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Diphenyl Sulphoxide Complexes of Lanthanide and Yttrium Perchlorates

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Diphenyl sulphoxide complexes of nine lanthanide perchlorates of the general composition $[Ln(DPSO)_6](ClO_4)_3$ where Ln=La, Ce, Pr, Nd, Sm, Gd, Ho and Yb and Y have been synthesised and characterized. Infrared studies indicate coordination through the oxygen atom of the ligand and the retention of the Td symmetry of the perchlorate group. The molar conductance and cryoscopic studies suggest a coordination number of six for the metal ions. Cryoscopic studies in DMSO indicate that DMSO is a better donor than DPSO. DTA and UV data are also presented.

The number of complexes of diphenyl sulphoxide (DPSO) reported in the literature is meagre compared with that of its alkyl analogue *viz.*, dimethyl sulphoxide (DMSO). Apart from the hydrogen-bonding[1,2] and the charge-transfer[3,4] studies involving complexes of DPSO in solution, the solid isolable complexes reported include the Lewis adducts with CdI_2,[5] BCl_3, tin halides,[6] BF_3, antimony halides,[7] Re_3Cl_9[8] and UCl_4,[9] the oxyhalide adducts of Nb and Ta[10]; and some transition and non-transition metal compounds.[11] An attempt to prepare $Hg(ClO_4)_2$ complex failed.[12] We have previously reported the DMSO complexes of some lanthanides.[13,14] It was of interest to investigate the DPSO complexes for two reasons: (i) due to its greater bulk than DMSO, DPSO can restrict the coordination number of the metal ion and (ii) DPSO may present a crystal field different from DMSO on account of the conjugation of its phenyl rings with the sulphoxide group. The present paper describes the isolation and characterization of nine new complexes of DPSO with lanthanide and yttrium perchlorates and the structural studies on them. The perchlorate salts were chosen due to their low anionic contribution to complexation.

Experimental

Materials. DPSO was prepared by the reaction of $SOCl_2$ with dry benzene in presence of anhydrous $AlCl_3$, as described by Shriner, Struck and Jorison.[15] The product was recrystallized from petroleum ether. Mp 71°C.

The hydrated lanthanide perchlorates were prepared from the respective oxides (Lindsey Chemical Co., U. S. A.) by treatment with aqueous perchloric acid (E. Merck).

The solvents, dimethyl formamide (DMF), nitrobenzene, nitromethane and acetonitrile were purified by standard methods.[16] DMSO was dried over CaO and fractionated under reduced pressure.

Preparation of the Complexes. All the complexes were prepared by the following general method. A solution of about 2.3 g of DPSO in 5 m*l* of dry methanol was added dropwise with stirring, to a solution of 1 g of the hydrated metal perchlorate in about 5 m*l* of methanol. The complex precipitated as fine crystals. It was filtered, washed with 2 m*l* of ice-cold methanol and then repeatedly shaken with small amounts of dry CCl_4. The product was filtered and dried in vacuum over P_2O_5 at room temperature. In some cases the complexes were recrystallized from acetonitrile.

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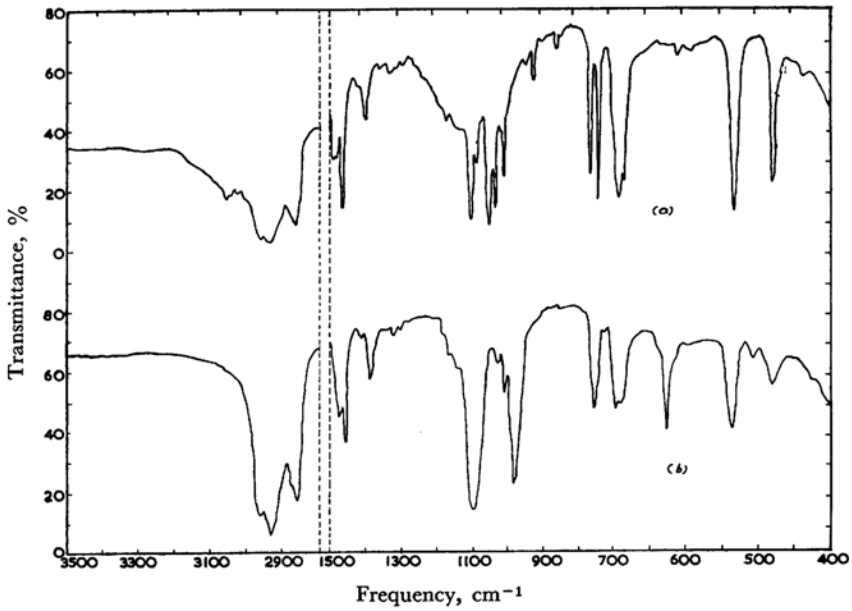

Fig. 1. Infrared spectra of (a) DPSO and (b) $Pr(DPSO)_6(ClO_4)_3$ in Nujol mull.

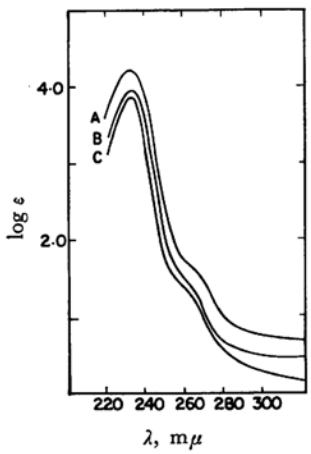

Fig. 2. UV spectra of DPSO (A) and its Pr (B) and Yb (C) complexes in CH_3CN.

Analyses. In the case of the lighter lanthanide complexes, the metal was estimated gravimetrically by the oxalate-oxide method. Y, Ho and Yb were estimated volumetrically by EDTA tritrations using xylenol orange as the indicator.[17] Perchlorate was estimated by the Kurz method.[18] Micro analyses of C, H and S were carried out for some representative complexes through the courtesy of the CIBA Research centre, Bombay. The analytical results along with some physical data are listed in Table 1.

Instrumentation. *Thermal Studies.* Owing to the explosive nature of the complexes, the differential thermal analysis (DTA) was carried out by diluting the complexes with alumina (~1 : 10 by weight). The apparatus employed was of a manual type provided with chromel-alumel thermocouples. The heating rate was 8°±1°C/min. The decomposition temperature is characterized by a sharp exotherm in the DTA profile. The DTA curves for three representative complexes are presented in Fig. 3.

Spectral Studies. The IR spectra of the complexes and of pure DPSO were measured in Nujol mulls in the region 4000—400 cm^{-1} employing Carl Zeiss UR-10 spectrophotometer. Spectral data for a typical case are presented in Table 2. The UV spectra were taken with a Beckman DB-10 recording spectrophotometer. Acetonitrile was used as the solvent and the concentration of the solutions was 10^{-5} M (*vide* Fig. 2).

Conductometric Measurements. The molar conductances of the complexes in various solvents were determined at 30°C in a Siemen's conductivity bridge with an immersion cell (Type LTA), previously calibrated with standard KCl solutions. It had a cell constant of 0.665. The data are given in Table 3.

Molecular Weight Data. These were obtained in nitrobenzene and DMSO using a crysocopic apparatus fitted with a Beckmann thermometer and a mercury-seal stirrer to exclude moistrure. The data are listed in Table 3.

Properties of the Complexes. In contrast to the high deliquescent nature of the lanthanide perchlorates, the complexes are non-hygroscopic. They are insoluble in solvents like CCl_4 and C_6H_6 but are appreciably soluble in acetone, acetonitrile, methanol, nitrobenzene, nitromethane, DMF and DMSO. In water they decompose to precipitate the insoluble ligand part. The colours of the complexes closely resemble those of their parent salts but are less in intensity. Some of the complexes under conditions of continuous evacuation over P_2O_5 develop a brown colour. Many of the physical and chemical data for all the complexes are very similar.

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18) E. Kurz, G. Kober and M. Berl, *Anal. Chem.*, **30**, 1983 (1958).

TABLE 1. PHYSICAL AND

Sl. No.	Complex	Colour	Melting point °C	% Metal Found	% Metal Cald
1	$La(DPSO)_6(ClO_4)_3$	white	171	8.38	8.43
2	$Ce(DPSO)_6(ClO_4)_3$	white	172—175	8.41	8.49
3	$Pr(DPSO)_6(ClO_4)_3$	pale green	173—177	8.58	8.53
4	$Nd(DPSO)_6(ClO_4)_3$	pale pink	154—158	8.61	8.72
5	$Sm(DPSO)_6(ClO_4)_3$	pale yellow	196—201	8.92	9.05
6	$Gd(DPSO)_6(ClO_4)_3$	white	177	9.36	9.43
7	$Y(DPSO)_6(ClO_4)_3$	white	156—160	5.66	5.56
8	$Ho(DPSO)_6(ClO_4)_3$	pale yellow	140—145	9.92	9.85
9	$Yb(DPSO)_6(ClO_4)_3$	white	168	10.39	10.28

TABLE 2. INFRARED DATA FOR DPSO AND ITS LANTHANIDE COMPLEXES

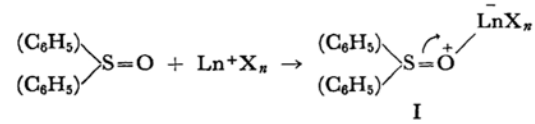
DPSO cm^{-1}	Complex	Assignment
3058 kink	3058 kink	C-H stretch (A_1)
1589 w	1590 w	C-C stretch (A_1)
1472 m	1470 m	C-C stretch (A_1)
1450 s	1454 s	C-C stretch (B_1)
1320 w	1320 w	C-C stretch (B_1)
1162 w, sh	1170 w, sh	C-H def. (A_1)
1092 vs	1090—1105 vs, bd	Mass dependent (A_1) and ν_3 ClO_4
1078 sh	—	C-H def. (B_1)
1043 vs	982 vs	S-O stretch
1028 s	1028 m	C-H def. (A_1)
1000 m	1004 m	Ring def. (A_1)
920 w	925 w, bd	C-H def. (B_1)
760 s	762 m	C-H def. (B_2)
740 s	750 s	—
696 s	695 m	Ring def. (B_2)
684 s	688 m	C-S stretch
—	625 m	ν_4ClO_4
538 s	535 s	—
—	508 w	—
480 s	482 m	Out of plane ring def.
438 w, bd	425 w	—

Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder and bd, broad
Note: The spectra of the different complexes (in Mulls) are quite similar (within $\pm 2\ cm^{-1}$). Except for the perchlorate bands the other assignments are based on the work of Lappert and Smith.[6]

Discussion

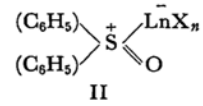
Single-crystal studies on diphenyl sulphoxide[19] have confirmed a pyramidal arrangement of the three bonds about the sulphur atom. With a semipolar S→O linkage and with unshared pairs of electrons on both S and O, it is possible that DPSO can form complexes with metal ions either through O or S atom. Hence it is of interest to determine the site of coordination.

Infrared studies of the complexes (Table 2 and Fig. 1) indicate that the DPSO molecules are bonded through their oxygen atom. This is evidenced by a considerable decrease in the S–O stretching frequency in the complexes ($\sim 60\ cm^{-1}$) compared to that in the free ligand. Such an inference stems from a consideration of the following structures for the complexes, where I represents O bonding and II, S bonding.



I

or



II

Ln is the lanthanide metal ion and X is the anion.

The S–O bond in the sulphoxide may be regarded as substantially, a double bond, with p_π-d_π $(\overset{-}{S}\text{–}\overset{+}{O})$ bonding from oxygen to sulphur, superimposed on the SO σ bond $(\overset{+}{S}\text{–}\overset{-}{O})$. Structure I implies a lengthening of the S–O bond accompanied by a decrease in the p_π-d_π back bonding in the complexes compared with the free ligand. Hence a decrease in S–O stretching frequency would be expected. On the other hand structure II requires an increase in the S–O stretching fundamental. Also the fact that the sulphoxide shift is nearly the same for all the lanthanide complexes studied, indicates that they all have nearly the same stability.

The unsplit IR band at 1096 (vs, bd) and the one at 625 (m) cm^{-1} suggest that the Td symmetry of the ionic perchlorate[20] is retained in the complexes. (Fig. 1)

Molar conductance data in solvents of different

19) S. C. Abrahams, *Acta Cryst.*, **10**, 417 (1957).

20) S. D. Ross, *Spectrochim. Acta*, **18**, 225 (1962).

ANALYTICAL DATA

% Perchlorate		% C		% H		% S	
Found	Cald	Found	Cald	Found	Cald	Found	Cald
18.21	18.09	52.21	52.44	3.97	3.64	11.51	11.64
18.17	18.08	—	—	—	—	—	—
18.18	18.07	—	—	—	—	—	—
18.14	18.03	—	—	—	—	—	—
17.86	17.97	—	—	—	—	—	—
17.84	17.88	51.62	51.84	3.91	3.60	11.34	11.51
18.82	18.66	—	—	—	—	—	—
17.95	17.81	—	—	—	—	—	—
17.87	17.73	51.06	51.39	3.76	3.57	11.26	11.41

TABLE 3. CONDUCTANCE AND CRYOSCOPIC DATA

Complex	Molar conductance Λ, $ohm^{-1} cm^2 mol^{-1}$			Molecular weight		Calcd. molecular weight	No. of species	
	NM	NB	DMSO	NB	DMSO		NB	DMSO
La	211.2	68.86	108.1	427.2	161.2	1649	3.86	10.23
Ce	213.7	—	107.2	441.2	160.5	1650	3.74	10.28
Pr	206.2	68.42	103.6	432.2	158.1	1651	3.82	10.44
Nd	—	72.10	103.1	446.1	162.5	1655	3.71	10.19
Sm	—	71.62	—	453.8	168.5	1661	3.66	9.86
Gd	214.7	70.59	—	—	163.2	1668	—	10.22
Y	213.2	69.85	104.6	412.2	155.2	1599	3.88	10.39
Ho	214.4	—	104.1	—	162.5	1675	—	10.31
Yb	217.6	70.24	103.7	439.3	166.0	1683	3.84	10.14

Note: 10^{-3} M solutions were used for conductance measurements. Λ for 1 : 1 electrolytes in nitromethane (NM),[21] nitrobenzene (NB)[21] and DMSO[22] lie in the range 70—100, 20—30 and ~40 mhos $cm^2 mol^{-1}$ respectively.

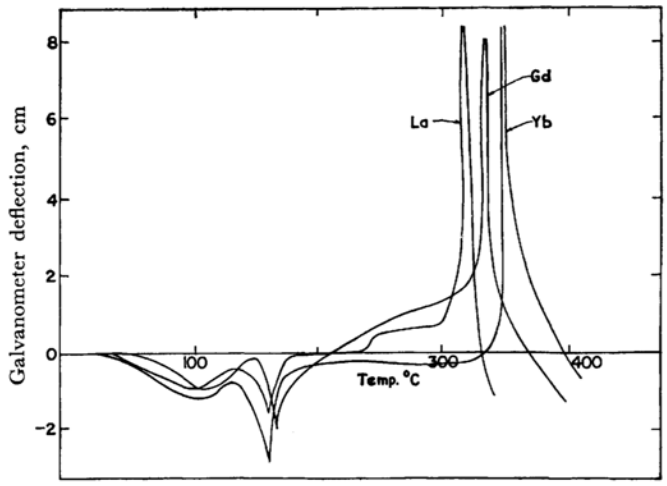


Fig. 3. DTA studies.

donor strengths such as nitromethane, nitrobenzene, acetonitrile and DMSO reveal a uni-trivalent structure for the complexes (see Table 3). Cryoscopic studies in nitrobenzene, a solvent of poor donor properties, show the presence of four species only, suggesting that the DPSO molecules bonded to the metal are not dissociated in solution. In accordance with these observations the complexes

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22) P. G. Sears, G. R. Lester and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956).

can be formulated as $[Ln(DPSO)_6]^{3+}$ $3(ClO_4)^-$, giving a coordination number six for the metal.

However, molecular weight studies of the complexes in DMSO show the presence of ten species, indicating that all the DPSO molecules are displaced from the coordination sphere by the solvent molecules. This implies that of the two ligands DMSO and DPSO, the former is a more powerful donor than the latter with respect to the lanthanide ions. This is probably a consequence of conjugation between the aromatic rings and the sulphoxide group. Hydrogen bonding[1,2] and charge-transfer[4] studies of some complexes of these ligands in solution, have also revealed a similar order of donor strengths for the two ligands.

The UV spectrum of DPSO in acetonitrile exhibits two maxima, one at 228mμ(log ε=4.2) and the other at 265mμ(inflection) (see Fig. 2). Presumably, the former band is attributable to the absorption arising from the S–O group and the latter to the benzanoid chromophore. In the spectra of the complexes there is no significant shift in the position of either band. In the visible region the complexes were transparent throughout. The limited solubility of the complexes in suitable solvents restricted work on this line.

The DTA studies suggest that the complexes have nearly the same thermal stability. The decomposition temperatures for the different complexes, characterized by sharp exothermic peaks, lie in a close range (315—360°C) (Fig. 3). The small endothermic peak at ~100°C represents the exclusion of any absorbed moisture and the one at 160—190°C represents the melting point of the complexes. The Yb complex heated separately at 350°C, on infrared analysis showed the absence of any perchlorate ion or DPSO.

The physical data, thus suggest a coordination number of six for the lanthanides and yttrium. In many DMSO complexes of the lanthanides[13,14,23] the coordination number has been shown to be eight. Thisreduction in the coordination capacity of the metal ions in the DPSO complexes is presumably due to steric factors.

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23) V. N. Krishnamurthy and S. Soundararajan, *J. Inorg. Nucl. Chem.*, **29**, 517 (1967).