analogy with the similar band found in DMSO complexes [19]. The metal-sulfur bond would be expected to absorb at lower frequencies [20].

The sulfoxide frequency shift ($\nu_{\text{uncomplexed SO}} - \nu_{\text{complexed SO}}$) has been used previously [21] to provide a measure of the extent to which electron density is removed from the S-O bond by coordination. In the present study, the shifts exhibited by the copper compounds are much larger than those of the other metals suggesting that the greatest weakening of the S-O bond occurs for each ligand when bonded to copper. This is also indicated by the M-O frequencies which are larger for Cu than for any other metal. It is likely that these results are due to the lower coordination number of copper as well as the expected trend of metal-oxygen bonding [22].

Visible Spectra

The visible and near ir spectral results are given in Table III along with the transition assignments while the ligand field parameters calculated from these spectra are given in Table IV where they can be compared with the values found for related compounds from other studies. From these data it is apparent that the field strengths (as reflected in Dq values) of the bidentate sulfoxides examined in this investigation are greater than those of all other

TABLE III. Near Infra-red and Visible Spectra.

Compound	λ_{max} , cm ⁻¹	Assignment
Co(MSP) ₃ (ClO ₄) ₂	8260	ν_1 ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	13510 (est)	ν_2 $\rightarrow {}^4A_{2g}(F)$
	18590	ν_3 $\rightarrow {}^4T_{1g}(P)$
	20490 (sh)	
Co(MSB) ₃ (ClO ₄) ₂	8260	ν_1 ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	14290 (est)	ν_2 $\rightarrow {}^4A_{2g}(F)$
	18800	ν_3 $\rightarrow {}^4T_{1g}(P)$
	20530 (sh)	
Co(ESE) ₃ (ClO ₄) ₂	8200	ν_1 ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	13890 (est)	ν_2 $\rightarrow {}^4A_{2g}(F)$
	18900	ν_3 $\rightarrow {}^4T_{1g}(P)$
	20410 (sh)	
Ni(MSP) ₃ (ClO ₄) ₂	8210	ν_1 ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$
	12940	
	14490	ν_2 $\rightarrow {}^3T_{1g}(F)$
Ni(MSB) ₃ (ClO ₄) ₂	23980	ν_3 $\rightarrow {}^3T_{1g}(P)$
	8000	ν_1 ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$
	12950	
Ni(ESE) ₃ (ClO ₄) ₂	14180	ν_2 $\rightarrow {}^3T_{1g}(F)$
	23920	ν_3 $\rightarrow {}^3T_{1g}(P)$
	8230	ν_1 ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$
Cu(MSP) ₂ (ClO ₄) ₂	13020	
	14490	ν_2 $\rightarrow {}^3T_{1g}(F)$
	24100	ν_3 $\rightarrow {}^3T_{1g}(P)$
Cu(MSP) ₂ (ClO ₄) ₂	13330	${}^2B_{1g} \rightarrow {}^2A_{1g}$ $\rightarrow {}^2E_{1g}$
	13070	${}^2B_{1g} \rightarrow {}^2A_{1g}$ $\rightarrow {}^2E_{1g}$
Cu(MSB) ₂ (ClO ₄) ₂	13070	${}^2B_{1g} \rightarrow {}^2A_{1g}$ $\rightarrow {}^2E_{1g}$
	12900	${}^2B_{1g} \rightarrow {}^2A_{1g}$ $\rightarrow {}^2E_{1g}$

TABLE IV. Ligand Field Parameters of Mono- and Bidentate Sulfoxides and Other Bidentate Oxygen Donors toward Ni(II).

Ligand	Dq (cm ⁻¹)	B (cm ⁻¹)	Ref.
MSE	928	772	2
MSP	898	761	this work
MSB	868	765	this work
ESE	901	783	this work
<i>rac</i> -PSE	809	899	3
<i>meso</i> -PSE	792	901	3
<i>rac</i> -PSM	822	866	3
<i>meso</i> -PSM	799	884	3
(CH ₃) ₂ S=O	800		a
(C ₄ H ₉) ₂ S=O	823		a
(C ₅ H ₁₀) ₂ S=O	851		a
(C ₆ H ₅) ₂ S=O	796		a
C ₆ H ₅ (CH ₃)S=O	823		a
(C ₃ H ₇ O) ₂ P(O)CH ₂ P(O)(OC ₃ H ₇) ₂	847		24
(C ₄ H ₉ O) ₂ P(O)CH ₂ P(O)(OC ₄ H ₉) ₂	864		24
(CH ₃) ₂ N ₂ P(O)OP(O)N(CH ₃) ₂	726		23
(CH ₃) ₂ NC(O)CH ₂ C(O)N(CH ₃) ₂	860		25

^aP.W.N.M. van Leeuwen and W.L. Groeneveld, *Rec. Trav. Chim. Pays Bas*, 86, 1219 (1967).

sulfoxides with the exception of the closely related MSE. They are also greater than those of the bidentate ligands; octamethylphosphoramidate [23], bis(di-isopropoxyphosphinyl)methane, bis(di-N-butylphosphinyl)methane [24], and tetramethylmalonamide [25], although they are clearly within the weak field range.

The Dq values of these ligands decrease in the order MSE > MSP > MSB, *i.e.*, as the size of the chelate ring increases from 7 to 9 members, and are influenced by the nature of R, decreasing with an increase in the size of this group. Thus, when the methyl group of MSE is replaced with an ethyl group (in ESE) a decrease in the value of Dq (from 928 to 901 cm⁻¹) is observed, which is followed by an even greater decrease (to ~800 cm⁻¹) when a benzene ring is the pendant group (in PSE). In contrast to Dq, the data in Table IV indicate that the Racah B parameter is influenced very little by the chelate ring size or the nature of the alkyl group present, although it is increased substantially by the presence of a phenyl group.

Even though the steric influence of the R group causes a decrease in the field strength, it does not appear to affect the overall stability of the resulting compounds. This is in contrast to complexes of the corresponding bidentate sulfur donors, in which the stability decreases markedly with increasing size of the R group [26, 27], as well as with ring size variations [28]. The most logical explanation for this difference in behavior between these two types of ligands is that the R group and carbon chain are attached directly to the donor atom in the sulfur donors but are one atom removed in the sulfoxides,

with the greater separation resulting in a smaller steric effect.

In summary, the three new bidentate sulfoxide ligands which have been synthesized produce 6-coordinate complexes with Mn⁺², Co⁺², Ni⁺² and Zn⁺² and 4-coordinate species with Cu⁺² and are coordinated to these "hard" metal ions via the oxygen. The ligands are all of the weak field type and their strength decreases slightly as the number of CH₂ groups between the sulfoxide moieties is increased (from 2 to 3 to 4) and as the steric requirements of the R group attached to the sulfur increase.

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