

NOTE

Infrared and Thermal Investigations of Dibenzyl Sulphoxide Complexes of Zinc(II) and Cadmium(II)†

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Dibenzyl sulphoxide (DBzSO) complexes of the formula $MX_2 \cdot 4DBzSO$ ($M = Zn$ or Cd ; $X = Cl, Br, I, NCS$ or CH_3COO) have been prepared and characterized by elemental analysis, molecular conductivity, molecular weight data and IR spectral measurements. TGA and DTA of the complexes were also studied.

Sulphoxides are an important class of ambidentate ligand capable of coordinating to metal ions through either sulphur or oxygen. In terms of Pearson's classification¹, sulphoxides may act as either hard bases (coordinating via oxygen) or as soft bases (coordinating via sulphur) and are thus potential ligands for the entire transitions, non-transitions and inner transition metal series. In the present note, we wish to report dibenzyl sulphoxide (DBzSO) complexes of zinc (II) and cadmium (II). Transition complexes of this ligand have already been reported¹⁻³.

The metal complexes were prepared by the following general method. An ethanolic solution of corresponding metal salt (0.01 mole in 45 ml) and a sufficient amount of dehydrating agent (2, 2'-dimethoxypropane) was refluxed with a solution of the ligand (0.04 mole) dissolved in ethanol (45 ml) on a steam bath for about 40 minutes. From the refluxate, the complexes separated gradually either on standing or on concentration and cooling at room temperature. The products were collected, washed with cold ethanol and finally with diethyl ether and dried in vacuo over P_4O_{10} . Elemental analysis and molecular weight determination of the complexes, of the type $MX_2 \cdot 4L$ ($M = Zn(II)$ or $Cd(II)$; $X = Cl, Br, I, NCS$ or CH_3OO and $L = DBzSO$). The compounds are soluble in common organic solvents. Molar conductance data ($3.2-6.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$) in nitrobenzene behave as non-electrolytes with the same molecular weight determination of the complexes. The magnetic movement of these complexes were measured at $300^\circ K$, the values lie in the range 2.3-3.7 B. M. These values are well within the range observed for the $Zn(II)$ and $Cd(II)$ complexes. All the complexes are diamagnetic (as expected for a d^{10} system):

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TABLE I
PERTINENT IR ABSORPTION FREQUENCIES (cm⁻¹) OF DBzSO AND ITS COMPLEXES WITH Zn(II) AND Cd(II)

Compound	Phenyl-S stretching	S=O stretching	Asym. C-S stretching	Sym. C-S stretching	$\nu(M-O)$	C-S-O deformation
DBzSO	1079 s	1032 vs	682 s	650 w	390 m	364 s, 328 s
ZnCl ₂ ·4DBzSO	1074 s	960 s	692 s	662 w	380 w	330 s, br
ZnBr ₂ ·4DBzSO	1072 s	962 s	702 sh	660 sh	402 w	322 m, br
ZnI ₂ ·4DBzSO	1070 s	966 m	698 s	668 w	390 w	320 w, br
Zn(NCS) ₂ ·4DBzSO	1072 s	964 s	690 s	670 w	400 m	332 m, br
Zn(CH ₃ COO) ₂ ·4DBzSO	1068 s	968 s	696 s	664 w	395 w	330 w
CdCl ₂ ·4DBzSO	1062 s	962 s	694 sh	668 w	392 w	334 w
CdBr ₂ ·4DBzSO	1066 s	964 s	704 s	666 sh	395 w	336 w, br
CdI ₂ ·4DBzSO	1064 m	968 m	698 s	664 w	400 w	322 w, br
Cd(NCS) ₂ ·4DBzSO	1068 s	966 s	706 s	662 w	405 w	326 s, br
Cd(CH ₃ COO) ₂ ·4DBzSO	1066 s	960 m	708 s	660 w	410 w	330 w, br

vs = very strong; s = strong; m = medium; w = weak; br = broad; sh = shoulder

In the IR spectra of DBzSO, two absorptions associated with S=O stretching frequency in free DBzSO appears as a strong absorption band at 1032 cm^{-1} and the other C-S stretching absorption at 682 cm^{-1} . In all the complexes are given in Table 1 studied here a significant negative shift of the S=O stretching frequency and a shift of the C-S stretching frequency towards a higher wave number indicative of the decrease in the double bond character of the S=O bond and an electron shift from the aryl group to the sulphur atom of the ligand. The data thus suggested coordinated from the oxygen atom of the DBzSO⁵. A very strong absorption attributed to phenyl-S stretching by previous workers⁶ has been identified at 1079 cm^{-1} in free DBzSO which did not suffer any significant change on complexation. It may be taken as an indication of the absence of coordination from the sulphur atom of the ligand. Several other absorptions, such as associated with C-H stretching, C-C stretching, ring deformation mode, C-H in-plane and out-of-plane deformation modes, appear at their usual positions. These have been identified in the spectra of the complexes and have been compared with the corresponding absorption in free ligand. The C-S-O symmetric and antisymmetric deformation modes appear in the spectrum of the free ligand at 364 and 328 cm^{-1} , respectively, which on complexation, in ever a distinct negative shift indicating electron donation from the oxygen atom. The IR spectra of the halo complexes closely resemble each other, while those of the thiocyanate and acetate complexes showed extra bands due to the corresponding anionic species.

All the TG and DT curves of these complexes indicate that they have no water of crystallization and are nonhygroscopic in nature. Between 180° and 240°C . The loss (44–39%) in halo, thiocyanate complexes occur. Finally at *ca.* 270°C , all the ligand molecules have been lost. The residue obtained at *ca.* 540°C to constant weight is very close to that expected for metal oxide (MO).

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REFERENCES

1. R. K. Agarwal, Pravesh Kumar and H. K. Rawat, *Thermochim. Acta*, **88**, 397 (1985).
2. R. K. Agarwal and Pravesh Kumar, *J. Indian Chem. Soc.*, **63**, 565 (1986).
3. R. K. Agarwal and G. Singh, *J. Indian Chem. Soc.*, **63**, 926 (1986).
4. A. Symal and B. K. Gupta, *J. Indian Chem. Soc.*, **58**, 513 (1981).
5. F. A. Cotton, R. Francis and W. D. Horrocks, *J. Phys. Chem.*, **64**, 1534 (1960).
6. R. M. Silverstein and G. C. Basslar, *Spectrometric Identification of Organic Compounds*, John Wiley, New York, 2nd Ed. (1967).

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