

Synthesis and Characterisation of Dibenzyl Sulphoxide Adducts with Lanthanide(III) Bromide and Nitrate

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THE paper reports the isolation and characterisation of dibenzyl sulphoxide adducts with lanthanide(III) bromides and nitrates: $LnX_n \cdot nDBzSO$, when $Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho$ or Yb ; $X = Br$, $n = 5$; $X = NO_2$, $n = 4$, on the basis of chemical analysis, conductance, molecular weight, magnetic moment, thermal, infrared and electronic spectral data.

Experimental

Dibenzyl sulphoxide (E. Merck), lanthanide nitrates (99.9%) and lanthanide oxides (Rare Earth Products Ltd., India) were used as such. The lanthanide bromides were prepared from lanthanide oxides and hydrobromic acid.

$Ln(DBzSO)_5Br_3$: The complexes were prepared as solids refluxing methanolic solutions of ligand

(DBzSO) and metal salt (5:1) for ~0.5 h on a water-bath. The complex $Ln(DBzSO)_5Br_3$ precipitated on cooling was filtered, washed with methanol and anhydrous diethyl ether and dried over P_2O_5 in vacuum desiccator (~67%).

$Ln(DBzSO)_4(NO_2)_2$: Hydrated lanthanide nitrate (0.5 mmol) in methanol (20 ml) was mixed with excess of ligand (2.5 mmol) in methanol (50 ml) and heated on a steam-bath with constant stirring. The resulting solid was stirred with benzene (10 ml), filtered off, washed with benzene and diethyl ether and dried as above (~70%).

The analytical and physical methods used were the same as described earlier^{1,2}.

Results and Discussion

Analytical data (Table 1) corresponds to the general formula of the complexes as $[Ln(DBzSO)_nX_n]$ ($n = 5, X = Br$; $n = 4, X = NO_2$; $Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho$ or Yb) (Table 1). All the complexes are non-hygroscopic having sharp melting point. The electrical conductance values in nitrobenzene suggest their non-electrolytic nature. The molecular weights determined by cryoscopy in freezing nitrobenzene suggest monomeric species.

TABLE I—ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Compd.	Analysis % : Found/(Calcd.)			Average Mol. wt. (Formula wt.)	Λ_M $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	μ_{eff} B.M.
	Metal	S	Anion			
$LaBr_3 \cdot 5DBzSO$	8.92 (9.09)	10.32 (10.46)	15.43 (15.69)	1521 (1529)	4.3	Diamag.
$PrBr_3 \cdot 5DBzSO$	9.11 (9.20)	10.90 (10.45)	15.45 (15.67)	1522 (1531)	4.6	3.57
$NdBr_3 \cdot 5DBzSO$	9.22 (9.38)	10.98 (10.43)	15.40 (15.64)	1524 (1534)	4.2	3.49
$SmBr_3 \cdot 5DBzSO$	9.60 (9.74)	10.25 (10.38)	15.39 (15.58)	1531 (1540)	3.9	1.57
$GdBr_3 \cdot 5DBzSO$	10.02 (10.14)	10.20 (10.34)	15.32 (15.51)	1535 (1547)	4.2	7.87
$TbBr_3 \cdot 5DBzSO$	10.11 (10.26)	10.20 (10.32)	15.30 (15.49)	1537 (1549)	4.7	9.22
$DyBr_3 \cdot 5DBzSO$	10.32 (10.46)	10.17 (10.30)	15.27 (15.45)	1542 (1552.5)	2.9	10.62
$HoBr_3 \cdot 5DBzSO$	10.47 (10.61)	10.14 (10.28)	15.24 (15.43)	1545 (1555)	3.7	10.25
$YbBr_3 \cdot 5DBzSO$	10.92 (11.06)	10.12 (10.28)	—	1552 (1563)	4.2	4.52
$La(NO_2)_4 \cdot 4DBzSO$	10.93 (11.16)	10.08 (10.28)	—	1238 (1245)	3.9	Diamag.
$Pr(NO_2)_4 \cdot 4DBzSO$	11.13 (11.30)	10.07 (10.26)	—	1241 (1247)	3.6	3.60
$Nd(NO_2)_4 \cdot 4DBzSO$	11.39 (11.52)	10.05 (10.21)	—	1243 (1250)	4.3	3.51
$Sm(NO_2)_4 \cdot 4DBzSO$	11.78 (11.94)	10.00 (10.19)	—	1249 (1256)	4.1	1.59
$Gd(NO_2)_4 \cdot 4DBzSO$	12.26 (12.43)	9.98 (10.13)	—	1256 (1263)	4.6	7.81
$Tb(NO_2)_4 \cdot 4DBzSO$	12.33 (12.56)	9.96 (10.11)	—	1258 (1265)	4.5	9.15
$Dy(NO_2)_4 \cdot 4DBzSO$	12.58 (12.81)	9.90 (10.09)	—	1261 (1268.5)	3.9	10.51
$Ho(NO_2)_4 \cdot 4DBzSO$	12.72 (12.98)	9.87 (10.07)	—	1264 (1271)	3.7	10.26
$Yb(NO_2)_4 \cdot 4DBzSO$	13.93 (13.52)	9.82 (10.00)	—	1273 (1279)	3.8	4.50

The La^{III} complexes are as usual diamagnetic, while all other lanthanum complexes are paramagnetic. The comparison of these observed values with those observed for 8-hydrated sulphates⁸ and those calculated for uncomplexed ion⁴, indicates that the 4f-electrons do not participate in bonding in these complexes.

The S=O stretching frequency in the ir spectra of free DBzSO appears as a strong band^{5,6} at 1 032 cm⁻¹, while it shifted to 965–950 cm⁻¹ in the spectra of its complexes, generally appearing as a very strong broad band. The ν_{C-S} band of free DBzSO appearing at 682 cm⁻¹ undergoes a slight positive shift on complexation. A negative shift of $\nu_{S=O}$ and a positive shift of the ν_{C-S} are 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 suggest coordination through the oxygen atom to the ligand. A very strong absorption attributed to phenyl-S stretch by previous workers⁷ has been identified at 1 079 cm⁻¹ in free DBzSO which does not undergo any significant change on complexation. It may be taken as an indication of the absence of coordination from the sulphur atom of the ligand. The ν_{Ln-O} band appeared in the region 400–360 cm⁻¹.

In the nitrate complexes, the occurrence of two strong bands at 1 525–1 510 and 1 310–1 290 cm⁻¹ region is attributed to ν_4 and ν_1 modes of the vibration of covalently bonded nitrate group, respectively, suggesting that the nitrate groups lie inside the coordination sphere^{9,10}. The nature of binding of the nitrate group can be predicted by examining^{10,11} the combination bands in the region 1 800–1 700 cm⁻¹. A separation of 55–30 cm⁻¹ in the combination bands suggests a bidentate nitrate coordination.

The thermal studies reveal that the complexes start losing mass (above 200°) with partial loss of the DBzSO ligand. A loss of 49.18–50.26% is observed in the range 200–320°, corresponding to the loss of 2.7 moles of the ligand. A further loss of 73.12–74.36% correspond to the complete loss of the ligand molecules. The residue obtained at about 780° corresponds to Ln₂O₃.

In the bromide complexes the lanthanide ions are linked by three Br⁻ ions and five oxygen atoms of DBzSO, resulting in eight-coordination. The NO₃⁻ groups are bidentate in the nitrate complexes, Ln(NO₃)₃·4DBzSO. Linking of Ln^{III} with 6 nitrate oxygen and 4 DBzSO oxygen results ten-coordination of lanthanum(III) in these complexes.

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Studies on Samarium(III) Complexes with some Substituted-dibenzoylmethanes at 0.1 M Ionic Strength and Apparent Molar Volume of 2'-Hydroxy-3,4-benzo-4-nitrodibenzoylmethane in Mixed Solvents

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THE formation constants of La^{III}, Ce^{III}, Pr^{III}, Nd^{III} and Sm^{III} chelates with substituted sulphonic acids in aqueous medium have been studied by Narwade¹. Sherry *et al.*² investigated the lanthanide complexes with carboxylic acids. Ramamoorthy and Manning studied exhaustively the mixed ligand chelates of mesoditartaric acid with divalent and trivalent metals³. Darnall and Birnbaum⁴ showed that a lanthanide ion could substitute for calcium ion and produce an active enzyme system⁴. The present work is aimed to investigate the complexing ability of 2'-hydroxy-3,4-benzodibenzoylmethane, 2'-hydroxy-3,4-benzo-4-methoxydibenzoylmethane and 2'-hydroxy-3,4-benzo-4-nitrodibenzoylmethane with samarium(III) ion. Millerio *et al.*⁵ determined solvation numbers for amino acids in aqueous solutions and in some cases in pure methanol and ethanol⁵. We have also undertaken a study of the apparent molar volume of 2'-hydroxy-3,4-benzo-4-nitrodibenzoylmethane (1.1×10^{-3} M) in different dioxane-water mixtures.