Synthesis and luminescence spectral properties of europium (III) and terbium (III) complexes with a new Schiff base ligand N,N,N′-tri-(2,4-dihydroxyl-acetophenone)-triaminotriethylamine

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A new Schiff base ligand with triposal structure, N,N,N′-tri-(2,4-dihydroxyl-acetophenone)-triaminotriethylamine (H₆L), and its complexes with europium (III) and terbium (III) have been synthesized. The complexes have been characterized by element analysis, IR spectra, mass spectra, thermal analysis and molar conductivity. The europium (III) and terbium (III) cations coordinate with the Schiff base nitrogen atoms, the bridgehead nitrogen atoms and phenolic hydroxyl oxygen atoms of the ligand. The luminescence properties of the complexes in DMSO, THF, DMF, MeCN and CH₃OH solvents have also been investigated. Under the excitation of UV light, these complexes exhibit characteristic of europium (III) and terbium (III). The solvent factors influencing the luminescence intensity are also discussed. Tentative structures for the complexes have been proposed based on the experimental results.

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Trivalent lanthanide ions can form stable coordination complexes with a variety of organic ligands. These chelates have been used in various applications including fluorimetric determination of ions, or conversely, of organic analytes used as ligand¹,⁵, and in the development of luminescent labels in clinical chemistry and molecular biology²,⁵.

Metal complexes of Schiff base ligand have received considerable attention over the past two decades⁶. This may be attributed to unusual structural features in the resultant metal complexes and their biological activities. Some of the metal complexes have antitumor properties², antioxidation activities⁸ and electronic and photophysical properties⁹,¹⁰. Although a lot of research has been reported, studies on lanthanide complexes with Schiff base as the ligands are rare. Some recent articles have reported Schiff base-lanthanide luminescence complexes¹¹-¹⁴. It is essential to design the appropriate ligand to optimize the luminescence properties of lanthanides by facilitating the well-known light conversion process, which shows efficient ligand-to-metal energy-transfer process (antenna effect)¹⁵. In order to understand further the coordination and the properties of rare earth complexes with Schiff base ligands, we have designed and synthesized a new and doubly functionalized Schiff base ligand (having both selective ability to coordinated lanthanide ions and enhancing luminescence of them) with a triposal structure, N,N,N′-Tri-(2,4-dihydroxyl-acetophenone)-triaminotriethylamine (H₆L). In this note, the synthesis, spectroscopic properties of europium (III) and terbium (III) nitrate complexes with this new ligand have been reported.

Experimental

All chemicals used for the synthesis were of analytical grade and used without further purification. Rare earth nitrates were prepared according to the literature method¹⁶.

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 FT-IR instrument. Mass spectra (fast atom bombardment) were recorded on a VG ZAB-HS mass spectrometer. The thermal behavior was monitored on a WCT-2A thermal analyzer. Conductivity measurements were carried out with a DDSJ-308 type conductivity bridge using 1.0×10⁻³ mol L⁻¹ solution in dimethylformamide (DMF) at 25°C. H NMR spectra were measured on a FT-80A spectrometer in acetone-d₆ solution, with tetramethylsilane (0.00 ppm) as internal standard. Chemical shift multiplicities are reported as s = singlet, d = doublet, t = triplet, and m = multiplet. Luminescence measurements were made on a Shimadzu RF-540 spectrophotometer equipped with quartz cuvettes of 1 cm path length. The excitation and emission slit widths were 10 nm.

Synthesis of N,N′,N″-tri-(2,4-dihydroxyl-acetophenone)-triaminotriethylamine (3)

Anhydrous ZnCl₂ (3.3 g, 24 m mol) was added slowly to hot glacial acetic acid (3.3 g, 54 m mol) solution. Then, 1,3-benzenediol (1) (2.2 g, 20 m mol)
was added and refluxed for 1 h. On cooling the mixture to room temperature, the product (2) was precipitated. It was washed with 1:3 HCl and water, respectively, and dried under vacuum to afford 2, 4-dihydroxyl-acetophenone (2) as brown powder.

A mixture of (2) (2.2823g, 15 mmol) and trimethyltriaminioamine (0.7312g, 5mmol) in anhydrous ethanol (20 mL) was refluxed for 5h at 60°C when a brown precipitate was formed. The precipitate was collected by filtration, washed with C2H5OH and dried under vacuum to afford ligand (3) as brown powder (Scheme 1). Yield: 78%, m.pt. 203-205°C. IR (cm⁻¹, KBr), 3074 (O-H), 1632 (C=N), 1602, 1583, 1599, 1498 (phenyl, C-C), 1241 (N-C). ¹H NMR (DMSO-d₆, ppm): 6.12 (d, 2H, ph-OH), 3.10 (s, 3H, CH₃), 2.34 (t, 4H, CH₂), 7.20-7.43 (m, 3H, Ar-H). FABMS: m/z = 549 (M+1). Found: C 66.83, H 6.48, N 10.03 %. Calc. for C₃₀H₃₉N₄O₉: C 65.69, H 6.57, N 10.22 %.

**Scheme 1**

**Synthesis of complexes**

Eu (NO₃)₂·6H₂O (1.0 mmol) in 10 mL ethanol was added dropwise to a solution of H₂L (1.0 mmol) in 10 mL ethanol. After stirring for 3 h at room temperature, the product which formed was collected by filtration, washed several times with ethanol and dried in vacuum. Yield: 68 %. Found: C 48.17 %, H 4.94 %, N 7.51 %, Eu 20.42 %. Analysis: Calc. for C₃₀H₃₉N₄O₉Eu: C 47.94 %, H 5.19 %, N 7.46 %, Eu 20.24 %. MS: m/z = 752 (M+1). The terbium complex was also synthesized by this method. Yield: 71 %. Found: C 47.85 %, H 4.98 %, N 6.95 %, Tb 21.21 %. Analysis: Calc. for C₃₀H₃₉N₄O₉Tb: C 47.49 %, H 5.15 %, N 7.39 %, Tb 20.98 %. MS: m/z = 759 (M+1).

**Results and discussion**

All complexes were soluble in DMSO, THF, DMF, MeCN and CH₃OH, but sparingly soluble in water and ethyl acetate. The molar conductivities were 11.4 S cm² mol⁻¹ and 9.7 S cm² mol⁻¹ for the europium and terbium complex respectively in DMF solution (1x10⁵ mol·L⁻¹), respectively, indicating that all complexes are non-electrolytes in DMF²⁷. Elemental analyses show the formula of the complexes to be Ln·H₂L·3H₂O (where Ln = Eu, Tb), which indicates that these complexes conform to 1:1 metal-to-ligand stoichiometry.

**IR spectra**

The IR spectra of the europium (III) and terbium (III) complexes are strikingly similar in relative positions and intensities of the peaks, which suggests a close structural relationship between the complexes. The IR spectrum of the free ligand (3) shows bands at 1632 cm⁻¹, which may be assigned to ν(C=N) of the Schiff base. The band is shifted ~ 27 cm⁻¹ (from 1632 to 1605) in the complexes, indicating that Schiff base nitrogen atom takes part in coordination. In addition, the vibration ν(C=N) of ligand (3) at 1241 cm⁻¹ is shifted to 1218 cm⁻¹ in europium (III) and terbium (III) complexes, indicating that the bridgehead nitrogen atom of ligand is coordinated to the lanthanide ions³⁸,³⁹. Furthermore, the mass spectral data for Eu (III) and Tb (III) complexes are consistent with deprotonation of three hydroxyl groups among the six-hydroxyl groups of the ligand. This supports the fact that the oxygen atom of phenolic hydroxyl is also coordinated to the metals ions. The conductivity measurement result for the two complexes in DMF solution that we have discussed above also supports this conclusion. The new bands at 432, 438 cm⁻¹ and 548, 551 cm⁻¹ in two complexes are assigned to the ν(Ln-O) and ν(Ln-N) vibrations, respectively, which could not be found at free ligand (3). In addition, the disappearance of bands characteristic of nitrates at ~ 1470 (ν₁), 810 (ν₂), 1290 (ν₃), and 1380 (ν₄) cm⁻¹, indicates that the complexes do not contain nitrates³⁰. The band corresponding to the ν(O-H) at 3257-3272 cm⁻¹ at complexes shows that the complexes contain water molecules, which is in accordance with the results of elemental analyses.

**Thermal analysis**

Both complexes are stable in air. The thermal analysis of the europium(III) complex has been studied in air using Al₂O₃ as reference. The DTA curve of the europium (III) complex shows two endothermic peaks at around 97 and 196°C, indicating weight loss of ~ 4.67 % at 83-121°C and ~ 2.28 % at 182-203. This corresponds to the loss of two water molecules (Calc., 4.79 %) and one coordinated water molecule (Calc., 2.40 %), respectively, indicating that both lattice water molecules and coordinated water
molecules are in the complex. On heating to 630°C, the complex decomposes step-by-step since there are two exothermic peaks at 304°C and 417°C. The residual weights fundamentally do not change beyond 540°C, which indicates that at 540°C lanthanide oxides are formed.

**Luminescence properties**

Since the ligands has multiple aromatic rings with a rigid planar structure, it can be predicted that its europium (III) and terbium (III) complexes have very strong luminescence due to antenna effect. Under identical experimental conditions, the luminescence properties of two complexes were investigated in DMSO, THF, DMF, MeCN and CH₃OH solutions (1.0 × 10⁻⁴ mol·L⁻¹ each) and are listed in Table 1. From Table 1 it can be seen that there is a small difference (15 nm) between the excitation maxima of the europium (III) complexes and that of the terbium (III) complexes. The characteristic luminescence emission wavelengths of the europium (III) and terbium (III) ions were observed. In DMSO solution, the europium (III) and terbium (III) complexes have the strongest luminescence. The order of luminescence is: DMSO > THF > DMF > MeCN > CH₃OH solutions (Figs 1 and 2).

Due to the presence of a scattering signal near 490 nm, the peak height at 545 nm for terbium (III) was used to measure the luminescence intensities. Comparing Figs 1 and 2, we can see that the luminescence intensities of europium (III) complex at 616 nm are stronger than those of terbium (III) complex at 545 nm in all the solutions. The luminescence of Ln³⁺ chelates is related to the

![Figure 1](image.png)

Table 1—Luminescence data for the complexes at room temperature

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Conc. (mol·L⁻¹)</th>
<th>Solvent</th>
<th>λₑₓ (nm)</th>
<th>λₑₘ (nm)</th>
<th>RFI ᵃ</th>
<th>Assignment</th>
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</thead>
<tbody>
<tr>
<td>Eu·H₂L·3H₂O</td>
<td>1.0×10⁻⁴</td>
<td>DMSO</td>
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<td>592</td>
<td>232</td>
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<td></td>
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<td>2426</td>
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<tr>
<td></td>
<td></td>
<td>DMF</td>
<td>365</td>
<td>592</td>
<td>436</td>
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<tr>
<td></td>
<td></td>
<td>MeCN</td>
<td>365</td>
<td>592</td>
<td>1638</td>
<td>⁶D₄₋→F₂</td>
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<tr>
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<td></td>
<td>CH₃OH</td>
<td>365</td>
<td>592</td>
<td>317</td>
<td>⁶D₄₋→F₂</td>
</tr>
<tr>
<td>Tb·H₂L·3H₂O</td>
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<td>492</td>
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<td>491</td>
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<td>¹⁵D₄₋→F₁</td>
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</tbody>
</table>

³RFI is relative luminescence intensity.
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 organic solution, the energy gap between the ligand triplet level and the emitting level of the europium (III) ion may be in favour of the energy transfer process.

We also can see the luminescence intensities of the europium (III) and terbium (III) complexes become weaker from DMSO, THF, DMF, MeCN to CH₃OH solution. This is due to the coordinating effects of solvents. Obviously, luminescence enhancement towards Ln³⁺-H₆L from organic solvents is due to not only removal of inner-sphere coordinating water molecules but also energy transfer from organic solvents to H₆L. That is to say, after absorbing radiation, organic solvents transfer energy to H₆L. Subsequent energy transfer from H₆L to the emission levels of Ln³⁺ ion causes a dramatic increase in luminescence intensity. H₆L simultaneously serves as the energy donor and acceptor.

The luminescence quantum yield (ϕ) of the Eu-H₆L-DMSO system was found to be 0.178 with quinine bisulfate (0.55) in 1 M H₂SO₄ as reference. UV-vis spectra of the Eu-H₆L system in DMSO solution showed absorption peak at about 367 nm, corresponding to the π-π* transition of the ligand. And the molar extinction coefficient is 6.34 × 10⁴ L·mol⁻¹·cm⁻¹. Since energy transfer processes in lanthanoid complexes occur via absorption of light by the ligand followed by intramolecular energy transfer from the ligand to the central metal ion. This strong absorption offers an efficient excitation mechanism for the Eu³⁺ ion.

We also can see that the luminescence intensities for both the complexes are weakest in CH₃OH solution. We believe that this is due to the O-H oscillators of CH₃OH 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 luminescence of the complexes in CH₃OH solution can be quenched easily because of the O-H oscillators.

Based on the above, the structures of the lanthanide complexes, Eu(III) and Tb(III) are proposed as shown in Fig. 3.

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References