

Synthesis and Infrared and Fluorescence Spectra of Europium and Terbium Complexes with a Novel Bis-Schiff Base Ligand Derived from 2,6-Diaminopyridine and Indole-2-carbaldehyde

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A new bis-Schiff base ligand 2,6-bis[(indol-2-ylmethylene)amino]pyridine, and its complexes with europium and terbium were synthesized. The complexes were characterized by elemental analysis, infrared spectra, and conductivity. The europium and terbium ions were found to coordinate to the C≡N nitrogen atoms, pyridine nitrogen atoms, and indole nitrogen atoms. The fluorescence properties of these complexes in DMSO, DMSO/CH₃OH, and CH₃OH were studied. Under the excitation of UV light, these complexes exhibit characteristic fluorescence of europium and terbium ions. The solvent factors influencing the fluorescence intensity are discussed.

The development of luminescence chemical probes and sensors is the subject of intensive research both in natural and medical science. Probes based on europium and terbium ions are of special interest because of the particularly suitable spectroscopic properties of these ions [1, 2]. Moreover, chemists have realized that it is essential to design the encapsulating ligand to optimize the luminescent properties of these lanthanide ions by facilitating the well-known light conversion process, the antenna effect [3]. Recently, calixarenes and terpyridine-like ligands have attracted much attention mainly because they can form highly stable and strongly luminescent europium and terbium ion complexes [4, 5]. In this paper, we designed and synthesized a new and doubly functionalized bis-Schiff base ligand (having both selective ability to coordinate lanthanide ions and to enhance luminescence of them), 2,6-bis[(indol-2-ylmethylene)amino]pyridine (L), which is of a terpyridine-like structure, and studied the fluorescence properties of europium and terbium complexes with the new ligand. The results indicated that the organic solvents affected the fluorescence characteristics of europium and terbium ions.

EXPERIMENTAL

All the starting materials used in the syntheses were anal. grade and used without further purification. Rare earth nitrates were prepared according to

the literature method [6].

The metal ions were determined by EDTA titration using xylenol orange as an indicator. Combustion analyses were determined using a Vario EL elemental analyzer. The IR spectra were recorded on a Nicolet Avatar 360 FTIR instrument. Conductivity measurements were carried out with a DDSJ-308 type conductivity bridge using 1.0×10^{-3} mol dm⁻³ solution in dimethylformamide (DMF) at 25°C. ¹H NMR spectra were measured on a FT-80A spectrometer in DMSO-*d*₆ solution, with TMS as internal standard. Fluorescence measurements were made on a Shimadzu RF-540 spectrofluorophotometer equipped with quartz cuvettes of 1 cm path length. The excitation and emission slit widths were 10 nm.

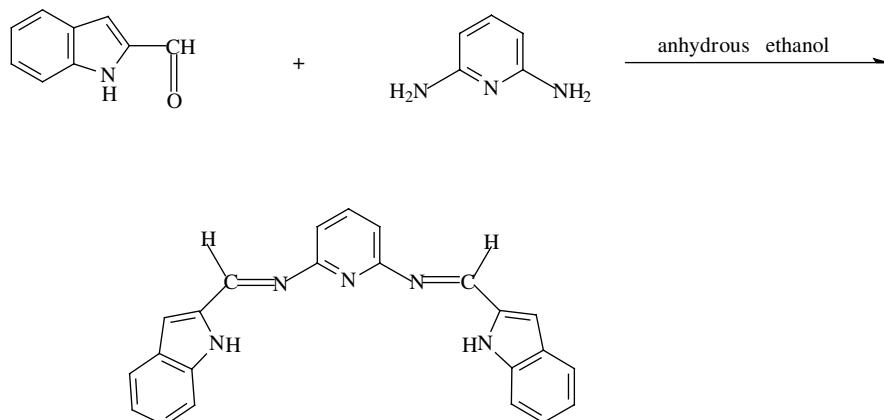
Ligand

A mixture of 2,6-diaminopyridine (11.8 mmol) and indole-2-carbaldehyde (23.6 mmol) in anhydrous ethanol (20 cm³) was stirred continuously for 8 h at room temperature. The gray precipitate was obtained by filtration and purified by crystallization with anhydrous ethanol. Yield 83 %, m.p. = 185—187°C.

Complexes

1.0 mmol of Eu(NO₃)₃ · 6H₂O or Tb(NO₃)₃ · 6H₂O in 10 cm³ of ethanol was added to the solution of the

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Scheme 1. The synthesis of ligand L.

Table 1. Elemental Analytical and Molar Conductivity Data for the Complexes

Complex	$w_i/\%$				A_m $S\text{ cm}^2\text{ mol}^{-1}$
	C	H	N	Ln	
L	75.80 (76.03)*	4.82 (4.68)	18.94 (19.28)		
$\text{Eu}(\text{NO}_3)_3 \text{L} \cdot 2\text{H}_2\text{O}$	37.82 (37.45)	2.97 (2.85)	14.83 (15.20)	20.94 (20.62)	87
$\text{Tb}(\text{NO}_3)_3 \text{L} \cdot 2\text{H}_2\text{O}$	36.76 (37.10)	2.75 (2.82)	14.58 (15.06)	21.06 (21.37)	79

*Calculated values are given in parentheses.

ligand (1.0 mmol) in 10 cm³ of ethanol. After stirring for 3 h at room temperature, the precipitate was separated by filtration, washed several times with ethanol and dried in a vacuum. Yield 61 %.

RESULTS AND DISCUSSION

The composition of the synthesized ligand (Scheme 1) has been confirmed by elemental analysis, ¹H NMR and IR spectra.

Analytical data for the complexes, presented in Table 1, conform to $\text{Eu}(\text{NO}_3)_3 \text{L} \cdot 2\text{H}_2\text{O}$ or $\text{Tb}(\text{NO}_3)_3 \text{L} \cdot 2\text{H}_2\text{O}$. Both the complexes are soluble in DMF, DMSO, and methanol, a little soluble in chloroform, ethanol, and acetone, insoluble in benzene, diethyl ether, and tetrahydrofuran. Conductivity measurements for these complexes in DMF solution (Table 1) indicate that the complexes are 1 : 1 ionic compounds [7].

The IR spectra of the complexes are similar. Table 2 gives the characteristic bands of ligand and its complexes. The IR spectrum of the free ligand shows bands at 3167 cm⁻¹, 1634 cm⁻¹, 712 cm⁻¹, and 634 cm⁻¹, which may be assigned to $\nu(\text{N—H})$, $\nu(\text{C=N})$, γ and δ (Py-ring, in-plane, and out-of-plane deformation vibrations), respectively. In the complexes, these bands for $\nu(\text{N—H})$, $\nu(\text{C=N})$, γ and δ are shifted by

about 29 cm⁻¹ (from 3167 cm⁻¹ to 3138 cm⁻¹) and 37 cm⁻¹ (from 1634 cm⁻¹ to 1597 cm⁻¹), 7 cm⁻¹ (from 712 cm⁻¹ to 719 cm⁻¹) and 8 cm⁻¹ (from 634 cm⁻¹ to 642 cm⁻¹), respectively, indicating that Schiff base nitrogen atoms, indole nitrogen atoms, and pyridyl nitrogen atoms take part in coordination to rare earth ions [8, 10]. The bands at 1594 cm⁻¹, 1568 cm⁻¹, and 1489 cm⁻¹ are assigned to the ring stretching vibrations of the pyridine ring. The new bands at 416—421 cm⁻¹ and 543—548 cm⁻¹ are assigned to the $\nu(\text{Ln—O})$ and $\nu(\text{Ln—N})$ vibrations. The band corresponding to the $\nu(\text{O—H})$ at 3341—3389 cm⁻¹ shows that the complexes contain water molecules, which is in accordance with the results of elemental analyses.

The absorption bands assigned to the coordinated nitrates were observed at about 1481 cm⁻¹ (ν_{as}) and 788 cm⁻¹ (ν_s) for the complexes. The ν_3 (E') free nitrates appear at approximately 1361 cm⁻¹ in the spectra of the complexes [9], in agreement with the results of the conductivity experiments. In addition, the separation of the two highest frequency bands $|\nu_4 - \nu_1|$ is approximately 184 cm⁻¹, thus the coordinated NO_3^- ions in the complexes are bidentate ligands [10].

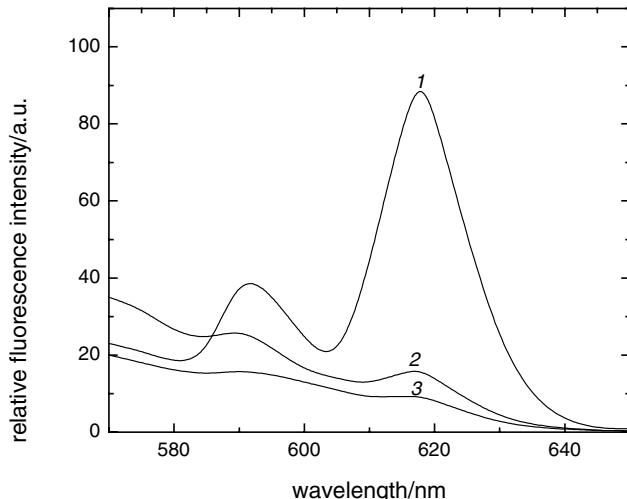
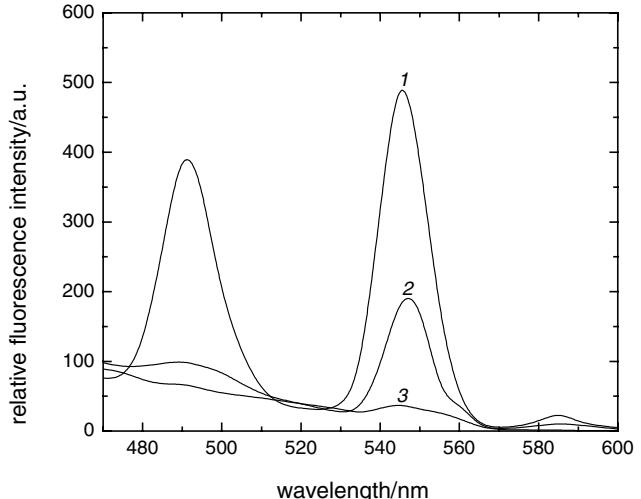
The fluorescence characteristics of the ligand and europium and terbium complexes in DMSO, DMSO/CH₃OH ($\varphi_r = 1 : 1$), and CH₃OH solution are listed in Table 3. The ligand has multiple aromatic rings

Table 2. The Relevant Characteristic IR Bands

Compound	$\tilde{\nu}_1/\text{cm}^{-1}$				
	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{H})$	$\nu(\text{NO}_3^-)$	$\nu_3(\text{NO}_3^-)$	$\nu_4(\text{NO}_3^-)$
L	1634	3167			
$\text{Eu}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$	1597	3138	1481	790	1298
$\text{Tb}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$	1598	3136	1479	788	1295
					1361
					1359

Table 3. Fluorescence Data for the Ligand and Complexes

	Solvent	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	RFT/a.u.	Assignment
L	DMSO	410	465	1020	
	CH_3OH	417	478	398	
$\text{Eu}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$	DMSO	395	592	39	$^5D_0 \rightarrow ^7F_1$
			617	87	$^5D_0 \rightarrow ^7F_2$
	DMSO/ CH_3OH		592	26	$^5D_0 \rightarrow ^7F_1$
			617	13	$^5D_0 \rightarrow ^7F_2$
	CH_3OH		592	14.5	$^5D_0 \rightarrow ^7F_1$
			617	8.6	$^5D_0 \rightarrow ^7F_2$
$\text{Tb}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$	DMSO	375	489	390	$^5D_4 \rightarrow ^7F_6$
			545	480	$^5D_4 \rightarrow ^7F_5$
			588	26	$^5D_4 \rightarrow ^7F_4$
	DMSO/ CH_3OH		489	99	$^5D_4 \rightarrow ^7F_6$
			545	197	$^5D_4 \rightarrow ^7F_5$
			588	11	$^5D_4 \rightarrow ^7F_4$
	CH_3OH		489	65	$^5D_4 \rightarrow ^7F_6$
			545	38	$^5D_4 \rightarrow ^7F_5$
			588	1.6	$^5D_4 \rightarrow ^7F_4$

**Fig. 1.** The emission spectrum of the europium complex. Concentration: $3.0 \times 10^{-4} \text{ mol dm}^{-3}$. 1. In DMSO, 2. in DMSO/ CH_3OH ($\varphi_r = 1 : 1$), 3. in CH_3OH solution.**Fig. 2.** The emission spectrum of the terbium complex. Concentration: $3.0 \times 10^{-4} \text{ mol dm}^{-3}$. 1. In DMSO, 2. in DMSO/ CH_3OH ($\varphi_r = 1 : 1$), 3. in CH_3OH solution.

with a rigid planar structure, so it is a strong fluorescence substance. It displays a fluorescence excitation maximum at $\lambda_{\text{ex}} = 410 \text{ nm}$ and an emission maximum at $\lambda_{\text{em}} = 465 \text{ nm}$ in DMSO solvent. But in DMSO/ CH_3OH solution, the excitation maximum

and emission maximum of the ligand are red-shifted. In CH_3OH solution, the excitation maximum and emission maximum of the ligand are red-shifted by approximately 7 nm and 13 nm compared with those in DMSO solvent, respectively. From Table 3 it could

be seen that the excitation and emission wavelengths of the europium and terbium complexes in organic solutions are quite different from those of the ligand, their λ_{ex} is shifted to 395 nm and λ_{em} to 592 nm and 615 nm (Fig. 1) for europium complex, and λ_{ex} to 375 nm and λ_{em} to 489 nm, 545 nm, 588 nm (Fig. 2) for terbium complex, respectively.

Due to the presence of a scattering signal near 490 nm, the peak height at 545 nm for terbium was used to measure the fluorescence intensities. From Table 3 we can see that the fluorescence intensities of terbium complex at 545 nm are stronger than those of europium complex at 615 nm, either in DMSO, DMSO/ CH_3OH , or CH_3OH solution. This property makes trivalent terbium ion desirable as luminescence labels or probes for analytical determinations. The luminescence of Ln^{3+} chelates is related to the efficiency of the intramolecular energy transfer between the triplet level of ligand and the emitting level of the ions, which depends on the energy gap between the two levels. In the organic solution, probably the energy gap between the ligand triplet levels and the emitting levels of the terbium favours to the energy transfer process for terbium.

We also can see that the fluorescence intensities for the complexes in DMSO solution are stronger than those in DMSO/ CH_3OH solution. We consider that this is due to the O—H oscillators of CH_3OH molecules. It is well known that the excited state of the lanthanide ions is efficiently quenched by interactions with high-energy vibrations like O—H groups. Therefore, the fluorescence of the complexes in CH_3OH solution can be quenched easily because of the O—H oscillators.

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