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MIXED-LIGAND COMPLEXES OF LANTHANIDE PERCHLORATE WITH 1,3-BIS(PHENYLSULPHINYL)PROPANE AND 1,10-PHENANTHROLINE

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Abstract—The mixed-ligand complexes of lanthanide perchlorate with 1,3-bis-(phenylsulphinyl)propane (bphsp) and 1,10-phenanthroline (phen) have been synthesized and characterized by elemental analysis, conductance, thermal analysis, magnetic and spectral (IR, UV–vis XPS) data. The complexes have the general formula $[La(bphsp)_3(phen)(ClO_4)](ClO_4)_2$ and $[Ln(bphsp)_{2.5}(phen)(ClO_4)](ClO_4)_2 \cdot nH_2O$ (where Ln = Pr, Nd, Sm, Tb, Ho, Er, Yb and Y, $n = 0–2$).

As a part of our studies on lanthanide complexes of disulphoxides, some complexes of lanthanide perchlorate with disulphoxides have been reported.[1] To study the influence of a second ligand upon the properties of lanthanide complexes of disulphoxide, mixed-ligand complexes of lanthanides with disulphoxide and organic base were synthesized. In this paper we report on the synthesis and characterization of mixed-ligand complexes of lanthanide perchlorate with bis(phenylsulphinyl)propane (bphsp) and 1,10-phenanthroline (phen).

EXPERIMENTAL

Materials

Lanthanide oxides (99.95%) were converted to the corresponding perchlorates. Bis(phenylsulphinyl)propane was prepared by the method in the literature;[1] m.p. 137–139°C, phenanthroline and other chemicals were analytical grade.

Synthesis

Anhydrous methanol solutions (10 cm^3) of lanthanide perchlorate (0.001 mol), phen (0.001 mol) and triethylorthoformate (2–3 cm^3) were mixed and refluxed for about 10 min. An anhydrous methanol solution (5 cm^3) of bphsp (0.002 mol) was added dropwise to the mixed solution. The mixture was stirred and refluxed for 6–8 h. The precipitated complex was filtered, washed several times with anhydrous methanol, ether and dried in a vacuum desiccator over $CaCl_2$.

Physical methods

Conductivities of the complexes in anhydrous methanol (10^{-3} mol dm^{-3} solution) were taken at room temperature using a DDS 11A conductometer. The IR spectra of the ligand and the complexes were recorded in the 400–4000 cm^{-1} range on a Nicolet DX V4 spectrometer using KBr discs. Magnetic susceptibilities were measured at room temperature by Gouy's method using $Ni(en)_3S_2O_3$ as the calibrant. Electronic spectra of the ligand and the complexes were recorded on a Shimadzu UV-240 spectrophotometer in the regions 340–850 (solid) and 190–325 nm (*ca* 10^{-5} mol dm^{-3} anhydrous methanol solution). Thermal characterization studies of the complexes were carried out on a Shimadzu DT thermal analyser and MP-500 melting point meter. The fluorescence spectrum of

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the Tb complex was measured using a Model F111 AI Fluorolog-2 spectrofluorometer at room temperature. X-ray photoelectron spectra were measured on a ESCALAB MK IIXPS meter. Metal contents were estimated by EDTA titration after decomposition of the sample with $HClO_4$. (Precaution : this reaction must be carried out in a fumehood.) Carbon, hydrogen and nitrogen analyses were performed on a Perkin–Elmer 240C elemental analyser.

RESULTS AND DISCUSSION

Analytical data of the complexes (Table 1) indicate that all the complexes have the general formula $La(bphsp)_3(phen)(ClO_4)_3$ and $Ln(bphsp)_{2.5}(phen)(ClO_4)_3 \cdot nH_2O$ (where Ln = Pr, Nd, Sm, Tb, Ho, Er, Yb and Y, $n = 0$–2). The complexes are soluble in dimethylformide and dimethylsulphoxide, and slightly soluble in methanol and acetonitrile. The electrical conductance values of the complexes in methanol are in the range 185–223 s mol^{-1} cm^{-2}, which indicates that the complexes behave as 2 : 1 electrolytes.[2]

Thermal analysis

The complexes are air stable at room temperature, with melting points in the range 195–213°C. Thermal analyses of the complexes show that decomposition starts when they are heated above 220°C after melting. The TGA data of Nd and Tb complexes show that the total weight loss [1.5% (Nd) and 1.5% (Tb) at 70–110°C and 50–90°C] respectively are consistent with the loss for one crystal water molecule (the theoretical weight loss for one water molecule is 1.3 and 1.3%).

IR spectra

In the IR spectra of the complexes, observed shifts in the ring vibration band (1509.8–1520.5 cm^{-1}) of phen suggest the presence of coordinated phen. The IR spectra of the complexes also indicated that the bphsp binds metals through the oxygen atoms of the sulphoxide moieties: the S=O bond stretching frequencies of the complexes (976–984 cm^{-1}) are lower than the corresponding ones in the free ligand (1039.8 cm^{-1}), and the S=O bond stretching band of the free ligand disappears.[1,3] IR data also indicate the presence of a unidentate perchlorate group ($\nu_{\mathrm{Cl-O}}$: 1140.0–1149.0, 920.0–934.2, 625.1–626.7 cm^{-1}) and ionic perchlorate groups ($\nu_{\mathrm{Cl-O}}$: 1076.0–1090.9 cm^{-1}) in the complexes.[3,4] Principal IR bands of the ligand and a complex were presented in Fig. 1.

Magnetic moments

The observed magnetic moments of the complexes are close to those given by Van Vleck,[5] indicating that the lanthanides in the complexes remain in the +3 oxidation state and the 4*f* electrons are little influenced by the ligand : bphsp and phen.

Table 1. Analytical and physical properties of the complexes

Complex	Colour	Found (Calc.) (%) M	C	H	N	μ_{eff} B.M.
$La(bphsp)_3(phen)(ClO_4)_3$	White	9.3 (9.3)	46.3 (45.8)	3.4 (3.7)	2.3 (1.9)	
$Pr(bphsp)_{2.5}(phen)(ClO_4)_3 \cdot H_2O$	Greenish	10.3 (10.3)	43.3 (43.4)	3.5 (3.7)	2.1 (2.1)	3.20
$Nd(bphsp)_{2.5}(phen)(ClO_4)_3 \cdot H_2O$	White	10.8 (10.5)	43.1 (43.3)	3.8 (3.7)	1.9 (2.0)	3.30
$Sm(bphsp)_{2.5}(phen)(ClO_4)_3 \cdot 2H_2O$	White	10.6 (10.8)	42.5 (42.6)	3.3 (3.8)	1.6 (2.0)	1.48
$Tb(bphsp)_{2.5}(phen)(ClO_4)_3 \cdot H_2O$	White	11.4 (11.5)	42.8 (42.9)	3.4 (3.6)	1.7 (2.0)	9.40
$Ho(bphsp)_{2.5}(phen)(ClO_4)_3$	White	11.4 (12.0)	43.7 (43.2)	3.2 (3.5)	1.8 (2.0)	
$Er(bphsp)_{2.5}(phen)(ClO_4)_3$	Pinkish	11.4 (12.2)	43.8 (43.2)	3.4 (3.5)	1.6 (2.0)	9.33
$Yb(bphsp)_{2.5}(phen)(ClO_4)_3$	White	12.1 (12.5)	43.8 (43.0)	3.4 (3.5)	1.8 (2.0)	4.22
$Y(bphsp)_{2.5}(phen)(ClO_4)_3$	White	6.4 (6.9)	46.7 (45.8)	3.6 (3.7)	2.0 (2.2)	

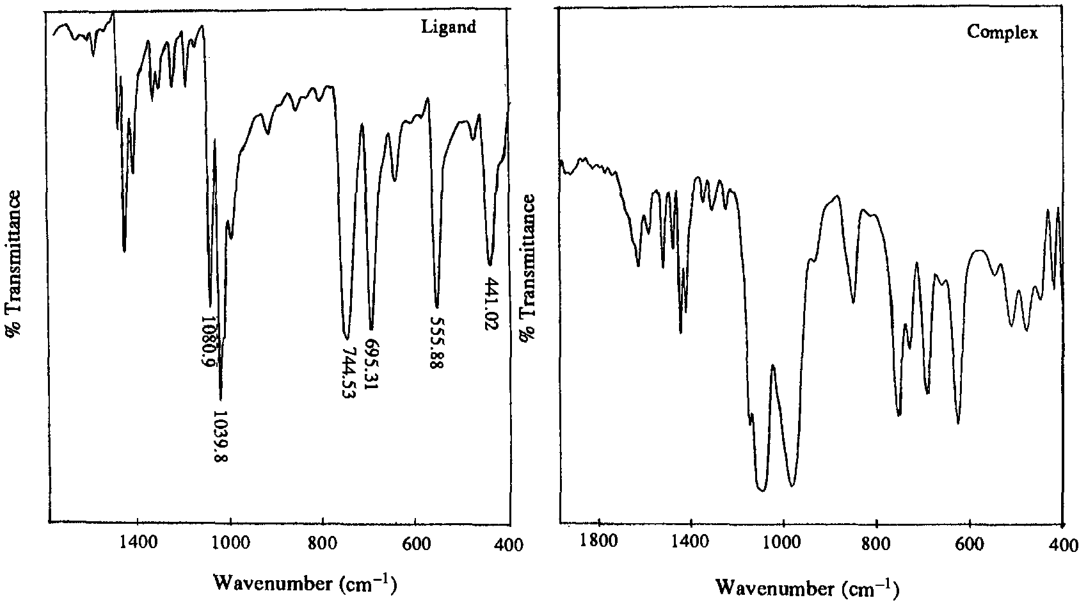

Fig. 1. IR spectra of the ligand (bphsp) and the complex [Tb(bphsp)$_{2.5}$(phen)(ClO$_4$)$_3$·H$_2$O].

Electronic spectra

The characteristic bands of the bphsp at 210 and 240, 270 nm are assigned to the n–π^* transition of the S=O group and two π–π^* transitions of the benzene ring.[6] The characteristic bands of phen at 203, 224 and 263 nm are π–π^* transitions of the ring. In the spectra of the complexes, the n–π^* band of the S=O group is slightly blue-shifted to 209–207 nm and the bands at 261–264 and 228–230 nm are π–π^* transitions of the ligands bphsp and phen. The results are presented in Fig. 2.

The electronic spectra of Pr, Nd, Ho and Er have been determined in the solid state in the 340–850 nm region. The absorption bands due to the f–f transitions of the lanthanide ions in the complexes show small red shifts compared with those of the respective aquo ions. The nephelauxetic parameter $(\bar{\beta})$,[7] the bonding parameter $(b^{1/2})$[8] and Sinha's[9] covalency parameter for the complexes of Pr^{3+}, Nd^{3+}, Ho^{3+} and Er^{3+} (Table 2) suggest a weak covalent character in the metal–ligand bond. The values of $b^{1/2}$ and δ in the complexes are in the order Pr, Nd > Ho, Er, which reveals that for the same ligand covalency in the lighter lanthanide ions is greater than in the heavier lanthanide ions.

Excitation and emission spectra

The excitation spectrum at 544 nm emission of [Tb(bphsp)$_{2.5}$(phen)(ClO$_4$)](ClO$_4$)$_2$·H$_2$O] at room temperature consists of five peaks at 288, 302, 316, 328 and 346 nm. The emission spectrum in 316 nm excitation shows the transitions $^5D_4 \rightarrow {}^7F_6$ as a hypersensitive transition at 496 nm with a strong

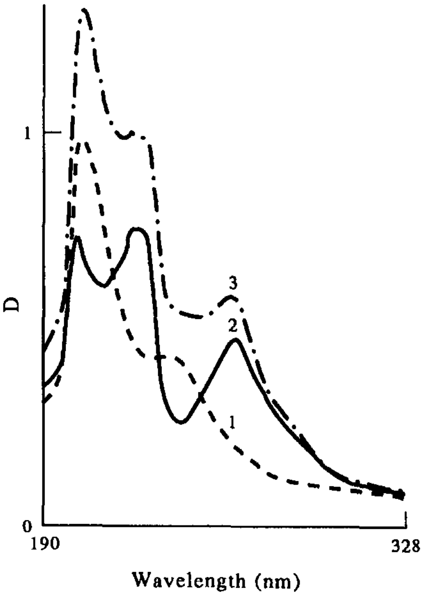

Fig. 2. UV spectra of bphsp, phen and complexes **1**, a methanol solution of bphsp, **2**, a methanol solution of phen and **3**, a methanol solution of Nd(bphsp)$_{2.5}$(phen)(ClO$_4$)$_3$·H$_2$O.

Table 2. Covalence parameters

Complex	$\bar{\beta}$	$b^{1/2}$	C
Pr^{2+}	0.9948	0.0510	0.5217
Nd^{3+}	0.9954	0.0480	0.4620
Ho^{3+}	0.9995	0.0158	0.0500
Er^{3+}	1.0020		

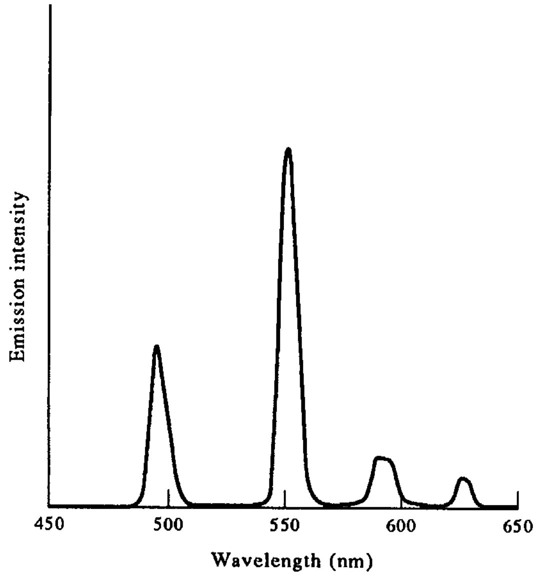

Fig. 3. Emission spectrum of solid $[Tb(bphsp)_{2.5}(phen)(ClO_4)](ClO_4)_2 \cdot H_2O$ by excitation with 316 nm radiation at room temperature.

emission, $^5D_4 \rightarrow {}^7F_5$ at 551 nm with a maximum emission, $^5D_4 \rightarrow {}^7F_4$ at 590 nm and $^5D_4 \rightarrow {}^7F_3$ at 628 nm with a weak emission.

X-ray photoelectron spectra for the complexes of Nd^{3+} and Ho^{3+}

The XPS data show that the bonding energy (E_b) peaks of 1*s* and 2*p* of the atoms in coordinated ligands are symmetric and single peaks and the N atoms of phen participate in coordination because of the N_{1s} bonding energy of the phen ligand in the complexes increase $\Delta E_b^N = 0.7$ eV (Table 3).

On the basis of the above evidence, it is concluded that these ligands have two coordination sites—the nitrogen atoms of phen and the oxygen atoms of bphsp, respectively. The complexes were assigned the formulae $[La(bphsp)_3(phen)(ClO_4)](ClO_4)_2$ and $[Ln(bphsp)_{2.5}(phen)(ClO_4)](ClO_4)_2 \cdot nH_2O$ (Ln = Pr, Nd, Sm, Tb, Ho, Er, Yb and Y, $n = 0$–2).

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Table 3. The bonding energies of electrons (E)

Complex	C_{1s}	N_{1s}	O_{1s}	S_{2p}	$Nd_{3d5/2}$	Ho_{4d}
$Nd(bphsp)_{2.5}(phen)(ClO_4)_3 \cdot H_2O$	284.6	399.1	531.9	166.3	983.1, (978.3)	
$Ho(bphsp)_{2.5}(phen)(ClO_4)_3$	284.6	399.1	531.8	166.4		162.6
phen	284.6	398.4				