

## DIMETHYL SULPHOXIDE COMPLEXES OF RARE-EARTH BROMIDES

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## ABSTRACT

Dimethyl sulphoxide (DMSO) complexes of six rare-earth bromides of the composition  $M(\text{DMSO})_8\text{Br}_3$  where  $M = \text{La, Pr, Nd, Sm, Ho and Y}$  have been prepared and characterized. Infrared studies of the complexes indicate that dimethyl sulphoxide coordinates to metal through oxygen. Conductivity data show a coordination number of ten for all rare-earths. The relative effect of halide ions on the coordination number of the rare-earth ions is discussed.

## INTRODUCTION

**D**IMETHYL sulphoxide complexes of rare-earth chlorides<sup>1</sup>, nitrates<sup>2</sup> and perchlorates<sup>3</sup> have been reported from this laboratory. In all these cases a coordination number of eight for the lighter lanthanides and seven for the heavier lanthanides and yttrium has been suggested from the conductance data. But from the crystal and molecular structure studies of dimethyl sulphoxide complexes of lanthanum nitrate<sup>4</sup> and ytterbium nitrate<sup>5</sup>, it has been shown that the coordination numbers for lanthanum and ytterbium should be ten and nine respectively. Recently rare-earth iodide complexes of dimethyl sulphoxide have been prepared and characterized in this laboratory<sup>6</sup>. A coordination number of nine for all the rare-earths has been suggested in these complexes from the conductivity data. So far very little work has been carried out on the effect of the bromide ion on the coordination number of the rare-earths. In the present paper, for the first time, the isolation and characterization of rare-earth bromide complexes with dimethyl sulphoxide are described.

## EXPERIMENTAL

**Materials.**—The hydrated rare-earth bromides were prepared from pure (99.9%) rare-earth oxides and hydrobromic acid.

Water white DMSO (Crown Zellerbach Co., U.S.A.) was used for the preparation of the complexes.

The commercial dimethylformamide (DMF) was shaken with KOH pellets for two hours and distilled under reduced pressure. The middle fraction distilling at 70° C at 10 mm pressure was collected and its specific conductance was  $9.1 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$  at 30° C.

Acetonitrile was purified by the standard method<sup>7</sup>. Its specific conductance was  $2.63 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

**Preparation of the Complexes.**—One gm. of the hydrated bromide was dissolved in 2 ml of DMSO and the excess of the ligand was removed under reduced pressure. The solid crystalline product

was washed with dry benzene to free it from DMSO and dried.

**Analyses.**—The complexes were analysed for their metal, bromide and DMSO parts. The metal content was estimated by EDTA titrations using xylenol orange as the indicator<sup>8</sup>. The bromide was estimated by Volhard's method and the DMSO by oxidation with excess of permanganate<sup>9</sup>. Since bromide is also oxidised by permanganate, it was removed as silver bromide by adding silver nitrate.

**Infrared Spectra.**—The infrared spectra of the complexes were taken in both nujol mulls and KBr pellets employing a Carl Zeiss UR-10 infrared spectrophotometer. The mull and KBr pellet spectra of the complexes were almost identical. The important absorption bands in the region 3600–600  $\text{cm}^{-1}$  and their assignments, similar to those given for other lanthanide-DMSO complexes, are presented in Table II.

**Conductivity Measurements.**—The molar conductances of the complexes in acetonitrile, dimethylformamide and water were determined with a Siemen's conductivity bridge using an immersion cell (Cell constant 0.665). The concentration of the solutions was ca. 0.001 M.

**Molecular Weight Measurements.**—The molecular weights for some representative complexes in water were determined by the freezing point depression method. However, molecular weight measurements could not be carried out in organic solvents because of their poor solubility in suitable solvents. Molecular weight and conductance data are presented in Table III.

## RESULTS AND DISCUSSION

Analytical results (Table I) show that the complexes have the formula  $M(\text{DMSO})_8\text{Br}_3$  where  $M = \text{rare-earth metal}$ . Unlike the corresponding perchlorate complexes, the metal: ligand ratio is eight for all the lanthanides and yttrium. However, the composition is similar to that of the iodide complexes.

The complexes are very hygroscopic, insoluble in non-polar solvents and acetone, and soluble in

TABLE I  
Analytical data for the complexes

| Compound                               | Metal (%) |       | Bromide (%) |       | DMSO (%) |       |
|--|-----------|-------|-------------|-------|----------|-------|
|  | calc.     | found | calc.       | found | calc.    | found |
| La (DMSO) <sub>8</sub> Br <sub>3</sub> | 13.87     | 13.74 | 23.93       | 23.89 | 62.23    | 62.05 |
| Pr (DMSO) <sub>8</sub> Br <sub>3</sub> | 14.03     | 14.04 | 23.84       | 23.58 | 62.10    | 62.50 |
| Nd (DMSO) <sub>8</sub> Br <sub>3</sub> | 14.32     | 14.42 | 23.82       | 23.43 | 61.93    | 61.65 |
| Sm (DMSO) <sub>8</sub> Br <sub>3</sub> | 14.84     | 14.77 | 23.67       | 23.39 | 61.58    | 61.16 |
| Ho (DMSO) <sub>8</sub> Br <sub>3</sub> | 16.03     | 16.05 | 23.31       | 23.20 | 60.66    | 60.53 |
| Y (DMSO) <sub>8</sub> Br <sub>3</sub>  | 9.43      | 9.42  | 24.33       | 24.22 | 66.24    | 65.95 |

TABLE II  
The principal absorption bands in the I.R. spectra of DMSO and its rare-earth bromide complexes (in cm<sup>-1</sup>)

|  | S = O stretch | CH <sub>3</sub> -rocking | Asym C—S stretch |
|--|---------------|--------------------------|------------------|
| DMSO*                                  | 1042 vs       | 962 s<br>905 w           | 695 m            |
| La (DMSO) <sub>8</sub> Br <sub>3</sub> | 1016 vs       | 966 s<br>914 w           | 720 m            |
| Pr (DMSO) <sub>8</sub> Br <sub>3</sub> | 1016 vs       | 964 s<br>909 w           | 718 m            |
| Nd (DMSO) <sub>8</sub> Br <sub>3</sub> | 1016 vs       | 966 s<br>910 w           | 718 m            |
| Sm (DMSO) <sub>8</sub> Br <sub>3</sub> | 1018 vs       | 964 s<br>912 w           | 720 m            |
| Ho (DMSO) <sub>8</sub> Br <sub>3</sub> | 1015 vs       | 965 s<br>916 w           | 720 m            |
| Y (DMSO) <sub>8</sub> Br <sub>3</sub>  | 1012 vs       | 964 s<br>914 w           | 718 m            |

\* Spectrum of DMSO was taken in the liquid phase. Spectra of the complexes taken in nujol mulls are presented.

Abbreviations: vs = very strong; s = strong; m = medium; w = weak.

polar solvents. The colours of the complexes are similar to those of the corresponding salts.

The molar conductances of the complexes in water and DMF are in good agreement with those reported for 1:3 and 1:2 electrolytes respectively<sup>10,11</sup>. The molar conductances in acetonitrile however, show that the complexes behave as 1:1 electrolytes<sup>11</sup> which suggest the possibility of two of the bromide ions being coordinated to the rare-earth ions. Thus a coordination number of ten can be postulated for all the rare-earth ions. This is the only example where a coordination number of

ten is suggested for a heavier lanthanide and yttrium in DMSO complexes, whereas for lighter lanthanides and coordination number of 10 has been postulated in rare-earth nitrate-DMSO complexes from crystal structure studies<sup>4</sup>.

The molecular weight data for the complexes in water show the presence of twelve species thereby suggesting the complete dissociation of the complexes in water.

The infrared spectra of all the complexes are similar showing no significant dependence on the central metal ion. The intense band occurring at



TABLE III  
Conductance and molecular weight data

| Compound                               | Molar conductance<br>(ohm <sup>-1</sup> cm <sup>2</sup> mole <sup>-1</sup> ) in |       |                    | Molecular weight in water |       |                |
|--|---|-------|--------------------|---------------------------|-------|----------------|
|  | Water   | DMF   | CH <sub>3</sub> CN | obtd.                     | calc. | No. of species |
| La (DMSO) <sub>8</sub> Br <sub>3</sub> | ..  | 159.7 | 91.88              | ..                        | ..    | ..             |
| Pr (DMSO) <sub>8</sub> Br <sub>3</sub> | 400.2   | 160.6 | 95.00              | 80.83                     | 1005  | 12             |
| Nd (DMSO) <sub>8</sub> Br <sub>3</sub> | 410.0   | 167.5 | 99.33              | ..                        | ..    | ..             |
| Sm (DMSO) <sub>8</sub> Br <sub>3</sub> | 403.4   | 163.6 | 94.71              | 84.14                     | 1014  | 12             |
| Ho (DMSO) <sub>8</sub> Br <sub>3</sub> | 411.4   | 164.1 | 96.00              | 84.76                     | 1029  | 12             |
| Y (DMSO) <sub>8</sub> Br <sub>3</sub>  | ..  | 164.7 | 92.94              | ..                        | ..    | ..             |

1045 cm<sup>-1</sup> attributable to the S=O stretch<sup>12</sup> in free DMSO shifts to about 1016 cm<sup>-1</sup> in the complexes, demonstrating the involvement of oxygen in the coordination. An enhancement in the C-S stretching fundamental (from 695 cm<sup>-1</sup> to about 718 cm<sup>-1</sup>) further confirms the oxygen coordination<sup>1</sup>. Absence of a band at 1045 cm<sup>-1</sup> indicates that no occluded or lattice held ligand is present in the complexes.

The extent of S=O shift, which is a measure of the metal-oxygen bond strength in the complexes, is less in bromide complexes (ca. 30 cm<sup>-1</sup>) than in the corresponding rare-earth perchlorate complexes of DMSO (ca. 50 cm<sup>-1</sup>)<sup>3</sup>. These shifts in the rare-earth chloride, bromide and iodide complexes (ca. 35, 30 and 25 cm<sup>-1</sup>) indicate that the metal-oxygen bond strength decreases as we go from chloride to iodide complexes. From the data obtained, the rare-earth bromide-DMSO complexes may be represented as [M(DMSO)<sub>8</sub>Br<sub>2</sub>]Br.

As pointed out in literature<sup>13</sup>, the number of ligands coordinated to the metal ion is dependent upon the anion in the complex. In the case of rare-earth chloride-DMSO complexes the maximum number of ligands coordinated to the metal ion is four, while in the case of the bromide complexes it is eight. In the rare-earth iodide complexes, however, the number of DMSO molecules coordinated to the metal ion remains eight as in the case of bromide complexes.

For the lanthanide ions, the coordination affinities of halide ions lie in the sequence F  $\gg$  Cl > Br > I<sup>14</sup>. Hence it is to be expected that rare-earths will add on more number of ligands in bromide complexes than in chloride ones. However, in the case of iodide complexes the number of ligands coordinated

to the metal ion is not further enhanced, probably due to the large ionic size of iodide ion. The interesting feature of the bromide complexes is that the lanthanides have a higher coordination number, as the number of anions coordinated to the metal ion is two (compared to one in the case of the iodide complexes) and the number of ligands coordinated is also the maximum.

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