

COORDINATION COMPOUNDS OF RARE EARTHS WITH  $Q_nX \rightarrow O$  TYPE LIGANDS  
 (X=N, P, As, S)

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**Abstract** — An increasing number of complexes formed by rare earths with  $Q_nX \rightarrow O$  type ligands are being reported in the literature. Sulphoxides, phosphine oxides and heterocyclic N-oxides are representatives of this type of coordinating agents, although some complexes of arsine oxides are also described.

HETEROCYCLIC N-OXIDES

Metal complexes of N-oxides of aromatic amine N-oxides (1) and aromatic diimines and diazines (2) have been recently reviewed. The preparation and properties of the ligands are described in the same papers. The number of rare earth complexes with these ligands is relatively small, but some aspects of their chemistry will be mentioned.

Some of the complexes formed by pyridine N-oxide are presented in Table 1. The complex perchlorates (3) were prepared by mixing the rare earth perchlorates and excess pyridine N-oxide; they are non-hygroscopic, soluble in polar solvents and insoluble in non-polar solvents. The i.r. spectra of the complexes are very similar. The very strong band at  $1265\text{ cm}^{-1}$  assigned to the N-O stretching vibration shifts to about  $1224\text{ cm}^{-1}$  in the complexes indicating coordination through oxygen resulting from a decrease in N-O double bond character. The shift in N-O stretching frequency, (about  $40\text{ cm}^{-1}$  in these complexes) which is a measure of the strength of the metal-oxygen bond, is less than for the trivalent transition metal ions, where a shift of about  $60\text{ cm}^{-1}$  has been observed (4); this shows that the rare earth complexes are less stable than those of the trivalent transition metal ions. The strong band around  $1085\text{ cm}^{-1}$  indicates the retention of  $T_d$  symmetry for the perchlorate ion in the complexes. The molar conductances in dimethylformamide and nitrobenzene are in good agreement with 1:3 electrolytes.

TABLE 1.

Pyridine N-oxide (PyNO)		
Perchlorates (3)	Iodides (5)	X = Nitrate Perchlorate (8) Tetraphenylborate
[ La(PyNO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[ La(PyNO) <sub>8</sub> ] I <sub>3</sub>	[ La(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
[ Ce(PyNO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>		
[ Pr(PyNO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[ Pr(PyNO) <sub>8</sub> ] I <sub>3</sub>	[ Pr(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
[ Nd(PyNO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[ Nd(PyNO) <sub>8</sub> ] I <sub>3</sub>	[ Nd(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
[ Sm(PyNO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>		[ Sm(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
		[ Eu(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
[ Gd(PyNO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>		[ Gd(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
	[ Tb(PyNO) <sub>8</sub> ] I <sub>3</sub>	[ Tb(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
	[ Dy(PyNO) <sub>8</sub> ] I <sub>3</sub>	[ Dy(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
		[ Ho(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
	[ Er(PyNO) <sub>8</sub> ] I <sub>3</sub>	[ Er(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
		[ Tm(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
	[ Yb(PyNO) <sub>8</sub> ] I <sub>3</sub>	[ Yb(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
		[ Lu(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>
[ Y(PyNO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[ Y(PyNO) <sub>8</sub> ] I <sub>3</sub>	[ Y(PyNO) <sub>4</sub> (NO <sub>3</sub> )] X <sub>2</sub>

The complex iodides (5) were prepared in acetone solution from which they precipitate as fine crystalline solids. The conductance data in acetonitrile and dimethylformamide suggest a 1:3 electrolytic behaviour in these solvents. Therefore the coordination number eight can be postulated for these complexes in these solvents. The lowering of the N-O stretching frequencies indicates coordination through the oxygen of the N-O group. On the basis of proton NMR data, a square antiprismatic geometry around the metal ion in solution is postulated. X-ray diffraction and fluorescence spectrometry studies of  $[\text{La}(\text{PyNO})_8](\text{ClO}_4)_3$  (6) and  $[\text{Eu}(\text{PyNO})_8]X_3$  ( $X = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{ClO}_4^-$ ) (7) have shown in a square antiprismatic geometry around the metal ion (Fig. 1).

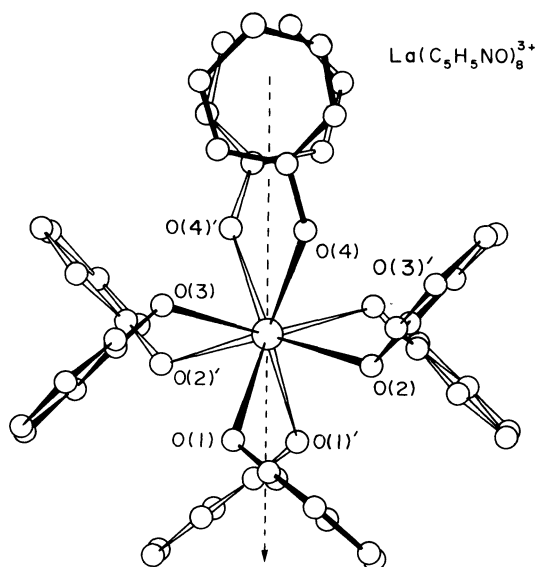


Fig. 1. The octakis (pyridine oxide) lanthanum (III) ion,  $\text{La}(\text{C}_5\text{H}_5\text{NO})_8^{3+}$  projected onto a plane containing the y crystal axis and whose normal is  $\alpha. 40^\circ$  from the crystal Z axis.

The complexes  $[\text{Ln}(\text{PyNO})_4(\text{NO}_3)]^{2+}$  were prepared in alcoholic solution (8) and can be precipitated either as nitrates from very concentrated solutions, or as perchlorates or tetraphenylborates from dilute solutions. Conductivity data confirm that these complexes are 2:1 electrolytes. The infrared spectra of all complexes are very similar and show the N-O stretching frequency split into two components, which are separated by about  $10\text{ cm}^{-1}$  and lowered by about  $15\text{ cm}^{-1}$  from the pyridine N-oxide value owing to coordination (4). Replacement of the nitrate ion band at about  $1380\text{ cm}^{-1}$  by two bands at about  $1450$  and  $1300\text{ cm}^{-1}$  in the spectra of all complexes indicates a covalently bonded nitrate ion. The coordination number six is tentatively assigned to all ions in these complexes. Rare earth pyridine N-oxide complexes with the anion  $[\text{Cr}(\text{SCN})_6]^{3-}$  are also known (9).

Complexes formed by 4-methylpyridine N-oxide, or 4-picoline N-oxide are presented in Table 2. The hydrated perchlorate complexes (10) were prepared by two procedures which yielded compounds with different stoichiometries even though excess ligand was present in both cases. In the first procedure (method A) the solvent was acetone and chloroform; in the second procedure (method B), for the preparation of the octakis(4-picoline N-oxide) complexes, the solvent was absolute ethanol. The complexes with the general formula  $[\text{Ln}(\text{PiNO})_8(\text{ClO}_4)_3(\text{H}_2\text{O})_2]$  contain water of crystallization which is expected to be in the outer coordination sphere. Attempts to remove the water from these complexes distorts the perchlorate ion from the apparent  $T_d$  symmetry. Water probably is associated with the ligand of the octakis complexes but is coordinated to the rare earth ions in the other complexes. The complexes prepared by method A have stoichiometries consistent with water molecules occupying in the inner coordination sphere, and an infrared band compatible with the M-OH<sub>2</sub> stretching frequency is observed.

The N-O stretching band appears at  $1260\text{ cm}^{-1}$  in the free ligand, but is shifted to  $1215$ – $1255\text{ cm}^{-1}$  in the various complexes. This is attributed to a decrease in bond order of the N-O bond as well as a mass effect due to coordination (11).

The emission spectrum of  $[\text{Eu}(\text{PiNO})_8(\text{ClO}_4)_3(\text{H}_2\text{O})_2]$  is identical to that reported for the anhydrous complex (12), and approximate  $D_{4d}$  symmetry is assigned to the configuration of the N-oxide oxygen atoms around the europium ion. The emission spectra of the aquo complex

TABLE 2.

4-Picoline N-oxide (piNO)					
Perchlorates (10)	Perchlorates (12)	Chlorides (12)	Iodides (12)	Hexafluoro- phosphates (12,13)	
	$[\text{Pr}(\text{PiNO})_8](\text{ClO}_4)_3(\text{H}_2\text{O})_2$				
	$[\text{Nd}(\text{PiNO})_8](\text{ClO}_4)_3(\text{H}_2\text{O})_2$				
$[\text{Sm}(\text{PiNO})_7(\text{H}_2\text{O})](\text{ClO}_4)_3$	$[\text{Sm}(\text{PiNO})_8](\text{ClO}_4)_3(\text{H}_2\text{O})_2$				
$[\text{Eu}(\text{PiNO})_6(\text{H}_2\text{O})_2](\text{ClO}_4)_3$	$[\text{Eu}(\text{PiNO})_8](\text{ClO}_4)_3(\text{H}_2\text{O})_2$	$[\text{Eu}(\text{PiNO})_3\text{Cl}_3]$	$[\text{Eu}(\text{PiNO})_8]\text{I}_3$	$[\text{Eu}(\text{PiNO})_8](\text{PF}_6)_3$	
	$[\text{Gd}(\text{PiNO})_8](\text{ClO}_4)_3(\text{H}_2\text{O})_2$				
	$[\text{Dy}(\text{PiNO})_8](\text{ClO}_4)_3(\text{H}_2\text{O})_2$				
$[\text{Er}(\text{PiNO})_7(\text{H}_2\text{O})](\text{ClO}_4)_3$					

$[\text{Eu}(\text{PiNO})_6(\text{H}_2\text{O})_2](\text{ClO}_4)_3$  is similar to that reported for  $[\text{Eu}(\text{PiNO})_3\text{Cl}_3]$  (12), although the lines appear much broader.

The anhydrous octakis(4-picoline N-oxide)europium perchlorate (12) was prepared from europium perchlorate and 4-picoline N-oxide (1:8 ratio) in water/isopropyl alcohol as a solvent. The product was purified from acetone/ethyl acetate. The anhydrous tris(4-picoline N-oxide)europium chloride and iodide (12) were prepared from europium chloride and iodide, respectively, in water/ethanol; the products were precipitated by ethyl acetate or acetone. The hexafluorophosphate complex (12) was prepared in water/acetone using ether as precipitant.

The iodide, perchlorate and hexafluorophosphate salts of the octakis(4-picoline N-oxide)europium cation present the same fluorescence emission spectra, which can be easily distinguished from the spectrum of tris(4-picoline N-oxide)europium trichloride.

The fluorescence emission spectrum of the octakis(4-picoline N-oxide)europium hexafluorophosphate (13) was measured at about 77°K and the analysis of the spectral data indicates that the europium is at a site with  $D_{4d}$  symmetry. Thus the complex appears to have the structure of a square antiprism.

Rare earth complexes of 2,6-lutidine N-oxide are shown in Table 3. They are prepared by reaching hydrated rare earth salts with an excess of the ligand and by evaporating the solution under vacuum to dryness (14). The perchlorates behave as 1:3 electrolytes, and the i.r. bands of the perchlorate ions indicate that they are not coordinated to the tripositive lanthanides. The five bands attributed to the nitrate ion were observed for the nitrate adducts, indicating that these ions are coordinated to the tripositive lanthanides. The shift of the N-O stretching mode to lower frequencies indicates coordination through the oxygen atoms. The electrolytic conductance data indicate that the nitrates behave as non-electrolytes in nitromethane and acetonitrile. The electrolytic data for the chlorides in methanol indicate the presence of 1:1 electrolytes, but this behavior may be due to the dissociative properties of the solvent. To the perchlorates the apparent coordination number eight may be attributed. For the nitrates and chlorides considerations concerning the coordination number may be mere speculations, because both ions act as monodentate or bidentate ligands, and may lie in a position between the lanthanide ions.

TABLE 3.

2,6-Lutidine N-oxide (LNO)		
Perchlorates	Nitrates (14)	Chlorides (14)
$[\text{La}(\text{LNO})_8](\text{ClO}_4)_3$	$[\text{La}(\text{LNO})_4(\text{NO}_3)_3]$	$[\text{La}(\text{LNO})_3\text{Cl}_3]$
$[\text{Nd}(\text{LNO})_8](\text{ClO}_4)_3$	$[\text{Nd}(\text{LNO})_4(\text{NO}_3)_3]$	$[\text{Nd}(\text{LNO})_3\text{Cl}_3]$
$[\text{Gd}(\text{LNO})_8](\text{ClO}_4)_3$	$[\text{Gd}(\text{LNO})_4(\text{NO}_3)_3]$	$[\text{Gd}(\text{LNO})_3\text{Cl}_3]$
$[\text{Er}(\text{LNO})_8](\text{ClO}_4)_3$	$[\text{Er}(\text{LNO})_4(\text{NO}_3)_3]$	$[\text{Er}(\text{LNO})_3\text{Cl}_3]$
$[\text{Y}(\text{LNO})_8](\text{ClO}_4)_3$	$[\text{Y}(\text{LNO})_4(\text{NO}_3)_3]$	$[\text{Y}(\text{LNO})_3\text{Cl}_3]$

Some rare earth complexes formed by pyrazine N-oxide and pyrazine 1,4-dioxide are summarized in Table 4. The complex perchlorates (15) were prepared in absolute ethanol from the hydrated rare earth perchlorates and excess of the ligand; the complexes were precipitated by addition of 2,2-dimethoxypropane. Only the lanthanum complex perchlorate shows water bands in the infrared spectrum; the other compounds are anhydrous. The N-O stretching mode is shifted to lower frequencies by about  $50\text{ cm}^{-1}$ , whereas practically no change in the CN stretching mode is observed. This indicates that coordination occurs only through the oxygen above. The bands observed for the perchlorate ions suggest that the  $T_d$  symmetry is maintained and that these ions are not coordinated to the tripositive lanthanides. The electrolytic behavior in nitromethane indicate that the complexes are 1:3 electrolytes in this solvent. The values for the nitromethane solutions are in accordance with the presence of 1:2 electrolytes and may be interpreted in terms of the existence of ion-pairs. The apparent coordination number nine is assumed for the compound of lanthanum whereas it is eight for the others.

The octakis(pyrazine N-oxide)lanthanide hexafluorophosphates (16) were prepared from a concentrated solution of lanthanide hexafluorophosphate in water with an excess of an ethanolic solution of  $\text{PyzNO}$ , by precipitation with triethylorthoformate. The complex chlorides

TABLE 4.

Perchlorates (15)	Pyrazine N-oxide (PyzNO)		Pyrazine 1,4-dioxide (PyzdNO)	
	Hexafluorophosphates (16)	Chlorides (16)	Perchlorates (18)	
[La(PyzNO) <sub>7</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	[La(PyzNO) <sub>8</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[La(PyzNO) <sub>2</sub> Cl <sub>3</sub> ]	[La(PyzdNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
[Pr(PyzNO) <sub>8</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Pr(PyzNO) <sub>8</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Pr(PyzNO) <sub>2.5</sub> Cl <sub>3</sub> ]	[Pr(PyzdNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
[Eu(PyzNO) <sub>8</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Eu(PyzNO) <sub>8</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Eu(PyzNO) <sub>2.5</sub> Cl <sub>3</sub> ]	[Eu(PyzdNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
[Er(PyzNO) <sub>8</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Er(PyzNO) <sub>8</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Er(PyzNO) <sub>3</sub> Cl <sub>3</sub> ]	[Er(PyzdNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
[Y(PyzNO) <sub>8</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Y(PyzNO) <sub>8</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Y(PyzNO) <sub>3</sub> Cl <sub>3</sub> ]	[Y(PyzdNO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	

(16) were prepared in ethanolic solution from the components, by adding triethylorthoformate for the precipitation of the compounds. The infrared spectra show in all cases the N-O stretching bands at lower frequencies, and practically no change in the CN stretching mode is observed, which indicates that coordination occurs only through the oxygen atom.

The strong  $\nu_3$  and  $\nu_4$  bands and the very weak forbidden band, which can be attributed to the PF<sub>6</sub><sup>-</sup> ion, were observed at about 830, 560 and 740 cm<sup>-1</sup> respectively, suggesting a small distortion of the octahedral symmetry of the PF<sub>6</sub><sup>-</sup> ion caused by solid state effects (17). The electrolytic conductance data for the hexafluorophosphates, in acetonitrile and nitromethane, show that they behave as 1:3 electrolytes. For the chlorides, the electrolytic conductance data in methanol indicate the behavior of 1:1 electrolytes, which may be due to the dissociative properties of this solvent.

It is interesting to note an apparent increase of the coordination number in the chloride adducts. Unfortunately the insolubility of these compounds and the extreme hygroscopicity limits a systematic investigation. Nevertheless, the fact that chloride ions may act as monodentate, bidentate or even as bridging ligands, and the existence of compounds of the composition LnCl<sub>2</sub>·2.5 PyzNO, in which PyzNO may at least in part be in a position between two lanthanide ions, discourages speculations about the coordination number in these compounds. The apparent coordination number of eight may be attributed to the lanthanide ions in the hexafluorophosphate adducts.

Pyrazine 1,4-dioxide complexes of some lanthanide perchlorates were also prepared (18). A small shift to lower frequencies of the N-O stretching mode (1258 cm<sup>-1</sup> for the free ligand to about 1254 cm<sup>-1</sup> for the complexes) suggests a weak coordination involving the oxygen above. As a consequence of coordination,  $\delta_{NO}$  is shifted to lower frequencies (875<sup>-1</sup> to about 850 cm<sup>-1</sup>). Splitting and shift of the CN out-of-plane deformation was also observed. The bands attributed to the perchlorate ions indicate that they have approximately T<sub>d</sub> point group symmetry and that they are not coordinated to the tripositive lanthanides. The ligands have two oxygen atoms in opposite positions that are able to coordinate with the lanthanide ions and may act as a bridge. The only evidence for the existence of polymeric species is that the compounds are extremely insoluble even in polar solvents.

The lanthanide complexes of quinoline N-oxide and 2,2'-bipyridine 1,1-dioxide are presented in Table 5. In methanol the tris- and tetrakis(quinoline N-oxide)lanthanide chlorides (19) dissociate giving conductivity values higher than expected for 1:1 electrolytes; identical results are obtained when dimethylformamide is used as solvent. On the basis of their thermal behavior, these complexes have been divided into two classes: the apparently seven-coordinated tris-complexes [M(QNO)<sub>3</sub>Cl<sub>3</sub>·H<sub>2</sub>O] and the tetrakis-complexes [M(QBO)<sub>4</sub>Cl<sub>3</sub>·H<sub>2</sub>O]. The tris-complexes are thermally more stable, whereas the tetrakis species lose two molecules of hydrogen chloride to form the seemingly six-coordinate oxychloride complexes MOCl(QNO)<sub>4</sub>.

The 2,2'-bipyridine 1,1-dioxide complexes were prepared in 95% ethanol and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> at room temperature (21,22); they appeared to be non-hygroscopic. Conductivity measurements indicate that in nitromethane there is a narrow concentration range in which these complexes behave as ionic 3:1 electrolytes. In 20 mM solutions molecular weight measurements show that there are 2.5 to 3.0 particles per molecule in solution i.e. between one and two perchlorate ions are dissociated per complex molecule. The NO stretching vibrations clearly show the effects of complexation i.e. the NO stretching bands do not only shift to lower frequencies, but also undergo splitting. The shift is approximately 25 cm<sup>-1</sup> and can be attributed to a decrease of the  $\pi$ -bond character of the NO bond due to the metal-oxygen coordination. The

TABLE 5.

Quinoline N-oxide (QNO)		2 2'-Bipyridine 1 1'-dioxide (BINDO)	
Chlorides (19)	[ Cr(SCN) <sub>6</sub> ] <sup>3-</sup> (20)	Perchlorates (21)(22)	Nitrate/Perchlorate (23)
	[ La(QNQ) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]	[ La(BINDO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
	[ Ce(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]		[ Ce(BINDO) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>
	[ Pr(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]	[ Pr(BINDO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
[ Nd(QNO) <sub>3</sub> Cl <sub>3</sub> ·H <sub>2</sub> O ]	[ Nd(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]	[ Nd(BINDO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
[ Sm(QNO) <sub>3</sub> Cl <sub>3</sub> ·H <sub>2</sub> O ]	[ Sm(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]	[ Sm(BINDO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
[ Eu(QNO) <sub>4</sub> Cl <sub>3</sub> ·H <sub>2</sub> O ]	[ Eu(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]	[ Eu(BINDO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
[ Gd(QNO) <sub>4</sub> Cl <sub>3</sub> ·H <sub>2</sub> O ]	[ Gd(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]	[ Gd(BINDO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
[ Tb(QNO) <sub>4</sub> Cl <sub>3</sub> ·H <sub>2</sub> O ]	[ Tb(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]	[ Tb(BINDO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
[ Dy(QNO) <sub>4</sub> Cl <sub>3</sub> ·H <sub>2</sub> O ]	[ Dy(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]	[ Dy(BINDO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
[ Ho(QNO) <sub>4</sub> Cl <sub>3</sub> ·H <sub>2</sub> O ]	[ Ho(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]	[ Ho(BINDO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
	[ Er(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]	[ Er(BINDO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
	[ Tm(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]		
[ Yb(QNO) <sub>4</sub> Cl <sub>3</sub> ·H <sub>2</sub> O ]	[ Yb(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]	[ Yb(BINDO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	
	[ Y(QNO) <sub>7</sub> ] [ Cr(SCN) <sub>6</sub> ]	[ Y(BINDO) <sub>4</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	

europium and terbium complexes (22) are fluorescent in the solid state and in nitromethane solution. The fluorescence spectrum of the europium complex at 300K, in nitromethane, shows a very broad band with a maximum at 612.5 mμ and no fine structure. It can be assigned to the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition. The fluorescence spectrum of the terbium complex in nitromethane shows a weak doublet at 480 nm <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>6</sub> transition).

The cerium (IV) complex (23) was prepared from (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> and 2 2'-bipyridine 1 1'-dioxide in water by addition of sodium perchlorate. The i.r. spectrum of the complex in a Nujol mull clearly indicates coordination of the bipyridyl-O<sub>2</sub> ligand to the cerium atoms through the oxygen atoms. The nitrate groups are also coordinated to the cerium atom, as indicated by a lowering of the symmetry of the nitrate group from D<sub>3h</sub> to C<sub>2v</sub>. The visible spectrum of the solid complex in Nujol and the magnetic susceptibility indicate that the complex is one of Ce(IV).

Some Ce(IV) complexes 2 2'-bipyridine 1 1'-dioxide are also reported (24) for which the coordination number eight is postulated.

Lanthanide complexes formed with triethylenediamine N-oxide (1,4-diazabicyclo [2,2,2] octane N-oxide), TEDANO (25) and triethylenediamine N-dioxide (1,4-diazabicyclo [2,2,2] octane 1,4-dioxide), TEDADO (26) are presented in Table 6. The infrared spectra of the TEDANO lanthanide perchlorate complexes (25) indicate that the T<sub>d</sub> symmetry is maintained and that the perchlorate ions are not coordinated to the tripositive lanthanide ions. For the PF<sub>6</sub><sup>-</sup> complexes the i.r. spectra indicate that the octahedral symmetry is unaltered and the ions are also not coordinated.

The NO stretching mode shows a small shift towards higher frequencies, when compared with that of the free ligand. This behavior can be explained by the fact that water molecules are coordinated to the ligand itself and are substituted by the lanthanide ion in the adducts

without modifying the shift of the NO band (27). The band at about  $1180\text{ cm}^{-1}$ , tentatively attributed to  $\nu_{\text{CN}}$ , is practically unaffected. According to conductance data, the compounds behave as 1:3 electrolytes. It is assumed that TEDANO is coordinated to the rare earth ions through the oxygen atom but bonding through the oxygen-free nitrogen atom may also occur, the ligand may act as a bridge and the existence of polymeric species is not excluded.

TABLE 6

Triethylenediamine N-oxide (TEDANO)		Triethylenediamine N,N'dioxide (TEDADO)
Perchlorates (25)	Hexafluorophosphates (25)	Perchlorates (26)
[La(TEDANO) <sub>7</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[La (TEDANO) <sub>5</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[La(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
[Ce(TEDANO) <sub>7</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Ce(TEDANO) <sub>5</sub> ](PF <sub>6</sub> ) <sub>3</sub>	
[Pr(TEDANO) <sub>7</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Pr(TEDANO) <sub>5</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Pr(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O
[Nd(TEDANO) <sub>7</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Nd(TEDANO) <sub>5</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Nd(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
[Sm(TEDANO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Sm(TEDANO) <sub>5</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Sm(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
[Eu(TEDANO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Eu(TEDANO) <sub>5</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Eu(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
[Gd(TEDANO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Gd(TEDANO) <sub>5</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Gd(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
[Tb(TEDANO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Tb(TEDANO) <sub>5</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Tb(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
[Dy(TEDANO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Dy(TEDANO) <sub>4.5</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Dy(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
[Ho(TEDANO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Ho(TEDANO) <sub>4.5</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Ho(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
[Er(TEDANO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Er(TEDANO) <sub>4.5</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Er(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
[Tm(TEDANO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Tm(TEDANO) <sub>4</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Tm(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
[Yb(TEDANO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Yb(TEDANO) <sub>4</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Yb(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
[Lu(TEDANO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Lu(TEDANO) <sub>4</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Lu(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O
[Y(TEDANO) <sub>6</sub> ](ClO <sub>4</sub> ) <sub>3</sub>	[Y(TEDANO) <sub>5</sub> ](PF <sub>6</sub> ) <sub>3</sub>	[Y(TEDADO) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>3</sub> ·3H <sub>2</sub> O

In the case of TEDADO perchlorate complexes (26), the bands attributed to the perchlorate ion suggest that the tetrahedral symmetry is maintained, indicating that the ion is not coordinated to the tripositive lanthanide in the solid state. The NO stretching mode is practically unaffected by the coordination, since the frequency shift of this band can be cancelled by changes of the other force constants (27). Electrolytic conductance data, measured in aqueous solutions, indicate the presence of 1:3 electrolytes. The existence of polymeric species may be expected; the compounds are extremely insoluble as are the adducts of pyrazine 1,4-dioxide (15).

## PHOSPHINE OXIDE

Complexes of Tri-*n*-butylphosphine oxide (28) have been described and the compounds are presented in Table 7. These complexes were studied in the solid state by infrared spectrometry. It is observed that the coordination of the nitrate ion is not the same throughout the lanthanide series; it is bidentate for the light earths (La to Eu) and monodentate for the heavy earths (Gd to Yb). It is also observed that the P=O stretching band is shifted to lower frequencies in the complexes free ligand  $1164\text{ cm}^{-1}$ . The P=O frequency does not vary monotonously with increasing atomic number of the rare earth; between La and Eu the variation

TABLE 7.

Tri- <i>n</i> -butylphosphine oxide (TBPO)
Nitrates (28)
La(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
Ce(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
Pr(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
Nd(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
Sm(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
Eu(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
Gd(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
Tb(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
Dy(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
Ho(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
Er(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
Tm(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
Yb(TBPO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>

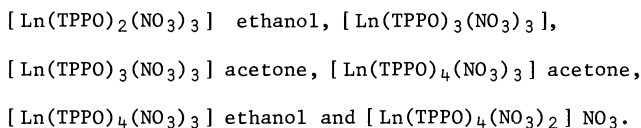
is approximately constant (1114–1118 cm<sup>-1</sup>), a break is observed for Gd (1115), and the frequency increases from Tb to Yb (1120–1127 cm<sup>-1</sup>). This is explained by back bonding, the decrease of the ionic radius and of the coordination number.

Many rare earth chlorides complexes with triphenylphosphine oxide (TPPO) were described (12, 29–32), see Table 8. The concentration of the solution and the temperature of the reaction determines which complex crystallises from solution, although extended refluxing generally yields the tritakis-complex (31). All observations indicate that the complexes are non-electrolytes and essentially monomeric (molecular weight). The six-coordinated tris-complexes [Ln(TPPO)<sub>3</sub>Cl<sub>3</sub>] seem to be more stable thermally than the seven-coordinate tetrakis-complexes (29, 31). The P=O stretching frequency is lowered. The coordination numbers 6 and 7 are postulated for the tris-complexes and for the tetrakis-complexes, respectively.

The tris(triphenylphosphine oxide)europium chloride (12) exhibits a strong fluorescence. The cerium(IV) compounds are not very stable thermally (32), are diamagnetic and behave as non-conductors in nitromethane and acetonitrile. The P=O stretching frequency is lowered from 1187 to about 1130 cm<sup>-1</sup> showing coordination through the oxygen atom of the PO group.

The thiocyanate complexes were also described (29), Table 8, and are very stable thermally. Millimolar solutions in acetone are weak electrical conductors indicating coordinated thiocyanate groups. Some distortion occurs for the tetrakis-complexes in chloroform. In all cases the P=O frequency is lowered in relation to that of the free ligand (1195 to about 1145 cm<sup>-1</sup>). It is also assumed (29) that the NCS ion is bonded to the rare earth atom through the nitrogen atom.

The rare earth nitrate complexes with TPPO were extensively studied (33), Table 9. Many compounds were prepared in various organic solvents, and the general formulae can be summarized in the following way:



Possibly, ethanol and acetone are coordinated to the metal ion; ethanol cannot be removed and severe treatment causes decomposition. Acetone, on the other hand, is not very firmly attached, since it can be removed completely under vacuum. For all complexes, except for the tetrakis(triphenylphosphine oxide) lanthanide nitrates, Ln(TPPO)<sub>4</sub>(NO<sub>3</sub>)<sub>3</sub>, the infrared spectra show strong



TABLE 8.

Triphenylphosphine oxide (TPPO)					
Chlorides (29)	Chlorides (30)	Chlorides (31)	Chlorides (12)	Chlorides (32)	Thiocyanates (29)
				[ CeCl <sub>4</sub> (TPPO) <sub>2</sub> ·ethanol ]	[ La(TPPO) <sub>4</sub> (NCS) <sub>3</sub> ]
				[ CeCl <sub>3</sub> OCH <sub>3</sub> (TPPO) <sub>2</sub> ]	[ Ce(TPPO) <sub>4</sub> (NCS) <sub>3</sub> ]
[ Nd(TPPO) <sub>3</sub> Cl <sub>3</sub> ]		[ Nd(TPPO) <sub>3</sub> Cl <sub>3</sub> ] H <sub>2</sub> O			[ Pr(TPPO) <sub>4</sub> (NCS) <sub>3</sub> ]
[ Nd(TPPO) <sub>4</sub> Cl <sub>3</sub> ]		[ Sm(TPPO) <sub>3</sub> Cl <sub>3</sub> ] H <sub>2</sub> O			[ Nd(TPPO) <sub>4</sub> (NCS) <sub>3</sub> ]
[ Sm(TPPO) <sub>3</sub> Cl <sub>3</sub> ]		[ Sm(TPPO) <sub>4</sub> Cl <sub>3</sub> ]			[ Sm(TPPO) <sub>4</sub> (NCS) <sub>3</sub> ]
[ Sm(TPPO) <sub>4</sub> Cl <sub>3</sub> ]		[ Eu(TPPO) <sub>3</sub> Cl <sub>3</sub> ] H <sub>2</sub> O	[ Eu(TPPO) <sub>3</sub> Cl <sub>3</sub> ]		[ Sm(TPPO) <sub>3</sub> (NCS) <sub>3</sub> ]
		[ Gd(TPPO) <sub>3</sub> Cl <sub>3</sub> ] H <sub>2</sub> O			[ Eu(TPPO) <sub>3</sub> (NCS) <sub>3</sub> ]
		[ Tb(TPPO) <sub>4</sub> Cl <sub>3</sub> ]			[ Gd(TPPO) <sub>3</sub> (NCS) <sub>3</sub> ]
		[ Tb(TPPO) <sub>4</sub> Cl <sub>3</sub> ] 2H <sub>2</sub> O			[ Dy(TPPO) <sub>3</sub> (NCS) <sub>3</sub> ]
		[ Dy(TPPO) <sub>4</sub> Cl <sub>3</sub> ] H <sub>2</sub> O			[ Ho(TPPO) <sub>3</sub> (NCS) <sub>3</sub> ]
	[ Y(TPPO) <sub>3</sub> Cl <sub>3</sub> ]	[ Ho(TPPO) <sub>3</sub> Cl <sub>3</sub> ] H <sub>2</sub> O			[ Er(TPPO) <sub>3</sub> (NCS) <sub>3</sub> ]
	[ Y(TPPO) <sub>3</sub> Cl <sub>3</sub> ] acetone				[ Tm(TPPO) <sub>3</sub> (NCS) <sub>3</sub> ]
	[ Y(TPPO) <sub>4</sub> Cl <sub>3</sub> ]				[ Lu(TPPO) <sub>3</sub> (NCS) <sub>3</sub> ]
					[ Y(TPPO) <sub>3</sub> (NCS) <sub>3</sub> ]

TABLE 9.

Triphenylphosphine oxide (TPPO) (33)	
$[\text{Ln}(\text{TPPO})_2(\text{NO}_3)_3] \cdot \text{ethanol}$	Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y
$[\text{Ln}(\text{TPPO})_3(\text{NO}_3)_3]$	Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y
$[\text{Ln}(\text{TPPO})_3(\text{NO}_3)_3] \cdot 2 \text{ acetone}$	Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y
$[\text{Ln}(\text{TPPO})_4(\text{NO}_3)_3] \cdot \text{acetone}$	Ln = La, Ce
$[\text{Ln}(\text{TPPO})_4(\text{NO}_3)_3] \cdot \text{ethanol}$	Ln = Tb, Ho, Er, Tm, Yb, Lu, Y
$[\text{Ln}(\text{TPPO})_4(\text{NO}_3)_2] \text{NO}_3$	Ln = Tb, Ho, Er, Tm, Yb, Lu, Y

bands which indicate coordinated nitrate groups; in the tetrakis-complexes additional bands characteristic of ionic nitrate appear. It is assumed that in complexes of the type presently described the nitrate group is bidentate. The  $P=O$  stretching frequency ( $1195\text{ cm}^{-1}$  for the free phosphine oxide) is lowered and split into two bands at about  $1150$  and  $1160\text{ cm}^{-1}$ . The exact frequency depends on the nature of the lanthanide ion.

The crystal and molecular structure of the tetranitratobis(triphenylphosphine oxide)cerium(IV) complex  $Ce\ TPPO_3(NO_3)_4$  has been determined (34) by single-crystal X-ray diffraction. Cerium is ten-coordinated to four bidentate nitrate groups and to two oxygen atoms from the triphenylphosphine oxide (Figs. 2 and 3).

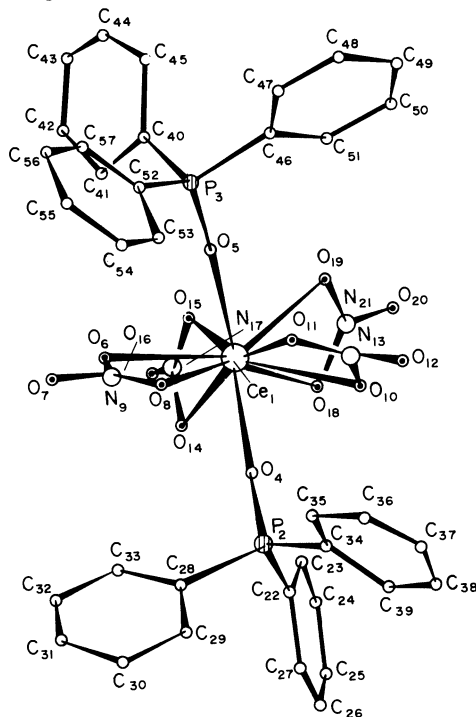


Fig. 2. The structure of tetranitratobis (triphenylphosphine oxide) cerium (IV).

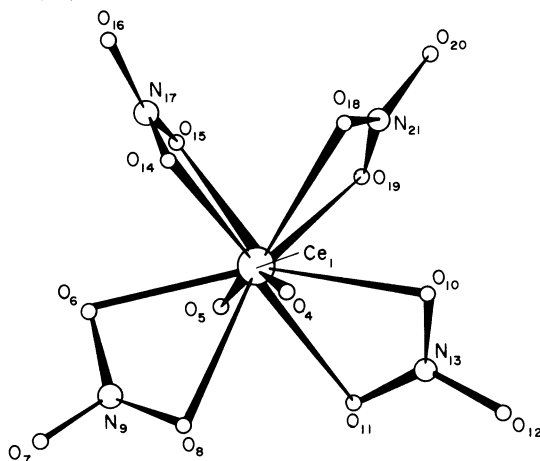


Fig. 3. Coordination of cerium.

Complexes of neodymium perchlorate with triphenylphosphine oxide (TPPO), diphenylmonobenzylphosphine oxide (DPMBPO), monophenyldibenzylphosphine oxide (MPDBPO) and tribenzylphosphine oxide (TBPO) were also described (35), see Table 10.

Conductance measurements indicate the existence of 1:1 species in nitromethane. The infrared spectra show that one perchlorate ion is not coordinated whereas the other two are, probably through one atom of oxygen (symmetry  $C_{3v}$ ).

TABLE 10.

$[\text{Nd}(\text{TPPO})_4(\text{ClO}_4)_2] \text{ClO}_4$	TPPO	= Triphenylphosphine oxide
$[\text{Nd}(\text{DPMBPO})_4(\text{ClO}_4)_2] \text{ClO}_4$	DPMBPO	= Diphenylmonobenzylphosphine oxide
$[\text{Nd}(\text{MPDBPO})_4(\text{ClO}_4)_2] \text{ClO}_4$	MPDBPO	= Monophenyldibenzylphosphine oxide
$[\text{Nd}(\text{TBPO})_4(\text{ClO}_2)] \text{ClO}_4$	TBPO	= Tribenzylphosphine oxide

The electronic spectra of the hypersensitive transition regions ( ${}^4\text{I}_{9/2} \rightarrow {}^4\text{G}_{7/2}$ ,  ${}^2\text{G}_{5/2}$ ) are very similar for all four complexes, indicating that the nature of the group attached to the phosphorus atom does not significantly affect the environment of the Nd(III) ion.

Many publications are known reporting on the extraction of lanthanide ions with *n*-butanol, *m*-xylene, *n*-hexane and other solvents, containing phosphine oxides such as tri-*n*-butylphosphine oxide, triphenylphosphine oxide, triisooamylphosphine oxide and tri-*n*-octylphosphine oxide.

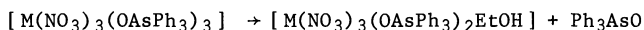
#### TRIPHENYLARSINE OXIDE

Triphenylarsine oxide complexes (see Table 11) with lanthanide thiocyanates (29) are thermally stable, melting at about 300°C, but decompose after several months in a desiccator. It is suggested (29) that these compounds are oxygen-bridged dimers with the formula  $[\text{M}(\text{NCS})_3(\text{OAsPh}_3)_3]_x$ . They provide the only case in which  $\nu_{\text{As-O}}$  is lower than for the free ligand and is split into as many as four peaks (926, 906, 887, 872  $\text{cm}^{-1}$  for the Pr compound).

Various complexes of rare earth nitrates with triphenylarsine oxide (36) were prepared in ethanol or acetone. Molar ratios of ligand to cation, concentration, temperature of mixing of the components and nature of the cation are among the factors which determine the type of species that is isolated.

The bis(triphenylarsine oxide) complexes retain the ethanol on heating at 0.1 mm at 100°C. It is suggested that the ethanol is coordinated and that the complex is polymeric, with bridging nitrate groups.

The tris(triphenylarsine oxide) complexes, prepared in warm acetone, form good crystals of the diacetone adducts. On being heated *in vacuo* at 70°C, the diacetones yield the unsolvated complexes  $[\text{M}(\text{NO}_3)_3(\text{OAsPh}_3)_3]$ ; they are soluble in chloroform, in which they tend to associate. This is in contrast to the triphenylphosphine oxide complexes, which are essentially monomeric. The association is probably brought about by bridging nitrate groups. In ethanol the complexes dissociate:



The infrared spectra of the complexes  $[\text{M}(\text{NO}_3)_3(\text{OAsPh}_3)_3]$  show an increase of  $\nu_{\text{As-O}}$  and a splitting of this band. All nitrate groups are coordinated.

The tetrakis(triphenylarsine oxide) complexes form as monoacetone or monoethanol adducts, when the hydrated lanthanide nitrates are treated with an excess of  $\text{Ph}_3\text{AsO}$  in warm acetone or alcohol. The solvent is removed at 80°C *in vacuo*. In these complexes the ionic formulation  $[\text{M}(\text{NO}_3)_2(\text{OAsPh}_3)_4] \text{NO}_3$  is suggested (36), because the infrared spectrum (Sm compound) shows band of ionic nitrate at 1355, 1339 ( $\nu_3$ ) and 832 ( $\nu_2$ )  $\text{cm}^{-1}$  and in addition bands arising from coordinated nitrate at 1484, 1453 ( $\nu_4$ ), 1292 ( $\nu_1$ ) and 820 ( $\nu_6$ )  $\text{cm}^{-1}$ ; these compounds are electrolytes in acetone.

The complexes of tribenzylarsine oxide with rare earth ions (37) were prepared in ethanol using ligand to metal ratios of 4:1 or 3:1 in some cases (Ce, Er, Gd). The molar conductivity in acetonitrile indicates that all of these complexes are weak electrolytes. There is a gradual increase of  $\nu_{\text{As-O}}$  from 870  $\text{cm}^{-1}$  in free  $\text{Bz}_3\text{AsO}$  to 885  $\text{cm}^{-1}$  in the Yb compound. The magnetic moments are similar to those of other rare earth compounds and usually correspond to the moment predicted for the free ion.

TABLE 11.  
Tribenzylarsine oxide (TBAsO)

Thiocyanates (29)	Triphenylarsine oxide (TPAsO)		Tribenzylarsine oxide (TBAsO)	
	Nitrates (36)	Nitrates (37)	Nitrates (36)	Nitrates (37)
	[ La(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	La(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>	La(TPAsO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub>	La(TBAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
[ Ce(TPAsO) <sub>3</sub> (NCS) <sub>3</sub>	[ Ce(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Ce(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>		Ce(TBAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
[ Pr(TPAsO) <sub>3</sub> (NCS) <sub>3</sub>	[ Pr(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Pr(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>		Pr(TBAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
	[ Nd(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Nd(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>	Nd(TPAsO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub>	Nd(TBAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
	[ Sm(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Sm(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>	Sm(TPAsO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub>	Sm(TBAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
	[ Eu(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Eu(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>	Eu(TPAsO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub>	
	[ Gd(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Gd(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>		Gd(TBAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
	[ Tb(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Tb(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>		Tb(TBAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
	[ Dy(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Dy(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>	Dy(TPAsO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub>	Dy(TBAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
	[ Ho(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Ho(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>	Ho(TPAsO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub>	Ho(TBAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
	[ Er(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Er(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>	Er(TPAsO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub>	Er(TBAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
	[ Tm(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Tm(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>	Tm(TPAsO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub>	
	[ Yb(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Yb(TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>	Yb(TPAsO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub>	Yb(TBAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>
	[ Lu(TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol		Lu(TPAsO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub>	
	[ Y (TPAsO) <sub>2</sub> (NO <sub>3</sub> ) <sub>3</sub>   Ethanol	Y (TPAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>	Y (TPAsO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub>	Y (TBAsO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub>

## SULPHOXIDES

Some complexes of rare earths with dimethyl- and diphenylsulfoxide were described in a general review on "Coordination Compounds of Sulphoxides" in 1968 (38). A survey of the general properties of sulphoxides was presented in the same paper (38). Since that time many other complexes formed from lanthanides and sulphoxides were characterized. Dimethylsulphoxide is an excellent coordinating agent and forms many coordination compounds, which are summarized in Tables 12 and 13. The perchlorate adducts were prepared and described by many authors (39-42) and the results, although not exactly the same, are in general agreement. The molar conductance data in dimethylformamide, nitrobenzene and water are in good agreement with those reported for 1:3 electrolytes (39). In all cases a shift of the S-O stretching frequency to lower wavelength is observed which suggests that coordination is through the oxygen atoms. The adducts show a decreased capacity of the rare earth ion to add ligand molecules as its radius decreases. The shift of the S-O stretching frequency (about  $60\text{ cm}^{-1}$ ) and the decrease in coordination number with decreasing ion radius are similar to those observed for the dimethylacetamide complexes of the rare earth perchlorates (43). The  $\nu_3$  and  $\nu_4$  bands of the perchlorate ions in the complexes appear as singlets in Nujol mull, suggesting the presence of  $T_d$  symmetry for the perchlorate ions (39).

The complex perrhenates were also described (44); a weak Raman and a very strong i.r. band at about  $1004\text{ cm}^{-1}$  can be assigned to the S-O mode, and the shift to a lower frequency relative to that of the free ligand ( $1058\text{ cm}^{-1}$ ) is consistent with coordination through the oxygen atom. The bands assigned to the perrhenate group remain virtually unchanged for all complexes. The spectral data can be interpreted by assuming a  $T_d$  symmetry.

Results for the hexafluorophosphate adducts (45) show that the complexes of the lighter lanthanides (La to Gd) are not very stable and contain more than seven ligands per lanthanide hexafluorophosphate; the complexes of the heavier lanthanides (Tb-Lu, Y), are more stable and contain 7 ligands per lanthanide hexafluorophosphate. The infrared spectra of all complexes are nearly the same. There is a displacement of the S-O stretching band towards lower frequencies ( $\Delta_{S-O}=35\text{ cm}^{-1}$ ) suggesting coordination of the lanthanide ion with the oxygen atom of the ligand. An enhancement of the C-S stretching frequency ( $\Delta_{C-S}=17\text{ cm}^{-1}$ ) confirms this interpretation. The ionic character of the  $PF_6^-$  groups is evidenced by two strong absorption bands at about  $835$  and  $556\text{ cm}^{-1}$ , assigned to  $\nu_3$  and  $\nu_4$  vibration bands at the  $PF_6^-$  (point group  $O_h$ ) in good agreement with the  $KPF_6$  of spectra (46).

The i.r. spectra of the chloride complexes (47) clearly show that the dimethylsulfoxide molecules are coordinated to the metal ions through the oxygen atom; an enhancement of the frequency of the C-S stretching mode ( $695-718\text{ cm}^{-1}$ ) confirms this view. Conductance data in acetonitrile and dimethylformamide suggest the coordination number 8 for the lanthanons and 7 for yttrium; a bridged structure involving chlorine is postulated.

The nitrate complexes were also described (48). Their i.r. spectra confirm the coordination of the lanthanide ion with the oxygen atom of the dimethylsulfoxide; the intense band at about  $1045\text{ cm}^{-1}$ , which is attributed to the S-O stretching mode in free dimethylsulfoxide, shifts to about  $1010\text{ cm}^{-1}$  in the complexes. An enhancement of the C-S stretching frequency further confirms complex formation through the oxygen atom of the ligand. The i.r. band of the nitrate groups indicates that all nitrate groups are covalently bonded. The presence of monodentate and bidentate nitrate groups is also evidenced by the i.r. spectra.

The nitrate complexes behave as non-electrolytes in acetone and acetonitrile, but as 1:2 electrolytes in dimethylformamide; considering this evidence, it is suggested that two nitrate groups are monodentate and the third is bidentate. The coordination number becomes 8 for the lighter lanthanides and 7 for yttrium and the two heavier lanthanides. Molecular weight determinations in acetonitrile show that the complexes are monomeric.

The crystal structure of the dimethylsulfoxide complex of lanthanum nitrate  $[La(DMSO)_4(NO_3)_3]$  was determined (49); the compound crystallizes in the monoclinic space group  $C_{2/c}$  and the La atom is coordinated by 10 oxygen atoms.

Complexes formed by other aliphatic sulfoxides are summarized in Table 14. In all cases the i.r. spectra show a decrease in the S=O stretching frequency of the ligand, indicative of coordination through the oxygen atom of the SO group. The i.r. spectra are also characterized by bands that can be assigned to ionic and coordinated perchlorate groups. In the case of the di-*n*-butylsulfoxide complexes (50), the Raman spectra give evidence of the presence of ionic and coordinated perchlorate groups. Conductivity data of these complexes in nitromethane are in the range expected for 1:2 electrolytes. It is suggested that the lanthanide perchlorate complexes  $[Ln_2(PSO)_{11}(ClO_4)_2(ClO_4)]$  have five sulfoxide ligands and one coordinated perchlorate group per metal atom. One sulfoxide group (probably bridging) is also present in the complex. This suggests a coordination number of seven.

TABLE 12.

Dimethylsulfoxide (DMSO)					
Perchlorates (39)	Perchlorates (40)	Perchlorates (41)	Perrhenates (44)	Hexafluorophosphates (45)	
[La(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[La(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[La(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[La(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[La(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Ce(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Ce(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Ce(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Ce(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Ce(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Pr(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Pr(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Pr(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Pr(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Pr(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Nd(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Nd(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Nd(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Nd(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Nd(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Sm(DMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Sm(DMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Sm(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Sm(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Sm(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Eu(DMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Eu(DMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Eu(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Eu(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Eu(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Gd(DMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Gd(DMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Gd(DMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Gd(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Gd(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
		[Tb(DMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Tb(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Tb(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
		[Dy(DMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Dy(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Dy(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
		[Ho(DMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Ho(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Ho(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
		[Er(DMSO) <sub>6</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Er(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Er(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
		[Tm(DMSO) <sub>6</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Tm(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Tm(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
		[Yb(DMSO) <sub>6</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Yb(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Yb(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
		[Lu(DMSO) <sub>6</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Lu(DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Lu(DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Y (DMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Y (DMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Y (DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Y (DMSO) <sub>8</sub> ] (ReO <sub>4</sub> ) <sub>3</sub>	[Y (DMSO) <sub>x</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	

 $x = 7.0 \sim 7.5$

TABLE 13.

Dimethylsulfoxide (DMSO)	
Chlorides (47)	Nitrates (48)
[ La(DMSO) <sub>4</sub> Cl <sub>3</sub> ]	[ La(DMSO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub> ]
[ Ce(DMSO) <sub>4</sub> Cl <sub>3</sub> ]	[ Ce(DMSO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub> ]
[ Pr(DMSO) <sub>4</sub> Cl <sub>3</sub> ]	[ Pr(DMSO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub> ]
[ Nd(DMSO) <sub>4</sub> Cl <sub>3</sub> ]	[ Nd(DMSO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub> ]
[ Sm(DMSO) <sub>4</sub> Cl <sub>3</sub> ]	[ Sm(DMSO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub> ]
[ Gd(DMSO) <sub>4</sub> Cl <sub>3</sub> ]	[ Gd(DMSO) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub> ]
	[ Ho(DMSO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]
	[ Yb(DMSO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]
[ Y(DMSO) <sub>3</sub> Cl <sub>3</sub> ]	[ Y(DMSO) <sub>3</sub> (NO <sub>3</sub> ) <sub>3</sub> ]

TABLE 14.

Di- <i>n</i> -propylsulfoxide (PSO)	Di- <i>n</i> -butylsulfoxide (BSO)	Di- <i>t</i> -butylsulfoxide (tBSO)
Perchlorates (50)	Perchlorates (51)	Perchlorates (53)
	La(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	La(tBSO) <sub>4</sub> (ClO <sub>4</sub> ) <sub>3</sub>
	Ce(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	Ce(tBSO) <sub>4</sub> (ClO <sub>4</sub> ) <sub>3</sub>
	Pr(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	Pr(tBSO) <sub>4</sub> (ClO <sub>4</sub> ) <sub>3</sub>
	Nd(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	Nd(tBSO) <sub>4</sub> (ClO <sub>4</sub> ) <sub>3</sub>
	Sm(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	Sm(tBSO) <sub>4</sub> (ClO <sub>4</sub> ) <sub>3</sub>
	Eu(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	Eu(tBSO) <sub>4</sub> (ClO <sub>4</sub> ) <sub>3</sub>
Gd <sub>2</sub> (PSO) <sub>11</sub> (ClO <sub>4</sub> ) <sub>6</sub>	Gd(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	
	Tb(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	
Dy <sub>2</sub> (PSO) <sub>11</sub> (ClO <sub>4</sub> ) <sub>6</sub>	Dy(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	
	Ho(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	
Er <sub>2</sub> (PSO) <sub>11</sub> (ClO <sub>4</sub> ) <sub>6</sub>	Er(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	
	Tm(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	
	Yb(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	
	Lu(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	
	Y(BSO) <sub>6</sub> (ClO <sub>4</sub> ) <sub>3</sub>	

Spectra of the di-*n*-butylsulfoxide complexes of the lighter lanthanides (51) show the bands of perchlorate ions and vibrational modes characteristic of a slight distortion of the anion indicating that some perchlorate groups are weakly coordinated to the lanthanide ions of larger radius. As one proceeds from lanthanum to the heavier lanthanides, these bands gradually decrease in intensity and disappear at terbium. Conductance studies in nitromethane show a similar trend. The shape of the hypersensitive band ( ${}^4I_{9/2} \rightarrow {}^4G_{5/2}$  of solid Nd(ClO<sub>4</sub>)<sub>3</sub>·6BSO compares reasonably well with that of neodymium in some six-coordinate β-diketonates (52), although such similarity is not conclusive. The partial coordination of the anion observed in the solid state and in nitromethane does not occur in acetonitrile.



Conductance data of the di-*t*-butylsulfoxide complexes (53) in nitromethane show a position between 1:1 and 1:2 electrolytes. Spectral evidence suggests that some of the  $\text{ClO}_4$  groups are coordinated and some are dissociated. The Raman spectrum of the lanthanum complex shows a band at  $440\text{ cm}^{-1}$ , with no correspondence in the infrared, and characteristic of the bidentate perchlorate group (symmetry  $\text{C}_{2v}$ ) (54). These facts were interpreted to indicate the gradual substitution of the bidentate  $\text{ClO}_4^-$  group ( $\text{C}_{2v}$ ) by the monodentate  $\text{ClO}_4^-$  group ( $\text{C}_{3v}$ ) as the lanthanide radius decreases.

Diphenylsulphoxide complexes of some rare earth ions were also described (55) see Table 15. Coordination through the oxygen atom of the ligand is evidenced by a considerable decrease in the  $\text{S}=\text{O}$  stretching frequency (down to about  $980\text{ cm}^{-1}$ ). Infrared data suggest that the  $\text{T}_d$  symmetry of the perchlorate ion is retained in the complexes. Molar conductance data in solvents of different donor strengths (nitromethane, nitrobenzene, acetonitrile) indicate electrolytes of the 1:3 type. Cryoscopic studies in nitrobenzene show the presence of four species, suggesting that the DPSO molecules bonded to the metal are not dissociated in solution. In accordance with these observation the complexes can be formulated as  $[\text{Ln}(\text{DPSO})_6]^{3+}3\text{ClO}_4^-$  giving the coordination number six for the metal. Some DTA studies were performed and they suggest that the complexes have nearly the same thermal stability.

TABLE 15.

Diphenylsulfoxide (DPSO)
Perchlorates (55)
$[\text{La}(\text{DPSO})_6] (\text{ClO}_4)_3$
$[\text{Ce}(\text{DPSO})_6] (\text{ClO}_4)_3$
$[\text{Pr}(\text{DPSO})_6] (\text{ClO}_4)_3$
$[\text{Nd}(\text{DPSO})_6] (\text{ClO}_4)_3$
$[\text{Sm}(\text{DPSO})_6] (\text{ClO}_4)_3$
$[\text{Gd}(\text{DPSO})_6] (\text{ClO}_4)_3$
$[\text{Ho}(\text{DPSO})_6] (\text{ClO}_4)_3$
$[\text{Yb}(\text{DPSO})_6] (\text{ClO}_4)_3$
$[\text{Y}(\text{DPSO})_6] (\text{ClO}_4)_3$

Tetramethylenesulfoxide (TMSO) forms many complexes with the rare earths. They are summarized in Table 16.

The perchlorate complexes (56) were prepared from concentrated solutions of the hydrated lanthanide perchlorates in ethanol and a small excess of TMSO. Conductivity measurements in nitromethane show that all the adducts behave as 1:3 electrolytes. The very strong  $\nu_3$  band and a strong  $\nu_1$  band for the perchlorate ion are observed, indicating that the tetrahedral symmetry is maintained. The  $\text{S}=\text{O}$  stretching mode of TMSO ( $\sim 1020\text{ cm}^{-1}$ ) is shifted to lower frequencies ( $\sim 960\text{ cm}^{-1}$ ), indicating that coordination occurs through the oxygen atom. The existence of compounds of the composition  $\text{Ln}(\text{ClO}_4)_3 \cdot 7.5\text{ TMSO}$  suggest that one molecule of the ligand may lie in a position between two lanthanide ions.

The whole series of the nitrate complexes (57) was prepared by direct reaction of the hydrated lanthanide nitrates with an excess of tetramethylenesulfoxide, followed by drying. Bertan and Madan (58) prepared the La, Nd, Sm, Gd, Dy, Er and Yb compounds by the reaction of the components

TABLE 16.

Tetramethylenesulfoxide (TMSO)						
Perchlorates (56)	Nitrates (57) (58)	Isothiocyanates (59)	Chlorides (60)	Bromides (61)	Hexafluorophosphates (62)	
[La(TMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[La(TMSO) <sub>4</sub> ] (NO <sub>3</sub> ) <sub>3</sub>		[La(TMSO) <sub>2</sub> ] Cl <sub>3</sub>	[La(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[La(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Ce(TMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Ce(TMSO) <sub>4</sub> ] (NO <sub>3</sub> ) <sub>3</sub>		[Ce(TMSO) <sub>2</sub> ] Cl <sub>3</sub>	[Ce(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Ce(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Pr(TMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Pr(TMSO) <sub>3,5</sub> ] (NO <sub>3</sub> ) <sub>3</sub>		[Pr(TMSO) <sub>2</sub> ] Cl <sub>3</sub>	[Pr(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Pr(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Nd(TMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Nd(TMSO) <sub>3,5</sub> ] (NO <sub>3</sub> ) <sub>3</sub>		[Nd(TMSO) <sub>2</sub> ] Cl <sub>3</sub>	[Nd(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Nd(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Sm(TMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Sm(TMSO) <sub>3,5</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Sm(TMSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Sm(TMSO) <sub>3</sub> ] Cl <sub>3</sub>	[Sm(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Sm(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Eu(TMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Eu(TMSO) <sub>3,5</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Eu(TMSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Eu(TMSO) <sub>3</sub> ] Cl <sub>3</sub>	[Eu(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Eu(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Gd(TMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Gd(TMSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Gd(TMSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Gd(TMSO) <sub>3</sub> ] Cl <sub>3</sub>	[Gd(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Gd(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Tb(TMSO) <sub>7,5</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Tb(TMSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Tb(TMSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Tb(TMSO) <sub>3</sub> ] Cl <sub>3</sub>	[Tb(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Tb(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Dy(TMSO) <sub>7,5</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Dy(TMSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Dy(TMSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Dy(TMSO) <sub>3</sub> ] Cl <sub>3</sub>	[Dy(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Dy(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Ho(TMSO) <sub>7,5</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Ho(TMSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Ho(TMSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Ho(TMSO) <sub>3</sub> ] Cl <sub>3</sub>	[Ho(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Ho(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Er(TMSO) <sub>7,5</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Er(TMSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Er(TMSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Er(TMSO) <sub>3</sub> ] Cl <sub>3</sub>	[Er(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Er(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Tm(TMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Tm(TMSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Tm(TMSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Tm(TMSO) <sub>3</sub> ] Cl <sub>3</sub>	[Tm(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Tm(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Yb(TMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Yb(TMSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Yb(TMSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Yb(TMSO) <sub>3</sub> ] Cl <sub>3</sub>	[Yb(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Yb(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Lu(TMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Lu(TMSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>0</sub>	[Lu(TMSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Lu(TMSO) <sub>3</sub> ] Cl <sub>3</sub>	[Lu(TMSO) <sub>6</sub> Br <sub>2</sub> ] Br	[Lu(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Y(TMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Y(TMSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Y(TMSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Y(TMSO) <sub>3</sub> ] Cl <sub>3</sub>	[Y(TMSO) <sub>7</sub> Br <sub>2</sub> ] Br	[Y(TMSO) <sub>7,5</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	

in absolute ethanol in the presence of dimethoxypropane. In both cases the complexes showed the same composition; however, Bertan and Madan (58) represent the compounds as dimers, except for La. The infrared spectra indicate that, in all cases, coordination occurs through the oxygen atom of TMSO; a significant shift of the S=O stretching band to lower frequencies (about  $975\text{ cm}^{-1}$ ) is observed. Although no doubt exists about the coordination of the nitrate group (20) (21) it is difficult to assign a monodentate, bidentate or bridging role to the coordinated nitrate group on the basis of the infrared spectra alone (21). Conductance data obtained in nitromethane suggest that an essentially neutral complex is present. The coordination number is believed to be eight and the nitrate coordination changes from predominantly monodentate to predominantly bidentate across the period.

Visible absorption bands were observed (21) for the hypersensitive transition ( ${}^4I_{9/2} \rightarrow {}^4G_5/2, {}^2G_7/2$ ) for the Nd complex and ( ${}^4I_{15/2} \rightarrow {}^2H_{11/2}$ ) for the Er complex in nitromethane. The shapes, intensities and wavelengths of these bands compare with those which Karraker (14) established for 8-coordinate Nd- $\beta$ -diketones and 6-coordinate Er- $\beta$ -diketones.

The isothiocyanate complexes (59) were prepared by the reaction of the hydrated lanthanide isothiocyanates with TMSO in *n*-butanol, from which they precipitate. The infrared spectra show a considerable shift of the S=O stretching mode to lower frequencies ( $\Delta ca. 50\text{ cm}^{-1}$ ) which is interpreted in terms of coordination through the oxygen atom of the SO group. The conductance data for millimolar solutions in nitromethane indicate that the adducts are practically non-electrolytes in this solvent. According to the infrared and conductance data it is considered that the NCS<sup>-</sup> ion is coordinated to the lanthanide ion through nitrogen, and that a coordination number of seven may be attributed to the rare earth ions in the complexes.

The infrared spectra of the chloride complexes (60) show a considerable shift of the S=O stretching mode to lower frequencies in relation to that of the free ligand ( $1015\text{ cm}^{-1}$  to about  $960\text{ cm}^{-1}$ ) suggesting coordination through the oxygen atom of the SO group. The complexes are non-electrolytes in nitromethane indicating that the chloride ions are coordinated to the tripositive lanthanide ions. Conductance data in methanol indicate the presence of 1:1 electrolytes, that may be attributed to the dissociative properties of the solvent. Considering the TMSO and the chloride ions as monodentate ligands, the coordination number will be unexpectedly low for the tripositive lanthanides. This may suggest the existence of halogen bridges in the complexes. Unfortunately the low solubility of these complexes in the usual solvents does not permit molecular weight determinations.

The formulation of the bromide complexes as  $[\text{Ln}(\text{TMSO})_7\text{Br}_2]\text{Br}$  is in accordance with infrared data and conductivity measurements in nitromethane (61).

The octahedral symmetry of the hexafluorophosphate complexes (62) is maintained since only two bands at  $840(\nu_3)$  and  $560(\nu_4)\text{ cm}^{-1}$  were observed. The S=O stretching mode for all the compounds is observed at a frequency lower than that of the free ligand (a shift from about  $1020$  to about  $980\text{ cm}^{-1}$ ) showing that coordination occurs through the oxygen atom. Considering the general formula  $\text{LnPF}_6 \cdot 7.5\text{TMSO}$  the existence of a molecule of the ligand in position between two lanthanide ions has been proposed.

Thioxane oxide (TSO) complexes formed with rare earths are summarized in Table 17.

The perchlorate complexes (26) (27) exhibit a  $T_d$  symmetry for the perchlorate ion in the i.r. spectra, but behave as 1:2 electrolytes in nitromethane; it is suggested that they exist partly as ion pairs in that solvent. The i.r. spectra show a considerable shift to lower frequencies, with a splitting, of the S=O stretching mode; this, together with the fact that the C-O-C stretching vibrations are virtually unchanged in relation to those of the free ligand, indicates that coordination occurs only through the sulfoxide oxygen atom.

The nitrate and chloride complexes (65) are formed when ethanolic solutions of the components are mixed in appropriate ratios. All the compounds, in particular the chlorides, are hygroscopic.

The i.r. spectra of the nitrates and chlorides show a shift to lower frequencies, and a splitting, of the S=O stretching mode and practically no changes in the symmetric and anti-symmetric C-O-C stretching modes, indicating coordination through the sulfoxide oxygen atom. Five or six bands are observed for the nitrate ion, indicating that this ion is coordinated to the tripositive rare earth ion.

Conductance measurements show that all the nitrates are non-electrolytes in nitromethane; the chloride adducts are 1:1 electrolytes in methanol. It is interesting to note the existence of compounds having 3.5 and 4.5 moles of TSO per mole of lanthanide (in the case of the chloride). No evidence is available for the nature of the coordination in these compounds, but considering the electrostatic nature of the bonding in the case of the tripositive lanthanides (ion-dipole attraction) it is suggested that at least one molecule may lie in position between two lanthanide ions in the solid state.

TABLE 17.

Thioxane Oxide (TSO)						
Perchlorates (63,64)	Nitrates (65)	Chlorides (65)	Bromides (66)	Isothiocyanates (67)	Hexafluorophosphates (67,68)	
[La(TSO) <sub>9</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[La(TSO) <sub>4</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[La(TSO) <sub>6</sub> ] Cl <sub>3</sub>	[La(TSO) <sub>6</sub> ] Br <sub>3</sub>	[La(TSO) <sub>5</sub> ] (NCS) <sub>3</sub>	[La(TSO) <sub>8</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Ce(TSO) <sub>9</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Ce(TSO) <sub>4</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Ce(TSO) <sub>6</sub> ] Cl <sub>3</sub>	[Ce(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Ce(TSO) <sub>5</sub> ] (NCS) <sub>3</sub>	[Ce(TSO) <sub>8</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Pr(TSO) <sub>9</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Pr(TSO) <sub>4</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Pr(TSO) <sub>6</sub> ] Cl <sub>3</sub>	[Pr(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Pr(TSO) <sub>5</sub> ] (NCS) <sub>3</sub>	[Pr(TSO) <sub>8</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Nd(TSO) <sub>9</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Nd(TSO) <sub>4</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Nd(TSO) <sub>6</sub> ] Cl <sub>3</sub>	[Nd(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Nd(TSO) <sub>5</sub> ] (NCS) <sub>3</sub>	[Nd(TSO) <sub>8</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Sm(TSO) <sub>8.5</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Sm(TSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Sm(TSO) <sub>4.5</sub> ] Cl <sub>3</sub>	[Sm(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Sm(TSO) <sub>5</sub> ] (NCS) <sub>3</sub>	[Sm(TSO) <sub>8</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Eu(TSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Eu(TSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Eu(TSO) <sub>4.5</sub> ] Cl <sub>3</sub>	[Eu(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Eu(TSO) <sub>5</sub> ] (NCS) <sub>3</sub>	[Eu(TSO) <sub>8</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Gd(TSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Gd(TSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Gd(TSO) <sub>4.5</sub> ] Cl <sub>3</sub>	[Gd(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Gd(TSO) <sub>5</sub> ] (NCS) <sub>3</sub>	[Gd(TSO) <sub>8</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Tb(TSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Tb(TSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Tb(TSO) <sub>3.5</sub> ] Cl <sub>3</sub>	[Tb(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Tb(TSO) <sub>5</sub> ] (NCS) <sub>3</sub>	[Tb(TSO) <sub>8</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Dy(TSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Dy(TSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Dy(TSO) <sub>3.5</sub> ] Cl <sub>3</sub>	[Dy(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Dy(TSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Dy(TSO) <sub>8</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Ho(TSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Ho(TSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Ho(TSO) <sub>3.5</sub> ] Cl <sub>3</sub>	[Ho(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Ho(TSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Ho(TSO) <sub>8</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Er(TSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Er(TSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Er(TSO) <sub>3.5</sub> ] Cl <sub>3</sub>	[Er(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Er(TSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Er(TSO) <sub>8</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	
[Tm(TSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Tm(TSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Tm(TSO) <sub>3.5</sub> ] Cl <sub>3</sub>	[Tm(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Tm(TSO) <sub>4</sub> ] (NCS) <sub>3</sub>		
[Yb(TSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Yb(TSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Yb(TSO) <sub>3.5</sub> ] Cl <sub>3</sub>	[Yb(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Yb(TSO) <sub>4</sub> ] (NCS) <sub>3</sub>		
[Lu(TSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Lu(TSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Lu(TSO) <sub>3.5</sub> ] Cl <sub>3</sub>	[Lu(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Lu(TSO) <sub>4</sub> ] (NCS) <sub>3</sub>		
[Y(TSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Y(TSO) <sub>3</sub> ] (NO <sub>3</sub> ) <sub>3</sub>	[Y(TSO) <sub>3.5</sub> ] Cl <sub>3</sub>	[Y(TSO) <sub>6</sub> ] Br <sub>3</sub>	[Y(TSO) <sub>4</sub> ] (NCS) <sub>3</sub>	[Y(TSO) <sub>8</sub> ] (PF <sub>6</sub> ) <sub>3</sub>	

The complex bromides (61) behave as non-electrolytes in nitromethane, and the i.r. spectra show that coordination of the rare earth ion occurs through the oxygen atom of the sulfoxide group.

In the case of the isothiocyanates (66) a considerable shift of the S=O stretching mode to lower frequencies in relation to that of the free ligand ( $1018\text{ cm}^{-1}$  to about  $995\text{ cm}^{-1}$ ) indicates that coordination of the rare earth occurs through the sulfoxide oxygen atom. The symmetric and asymmetric C-O-C stretching modes are practically unaltered relative to those of the free TSO, indicating that the ether oxygen atom is not bonded to the tripositive lanthanide ion. The frequencies observed for all three vibrational modes of the  $\text{NCS}^-$  ion ( $\nu_{\text{CN}}, \nu_{\text{CS}}, \nu_{\text{NCS}}$ ) indicate that this ion is bonded to the rare earth ion through the nitrogen atom. Conductance measurements in nitromethane indicate that the complexes are non-electrolytes in this solvent.

In the i.r. spectra of the hexafluorophosphate complexes (67) (68) the strong band of the free ligand, assigned to the S=O stretching vibration, has shifted to the lower frequency region ( $1019$  to about  $975\text{ cm}^{-1}$ ) as would be expected for metal-oxygen bonding. The bands attributed to the  $\text{PF}_6^-$  ion indicate that the octahedral symmetry is maintained and that these  $\text{PF}_6^-$  ions are not coordinated to the tripositive lanthanide ions.

The complexes were prepared from the lanthanide hexafluorophosphates and an excess of the ligand in methanol. By using water/ethanol instead of methanol, compounds with the composition  $\text{Ln}(\text{PF}_6)_3 \cdot 7.5\text{TMSO}$  were obtained, including complexes of Tm, Yb and Lu.

Complexes formed by 1,4-dithiane monoxide (DTMSO) and *trans*-1,4-dithiane 1,4-dioxide (TDTD) are presented in Table 18. In the complexes formed by DTMSO (69) the  $T_d$  symmetry of the perchlorate ion is maintained. Solid DTMSO shows four bands at  $1064, 1045, 1035$  and  $1020\text{ cm}^{-1}$  mainly attributed to S=O stretching vibrations (70); in the complexes the S=O stretching mode is found at about  $980\text{ cm}^{-1}$ , indicating that the coordination occurs through the oxygen atom. The compounds of La, Nd, Tb and Y behave as 1:2 electrolytes in nitromethane; the data for Er and Yb compounds approach those of 1:3 electrolytes. The existence of ion pairs may be responsible for the observed behavior.

TABLE 18.

1,4-Dithiane monoxide (DTMSO)	<i>trans</i> -1,4-Dithiane 1,4-dioxide (TDTD)	
Perchlorates (69)	Perchlorates (71)	Hexafluorophosphates (72)
[La(DTMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[La(TDTD) <sub>5</sub> ] (ClO <sub>4</sub> ) <sub>3</sub> · 5H <sub>2</sub> O	[La(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
		[Ce(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
		[Pr(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
[Nd(DTMSO) <sub>8</sub> ] (ClO <sub>4</sub> ) <sub>3</sub>	[Nd(TDTD) <sub>6</sub> ] (ClO <sub>4</sub> ) <sub>3</sub> · 3H <sub>2</sub> O	[Nd(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
		[Sm(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
		[Eu(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
		[Gd(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
[Tb(DTMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub> · 2H <sub>2</sub> O	[Tb(TDTD) <sub>6</sub> ] (ClO <sub>4</sub> ) <sub>3</sub> · 3H <sub>2</sub> O	[Tb(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
		[Dy(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
		[Ho(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
[Er(DTMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub> · 2H <sub>2</sub> O	[Er(TDTD) <sub>6</sub> ] (ClO <sub>4</sub> ) <sub>3</sub> · 3H <sub>2</sub> O	[Er(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
		[Tm(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
[Yb(DTMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub> · 2H <sub>2</sub> O		[Yb(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
	[Lu(TDTD) <sub>6</sub> ] (ClO <sub>4</sub> ) <sub>3</sub> · 3H <sub>2</sub> O	[Lu(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O
[Y(DTMSO) <sub>7</sub> ] (ClO <sub>4</sub> ) <sub>3</sub> · 2H <sub>2</sub> O	[Y(TDTD) <sub>6</sub> ] (ClO <sub>4</sub> ) <sub>3</sub> · 3H <sub>2</sub> O	[Y(TDTD) <sub>4</sub> ] (PF <sub>6</sub> ) <sub>3</sub> · 4H <sub>2</sub> O

In the case of the perchlorate complexes (71) the symmetry of the perchlorate ion is maintained, since only two bands at 1080 ( $\nu_3$ ) and 620 ( $\nu_4$ )  $\text{cm}^{-1}$  are observed. The S=O stretching bands are observed at lower frequencies in relation to that of the free ligand indicating that coordination occurs through oxygen. Some observations indicate that the ligand functions at least partially as a unidentate ligand.

In the case of the hexafluorophosphate (72), coordination of the ligand through oxygen is evidenced by a shift of the S=O stretching mode to lower frequencies in relation to that of the free ligand (1016 to 1002 - 986  $\text{cm}^{-1}$ ). The octahedral symmetry of the  $\text{PF}_6^-$  ion is maintained, indicating that this ion is not coordinated to the tripositive lanthanide ion. Conductance data of approximately millimolar aqueous solutions indicate that the compounds are 1:3 electrolytes. It is interesting to consider that the ligand TDTD, having two oxygen atoms, should be able to coordinate as a bridge. The existence of polymeric species may be expected but no experimental evidence has been presented.

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