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SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND COMPLEXES OF YTTRIUM AND LANTHANIDE(III)–BIS(PHENYLSULPHINYL)PROPANE AND BIPYRIDYL

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Abstract—A series of novel mixed ligand complexes of yttrium and lanthanide(III) ions with bis(phenylsulphinyl)propane and bipyridyl have been synthesized. The complexes were assigned the formula $[Ln(bphsp)_3(bipy)(ClO_4)](ClO_4)_2$ (bphsp = bis(phenylsulphinyl)propane; bipy = bipyridyl; Ln = La, Pr, Eu, Gd, Tb, Ho, Er, Yb, Y) and $[Nd(bphsp)_3(bipy)(ClO_4)](ClO_4)_2 \cdot 2H_2O$ on the basis of analytical, conductance and spectral (IR, electronic) and magnetic data. In all cases, the lanthanide ion bonds to the sulphoxide moiety via the oxygen atoms and to the bipy via the nitrogen atom. The coordination number of the complexes may be nine. The spectral strength for emission spectrum ($^5D_0 \rightarrow {}^7F_2$) of $Eu(bphsp)_3(bipy)(ClO_4)_3$ was increased by the coordination of bipy.

Lanthanide complexes of disulphoxide have been reported,[1] but very few papers have appeared on mixed-ligand complexes of lanthanides with disulphoxide. The present paper reports a series of novel mixed-ligand complexes of lanthanide-bis(phenylsulphinyl)propane (bphsp) and bipyridyl (bipy). The aim of this work was to explore the influence of bipy on the properties of bphsp complexes of lanthanides.

EXPERIMENTAL

Materials and methods

The lanthanide perchlorates were prepared by dissolving the respective oxide (99.95%) in $HClO_4$. The ligand, bphsp, was prepared by nitric acid oxidation of the parent disulphide. The parent disulphide was obtained by adding equimolar amounts of propyl bromide to a solution of thiophenol. The melting point of bphsp is 137–139°C.[2] Other chemicals were analytical reagent grade.

The complexes were prepared as follows. A solution of 1 mmol bphsp in 5 cm^3 anhydrous methanol was added dropwise to a refluxing solution of 0.5 mmol metal perchlorate and 0.5 mmol bipy in 10 cm^3 anhydrous methanol and 3 cm^3 triethylthioformate. The mixture was stirred and refluxed for 4–6 h to give the complex as a precipitate. The complex was filtered, washed with anhydrous methanol and ether, and dried in a desiccator over $CaCl_2$ *in vacuo*. Yield >80% (refer to bphsp).

Physical measurements

Conductance measurements were carried out on a 10^{-3} mol dm^{-3} anhydrous methanol at 25°C with a DDS-IIA conductometer. IR spectra were recorded with a Nicolet DX V4 spectrometer using KBr plates in the range of 400–4000 cm^{-1}. 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

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the complexes were recorded on a Shimadzu UV-240 spectrophotometer. The solid state electronic spectra of the complexes were recorded in the 340–850 nm region by a reflectance technique using $BaSO_4$ as the reference material. The methanol solution of the ligands and complexes (10^{-5} mol dm^{-3}) were used to record UV spectra. Visible spectra of the complexes in methanol–chloroform (1 : 2) were recorded in the range 340–850 nm. Thermal decomposition study in nitrogen was carried out on a Shimadzu DT-30 thermal analyser. Melting points of the complexes were measured using a MP-500 melting point meter. Solid state emission spectrum was recorded by a Model F111 AI Fluorolog-2 spectofluorometer at room temperature.

Analysis

The lanthanide ion content was determined by the standard EDTA complexometric titration. Carbon, hydrogen and nitrogen analyses were obtained on a Perkin–Elmer 240C elemental analyser.

RESULTS AND DISCUSSION

Analytical data of the complexes (Table 1) show that all 10 complexes have the general formula $Ln(bphsp)_3(bipy)(ClO_4)_3 \cdot nH_2O$ (where Ln = La, Pr, Eu, Gd, Tb, Ho, Er, Yb, Y, $n = 0$; Ln = Nd, $n = 2$). All the complexes are soluble in dimethylformamide, disulphoxide, slightly soluble in methanol, acetonitrile, chloroform and ethanol and insoluble in benzene. The conductance in methanol (Table 1) show that the complexes are 2 : 1 electrolytes and that one ClO_4 is coordinated.[3]

All the complexes are air stable and melt up to 200–230°C. The DTA data of $[Tb(bphsp)_3(bipy)(ClO_4)](ClO_4)_2$ show that the complex is stable up to ~230°C and undergo decomposition around 230 (strong peak) and 620°C.

IR spectra and the nature of coordination

In the spectra of the complexes, the absorptions associated with the S═O stretching modes undergo significant shifts on coordination. The S═O stretching frequency in free bphsp appears as a strong absorption at 1039.8 cm^{-1}, which disappears on complex formation with a new band appearing in the 972–988 cm^{-1} region (Table 2), showing coordination of bphsp to the metal ion through its oxygen atoms. A shift of the S═O stretching frequency towards lower wavenumbers is an indication of a decrease in the double bond character of S═O, suggesting oxygen coordination of S═O.[4] In the IR spectra of the complexes, the appearance of a band at 1589–1601 cm^{-1} assigned to $\nu_{(C=N)}$ of bipy confirms the presence of bipy in the complexes.

Table 1. Analytical, magnetic and conductance data of the complexes

Complex	M.p. (°C)	Found (Calc.), %				Λ_m (s cm^2 mol^{-1})	μ_{eff} (B.M.)
		Ln	C	H	N		
$La(bphsp)_3(bipy)(ClO_4)_3$	200–203	9.5	44.7	3.8	2.0	171	
		(9.5)	(44.9)	(3.8)	(1.9)		
$Pr(bphsp)_3(bipy)(ClO_4)_3$	221–222	9.6	44.9	3.6	1.6	207	3.34
		(9.6)	(44.9)	(3.8)	(1.9)		
$Nd(bphsp)_3(bipy)(ClO_4)_3 \cdot 2H_2O$	213–216	9.7	43.8	3.7	1.8	214	3.55
		(9.5)	(43.7)	(4.0)	(1.9)		
$Eu(bphsp)_3(bipy)(ClO_4)_3$	221–224	10.2	44.6	3.5	1.9	217	3.30
		(10.3)	(44.5)	(3.8)	(1.9)		
$Gd(bphsp)_3(bipy)(ClO_4)_3$	228–229	10.7	44.2	3.5	1.8	210	7.92
		(10.3)	(44.4)	(3.8)	(1.9)		
$Tb(bphsp)_3(bipy)(ClO_4)_3$	226–228	10.1	44.2	3.6	1.7	221	9.76
		(10.7)	(44.3)	(3.8)	(1.9)		
$Ho(bphsp)_3(bipy)(ClO_4)_3$	228–230	10.7	43.9	3.6	1.8	216	10.04
		(11.0)	(44.1)	(3.7)	(1.9)		
$Er(bphsp)_3(bipy)(ClO_4)_3$	225–227	11.1	43.7	3.4	1.8	217	9.17
		(11.2)	(44.1)	(3.7)	(1.9)		
$Yb(bphsp)_3(bipy)(ClO_4)_3$	223–226	11.6	43.3	3.5	1.5	224	4.25
		(11.5)	(43.9)	(3.7)	(1.9)		
$Y(bphsp)_3(bipy)(ClO_4)_3$	228–230	6.4	46.2	3.9	1.7	219	
		(6.7)	(46.5)	(3.9)	(2.0)		

Table 2. Important IR frequencies (cm^{-1}) of complexes

Complex	ν(S—O)	ν(C=N)	ν(Cl—O) (coordinated ClO_4) $\nu_4(E)$	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$ $\nu_5(E)$	ν(Cl—O) (ClO_4^-)
La	983.6	1593.7	1145.9	1013.3	936.6	625.5	1089.9
Pr	981.6	1598.3	1146.0	1011.0	937.2	626.0	1089.8
Nd	983.1	1598.6	1146.0	1004.4	937.5	624.8	1089.6
Eu	982.4	1597.7	1146.5	1008.0	932	627.5	1089.1
Gd	972.2	1589.9	1145.9	1004.0	936.9	624.9	1090.2
Tb	984.2	1600.3	1146.2	1008.0	936.2	626.3	1089.5
Ho	985.1	1600.9	1146.3	1006.0	936.4	625.9	1089.1
Er	983.5	1600.9	1146.3	1006.0	936.4	625.1	1089.7
Yb	988.3	1601.8	1146.8	1008.0	936.8	626.5	1088.8
Y	986.6	1600.7	1146.2	1016.0	936.3	626.2	1089.2

The IR spectra of the complexes show a strong absorption at 1089.9–1090.2 cm^{-1}, which is assigned to the $\nu_3(T_2)$ vibration of ionic ClO_4^-. The IR spectra of the complexes also exhibit bands associated with monodentate coordinated ClO_4^- with C_{3v} symmetry.[5] The IR bands and assignments are listed in Table 2.

Magnetic studies

The magnetic data of the complexes are presented in Table 1. All the complexes, except those of lanthanum and yttrium, are paramagnetic. The observed magnetic moments show little deviation from the Van Vleck values,[6] indicating that the 4*f* electrons do not participate in bond formation in these complexes.

Electronic spectra

The UV spectra of the ligand and complexes are presented in Table 3. From Table 3, it is indicated that the band at 203–204 nm is assigned to n–π^* of S=O, the bands in the region of 225–325 nm are the π–π^* and n–π^* of the bipy ring and benzene ring of bphsp.[7] The data also shown that bphsp and bipy are coordinated to the metal.

Table 3. UV spectra (nm) of the ligand and complex

Compound	n–π^* (S=O)	n–π^* and π–π^* (bipy and benzene)			
biby		201	234	282	305
bphsp	208		239	272	
La	204		237	282	304
Pr	204		238	282	304
Nd	204		238	282	304
Eu	204		238	282	302
Gd	204		238	283	302
Tb	204		238	282	302
Ho	204		238	282	302
Er	204		238	283	304
Yb	204		238	283	304
Y	204		238	283	306

The solution and solid state spectra of the complexes in the visible range show a shift of spectral bands towards lower energy as compared to those of the respective aqua ions, which is known as the nephelauxetic effect.[8] The nephelauxetic parameter is less than one, $b^{1/2}$ and δ[9] (Table 4) are positive for these complexes, which show weak covalent bonding between the metal and the ligands. The values of $b^{1/2}$ and δ in these complexes are in the order Pr, Nd > Ho, Er. The results are the same as those of bphsp complexes in which the lighter lanthanide has greater values than in the heavier lanthanide.[2] A comparison of the covalent parameters (β, $b^{1/2}$, δ) calculated from the solid state spectra with those of values obtained from solution spectra indicate that the covalency is greater in the solid.

The intensity of *f*–*f* transitions of the complexes are presented in Table 5. The oscillator strengths of the hypersensitive transition in Nd^{3+}, Ho^{3+} and Er^{3+} complexes in CH_3OH–$CHCl_3$ (1 : 2) display larger changes compared to the corresponding aqua ion and are larger than those of pure bphsp complexes. The increase of the oscillator strength is related to the basicity of the ligand around Ln^{3+} and the symmetry: bipy substituting for H_2O or ClO_4^- can increase the basicity of the ligand around Ln^{3+} and can change the symmetry of the complexes.

Fluorescence spectrum

The fluorescence spectrum of $[Eu(bphsp)_3(bipy)(ClO_4)](ClO_4)_2$ at room temperature is presented in

Table 4. Covalency parameters

Complex	$\bar{\beta}$ solid	$\bar{\beta}$ solution	$b^{1/2}$ solid	$b^{1/2}$ solution	δ solid	δ solution
Pr	0.9940	0.9970	0.0549	0.0387	0.6036	0.3092
Nd	0.9940	0.9947	0.0549	0.0515	0.6036	0.5328
Ho	0.9971	1.000	0.0336	0	0.2908	0
Er	0.9990	0.9992	0.0224	0.020	0.1001	0.0800

Table 5. Oscillator strength of complexes

Complex	Transition	Energy CH_3OH–$CHCl_3$	Solid	$P_{exptl}(10^6)$ CH_3OH–$CHCl_3$
$[Pr(bphsp)_3(bipy)(ClO_4)](ClO_4)_2$	$3H_4 \rightarrow {}^1D_2$	593.6	596.6	2.88
	${}^3P_0$	481.5	482.4	3.23
	${}^3P_1$	469	469.6	6.59
	${}^3P_2$	444.5	445	14.31
$[Nd(bphsp)_3(bipy)(ClO_4)](ClO_4)_2 \cdot 2H_2O$	${}^4I_{9/2} \rightarrow {}^4F_{5/2}$	799.2	801.8	9.80
	${}^4F_{7/2}$	748.4	748.4	11.59
	${}^4G_{5/2}, {}^2G_{7/2}$	579.5	584.0	17.44
	${}^4G_{7/2}$	522.5	526.1	4.27
	${}^4G_{9/2}$	510.5	513.2	2.80
$[Ho(bphsp)_3(bipy)(ClO_4)](ClO_4)_2$	${}^5I_8 \rightarrow {}^5F_5$	639.7	642	2.38
	${}^5S_2, {}^5F_4$	535.8	537.6	4.54
	${}^5F_3$	484.3	484.8	1.10
	${}^5F_2, {}^3K_8$	467.3	472	1.51
	${}^5G_6$	451.9	450.6	10.06
	${}^3H_6, ({}^5G, {}^3H)_5$	360.5	360.2	3.77
$[Er(bphsp)_3(bipy)(ClO_4)](ClO_4)_2$	${}^4I_{15/2} \rightarrow {}^4F_{9/2}$	651.9	652.4	1.62
	${}^2H_{11/2}$	521.0	521.4	4.82
	${}^4F_{7/2}$	486.2	487.2	3.18
	${}^4G_{11/2}$	378.2	378.2	11.03
	${}^4G_{9/2}$	363.6	363.9	1.70

Fig. 1. The analysis of this spectrum indicates the following attributions: the ${}^5D_0 \rightarrow {}^7F_0$ transition at 577.5 nm is observed to be a weak band; the ${}^5D_0 \rightarrow {}^7F_1$ transition around 590 nm is separated into two bands (588.0, 591.0 nm); three strong bands that appear at 609.5, 614.5 and 619.0 nm are assigned to the ${}^5D_0 \rightarrow {}^7F_2$ transition; the weak band at 648.5 nm may be ${}^5D_0 \rightarrow {}^7F_3$, the ${}^5D_0 \rightarrow {}^7F_4$ transition appears at 688.0, 693.5 and 699.5 nm. The presence of the ${}^5D_0 \rightarrow {}^7F_0$ transition indicates the absence of inversion symmetry at the europium(III) site. The electric dipole transition (${}^5D_0 \rightarrow {}^7F_2$) is clearly stronger than the magnetic dipole (${}^5D_0 \rightarrow {}^7F_1$), which also shows the lower symmetry of the europium(III) site. The C.F. splitting of ${}^7F_j$ levels observed suggests possible nine-fold coordination. According to the splittings of ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$, the Eu^{3+} ion occupies a site of lower symmetry than C_{4v} or D_{3h}.[10,11]

Thus, the complexes, on the basis of their elemental analyses, molar conductance, magnetic moments, thermal analyses, IR and electronic and

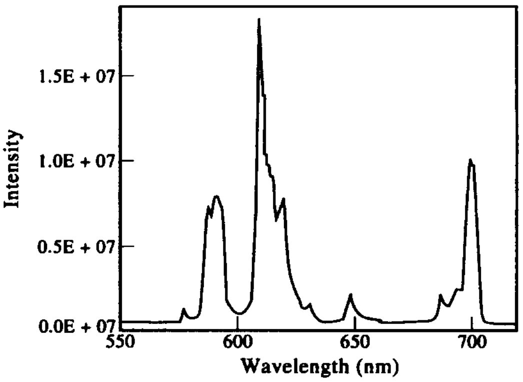

Fig. 1. Fluorescence spectrum of $[Eu(bphsp)_3(bipy)(ClO_4)](ClO_4)_2$.

fluorescence spectral studies, have been assigned the general formula: $[Ln(bphsp)_3(bipy)ClO_4)](ClO_4)_2 \cdot nH_2O$ ($n = 0, 2$). The lanthanide ions in the complexes exhibit coordination number nine. The eunpium site symmetry is lower than C_{4v} or D_{3h}.

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