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# Synthesis and infrared and luminescence spectra of rare earth complexes with a new hexapodal ligand

Yu Tang, De-Bo Liu, Wei-Sheng Liu, Min-Yu Tan\*

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

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### Abstract

Solid complexes of rare earth nitrates and picrates with a new hexapodal ligand, 1,2,3,4,5,6-hexa{[(2'-benzylamino-formyl)phenoxyl] methyl}-benzene (L) have been prepared. These complexes were characterized by elemental analysis, IR and molar conductivity. At the same time, the luminescence properties of the Eu(III) and Tb(III) nitrates and picrates complexes in solid state were also investigated. Under the excitation of UV light, these complexes exhibited characteristic emission of europium and terbium ions. The influence of the counter anion on the luminescent intensity was also discussed.

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Keywords: Hexapodal ligand; Rare earth complexes; Luminescence properties

# 1. Introduction

The specific spectroscopic and magnetic properties of rare earth ions have made them essential components in the preparation of new materials and ideal as probes in studies of biological systems [1]. Macrocyclic, macrobicyclic (cryptand) and podand-type ligands have been extensively used for these purposes [2-5]. These complexes have been studied as supramolecular devices, as contrast-enhancing agents in magnetic resonance imaging, as effective chelators in the separation and purification of rare earths, and as fluorescent probes and luminescent labels in fluoroimmunoassays. Among these studies, the luminescence properties of rare earth complexes are of special interest because these complexes could show narrow emission bands, a large Stokes' shift and long luminescence decay times [6]. Podandtype ligands have drawn much attention in recent years, mainly due to their possessing spheroidal cavities and binding sites that are hard, therefore, stabilizing their complexes and shielding the encapsulated ion from interaction with the surroundings [7]. Ligands containing many of the common donor groups have been synthesized. Among these numerous podands which have demonstrated their potential use in functional supramolecular chemistry [8-10], amide type podands have been attracted more attention in preparing the rare earth complexes possessing strong luminescence properties. It is expected that the amide type podands, which are flexible in structure and have 'terminal-group effects' [11], will shield the encapsulated rare earth ion from interaction with the surroundings effectively, and thus to achieve strong luminescent properties. As a part of our systematic studies, a new hexapodal ligand (L, Scheme 1), 1,2,3,4,5,6-hexa{[(2'benzylaminoformyl)phenoxyl]-methyl}-benzene, has been designed and prepared successfully with the goal of expanding the pool of ligand type and studying the coordination and luminescence properties of rare earth ions with the hexapodal ligand, which were not very familiar. The results indicated that counter anion notably affected the luminescence characteristics of europium and terbium ions.

# 2. Experimental

## 2.1. Materials

*N*-Benzylsalicylamide was prepared according to the literature methods [12]. Other chemicals were obtained

<sup>\*</sup> Corresponding author. Tel.: +86 9318912552; fax: +86 9318912582. *E-mail address:* tangyu@lzu.edu.cn (M.-Y. Tan).

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Scheme 1. The synthetic route for the hexapodal ligand L.

from commercial sources and used without further purification.

#### 2.2. Methods

The RE(III) ion was determined by EDTA titration using xylenol-orange as an indicator. Carbon, nitrogen and hydrogen were determined using an Elementar Vario EL (see Table 1). Conductivity measurements were carried out with a DDS-307 type conductivity bridge using  $10^{-3}$  mol cm<sup>-3</sup> solutions at 25 °C. The IR spectra were recorded in the 4000–400 cm<sup>-1</sup> region using KBr pellets and a Nicolet Nexus 670 FTIR spectrometer (see Tables 2 and 3). <sup>1</sup>H NMR spectra were measured on a Varian Mercury 200 spectrometer in CD<sub>3</sub>COCD<sub>3</sub> solutions, with TMS as internal standard. Luminescence spectra were obtained on a Hitachi F-4500 spectrophotometer at room temperature.

# 2.3. Preparation of hexapodal ligand L

The synthetic route for the hexapodal ligand is shown in Scheme 1. *N*-Benzylsalicylamide (1.08 g, 4.75 mmol), potas-

sium carbonate (1.0 g, 3.6 mmol) and DMF (20 cm<sup>3</sup>) were warmed to ca. 60 °C and 1,2,3,4,5,6-hexakis(bromomethyl)benzene (0.48 g, 0.75 mmol) was added. The reaction mixture was stirred at 60–65 °C for 2 h. After cooling down, the mixture was poured into water (100 cm<sup>3</sup>). The resulted solid was treated with column chromatography on silica gel [petroleum ether:ethyl acetate (2:1)] to get hexapodal ligand L, yield 78%, mp 175–178 °C; <sup>1</sup>H NMR (CD<sub>3</sub>COCD<sub>3</sub>, 200 MHz)  $\delta$ : 4.17 (d, 12H, –CH<sub>2</sub>–N), 5.43 (s, 12H, –CH<sub>2</sub>–O), 7.02–7.34 (m, 54H, Ar–H), H<sub>(N–H)</sub> not detected; IR (KBr)  $\nu$ : 2922, 1648, 1451, 1218, 1105 cm<sup>-1</sup>; anal. data, calc. for C<sub>96</sub>H<sub>84</sub>N<sub>6</sub>O<sub>12</sub>: C, 76.17; H, 5.59; N, 5.55. Found: C, 76.31; H, 5.84; N, 5.40.

## 2.4. Preparation of the complexes

A solution of 0.10 mmol L in 10 cm<sup>3</sup> of ethyl acetate was added drop wise to a solution of 0.15 mmol rare earth nitrates (RE = La, Nd, Eu, Tb, Ho, Lu) in 10 cm<sup>3</sup> of ethyl acetate. The mixture was stirred at room temperature for 4 h. The precipitated white solid complex was filtered, washed with ethyl acetate and dried in vacuo over  $P_4O_{10}$  for 48 h and submitted for elemental analysis, yield 65%.

Table	1
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Analy	tical a	and mola	conductance	data of the	complexes	(calculated	values in	parentheses)
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Complexes	Analysis (%)	$\Lambda m (\mathrm{cm}^2(\Omega\mathrm{mol})^{-1})$			
	С	Н	Ν	RE	
$[La_3(NO_3)_9L_2]\cdot 3C_4H_8O_2$	57.61 (57.43)	4.24 (4.54)	6.86 (6.89)	9.60 (9.77)	60.4 <sup>a</sup>
$[Nd_3(NO_3)_9L_2]\cdot 3C_4H_8O_2$	57.33 (57.21)	4.48 (4.52)	6.75 (6.87)	10.27 (10.10)	65.0 <sup>a</sup>
$[Eu_3(NO_3)_9L_2]\cdot 3C_4H_8O_2$	56.85 (56.91)	4.80 (4.49)	6.52 (6.83)	10.37 (10.59)	57.8 <sup>a</sup>
$[Tb_3(NO_3)_9L_2]\cdot 3C_4H_8O_2$	56.54 (56.63)	4.40 (4.47)	6.89 (6.80)	10.86 (11.02)	75.1 <sup>a</sup>
$[Ho_3(NO_3)_9L_2]\cdot 3C_4H_8O_2$	56.35 (56.40)	4.33 (4.45)	6.81 (6.77)	11.10 (11.39)	50.9 <sup>a</sup>
$[Lu_3(NO_3)_9L_2]\cdot 3C_4H_8O_2$	56.28 (56.01)	4.56 (4.42)	6.39 (6.72)	11.88 (12.00)	63.7 <sup>a</sup>
$[La_4(Pic)_{12}L_3] \cdot C_2H_5OH$	55.27 (55.18)	3.47 (3.61)	9.50 (9.60)	7.33 (7.05)	63.7 <sup>b</sup>
$[Nd_4(Pic)_{12}L_3] \cdot C_2H_5OH$	54.86 (55.03)	3.55 (3.60)	9.54 (9.57)	7.51 (7.30)	51.8 <sup>b</sup>
$[Eu_4(Pic)_{12}L_3] \cdot C_2H_5OH$	54.74 (54.81)	3.50 (3.58)	9.37 (9.54)	7.50 (7.66)	42.0 <sup>b</sup>
$[Tb_4(Pic)_{12}L_3] \cdot C_2H_5OH$	54.42 (54.62)	3.53 (3.57)	9.47 (9.50)	7.75 (7.99)	55.7 <sup>b</sup>
$[Ho_4(Pic)_{12}L_3] \cdot C_2H_5OH$	54.35 (54.46)	3.60 (3.56)	9.56 (9.47)	8.01 (8.26)	47.5 <sup>b</sup>
$[Er_4(Pic)_{12}L_3] \cdot C_2H_5OH$	54.52 (54.39)	3.63 (3.56)	9.29 (9.46)	8.09 (8.37)	39.7 <sup>b</sup>
$[Y_4(Pic)_{12}L_3] \cdot C_2H_5OH$	56.48 (56.61)	3.77 (3.70)	9.74 (9.85)	4.79 (4.63)	37.5 <sup>b</sup>

<sup>a</sup> Measured in acetone.

<sup>b</sup> Measured in methanol  $(10^{-3} \text{ mol } L^{-1})$ .

Table 2
The most important IR bands of the rare earth nitrate complexes (cm <sup>-1</sup> )

Compound	ν(C=O)	v(C-O-C)	ν(NO <sub>3</sub> <sup>-</sup> )				
			$\nu_1$	$\nu_4$	v <sub>1</sub> -v <sub>4</sub>	ν <sub>2</sub>	<i>v</i> <sub>3</sub>
L	1649s	1105m					
$[La_3(NO_3)_9L_2]\cdot 3C_4H_8O_2$	1609s 1638s	1108m	1451s 1482s	1299s	152 183	1029w	813w
$[Nd_{3}(NO_{3})_{9}L_{2}]\cdot 3C_{4}H_{8}O_{2}$	1610s 1638s	1107m	1451s 1481s	1300s	151 181	1029w	814w
$[Eu_3(NO_3)_9L_2]\cdot 3C_4H_8O_2$	1609s 1638s	1108m	1450s 1481s	1299s	151 182	1028w	814w
$[Tb_{3}(NO_{3})_{9}L_{2}]\cdot 3C_{4}H_{8}O_{2}$	1609s 1638s	1108m	1451s 1482s	1299s	152 183	1029w	813w
$[Ho_{3}(NO_{3})_{9}L_{2}]\cdot 3C_{4}H_{8}O_{2}$	1610s 1638s	1108m	1451s 1481s	1300s	151 181	1028w	816w
$[Lu_3(NO_3)_9L_2]\cdot 3C_4H_8O_2$	1609s 1638s	1108m	1450s 1481s	1299s	151 182	1029w	814w

Table 3

The most important IR bands of the rare earth picrate complexes (cm<sup>-1</sup>)

Compound	ν(C=O)	v(C-O-C)	ν(C–O)	$v_{as}(-NO_2)$	$v_{s}(-NO_{2})$	ν(OH)
HPic			1265s	1555m	1342s	
L	1649s	1111m				
$[La_4(Pic)_{12}L_3] \cdot C_2H_5OH$	1613s	1108m	1274m	1574m 1542m	1363m 1326m	3403w
$[\mathrm{Nd}_4(\mathrm{Pic})_{12}\mathbf{L}_3]{\cdot}\mathrm{C}_2\mathrm{H}_5\mathrm{OH}$	1613s	1108m	1275m	1575m 1542m	1364m 1328m	3404w
$[Eu_4(Pic)_{12}L_3] \cdot C_2H_5OH$	1614s	1108m	1274m	1574m 1542m	1366m 1330m	3402w
$[Tb_4(Pic)_{12}L_3] \cdot C_2H_5OH$	1613s	1108m	1274m	1574m 1542m	1363m 1326m	3402w
$[\mathrm{Ho}_4(\mathrm{Pic})_{12}\mathbf{L}_3]{\cdot}\mathrm{C}_2\mathrm{H}_5\mathrm{OH}$	1613s	1108m	1275m	1575m 1543m	1367m 1330m	3403w
$[\mathrm{Er}_4(\mathrm{Pic})_{12}\mathbf{L}_3]\cdot \mathbf{C}_2\mathbf{H}_5\mathrm{OH}$	1613s	1108m	1274m	1575m 1543m	1363m 1327m	3404w
$[Y_4(Pic)_{12}L_3] \cdot C_2H_5OH$	1613s	1108m	1274m	1574m 1542m	1364m 1327m	3401w

A solution of 0.10 mmol L in 10 cm<sup>3</sup> of ethanol was added drop wise to a solution of 0.14 mmol rare earth picrates (RE = La, Nd, Eu, Tb, Ho, Er, Y) in 10 cm<sup>3</sup> of ethanol. The mixture was stirred at room temperature for 6 h. The precipitated yellow solid complex was filtered, washed with ethyl ethanol and dried in vacuo over P<sub>4</sub>O<sub>10</sub> for 48 h and submitted for elemental analysis, yield 62%. Analytical data and molar conductance values of these rare earth nitrates and picrates complexes are given in Table 1.

# 3. Results and discussion

# 3.1. Properties of the complexes

Analytical data for the newly synthesized complexes, listed in Table 1, indicate that the six nitrates com-

plexes conform to a 3:2 metal-to-ligand stoichiometry  $[RE_3(NO_3)_9L_2]\cdot 3C_4H_8O_2$  and seven picrates complexes conform to a 4:3 metal-to-ligand stoichiometry  $[RE_4(Pic)_{12}L_3]\cdot C_2H_5OH$ .

All the rare earth nitrates complexes are soluble in DMF, DMSO, methanol, ethanol, acetone and THF, but slightly soluble in AcOEt and CHCl<sub>3</sub>. The molar conductances of the complexes in acetone (see Table 1) indicate that all complexes act as noneletrolytes [13], implying that all nitrate groups are in coordination sphere.

All the rare earth picrates complexes are soluble in DMF, DMSO, methanol, acetone and acetonitrile, but slightly soluble in ethanol, AcOEt and CHCl<sub>3</sub>. The molar conductances of the complexes in methanol (see Table 1) indicate that all complexes act as noneletrolytes [13], implying that all picrate groups are in coordination sphere.

#### 3.2. IR spectra

The most important IR peaks of the ligand and the complexes are reported in Tables 2 and 3.

The "free" ligand **L** exhibit two absorption bands at 1649 and 1105 cm<sup>-1</sup> which are assigned to  $\nu$ (C=O) and  $\nu$ (C=O-C), respectively. In the nitrate complexes, the low-energy band remains unchanged, but the high-energy band red shifts to about 1609 cm<sup>-1</sup> ( $\Delta \nu = 40$  cm<sup>-1</sup>) as compared to its counterpart for the "free" ligand, indicating that only the oxygen atom of C=O takes part in coordination to the metal ions.

The characteristic frequencies of the coordinating nitrate groups  $(C_{2v})$  appear at ca. 1450 and 1480 cm<sup>-1</sup>  $(v_1)$ , 1300 cm<sup>-1</sup>  $(v_4)$ , 1030 cm<sup>-1</sup>  $(v_2)$  and 815 cm<sup>-1</sup>  $(v_3)$  cm<sup>-1</sup> [14], and the difference between two strongest absorptions  $(v_1 \text{ and } v_4)$  of the nitrate groups is about 150–180 cm<sup>-1</sup>, clearly establishing that the NO<sub>3</sub><sup>-</sup> groups in the solid complexes coordinate to the rare earth ion as bidentate ligands [15]. Additionally, no bands at 1380, 820 and 720 cm<sup>-1</sup> in the spectra of complexes indicates that free nitrate groups  $(D_{3h})$  are absent. Additionally, band at 1638 cm<sup>-1</sup> indicates that ethyl acetate is existent in the complexes, confirming the elemental analysis.

In the picrate complexes, after the formation of the complex, the characteristic frequency of the free ligand  $\nu$ (C=O) at 1649 cm<sup>-1</sup> shifts ca. 35 cm<sup>-1</sup> towards lower wave numbers and the  $\nu$ (C–O–C) absorption band also remains unchanged, indicating that only the oxygen atom of C=O coordinate to the rare earth ion.

The OH out-of-plane bending vibration of the free HPic at  $1151 \text{ cm}^{-1}$  disappears, indicating that the H-atom of the OH group is replaced by RE(III). The vibration  $v_{C-O}$  of

Pic<sup>-</sup> at 1265 cm<sup>-1</sup> is shifted toward higher frequency by ca. 10 cm<sup>-1</sup> in the complexes. This is due to the following two effects. First, the hydrogen atom of the OH group is replaced by RE(III), increasing the  $\pi$ -bond character in the C–O bond. Secondly, coordination of the nitrogen atom of L to RE(III) decreases the  $\pi$ -character. The free HPic has  $\nu_{as}(-NO_2)$  and  $\nu_s(-NO_2)$  at 1555 and 1342 cm<sup>-1</sup>, respectively, which split into two bands at ca. 1575, 1542 cm<sup>-1</sup> and ca. 1365, 1330 cm<sup>-1</sup>, respectively, in the complexes. This indicates that some O-atoms in the nitro group of Pic<sup>-</sup> take part in coordination [16]. Additionally, broad bands at 3400 cm<sup>-1</sup> could be attributed to the O–H stretching vibrations of ethanol molecule.

#### 3.3. Luminescence properties of the complexes

Ligand-based excitations cause the characteristic emission of rare earth complexes while the ligand fluorescence is completely quenched. This indicates the presence of ligandto-metal energy transfer [17]. The ability to transfer energy from ligand to metal is important in the design of RE(III) supramolecular photonic devices [18,19]. The luminescence spectra of the ligand and its  $Eu^{3+}$  and  $Tb^{3+}$  complexes in solid state were recorded at room temperature. Among these four complexes, luminescence of the complexes of Eu, Tb nitrates and Eu picrate were observed but not for the Tb picrate complexes. The emission spectra of the ligand and complexes are shown in Fig. 1.

Excited by the absorption band at 325 nm, the "free" ligand exhibits broad emission bands ( $\lambda_{max} = 450$  nm). It is shown in Fig. 1 that the complexes show the characteristic emissions of Eu<sup>3+</sup> or Tb<sup>3+</sup>. This indicates that the ligand **L** is a good organic chelator to absorb and transfer energy to metal ions.



Fig. 1. (A) Emission spectra of L in solid state; (B) emission spectra of  $[Eu_3(NO_3)_9L_2] \cdot 3C_4H_8O_2$  in solid state; (C) emission spectra of  $[Tb_3(NO_3)_9L_2] \cdot 3C_4H_8O_2$  in solid state; (D) emission spectra of  $[Eu_4(Pic)_{12}L_3] \cdot C_2H_5OH$  in solid state.

In the spectrum of Eu(NO<sub>3</sub>)<sub>3</sub> complex, the relative intensity of  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  is stronger than that of  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ , showing that the Eu(III) ion is not in a centro-symmetric coordination site [20]. In addition, the  $Tb(NO_3)_3$  and Eu(Pic)<sub>3</sub> complexes show no ligand-based emission bands in ca. 450 nm, but this emission bands in the  $Eu(NO_3)_3$ complex are still visible which means the energy transfer in the Tb(NO<sub>3</sub>)<sub>3</sub> and Eu(Pic)<sub>3</sub> complexes are more efficient than that in the Eu(NO<sub>3</sub>)<sub>3</sub> complex. Intramolecular energy transfer from the triplet state of the ligand to the resonance level of the RE(III) ion is one of the most important processes influencing the luminescence quantum yields of RE(III) complexes [21]. The energy difference between the triplet state energy level of the ligand and the lowest excited state level of RE(III) cannot be too large or too small. So considering the emission spectra of these three complexes, it can be concluded that the triplet energy of L is in an appropriate level to  $Tb^{3+}$  in the  $Tb(NO_3)_3$  complex and  $Eu^{3+}$  in the  $Eu(Pic)_3$ complex, which makes the energy transition from the ligand to RE(III) more easily in these two complexes. We deduced that the electrostatic factors in the ligand-metal bonding, which may be affected by the different counter anion in these two series complexes, influenced the triplet state energy level of the ligand L [6] and made this  $T_1$  energy be lowered in the picrates complexes, thus intensified the emission of the Eu(III) and quenched the emission of the Tb(Pic)<sub>3</sub> complex.

#### 4. Conclusions

In this paper, we report the preparation, IR aspectra and luminescent properties of the solid complexes of rare earth nitrates and picrates with a new hexapodal ligand, 1,2,3,4,5,6hexa{[(2'-benzylamino-formyl)phenoxyl]methyl}-benzene (L). Comparing the luminescence spectra of the nitrate complexes of europium(III) and terbium(III), we found that the hexapodal ligand L in  $Tb(NO_3)_3$  complex is more effective in energy-transfer than in Eu(NO<sub>3</sub>)<sub>3</sub> complex. The  $Tb(NO_3)_3$  complex show no emission bands from the ligand L in ca. 450 nm, but the emission bands in the Eu(NO<sub>3</sub>)<sub>3</sub> complex are still visible (Fig. 1). And the compare between the luminescence spectra of the Eu(NO<sub>3</sub>)<sub>3</sub> complex and the  $Eu(Pic)_3$  complex showed that the ligand L in Eu(Pic)<sub>3</sub> complex is more effective in energy-transfer than in  $Eu(NO_3)_3$  complex. This is maybe due to the suitable lowest triplet energy of L in its  $Eu(Pic)_3$  complex. And the Tb(Pic)<sub>3</sub> complex does not show its characteristic emission spectrum. So, we may deduce that the counter anion of the

complexes is very essential in determining the luminescent properties of the rare earth complexes by influencing the electrostatic factors in the ligand–metal bonding.

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