

Studies on Synthesis and Fluorescence Spectra of New Europium Complex with an Amide-Based Tripod-Type Compound

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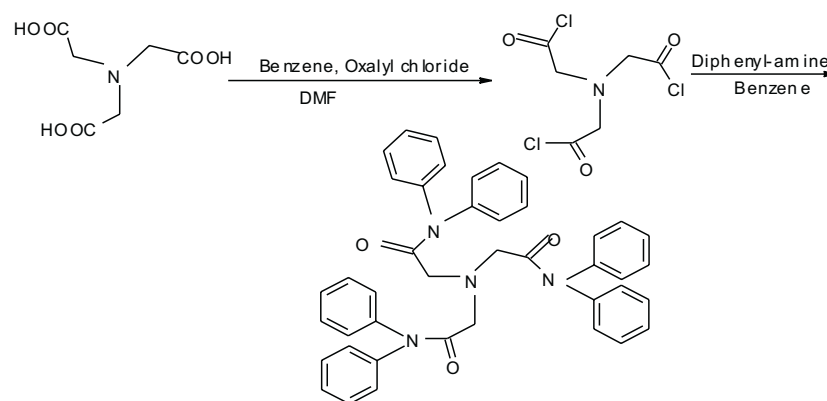
The development of luminescent chemical probes and sensors is the subject of intensive research, both in natural [1] and medical sciences [2]. The design of complexes of Ln(III) ions with encapsulating ligands is an important theme in the field of supramolecular chemistry because it offers the possibility to obtain stable luminescent compounds. A relevant aspect of this research consists in the possibility to optimize the luminescence properties of the metal ion by a suitable choice of ligand [3]. One of the most important methods, that can increase the complex fluorescence intensity, is to design and synthesize a ligand that can form stable complex with Ln(III) ions and protect the metallic site from attacking by solvent molecules [4]. Recently, the amide-based tripod-type compounds have been widely studied in the energy transfer between ligands and Ln(III) ions. The probes based on Eu(III) ions are of special interest because of the particularly suitable spectroscopic properties [5].

Recently, we have designed and synthesized a new amide-base tripod-type ligand L (2-(bis-diphenylcarbamoylmethyl-amino)-*N,N*-diphenyl-acetamide), and studied its fluorescence properties with Eu(III) ion. We found that the amide groups of the ligand possess suitable molecular structure, that can form a suitable complex with Eu(III) ion, and the solvent effect on the fluorescence properties has been discussed.

The lanthanide picrate [6] and L [7] were prepared according to literature methods. All commercially available chemicals were of reagent grade and were used without further purification. The metal ion was determined by EDTA titration, using Xylenol Orange as an indicator. Combustion analyses were determined by a Vario EL elemental analyzer. ^1H NMR spectrum was measured on a FT-80A spectrometer in CDCl_3 solution, with TMS as an internal standard. IR spectra were recorded on a Ni-

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colet AVATAR 360 FT-IR instrument, using KBr discs in the 400–4000 cm^{-1} region. Conductivity measurements were carried out with a DDS-307 type conductivity bridge, using $1.0 \times 10^{-3} \text{ mol l}^{-1}$ solution in acetone at room temperature. Fluorescence measurements were made on a Shimadzu F-4500 spectrofluorophotometer, equipped with quartz cuvettes of 1 cm path length. The excitation and emission slit widths were 5 nm. The ligand was prepared according to Scheme 1.



Scheme 1. The synthesis of ligand L.

Oxalyl chloride (10.0 ml) was added dropwise to the mixture of (bis-carboxymethyl-amino)-acetic acid (1.5 g, 7.85 mmol, in 20 ml benzene) with two drops of DMF as catalyst. The mixture was stirred at 30°C for 6 h, the benzene and extra oxalyl chloride were removed by decompress distillation under 60°C. Diphenyl-amine (8.0 g, 47.38 mmol, in 20 ml benzene) was added. After the mixture had been stirred about 8 h at room temperature, the precipitated solid was filtered, and the solvent was removed by decompress distillation. The crude product was chromatographed on silica gel (petroleum ether/ $\text{CH}_3\text{COOC}_2\text{H}_5$, 1:1(v:v)) to afford pure product as red-brown oil in 45% yield (Scheme 1).

The complex was obtained as follows: A solution of L (0.1 mmol, in 15 ml ethanol) was added dropwise to a solution of the europium picrate (0.1 mmol, in 10 ml ethanol). The mixture was stirred at room temperature for 8 h, and yellow precipitate formed. The precipitate was filtered and washed three times with ethanol. Further drying in vacuum over P_4O_{10} for 48 h afforded yellow powder, yield 51%. Anal. Calc. For $\text{C}_{60}\text{H}_{42}\text{N}_{13}\text{O}_{24}\text{Eu}$: C, 48.65; H, 2.84; N, 12.30; Eu, 10.27. Found: C, 48.76; H, 2.81; N, 12.17; Eu, 10.08.

Analytical data for the complex conformed to a 1:3:1 metal-to-picrate-to-L stoichiometry $\text{Eu}(\text{pic})_3\text{L}$. The complex is soluble in DMSO, DMF, acetone, acetonitrile, tetrahydrofuran, but sparingly soluble in methanol, ethanol and chloroform. Conductivity measurement for this complex in acetone solution ($50.3 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) indicates that this complex is nonelectrolyte and all the three picrate groups coordinate to Eu(III) in complex [8]. The complex has constant composition and is stable in air.

The ^1H NMR spectrum of the ligand exhibits one single peak at 3.66 ppm assigned to $\text{N-CH}_2\text{-C=O}$ protons, and one multiples at 6.73–7.39 ppm assigned to benzene ring H, respectively.

Free L shows a band at 1673 cm^{-1} , which may be assigned to $\nu(\text{C=O})$. In the IR spectrum of the europium complex, the band of $\nu(\text{C=O})$ of free L shift about 57 cm^{-1} towards lower wavenumber, indicating that the C=O groups take part in coordination to the Eu(III) . The larger band shift for $\nu(\text{C-O})$ (63 cm^{-1}) in the spectrum of complex suggests that the Eu-O (phenol) band is stronger than Eu-O (carbonyl) one [9]. Furthermore, the characteristic frequencies ($1555, 1342\text{ cm}^{-1}$) of free picrate were divided into two double peaks (about $1583, 1541\text{ cm}^{-1}$ and $1367, 1329\text{ cm}^{-1}$), indicating that the picrate groups coordinate to the Eu(III) as bidentate ligands [10] (Table 1).

The fluorescence characteristics of the complex in CHCl_3 and acetone solutions are listed in Table 2. The ligand is a strong fluorescence substance. It displays a fluorescence excitation maximum at 398 nm and an emission maximum at 614 nm in acetone solution. In CHCl_3 solution, the excitation maximum at 390 nm and an emission maximum at 614 nm are observed. We also can see the fluorescence intensity for the complex in CHCl_3 solution stronger than that in acetone solution (Table 2).

Table 1. The relevant characteristic IR bands (cm^{-1}).

Compound	$\nu(\text{C=O})$	$\nu(\text{O-H})$	$\nu(\text{C-O})$	$\nu_{\text{as}}(-\text{NO}_2)$	$\nu_{\text{s}}(-\text{NO}_2)$
Ligand (L)	1673				
Picrate acid		3445	1213	1555	1342
$\text{Eu(pic)}_3\text{L}$	1617		1276	1583, 1541	1367, 1329

Table 2. Fluorescence data for complex (concentration: $1.0 \times 10^{-4}\text{ mol l}^{-1}$).

	Solvent	Ex (nm)	Em (nm)	RFI	Assignment
$\text{Eu(pic)}_3\text{L}$	CHCl_3	390	579	6.43	$^5\text{D}_0 \rightarrow ^7\text{F}_0$
			590	10.38	$^5\text{D}_0 \rightarrow ^7\text{F}_1$
			614	131.5	$^5\text{D}_0 \rightarrow ^7\text{F}_2$
$\text{Eu(pic)}_3\text{L}$	acetone	398	577.5	2.52	$^5\text{D}_0 \rightarrow ^7\text{F}_0$
			591	4.69	$^5\text{D}_0 \rightarrow ^7\text{F}_1$
			614	9.11	$^5\text{D}_0 \rightarrow ^7\text{F}_2$

As can be seen from Fig. 1 and Table 2, emission spectra for this complex are composed of three main bands corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_{0,1,2}$. The band of $^5\text{D}_0 \rightarrow ^7\text{F}_0$ is very weak, and the fluorescence intensity for the complex in CHCl_3 solution is stronger than that in acetone solution.

The influence of the concentration of complex in the acetone and CHCl_3 solutions on the relative fluorescence intensity is shown in Fig. 2. In acetone solution, when the

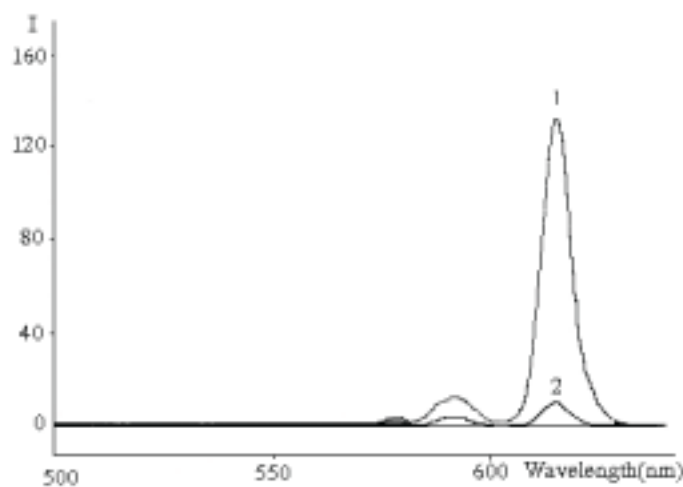


Figure 1. The emission spectrum of the europium complex. Concentration: $1.0 \times 10^{-4} \text{ mol l}^{-1}$. (1) CHCl_3 solution, (2) acetone solution.

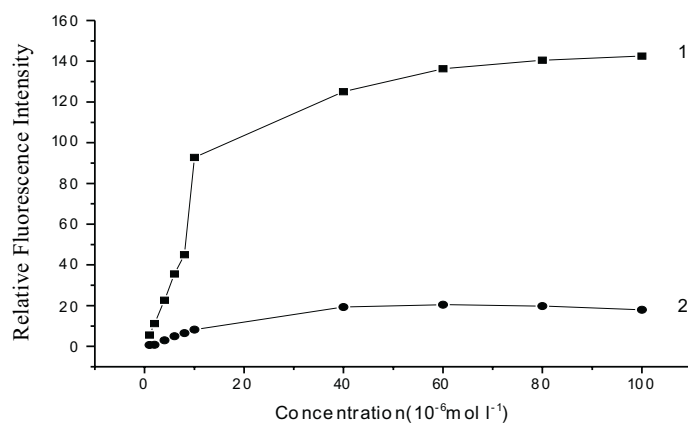


Figure 2. Effect of concentration on the relative fluorescence intensity of complex. (1) CHCl_3 solution, (2) acetone solution.

concentration is lower than $6.0 \times 10^{-5} \text{ mol l}^{-1}$, the fluorescence intensity of complex increases with concentration increasing, but, with the concentration continuously increasing, the fluorescence intensity drops. In CHCl_3 solution, the fluorescence intensity of complex increases with the concentration and no maximum is observed on the fluorescence intensity-concentration dependence.

The fluorescence spectra of europium complex also provide information about the geometry of the complex. The probability of magnetism dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_1$) of europium ion is smaller than that of electric dipole transition ($^5\text{D}_0 \rightarrow ^7\text{F}_2$). This is expected considering low site symmetry for the europium ion in the complex [11].

According to the data and discussion above, the amide-base tripod-type ligand could form stable complex with europium ion. Obvious IR spectrum changes were observed after the ligand formed complex. The complex exhibited characteristic fluorescence of europium ion. The metal-centered emission bands were recorded and assigned as $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$. Based on these results, we can design and synthesize a series of new tripod-type ligands to optimize the luminescence properties of lanthanide ions.

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