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# Synthesis and luminescence properties of lanthanide complexes with a new aryl amide bifunctional bridging ligand

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# Abstract

A new aryl amide type bifunctional bridging ligand 4,4'-bis{[(2"-benzylaminoformyl)phenoxyl]methyl}-1,1'-biphenyl (**L**) and its complexes with lanthanide ions (Ln = Pr, Eu, Gd, Tb, Ho, Er) were synthesized and characterized by elemental analysis, infrared spectra, conductivity measurements and thermal analysis. At the same time, the luminescence properties of the Eu and Tb complexes in acetone solutions were investigated. Under the excitation of UV light, these two complexes exhibited characteristic emission of europium and terbium ions. And the lowest triplet state energy level T<sub>1</sub> of this ligand matches better to the lowest resonance energy level of Tb(III) than to Eu(III) ion. © 2005 Elsevier B.V. All rights reserved.

Keywords: Aryl amide bifunctional bridging ligand; Lanthanide(III) complexes; Synthesis; Luminescence properties

## 1. Introduction

The emission of light from lanthanide ions arises from f-f transitions, which result in emission bands with extremely narrow bandwidth and no theoretical cap on the quantum efficiency. This makes lanthanide ions very attractive for a variety of applications, such as chromophores for LEDs and as probes and labels in a variety of biological and chemical applications [1]. And the probes based on europium and terbium ions are of special interest because of the particularly suitable spectroscopic properties of these ions, such as their large stokes shift and narrow emission profiles [2,3]. Since the f-f transitions are spin- and parity-forbidden, the excited state of the lanthanide ion is populated through intramolecular energy transfer from the ligand or ligands, which, therefore, serve as sensitizers (antenna effect) [4,5]. The role of the ligands is on one hand, to collect the photons provided by the light source in order to allow an energy transfer to the emitting levels of the Ln(III) ion and on the other to shield it against the solvent in order to avoid non-radioactive deactivation processes. It is generally accepted that the energy transfer from ligand to Ln(III) ion occurs from the lowest triplet state

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energy level  $T_1$  of the ligand to the resonance level of Ln(III) [6]. And this energy transfer process is one of the most important processes having influence on the luminescence properties of the lanthanide complexes.

Recently, polynuclear lanthanide complexes, especially with luminescence properties, are attracting more and more chemists [7]. Our group is interested in the supramolecular coordination chemistry of lanthanide ions with amide type ligands that have strong coordination capability to the lanthanide ions and terminal group effects [8]. We have designed a series of polyfunctional ligands having both selective ability to coordinate more than one lanthanide ions and enhanced luminescence of lanthanide complexes by providing some of proper conjugate absorption groups suitable for energy transfer. In the present work, we designed and synthesized a new aryl amide type bifunctional bridging ligand 4,4'-bis{[(2"-benzylaminoformyl)phenoxyl]methyl}-1,1'-biphenyl (L) (Scheme 1) and studied the luminescence properties of europium and terbium complexes with this new ligand. Under the excitation of UV light, Eu and Tb complexes exhibited characteristic emission of lanthanide ions. The lowest triplet state energy level of the ligand was calculated from the phosphorescence spectrum of the Gd complex at 77 K. The result indicate that the triplet state energy level of the ligand matches better to the resonance level of Tb(III) than to Eu(III) ion.

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Scheme 1. The synthetic route for the ligand L.

#### 2. Experimental

## 2.1. Materials

*N*-Benzylsalicylamide was prepared according to the literature methods [9]. Other chemicals were obtained from commercial sources and used without further purification.

#### 2.2. Methods

The metal ions were determined by EDTA titration using xylenol orange as an indicator. Carbon, nitrogen and hydrogen analyses were determined using an Elementar Vario EL (see Table 1). Conductivity measurements were carried out with a DDSJ-308 type conductivity bridge using  $1.0 \times 10^{-3}$  mol cm<sup>-3</sup> solutions in acetone at 25 °C. IR spectra were recorded on a Nicolet 360 FT-IR instrument using KBr discs in the 4000–400 cm<sup>-1</sup> region. <sup>1</sup>H NMR spectrum was measured on a Varian Mercury-300B spectrometer in d-DMSO solution with TMS as internal standard. Luminescence and phosphorescence spectra were obtained on a Hitachi F-4500 spectrophotometer. The excitation and emission slit widths were 10 nm.

# 2.3. Synthesis of the ligand L

The synthetic route for the ligand **L** is shown in Scheme 1. *N*-Benzylsalicylamide (2.0 mmol), potassium carbonate (3.6 mmol) and DMF (20 cm<sup>3</sup>) were warmed to ca. 90 °C and 4,4'-bisbromomethyl-1,1'-biphenyl (0.75 mmol) was added. The reaction mixture was stirred at 90–95 °C for 8 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 (1:1)] to get the ligand

L, yield 80%, m.p. 132–134 °C; <sup>1</sup>H NMR (DMSO, 300 MHz): 4.46–4.49 (s, 4H), 5.29 (d, 4H), 7.02–7.09 (t, 2H), 7.18–7.30 (q, 12H), 7.43–7.75 (m, 12H), 8.66 (s, 2H). IR (KBr): 3398 (m), 3320 (m), 1639 (s, C=O), 1600 (m), 1534 (m), 1486 (m), 1451 (m), 1299 (m), 1229 (m, Ar–O), 1107 (w, Ar–O), 807 (w), 755 (s), 700 (m). Analytical data, calculated for L·H<sub>2</sub>O–C: 77.52, H: 5.89, N: 4.30. Found–C: 77.29, H: 5.41, N: 4.14.

#### 2.4. Preparation of the complexes

An ethyl acetate solution  $(5 \text{ cm}^3)$  of  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Ln = Pr, Eu, Gd, Tb, Ho, Er) (0.1 mmol) was added dropwise to a solution of 0.1 mmol ligand **L** in the chloroform  $(5 \text{ cm}^3)$ . The mixture was stirred at room temperature for 8 h. And then the precipitated solid complex was filtered, washed with ethyl acetate and chloroform, dried in vacuo over P<sub>4</sub>O<sub>10</sub> for 48 h and submitted for elemental analysis, yield: 70%.

## 3. Result and discussion

#### 3.1. Properties of the complexes

Analytical data for the newly synthesized complexes, listed in Table 1, indicate that the six nitrates complexes conform to a 2:3 metal-to-ligand stoichiometry  $Ln_2(NO_3)_6L_3 \cdot 2H_2O$  (Ln = Pr, Eu, Gd, Tb, Ho, Er). All complexes are soluble in DMF and DMSO, slightly soluble in acetone and acetonitrile, but sparingly soluble in methanol, ethanol, chloroform and ethyl acetate. Conductivity measurements for these complexes in acetone solution (Table 1) indicate that all the complexes are non-electrolyte [10].

Table 1 Analytical and molar conductance data of the complexes (calculated values in parentheses)

Complexes	Analysis (%)	$\Lambda_{\rm m}~({\rm S~cm^2~mol^{-1}})$			
	С	Н	Ν	Ln	
$Pr_2(NO_3)_6L_3\cdot 2H_2O$	58.61 (58.47)	3.90 (4.36)	6.71 (6.49)	10.78 (10.89)	62.1
$Eu_2(NO_3)_6L_3\cdot 2H_2O$	57.86 (57.98)	3.84 (4.32)	6.67 (6.44)	11.40 (11.64)	51.6
$Gd_2(NO_3)_6L_3\cdot 2H_2O$	57.94 (57.74)	3.88 (4.31)	6.74 (6.41)	11.55 (12.00)	45.8
$Tb_2(NO_3)_6L_3\cdot 2H_2O$	57.91 (57.67)	3.98 (4.30)	6.67 (6.41)	12.00 (12.11)	39.2
$Ho_2(NO_3)_6L_3\cdot 2H_2O$	57.34 (57.41)	4.01 (4.28)	6.73 (6.38)	12.25 (12.51)	35.4
$Er_2(NO_3)_6L_3\cdot 2H_2O$	57.37 (57.31)	3.92 (4.27)	6.63 (6.36)	12.78 (12.67)	36.8

Table 2 IR spectral data of the ligand and its complexes  $(cm^{-1})$ 

Compounds	ν(C=0)	ν(Ar–O–C)	v(NO <sub>3</sub> <sup>-</sup> )	ν(NO <sub>3</sub> <sup>-</sup> )				
			$\nu_1$	$\nu_4$	$\nu_2$	<i>v</i> <sub>3</sub>	<i>v</i> <sub>1</sub> - <i>v</i> <sub>4</sub>	
L	1639	1229, 1107						
$Pr_2(NO_3)_6L_3 \cdot 2H_2O$	1610	1232, 1109	1483	1300	1030	810	183	
$Eu_2(NO_3)_6L_3 \cdot 2H_2O$	1611	1231, 1108	1486	1301	1028	811	185	
$Gd_2(NO_3)_6L_3 \cdot 2H_2O$	1612	1233, 1109	1484	1298	1029	812	186	
$Tb_2(NO_3)_6L_3 \cdot 2H_2O$	1611	1231, 1108	1486	1304	1029	811	182	
$Ho_2(NO_3)_6L_3\cdot 2H_2O$	1612	1231, 1108	1485	1301	1030	812	184	
$Er_2(NO_3)_6L_3\cdot 2H_2O$	1612	1231, 1108	1485	1302	1030	812	183	

# 3.2. IR spectra

The most important IR peaks of the ligand and the complexes are reported in Table 2. The IR spectra of the complexes are similar.

The IR spectrum of the free ligand shows bands at 1639, 1229 and 1107 cm<sup>-1</sup>, which may be assigned to  $\nu$ (C=O) and  $\nu$ (Ar–O–C), respectively. In the complexes, the low-energy band remains unchanged, but the high-energy band red shifts to about 1611 cm<sup>-1</sup> ( $\Delta \nu = 28$  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. 1485 cm<sup>-1</sup>  $(v_1)$ , 1300 cm<sup>-1</sup>  $(v_4)$ , 1030 cm<sup>-1</sup>  $(v_2)$  and 810 cm<sup>-1</sup>  $(v_3)$  cm<sup>-1</sup>, and the difference between the two strongest absorptions  $(v_1 \text{ and } v_4)$  of the nitrate groups is about 180 cm<sup>-1</sup>, clearly establishing that the NO<sub>3</sub><sup>-</sup> groups in the solid complexes coordinate to the lanthanide ion as bidentate ligands [11,12]. 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, in agreement with the results of the conductivity experiments.

# 3.3. Thermal analysis

The TG and DTA curves for the Pr and Er complexes show that the complexes has no melting point and the water molecules containing in the complexes are all coordinated water molecules, because the only one endothermic peak appear at ca. 125 °C. And the percent of water is consistent with the results of elemental analysis. The complexes are stable up to ca. 445 °C and then decompose in the temperature range 445–800 °C, producing two exothermic peaks. The residual weights are approximately consistent with the values required for the metal oxide. So the

Table 3

Luminescence data for the Eu and Tb complexes

formula of these six nitrate complexes could be indicated as  $[Ln_2(NO_3)_6L_3(H_2O)_2]$  (Ln = Pr, Eu, Gd, Tb, Ho, Er).

## 3.4. Luminescence properties of the complexes

Ligand-based excitations cause the structural emission of lanthanide complexes and the ligand luminescence is quenched show that the ligand-to-metal energy transfer occurs [13]. The ability to transfer energy from ligand-centered to metal-centered is important in the design of lanthanide(III) supramolecular photonic devices [14]. As the complexes were stable in acetone, the luminescent investigations were carried out in this solution.

Under identical experimental conditions, the luminescence characteristics emissions of the complexes in acetone are listed in Table 3. The emission spectra of the Eu and Tb complexes in acetone solution are shown in Fig. 1. The ligand having multiple aromatic rings has a strong antenna effect. So its complexes could have strong luminescence properties. From Table 3 it can be seen that great difference (87 nm) between the excitation maxima of the europium complex and that of the terbium one. The luminescence characteristic emission wavelengths of the europium and terbium ions are observed. This indicates that the ligand L is a good organic chelator to absorb energy and transfer them to metal ions. In the spectrum of Eu complex, the relative intensity of  ${}^5D_0 \rightarrow {}^7F_2$  is more intense than that of  ${}^5D_0 \rightarrow {}^7F_1$ , showing that the Eu(III) ion does not lie in a centro-symmetric coordination site [15].

Due to the presence of a scatting signal near 490 nm, the peak height at 547 nm for terbium was used to measure the luminescence intensity. Comparing the spectra of Eu and Tb complexes (Fig. 1), we can see that the luminescence intensity of terbium complex at 547 nm is greatly stronger than that of europium complex at 618 nm. As we know, the luminescence of  $Ln^{3+}$  chelates is related to the efficiency of the intramolecular energy transfer

Complexes	Concentration ( $\times 10^{-4} \text{ mol } L^{-1}$ )	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm)	RFI <sup>a</sup>	Assignment
$[Eu_2(NO_3)_6L_3(H_2O)_2]$	1	397	592 618	38 83	
$[Tb_2(NO_3)_6L_3(H_2O)_2]$	1	310	493 547 587	4244 8666 495	

<sup>a</sup> RFI: relative fluorescence intensity.



Fig. 1. The emission spectra of Eu complex (A) and Tb complex (B) in acetone solutions.

between the triplet excited state  $T_1$  of the ligand and the lowest excited resonance level of the lanthanide ions, which depends on the energy gap between the two levels. So we may deduce that the energy gap between the ligand triplet excited state  $T_1$ and the lowest excited state of the terbium ion may be in favour of the energy transfer process. A triplet excited state T1 which is localised on one ligand only and is independent of the lanthanide nature [16]. In order to acquire the triplet excited state  $T_1$  of the ligand L, the phosphorescence spectrum of the Gd(III) complex was measured at 77 K in a methanol-ethanol mixture (v/v, 1:1). The triplet state energy level  $T_1$  of the ligand L, which was calculated from the shortest-wavelength phosphorescence band [6], is  $22,523 \text{ cm}^{-1}$ . This energy level is above the lowest excited resonance level  ${}^{5}D_{0}$  of Eu(III) (17,286 cm<sup>-1</sup>) and the lowest excited resonance level  ${}^{5}D_{4}$  (20,545 cm<sup>-1</sup>) of Tb(III). Thus, the energy could be transferred from ligand to the Eu and Tb ions. And this result also indicates that the triplet state energy level T<sub>1</sub> of this ligand **L** matches better to the lowest resonance level of Tb(III) ( $\Delta v = 1978 \text{ cm}^{-1}$ ) than to Eu(III) ( $\Delta v = 5237 \text{ cm}^{-1}$ ) ion [16,17].

# 4. Conclusion

According to the data and discussion above, the ligand could form stable polynuclear complexes with lanthanide ions (metal: $\mathbf{L} = 2:3$ ). We have reported a novel 1D metal-losupramolecular polymer { $[Eu(NO_3)_3]_2 \mathbf{L}_3^1$ }<sub>n</sub> generated from the reaction of Eu(NO<sub>3</sub>)<sub>3</sub> with  $\mathbf{L}^1$ , 1,4-bis{[(2'-



Scheme 2. The chemical formula of the ligand  $L^{I}$ .

benzylaminoformyl)phenoxyl]methyl}benzene (Scheme 2) [18].

Based on the comparability of these two ligands and the stoichiometries of the complexes, we deduce that ligand L also acts as a bi(unidentate) bridging ligand connecting two lanthanide(III) ions in these complexes. Scheme 3 shows the most probable coordination structure with the lanthanide ions. And the coordination number of the lanthanide ions is 10.

When the ligand formed the lanthanide complexes, obvious changes in IR spectra were observed. In the complexes, lanthanide ions were coordinated to the C=O oxygen atoms of the ligand L. The luminescence properties of the Eu and Tb complexes in acetone solutions were investigated. Under the excitation of UV light, these complexes exhibited characteristic emission of europium and terbium ions. The lowest triplet state energy level  $T_1$  of this ligand L matches better



Scheme 3. The most probable coordination structure of the complexes.

to the lowest exicted resonance energy level of Tb(III) than to Eu(III) ion.

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