Synthesis and fluorescent properties of Eu and Tb complexes of a new aryl amide ligand Yanhua Zhang, Xiang Chen and Damin Tian*

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A new ligand, 1,2-bis[(2-benzyloxy)benzoylamino]ethane, and its complexes of europium and terbium have been synthesised and characterised. Under UV light, the europium and terbium complexes exhibited characteristic emissions and measurement of the lowest triplet state energy level of the ligand indicates that it matches better to the lowest resonance energy level of the Tb(III) ion than to that of the Eu(III) ion.

Keywords: aryl amide ligand, rare earth, complexes, fluorescence

Compounds containing lanthanide(III) ions have widely been used as probes and labels in a variety of biological and chemical applications^{1,2} because of their unique luminescence properties, such as long fluorescent decay time³ and narrow emission bands.^{4,5} Since f-f transitions are spin- and parityforbidden, the exited state of the lanthanide ion is populated through intramolecular energy transfer from the ligand to the lanthanide ion (antenna effect).⁶ It is generally accepted that the energy transfer from ligand to lanthanide(III) ion occurs from the lowest triplet state energy level T₁ of the ligand to the resonance level of the lanthanide(III) ion.⁷ This energy transfer process is one of the most important processes influencing the luminescence properties of lanthanide complexes, so it is essential to design the ligand to optimise the luminescent properties of these lanthanide ion by facilitating the well-known light conversion process and forming strongly luminescent lanthanide ion complexes.8 We have designed and prepared a new aryl amide ligand 1,2-bis[(2-benzyloxy)benzoylamino]et hane (1, Scheme 1) and its europium(III) and terbium(III) complexes, and studied the fluorescent properties of the complexes in detail. The lowest triplet state energy level T_1 of 1 matches the lowest resonance level of the Tb(III) ion better than that of the Eu(III) ion.

Experimental

1,2-bis(2-hydroxybenzoylamino)ethane⁹ and rare earth nitrates¹⁰ were prepared according to the literature methods. All commercially available chemicals were of A.R. grade and were used without further purification. The metal ions were determined by EDTA titration using xylenol orange as an indicator. Carbon, hydrogen and nitrogen analyses were determined using a PE-2400(II) Elementar instrument. IR spectra were recorded on a Perkin-Elmer Spectrum One instrument using KBr pellets in the 4000–400 cm⁻¹ region. Conductivity measurements were carried out with a DDS-11A conductivity bridge using 1.0×10^{-4} mol·L⁻¹ solution in acetone at 25 °C. ¹H NMR spectra were measured on a Bruker Avance 400 spectrometer in CDCl₃ solution with TMS as internal standard. Luminescence spectra were obtained on a Hitachi F-4500 spectrofluorometer. The excitation and emission slit widths were 2.5 nm and the PMT voltage was 700 V.

Preparation of ligand 1: The synthetic route for 1 is shown in Scheme 1. 1,2-bis(2-hydroxybenzoylamino)ethane (10 mmol), potassium carbonate (24 mmol) and DMF (100 mL) were warmed to *ca* 92 °C. After half an hour, benzyl bromide (20 mmol) was added. The reaction mixture was stirred at 92–95 °C for 15 h. After cooling down, the mixture was poured into pure water (200 mL). The resulted solid was filtered and washed by pure water several times, then dried to get the white ligand 1, yield 90%, m. p. 172–174 °C; 'H NMR (CDCl₃, 400 MHz): 3.55 (d, 4H, $-CH_2-N$), 5.15 (s, 4H, $-CH_2-O$), 6.95–7.95 (m, 18H, ArH), 8.29 (s, 2H, N–H); IR (KBr): 1642 (s, C=O), 1594 (m), 1531 (m), 1486 (m), 1450 (m), 1299 (m), 1218 (m, ArO), 1100 (m, C–O–C), 810 (w), 750 (s), 698 (m). Anal. (Calcd) C, 74.96 (74.98); H, 5.94 (5.87); N, 5.69 (5.83); O, 13.29 (13.32)%.

Preparation of the complexes: An ethyl acetate solution (5 mL) of $Ln(NO_3)_3$ ·6H₂O (Ln = Eu or Tb) (0.1 mmol) was added dropwise to a solution of 0.1 mmol of 1 in chloroform (5 mL). The mixture was stirred at room temperature for 5 h, then the precipitated complex was filtered, washed with ethyl acetate and chloroform and dried *in vacuo* over P₄O₁₀ for 48 h. Both complexes were obtained as white powders, yield 70–78 %.

Results and discussion

Analytical data for the complexes listed in Table 1 show a 1:1 metalto-1 stoichiometry. Both complexes are soluble in DMF, DMSO, acetonitrile and acetone, and slightly soluble in methanol, ethanol, chloroform and ethyl acetate. Conductivity measurement results in acetone (Table 1) indicate that both complexes act as nonelectrolytes¹¹, implying that all nitrate groups are in the coordination sphere.

The most important IR peaks of the ligand and its complexes are presented in Table 2. The IR spectra of the complexes are similar to each other, which indicates that their structures are similar. The IR spectrum of the free ligand shows strong bands at 1642 and 1100 cm⁻¹, which are attributable to [ν (C=O)] of the amide group and ν (C-O-C), respectively. In the synthesised complexes, the low-energy band remains unchanged, but the high-energy band red shifts to about 1615 cm⁻¹ ($\Delta \nu = 27$ cm⁻¹) as compared to its counterpart for the free ligand, thus indicating that only the oxygen atom of C=O takes part in



Scheme 1 The synthetic route for the ligand 1.

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Found (Calcd)					$\Lambda_{\rm m}/{\rm S~cm^2 \cdot mol^{-1}}$
%C	%Н	%N	%Ln		
42.76 (42.72)	3.61 (3.58)	8.28 (8.30)	18.82 (18.84)	843.12	61.2
	%C 42.76 (42.72) 43 11 (43 07)	Found %C %H 42.76 (42.72) 3.61 (3.58) 43.11 (43.07) 3.66 (3.61)	Found (Calcd) %C %H %N 42.76 (42.72) 3.61 (3.58) 8.28 (8.30) 43.11 (43.07) 3.66 (3.61) 8.35 (8.37)	Found (Calcd) %C %H %N %Ln 42.76 (42.72) 3.61 (3.58) 8.28 (8.30) 18.82 (18.84) 43.11 (43.07) 3.66 (3.61) 8.35 (8.37) 18.24 (18.17)	Found (Calcd) m/z %C %H %N %Ln 42.76 (42.72) 3.61 (3.58) 8.28 (8.30) 18.82 (18.84) 843.12 43.11 (43.07) 3.66 (3.61) 8.35 (8.37) 18.24 (18.17) 837.16

Table 1	Analytical	and mo	ar conductance	e data o	of the	complexes
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 Table 2
 The most important IR bands of the complexes (cm⁻¹)

Compounds	υ(C=O)	υ(C–O–C)	υ(NO ₃)					
			υ_1	υ_4	υ_2	υ_3	$ v_1-v_4 $	
1	1642	1100	_	_	_	_	_	
$[Tb(NO_3)_31] \cdot H_2O$	1615	1101	1480	1299	1031	814	181	
[Eu(NO ₃) ₃ 1]·H ₂ O	1618	1100	1478	1298	1032	813	180	

coordination to rare earth ions. The characteristic frequencies of the coordinating nitrate groups (C_{2v}) appear at ca 1480 cm⁻¹(v_1), 1299 cm⁻¹ (v_4), 1031 cm⁻¹ (v_2) and 814 cm⁻¹ (v_3), and the difference between the two strongest frequency bands (v_1 and v_4) of the nitrate groups is about 181 cm⁻¹, clearly establishing that the NO₃⁻ groups in the solid complexes coordinate to the lanthanide ion as bidentate ligands.¹²⁻¹⁴ No bands at 1380, 820 and 720 cm⁻¹ in the spectra of complexes indicate that free nitrate groups (D_{3h}) are absent, in agreement with the results of the conductivity experiments. Additionally, broad bands at 3362 cm⁻¹ can be attributed to the O–H stretching vibrations of H₂O molecule, which indicates that H₂O is present in the complexes, confirming the elemental analysis.

The fluorescence characteristics of the complexes are listed in Table 3. Comparing the fluorescence intensities of the complexes at their characteristic emission wavelengths in Fig. 1, it can be found that the relative fluorescence intensity of the Tb complex at 544 nm is greater than that of the Eu complex at 612 nm. This indicates that energy transfer from the triplet state of the ligand to the resonance

level of Tb (III) is more effective than to that of Eu (III), As we know, the luminescence of Ln³⁺ chelates is related to the efficiency of the intramolecular energy transfer between the lowest excited triplet state T₁ of the ligand and the 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 excited triplet state T₁ of the ligand and the lowest excited state of the terbium ion may be in favour of the energy transfer process. This is confirmed by the phosphorescence spectra. In addition, the relative intensity of ${}^5D_0 \rightarrow {}^7F_2$ emission of Eu(III) ion is stronger than that of ${}^5D_0 \rightarrow {}^7F_1$, showing that the Eu(III) ion is not in a centro-symmetric coordination site.¹⁵

In order to acquire the lowest excited triplet state energy T_1 of **1**, the phosphorescence spectrum of $[Gd(NO_3)_3L] \cdot H_2O$ was determined at 77K in a solution of methanol–ethanol (1:1). The Gd(III) complex displays only one phosphorescent emission band at 441 nm (shown in Fig. 2), and it can be assumed to be the 0–0 transition.¹⁶ The triplet state energy was determined. The triplet state energy level T_1 of **1**, which was calculated from the shortest-wavelength phosphorescence

 Table 3
 Fluorescence data for 1 and complexes

Compound	Solvent	Slit/nm	λ _{ex} /nm	λ _{em} /nm	RFT ^a	Assignment
 [Tb(NO ₂)2 1].H2O	Solid state	2.5	325	490	1073	⁵ D,→ ⁷ F,
[15(1003/31]1120			010	544	2813	${}^{5}D_{4} \rightarrow {}^{7}F_{5}$
				583 620	140 84	$^{5}D_{4} \rightarrow ^{7}F_{4}$ $^{5}D_{4} \rightarrow ^{7}F_{3}$
$[Eu(NO_3)_3 1] \cdot H_2O$	Solid state	2.5	314	591 612	204 1247	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$

^a RFI is relative fluorescence intensity.





Fig. 1 Emission spectra of $[Tb(NO_3)_3L]\cdot H_2O$ (1) and $[Eu(NO_3)_3L]\cdot H_2O$ (2).

Fig. 2 The phosphorescence spectrum of Gd(III) complex $[Gd(NO_3)_3L]{\cdot}H_2O$ in methanol–ethanol (1:1) at 77K.

band,¹⁷ is 22676 cm⁻¹. This energy level is above the lowest excited resonance levels ${}^{5}D_{1}$ of Eu(III) (19020 cm⁻¹) and ${}^{5}D_{4}$ (20430 cm⁻¹) of Tb(III). Thus, energy can be transferred from the ligand to the Eu(III) and Tb(III) ions. The intramolecular transfer efficiency has a close relationship to the energy difference between the lowest triplet energy level (T) of 1 and ⁵D of the Ln(III) ion (Ln = Eu or Tb).¹⁸ The relationship indicates that at room temperature, when $\Delta E(T^{-5}D_4) = 2400\pm$ 300 cm⁻¹, the organic ligand would more efficiently sensitize luminescence of the Tb(III) ion. When $\Delta E(T^{-5}D_1)$ for Eu(III) is in the range of 1000-2000 cm⁻¹, the fluorescence yield of the Eu(III) complexes is very high, whilst for the Eu(III) complex, if $\Delta E(T^{-5}D_1) > 4000 \text{ cm}^{-1}$, and for the Tb(III) complex, if $\Delta E(T^{-5}D_4) < 1500 \text{ cm}^{-1}$, the fluorescence yield is much lower.19 Accordingly the strong luminescence of the Tb(III) complex should be due to the optimal energy gap between the lowest triplet energy level of the ligands (T) and ${}^{5}D_{4}$ of Tb(III) ion; while the relatively weak luminescence of the Eu (III) complex may be caused by the larger energy gap. So, the triplet state energy level T₁ of 1 matches better to the lowest resonance level of the Tb(III) ion $(\Delta v = 2246 \text{ cm}^{-1})$ than to that of the Eu(III) ion $(\Delta v = 3656 \text{ cm}^{-1})$.

Conclusion

According to the data and discussion above, ligand 1can form stable complexes with lanthanide ions (metal:1 = 1:1), causing obvious changes in the IR spectra. In the complexes, lanthanide(III) ions were coordinated to the C=O oxygen atoms of 1. The NO₃⁻ group coordinates to the lanthanide(III) ions as a bidentate ligand, the coordination number of lanthanide ions being 8.

The europium(III) and terbium(III) complexes exhibited strong characteristic fluorescence of the europium and terbium ions, respectively. The triplet state energy level T_1 of the ligand

L is 22676 cm⁻¹, which matches better to the lowest resonance level of the Tb(III) ion than to that of the Eu(III) ion.

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