

SYNTHESIS AND CHARACTERIZATION OF SOME NOVEL HEXA-COORDINATED MIXED-LIGAND COMPLEXES OF LANTHANIDES WITH 4-(3,5-DIPHENYL-2-PYRAZOLIN- 1-YL) BENZENESULPHONIC ACID

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Abstract—Novel mixed-ligand 1,10-phenanthroline complexes of some lanthanides of the formula $[M(\text{phen})_2(\text{DPBS})_2] \cdot \text{DPBS}$, where phen = 1,10-phenanthroline, DPBS = 4-(3,5-diphenyl-2-pyrazolin-1-yl)benzene sulphonate ion and M = lanthanide and yttrium have been synthesized by the interaction of $M(\text{phen})_2(\text{ClO}_4)_3$ with HDPBS in methanol. These complexes have been characterized by elemental analyses, molar conductances, magnetic measurements, thermogravimetric analyses, XPS, IR and UV-vis spectral studies. An octahedral structure has been proposed for all the complexes, where phen is *trans* to phen in the equatorial position and two DPBS ligands are *trans* to each other at the axial positions.

2-Pyrazoline compounds have been used as optical brighteners,^{1,2} scintillators^{3,4} and photoconductive materials,⁵ and in recent years there has been great interest in the synthesis and study of new 2-pyrazoline derivatives.^{6,7} However, the synthesis and properties of lanthanide mixed-ligand complexes have not been reported so far. As part of our systematic investigation on the coordination chemistry of 2-pyrazoline ligands, the present study describes the synthesis and characterization of new lanthanide mixed-ligand 2-pyrazoline complexes.

EXPERIMENTAL

Materials

HDPBS (Fig. 1) was prepared according to the literature method⁶ and 1,10-phenanthroline was

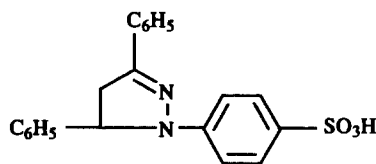


Fig. 1. Structure of HDPBS.

chemical reagent grade. Lanthanide perchlorates were prepared from their oxides and perchloric acid by the following procedure.⁸ Lanthanide(III) perchlorate were obtained by treating 1 mmol of lanthanide(III) oxide with 10 cm³ of hot aqueous perchloric acid (1 : 1). The resulting solution evaporated to dryness. The crystals, $M(\text{ClO}_4)_3 \cdot 6-8\text{H}_2\text{O}$, were dried in a vacuum desiccator over CaCl_2 (yield 0.18–0.27 g, 80–92%). Thermoanalyses show that these compounds lose combined water between 60 and 170°C and begin to decompose over the range of 250–300°C and then MOCl is formed.

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CAUTION: the concentrated solution should not be heated directly but slowly on a water bath.

Preparation of the parent compound

The parent compound, $M(\text{phen})_2(\text{ClO}_4)_3$, was prepared by refluxing a mixture of lanthanide(III) perchlorate (1 mmol) and 1,10-phenanthroline (0.3610 g, 2 mmol) in 20 cm³ dioxane for 5 h. The solid which formed when the mixture cooled was collected and washed with ether and dried *in vacuo* (80 mmHg) at 80°C for 1 h; yield 0.50–0.58 g, 60–70%. Thermolysis indicated that these parent compounds began to decompose gradually at about 200°C.

CAUTION: the parent compounds, together with the complexes, should not make contact with hot conc. acids and especially not with oxidative acids.

Synthesis of the complexes

To a filtered methanol solution of the parent compound, $M(\text{phen})_2(\text{ClO}_4)_3$ (1 mmol, 30 cm³), a solution (20 cm³) of HDPBS (1.135 g, 3 mmol) was added dropwise with stirring, and a yellow precipitate was immediately produced. The reaction mixture was heated at 60°C for 2 h. The solid was filtered, washed several times with methanol and finally with ether and dried to a constant weight *in vacuo* over silica gel; yield 0.95–1.27 g, 64–81%. Analytical data are given in Table 1.

Analyses

After destruction of organic matter with HClO_4 , the metal ions were measured by EDTA titration in the buffer solution (urotropic buffer, pH 5.5) using xylenol orange as indicator.⁹ Carbon, hydrogen and nitrogen were determined by the Instrument Analysis and Research Centre of Lanzhou University.

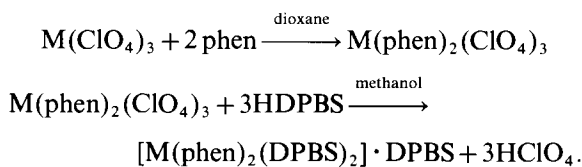
Physical methods

The IR spectra were obtained on CsI pellets using an NIC-5DX spectrophotometer. UV spectra were recorded in the 200–700 nm region in methanol with a DJ-240 spectrophotometer. Electrolyte conductivities were measured on a DDS-IIA conductometer using 10⁻³ mol dm⁻³ methanol and dimethylformamide (DMF) solutions of the complexes at 25°C. The magnetic moments were measured on a Guoy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant.¹⁰ X-ray photoelectron spectra (XPS) were recorded on a PHI-550 X-ray photoelectron spectrophotometer using a Mg-K_α irradiation unit.

TG and DTA measurements were made in a nitrogen atmosphere between room temperature and 800°C using a Thermoflex TG-DTA meter (Japan).^{11,12}

RESULTS AND DISCUSSION

The mixed-ligand complexes $[M(\text{phen})_2(\text{DPBS})_2] \cdot \text{DPBS}$ were synthesized according to the following equations:



Replacement of all perchlorate ions in the parent compound, $M(\text{phen})_2(\text{ClO}_4)_3$, by three molecules of the ligand, DPBS, was accomplished and is consistent with the above equations.

All the complexes are air stable, yellow solids. They are soluble in ethanol, methanol, ethyl acetate, DMF, dimethylsulphoxide and chloroform, but insoluble in water and benzene. They are thermally stable and do not melt or decompose up to 200°C. They are decomposed in dilute alkalis and acids only on heating.

The complexes were characterized on the basis of the following results.

IR spectra

The important IR spectral frequencies along with their relative assignments are given in Table 2. The IR spectra of the complexes $[M(\text{phen})_2(\text{DPBS})_2] \cdot \text{DPBS}$ show significant changes as compared with those of the parent ligands.

It can be seen that the $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$ frequencies of the phen shift from 1616 and 1587 cm⁻¹ to lower frequencies at *ca* 1595 and 1540 cm⁻¹. The changes of these frequencies suggest that the nitrogen atoms (in phen) participate in coordination with the metal ion. The $\nu(\text{C}=\text{N})$ and $\nu(\text{N}=\text{N})$ absorption bands of DPBS show no significant changes which indicate that the nitrogen atoms of HDPBS do not coordinate to the metal ion. In addition, the band due to $\nu(\text{SO}_3^-)$ of HDPBS appeared at 1181 cm⁻¹, but in the complexes became two bands at *ca* 1147 and 1226 cm⁻¹ and shifted to lower frequency by 33–35 cm⁻¹, or to higher frequency by 39–52 cm⁻¹. It was also observed that the relative intensity of the two bands is about 2:1. This means that only two ligands molecules (HDPBS) are coordinated to the metal ion in the unidentate form and the other one is in the outer sphere of the complex, which can be

Table 1. Physical properties and elemental analyses of the complexes

Complex	Formula ^a	Found (Calc.), %				Yield (%)	Decomp. temp. (°C)	Λ_M (S cm ² mol ⁻¹) in	
		M	C	H	N			Methanol	DMF ^b
I	La(phen) ₂ (DPBS) ₃	8.5 (8.5)	64.1 (64.0)	4.1 (4.1)	8.6 (8.6)	74	238	89.0	67.4
II	Pr(phen) ₂ (DPBS) ₃	8.6 (8.6)	64.0 (63.9)	4.1 (4.1)	8.6 (8.6)	65	230	94.8	66.2
III	Nd(phen) ₂ (DPBS) ₃	8.8 (8.8)	64.0 (64.8)	4.1 (4.1)	8.6 (8.6)	81	234	91.7	53.3
IV	Sm(phen) ₂ (DPBS) ₃	9.2 (9.2)	63.7 (63.6)	4.1 (4.1)	8.6 (8.5)	80	236	94.3	56.1
V	Eu(phen) ₂ (DPBS) ₃	9.3 (9.2)	63.6 (63.5)	4.1 (4.1)	8.5 (8.5)	67	237	97.1	58.9
VI	Gd(phen) ₂ (DPBS) ₃	9.6 (9.5)	63.4 (63.4)	4.1 (4.1)	8.5 (8.5)	72	237	96.1	57.4
VII	Tb(phen) ₂ (DPBS) ₃	9.6 (9.6)	63.3 (63.2)	4.1 (4.1)	8.5 (8.5)	78	232	89.5	61.2
VIII	Dy(phen) ₂ (DPBS) ₃	9.9 (9.8)	63.2 (63.1)	4.1 (4.1)	8.5 (8.5)	78	234	85.7	63.4
IX	Ho(phen) ₂ (DPBS) ₃	10.0 (10.0)	63.1 (63.0)	4.1 (4.1)	8.5 (8.5)	76	233	90.1	66.6
X	Er(phen) ₂ (DPBS) ₃	10.0 (10.1)	63.1 (63.0)	4.1 (4.1)	8.5 (8.4)	68	233	93.4	59.7
XI	Tm(phen) ₂ (DPBS) ₃	10.2 (10.1)	62.9 (62.9)	4.1 (4.1)	8.4 (8.4)	68	229	97.2	58.4
XII	Yb(phen) ₂ (DPBS) ₃	10.4 (10.3)	62.9 (62.7)	4.1 (4.1)	8.4 (8.4)	66	230	96.7	54.3
XIII	Lu(phen) ₂ (DPBS) ₃	10.5 (10.5)	62.7 (62.7)	4.1 (4.1)	8.4 (8.4)	65	226	88.4	55.6
XIV	Y(phen) ₂ (DPBS) ₃	5.6 (5.6)	66.1 (66.0)	4.3 (4.2)	8.9 (8.8)	64	235	89.9	57.8

^a MC₈₇H₆₇N₁₀O₉.^b At the 10⁻³ mol dm⁻³ level.

confirmed by the observation of a weak shoulder band at *ca* 1185 cm⁻¹.

In far-IR spectra of the complexes two new bands appeared due to the presence of terminal M—O band (*A*_{2u}) at *ca* 451 cm⁻¹ and the band at *ca* 310 cm⁻¹ can be attributed to the M—N(*E*_u) stretching vibration of the square planar structure.¹³⁻¹⁵

UV spectra

UV absorption spectra of the ligands and their complexes in methanol are shown in Table 3. The UV spectra of all complexes are similar, but they are different from those of the ligands. There is a strong peak at 313 nm and two shoulder peaks at 265 and 365 nm, attributed to the $\pi \rightarrow \pi^*$ transition of the phenyl ring, the pyrazoline ring and the chromophores C=N—N, respectively, and two peaks at 229 and 263 nm arising from phen. After complexing, five absorption bands appeared at *ca* 227,

261, 264, 309 and 358 nm which shift to short wavelength. In addition, a new band near 348 nm appeared, suggesting that the whole molecule changed into a large conjugate system due to chelation.¹⁶

Electrolytic conductance

Pale-yellow solutions were obtained on dissolving the complex [M(phen)₂(DPBS)₂] · DPBS in DMF or methanol. The molar conductances (Table 1) of the complexes approached those reported for 1:1 electrolytes.¹⁷

Magnetic moments

The paramagnetic behaviour of lanthanide(III) ions is consistent with the presence of unpaired electrons. The room temperature magnetic moments of all the mixed-ligand complexes show very little deviation from the Van Vleck values,¹⁸

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

Complex	Phen		$-\text{SO}_3^-$			HDPBS			
	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	ν_{as}	ν_{s}	$\Delta\nu$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
phen	1587	1616							
HDPBS			1178	1036	142	1605	1128		
I	1545	1596	1147	1032	115	1596	1124	452	320
			1220		188				
II	1540	1596	1146	1032	114	1596	1124	451	317
			1224		192				
III	1542	1595	1147	1032	115	1595	1124	450	309
			1221		189				
IV	1540	1595	1148	1032	116	1595	1124	452	310
			1226		194				
V	1543	1595	1148	1032	116	1595	1124	449	317
			1226		194				
VI	1542	1596	1149	1032	117	1596	1124	448	309
			1227		195				
VII	1540	1595	1150	1032	118	1595	1124	445	315
			1226		195				
VIII	1542	1595	1151	1032	119	1595	1124	455	325
			1227		198				
IX	1540	1595	1146	1032	114	1595	1124	445	323
			1233		201				
X	1542	1595	1146	1032	114	1595	1124	447	315
			1228		196				
XI	1542	1595	1151	1032	119	1595	1124	445	310
			1229		198				
XII	1540	1595	1146	1032	114	1595	1124	446	310
			1233		201				
XIII	1542	1595	1146	1032	114	1595	1124	445	310
			1228		196				

Table 3. Magnetic moments and UV spectra of the ligands and complexes

Compound	μ_{eff} (B.M.)	Characteristic absorption bands λ_{max} (nm)					
		1	2	3	4	5	6
phen		229	263				
HDPBS				265	313	365	
I	dia.	227	262	264	309	360	347
II	3.30	227	262	263	309	360	347
III	3.40	226	261	263	309	358	347
IV	3.15	225	261	263	309	358	347
V	3.18	228	263	264	310	360	348
VI	7.4	226	262	263	309	358	347
VII		226	261	263	309	358	347
VIII	9.5	226	261	264	309	358	347
IX		225	261	264	308	356	345
X		225	260	264	308	356	345
XI		225	260	263	308	356	345
XII		225	260	263	308	356	345
XIII		225	260	264	308	356	347
XIV		224	261	263	309	357	346

Table 4. Binding energies (eV) of the complexes and ligands

Peaks	N (phen)	S (HDPBS)	I	IV	X
4s			275.4		450.1
4p _{3/2}			193.6	252.4	331.6
4p _{1/2}			209.5		
4d _{5/2}			103.9	143.6	168.5
4d _{3/2}			105.7		184.9
N 1s	401.2		400.1	399.9	399.6
S 2p		166.2	166.1, 165.8	166.2, 165.4	166.1, 165.1

indicating negligible participation of 4f electrons in bond formation (Table 3).

XPS studies

To get further insight into the nature of binding, XPS of the three complexes and ligand were recorded in powder form at room temperature. We found that the nitrogen 1s peak arises from phen and in the complexes occurs in the same chemical environment, which indicates the nitrogen atoms of phen coordinate with the metal ion in an identical form, i.e. it may be a planar form with two sulphur 2p peaks for the complexes relative to one for the HDPBS, as shown in Table 4. This behaviour, combined with the intensity ratio (2:1) of the peak, suggests that two HDPBS molecules participate in coordination with the metal ion.

Thermogravimetric analyses

The TG-DTA diagrams of all the complexes are similar. It can be seen from these diagrams that the complexes $[M(\text{phen})_2(\text{DPBS})_2] \cdot \text{DPBS}$ begin to decompose at ca 230°C (Table 1), accompanied by the release of a great amount of heat and weight loss. Then they continue to decompose exothermally at about 312, 523, 554 and 607°C, and the decomposition is completed at about 780°C.

The analytical data and all the above results suggest that these hetero complexes may be formulated

as $[M(\text{phen})_2(\text{DPBS})_2] \cdot \text{DPBS}$, and it is reasonable to propose an octahedral structure where phen molecules are *trans* to each other in equatorial positions, and DPBS is *trans* to DPBS in an axial position, as shown in Fig. 2.

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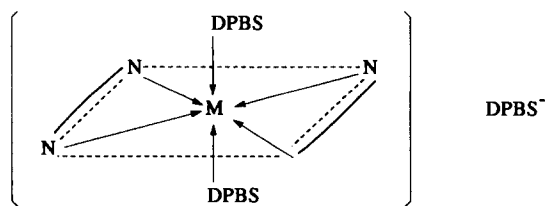


Fig. 2. Proposed octahedral structure of $[M(\text{phen})_2(\text{DPBS})_2] \cdot \text{DPBS}$.