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Diphenyl Sulphoxide Complexes of Some Divalent Metal Ions*

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Diphenyl sulphoxide (DPSO) complexes of some divalent metal perchlorates and chlorides are prepared. The perchlorates of Mn, Co, Ni, Zn and Cd have the general formula $[M(DPSO)_6](ClO_4)_2$. *The Cu(II) complex is found to have the composition* $[Cu(DPSO)_4](ClO_4)_2$. *The chloro complexes having the formula* $ZnCl_2 . 2\,DPSO$, $CdCl_2 . DPSO$, $HgCl_2 . DPSO$ *and* $PdCl_2 . 2\,DPSO$ *have also been obtained. Infrared spectra indicate that the DPSO complexes of Mn, Co, Ni, Cu and Zn are oxygen-bonded while those of Cd, Hg and Pd are sulphur-bonded. The magnetic susceptibility and the optical spectral data reveal octahedral coordination for Mn, Co and Ni complexes. From the electronic spectra of Co and Ni complexes, the ligand field parameters, Dq and β, are calculated.*

Introduction

The interest in sulphoxides as ligands arises from their ability to coordinate either through oxygen or sulphur. Although the complexes of dimethyl sulphoxide (DMSO) have been investigated,[1-3] those of diphenyl sulphoxide (DPSO) are not known, except for the Lewis adducts of BCl_3 and $SnCl_4$ and complexes of UCl_4 and $SnCl_2$.[4] We have studied the complexes of DPSO with some divalent metal perchlorates and chlorides to ascertain the donor properties of the ligand and to characterize the nature of the complexes formed. When this work was pending for publication, a short-communication by Van Leeuwen and Groenveld[5] appeared, describing the preparation of some of the complexes of DPSO.

Experimental Section

Materials. DPSO was prepared by reacting pure dry benzene with thionyl chloride in presence of anhydrous aluminium trichloride.[6] The recrystallized product melted at 70°C. The hydrated metal perchlorates were prepared by dissolving pure metal carbonates or hydroxides in dilute (10%) perchloric acid (60% Merck reagent). Other reagents were of Analar grade. Acetone, ethanol, acetonitrile and nitrobenzene were purified by standard methods.[7]

Preparation of the complexes. The following general method for the preparation of most of the complexes was employed. About 1 g of hydrated metal perchlorate or chloride and 3 g of DPSO, each dissolved in 25 ml of acetone, were mixed slowly with stirring. The solution, on slow evaporation by passing dry air at room temperature, yielded crystals of the complex in about a day. These were separated, washed several times with petroleum ether to remove any adhering DPSO and recrystallized either from acetone or ethanol. Preparation of copper(II) perchlorate complex from ethanol was found to yield good crystals, whereas a pasty material was obtained from acetone. Cadmium(II) chloride complex was prepared using anhydrous salt in ethanol medium.

Analyses. The metal in the complexes was analysed by standard methods:[8] Co, Cu, Zn and Cd were determined gravimetrically as their pyridine thiocyanates, Pd and Ni as their dimethyl glyoximates, Mn as pyrophosphate and Hg as $[Cu(en)_2](HgI_4)$ complex. When the complexes (0.2 g) were dissolved in about 25 ml of 2% hydrochloric acid, DPSO got separated as a solid, which was filtered off before the metal was estimated. The perchlorate in the complex was estimated as chloride after reducing it with sodium nitrite at ~500°C.[9] Chloride was determined by Volhard's method after decomposing the complex by boiling with 2*N* nitric acid. Mercury(II) was found to interfere with chloride estimation and hence it was removed as HgS prior to the determination of chloride. The results of the analyses are summarised in Table I.

Properties. The complexes are crystalline. Cobalt (II) and zinc(II) perchlorate complexes are sligthly hygroscopic, while others are not. The complexes are insoluble in nonpolar solvents like benzene, carbon tetrachloride, *etc.*, but are soluble in polar solvents like ethanol, acetone and acetonitrile. The solubility of the coloured complexes in these solvents is not accompanied by any perceptible colour change.

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Table I. Analyses of DPSO Complexes

Compound	Colour	Found %		Calculated %	
		Metal	Anion	Metal	Anion
$Mn(DPSO)_6(ClO_4)_2$	Light yellow	3.80	13.62	3.75	13.57
$Co(DPSO)_6(ClO_4)_2$	Pink	4.12	13.60	4.01	13.53
$Ni(DPSO)_6(ClO_4)_2$	Light green	4.05	13.50	4.00	13.52
$Cu(DPSO)_4(ClO_4)_2$	Green	6.00	18.60	5.93	18.59
$Zn(DPSO)_6(ClO_4)_1$	Colourless	4.45	13.52	4.43	13.48
$Cd(DPSO)_6(ClO_4)_2$	Colourless	7.35	12.98	7.38	13.06
$PdCl_2$. 2 DPSO	Brown	18.38	12.35	18.30	12.21
$ZnCl_2$. 2 DPSO	Colourless	12.25	13.42	12.10	13.14
$CdCl_2$. DPSO	Colourless	29.08	18.50	29.16	18.43
$HgCl_2$. DPSO	Colourless	42.40	15.51	42.36	15.34

The experimental procedures for the determination of electrical conductance in acetonitrile and nitrobenzene, molecular weight in nitrobenzene by cryoscopy, paramagnetic susceptibility and electronic and infrared spectra were the same as described in a previous paper.[10] Infrared spectra were recorded both in Nujol mull and in KBr pellets.

Results and Discussion

The molar conductances of the perchlorate complexes in the concentration range 10^{-3} to $10^{-4}M$ in acetonitrile at 25°C are around 200-250 ohm^{-1}cm^{2}mole^{-1}, indicating uni-bivalent electrolytic nature of the complexes. The exchange of coordinated ligands with the solvent molecules in solution is not likely to affect the conductance. The molar conductance of $PdCl_2$. 2 DPSO complex is about 2 ohm^{-1} cm^2 mole^{-1} (conc : 6×10^{-3} *M*) in acetonitrile, showing its non-ionic nature. The nitrobenzene solutions of the complexes $ZnCl_2$. 2 DPSO, $CdCl_2$. DPSO and $HgCl_2$. DPSO (10^{-3} to $10^{-4}M$) are non-conducting, the resistance being around 10^6 ohms, thereby revealing their non-ionic nature. $ZnCl_2$. 2 DPSO and $HgCl_2$. DPSO are appreciably soluble in nitrobenzene which prompted us to determine their molecular weights by the cryoscopic method. The molecular weight of the zinc complex is around 540-550, which implies its existence as a monomer (calcd. 540) in nitrobenzene. The molecular weight of $HgCl_2$. DPSO (280-290) is less than the monomer weight (474), which indicates the removal of some of the DPSO molecules from the coordination sphere.

The magnetic susceptibility data of the solid complexes at room temperature (298°K) are given in Table II. The effective magnetic moments of the Mn(II), Co(II) and Ni(II) complexes are in the same range as other octahedral complexes.[11]

Table II. Magnetic susceptibility data on DPSO Complexes

Compound	$\chi_g \times 10^6$	$\chi_M \times 10^6$	μ_{eff} (B.M.)
$Co(DPSO)_6(ClO_4)_2$	7.03	10,720	5.09
$Ni(DPSO)_6(ClO_4)_2$	2.88	4,953	3.46
$Mn(DPSO)_6(ClO_4)_2$	8.08	13,020	5.56
$Cu(DPSO)_4(ClO_4)_2$	0.968	1,516	1.914

χ_M is the molar magnetic susceptibility corrected for diamagnetism.

The electronic spectral data of Co(II), Ni(II) and Cu(II) complexes in acetone are given in Table III. The spectra of the Ni(II) and Co(II) complexes are very similar to those of other octahedral complexes of these metals.[12] The electronic spectrum of the Cu(II) complex containing the ion $Cu(DPSO)_4^{2+}$ shows a broad absorption band in the 700-900 mμ region, similar to that of $Cu(Ph_3PO)_4^{2+}$.[13] The position and the low intensity ($\epsilon = 27$) of the band suggests a centrosymmetric square planar structure for the complex ion.

From the electronic spectral data on the Ni(II) and Co(II) complexes, the *Dq* values are calculated using the relations given by Underhill and Billing.[14] The calculated *Dq* values for Co(II) and Ni(II) complexes are 840 and 780 cm^{-1} respectively. The P-F term distances in the complexes, calculated from the spectral data using the weak-field formalism[15] are 12,400 and 13,800 cm^{-1} for Co(II) and Ni(II) complexes respectively, while the corresponding free ion values[15] are 14,500 and 15,840 cm^{-1}. The extent of the decrease in the P-F term distances from the free ion value is taken as a measure of the covalency in the complexes. The percentage lowering of the P-F term distances for Co(II) and Ni(II) complexes are 14.9 and 12.8 respectively, whereas those for the corresponding DMSO complexes are 14.9 and 12.7.[12] This shows that there is not much difference in the ligand field strength provided by these ligands, when the bonding occurs through oxygen of the sulphoxide.

Table III. Electronic Spectral Data on DPSO Complexes in acetone

Compound	λ max, cm^{-1}	ε_{max}	Band Assignment	Dq, cm^{-1}	E(P)—E(F), cm^{-1}
$[Co(DPSO)_6](ClO_4)_2$	(21,050)^a			840	12,400
	18,600	13	$^4T_1(F) \longrightarrow {}^4T_1(P)$		
	14,900	5	$\longrightarrow {}^4A_2(F)$		
$[Ni(DPSO)_6](ClO_4)_2$	24,000	10.7	$^3A_2(F) \longrightarrow {}^3T_1(P)$	780	13,800
	(14,300)				
	13,000	5	$\longrightarrow {}^3T_1(F)$		
$[Cu(DPSO)_4](ClO_4)_2$	11,750^b	26.2	...	...	...

^{a} The parantheses designate a shoulder on the main peak of the spectrum. ^{b} The band is very broad. ε_{max}-values are given in lit. mole^{-1} cm^{-1}.

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Table IV. Infrared frequencies (in cm^{-1}) of DPSO, its complexes and probable assignments of the frequencies

DPSO	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	$PdCl_2.2DPSO$	Assignment
1475 m	1485 m	1485 m	1483 m	1485 m	1485 m	1485 m	1485 m	δ(C—H)
1445 s	1450 s	1450 s	1453 s	1452 s	1450 s	1450 s	1450 s	
1320 w			1315 w	1320 w		1315 w	1310 w	
1155 w	1150 w	1155 w	1153 w	1150 w	1150 w	1150 w	1152 w	
1090 vs	1100 vs, br	1097 vs, br	1100 vs, br	1095 vs, br	1093 vs, br	1095 vs, br	1093 vs	ν(Ph—S) + ν_3ClO_4*
1045 vs	998 vs	992 vs	990 vs	965 vs	995 vs	1050 vs	1050 vs	ν(S—O)
1028 m	1030 m	1028 m	1028 m	1030 m	1025 m	1028 m	1028 m	ρ(C—H)
1000 w	1015 w	1010 w	1008 w	1002 w	1000 w	1000 w	1005 w	
755 m	760 m	765 m	765 m	765 m	760 m	760 m	760 m	π(C—H)
740 s	745 s	745 s	748 s	750 s	742 m	740 s	740 s	
695 s	697 s	697 s	698 s	695 s	695 s	695 s	695 s	ν_{as}(C—S)
687 s	685 s	685 s	685 s	688 s	688 s	687 s	685 s	
	625 s	625 s	626 s	625 s	625 s	625 s		ν_4ClO_4
535 s	535 s	540 s	540 s	540 s	535 s	540 s	540 s	• • •
480 s	480 s	480 s	480 s	480 s	485 s	485 s	485 s	δ(S—O)
—	405 w	420 w	425 w	435 w	—	—	—	ν(M—O)

* In perchlorate complexes only. v = very, s = strong, m = medium, w = weak, ν = stretching, ν_{as} = asymmetric stretching, δ = in-plane deformation, π = out-of-plane deformation, ρ = in-plane rocking.

Infrared absorption frequencies of the ligand and the complexes in KBr pellets are given in Table IV, together with their probable assignments. Representative infrared spectra of oxygen- and sulphur-bonded complexes are given in Fig. 1.

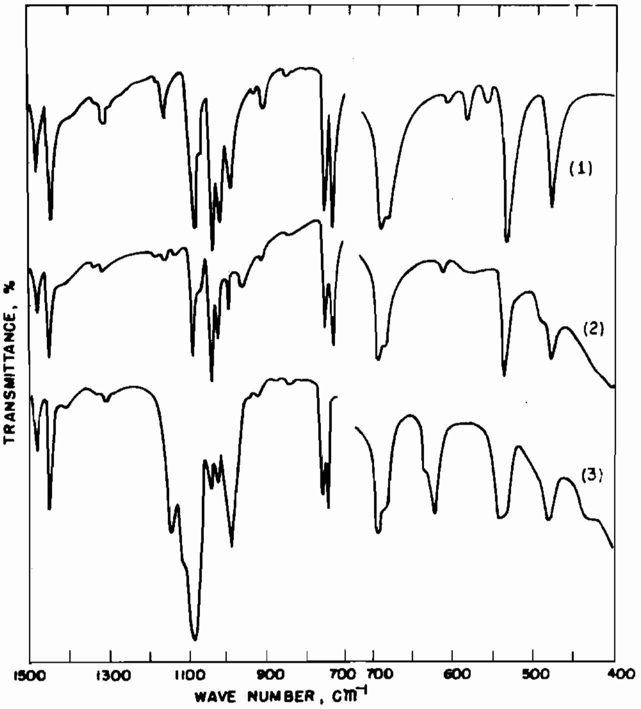

Figure 1. Infrared spectra of (1) DPSO (2) $PdCl_2$. 2 DPSO and (3) $[Co(DPSO)_6](ClO_4)_2$.

Like DMSO, DPSO has a pyramidal structure, the sulphur atom being at the apex of the pyramid.[16] Both sulphur and oxygen contain unshared pair of electrons. It can, therefore, form complexes by donation of a pair of electrons either from sulphur or from oxygen. In DMSO complexes, both the type of bonding have been found.[2,3] In this respect, it is of interest to compare the behaviour of DPSO complexes with that of DMSO complexes.

A strong band at 1045 cm^{-1} has been assigned to the S-O stretch of DPSO both in mull and in KBr pellet. This assignment is in agreement with that of Lappert and Smith.[4] In the perchlorate complexes of Mn, Co, Ni, Cu and Zn and in $ZnCl_2$. 2 DPSO, this band shifts to lower frequencies, showing the decrease of S-O bond order on complex formation through oxygen. However, in the complexes $Cd(DPSO)_6(ClO_4)_2$, $CdCl_2$.DPSO, $HgCl_2$. DPSO and $PdCl_2$. 2 DPSO, the S-O stretch occurs at 1045 - 1050 cm^{-1}, without undergoing any significant shift from the S-O stretch of the free ligand. This probably indicates that in these complexes the bonding occurs through sulphur of the sulphoxide. In the nitric acid adducts of DPSO and DMSO, Hadzi[17] found no shift in the S-O stretch of the former while in the latter a shift to higher frequency was observed. This behaviour was attributed to hydrogen bonding through sulphur in both the cases.

In the sulphur-bonded complexes of DMSO, a considerable increase in the S-O stretching frequency is observed and this is considered to be due to an increase in the S-O bond order on sulphur coordination.[1,3] However, the recently determined crystal structures of DMSO complexes by Bennett *et al.*[18] indicate that the S-O bond length (1.470±0.01Å) in the sulphur-bonded complex, $PdCl_2$. 2 DMSO, remains almost the same as the free DMSO (1.471±0.008 Å), whereas the S-O bond length in the oxygen-bonded complex, *trans*-$[FeCl_2(DMSO)_4](FeCl_4)$, is considerably larger than in the free DMSO. Accordingly, in the sulphur-bonded complexes, one should not observe any substantial change in the S-O stretch. The observed increase in DMSO complexes is attributed to the dynamical effect of attaching DMSO to heavy metal ions.[18] In the DPSO complexes, this effect is not expected to be significant because of the large size of the ligand.

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Further, the electron-withdrawing phenyl groups on the sulphur atom and the back-donation of the electron from the metal d-orbitals to the empty sulphur d-orbitals would leave the S-O bond order practically unchanged, resulting in almost no change in the S-O stretch of these complexes.

It may be worthwhile to note that those metal ions which are easily polarisable or having pronounced «b-character»,[19] like Cd(II), Hg(II) and Pd(II), form complexes with DPSO, through sulphur in preference to oxygen. It implies that back-donation from the metal d-orbitals to the vacant sulphur d-orbitals may be an essential feature for the sulphur-bonding in DPSO complexes. It may be pointed out that Cd(II) and Hg(II), although having b-character, form oxygen-bonded complexes with DMSO. This may be due to the electron donating tendency of the methyl groups attached to sulphur, resulting in a decrease in the back-donation from the metal to the sulphur. The increased tendency of DPSO to form sulphur-bonded complexes is perhaps associated with enhanced back-donation by the electron-withdrawing phenyl substituents on sulphur.

The strong band at 1095 cm^{-1} in DPSO and its complexes is assigned to phenyl-S stretching mode which interacts with a ring breathing vibration. From an infrared and Raman study of a large number of aromatic sulphur compounds, Ham *et al.*[20] concluded that the strong band around 1095 cm^{-1}, which is present in all aromatic sulphur compounds, is not due to inner vibrations of the benzene ring alone.

The occurrence of unsplit ν_3 and ν_4 bands of perchlorate around 1095 cm^{-1} (merged with Ph-S stretch) and 625 cm^{-1} respectively shows the ionic nature of the perchlorate in the complexes. A weak band in the region 400-435 cm^{-1} observed in the oxygen-bonded complexes is assigned to the metal-oxygen stretch. The variation in frequency of this band in transition metal complexes indicates that the strength of the metal-oxygen bond varies in the order Mn(II) < Co(II) < < Ni(II) < Cu(II). The same conclusion can be arrived at by comparing the decrease in the S-O stretching frequency of these complexes.

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