Polish J. Chem., **78**, 601–605 (2004) **COMMUNICATION**

Synthesis and Fluorescence Spectra of Europium(III) and Terbium(III) Complexes with a New Bis-Schiff Base Ligand N,N′-Bis(2,4-dihydroxyacetonephenone)-2,6-diaminopyridine (H_4L)

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(Received July 15th, 2003; revised manuscript December 18th, 2003)

Metal complexes of Schiff base ligand have received considerable attention over the past two decades [1]. This may be attributed to unusual structural features in the resultant metal complexes and their biological activities. Some of the metal complexes have antitumor properties [1,2], antioxidative activities [3], electronic and photophysical properties [4]. Although a lot of research has been reported, the lanthanide complexes of these ligands are rare. It has been indicated that lanthanide luminescence enhancement can be facilitated in complexes possessing an aromatic ring that has a nitrogen atom, such as 1,10-phenanthroline or bipyridine. The nitrogen lone pair appears to form an efficient energy bridge to the lanthanide ion [5,6], which exhibits a good light conversion process, the antenna effect [7]. In order to understand further the coordination and the properties of rare earth complexes with Schiff base ligands, we designed and synthesized a new and doubly functionalized bis-Schiff base ligand (having both selective ability to coordinate lanthanide ions and to enhance their luminescence), N,N′-bis(2,4-dihydroxyacetonephenone)-2,6-diaminopyridine (H_4L), and studied the synthesis, spectroscopic properties of europium and terbium nitrates complexes with the new bis-Schiff base ligand.

The synthesis route of the ligand was described by Scheme 1. Anhydrous $ZnCl_2$ (3.3 g, 24 mmol) was slowly added dropwise to a hot glacial acetic acid (3.3 g, 54 mmol) solution. Then 1,3-benzenediol (2.2 g, 20 mmol) was added and refluxed for 1 h. When cooling the mixtures to room temperature, the products (**2**) were precipitated from solutions, washed with 1:3 HCl and water, respectively. The precipitates were dried under vacuum to afford 2,4-dihydroxyl-acetophenone as yellow powders.

A mixture solution of (**2**) (1.5215 g, 10 mmol) and 2,6-diaminopyridine (0.5457 g, 5 mmol) in C_2H_5OH (20 mL) was refluxed for 6 h at 65°C and brown precipitate (H_4L) formed. The precipitate was obtained by filtration and purified by crystallization with

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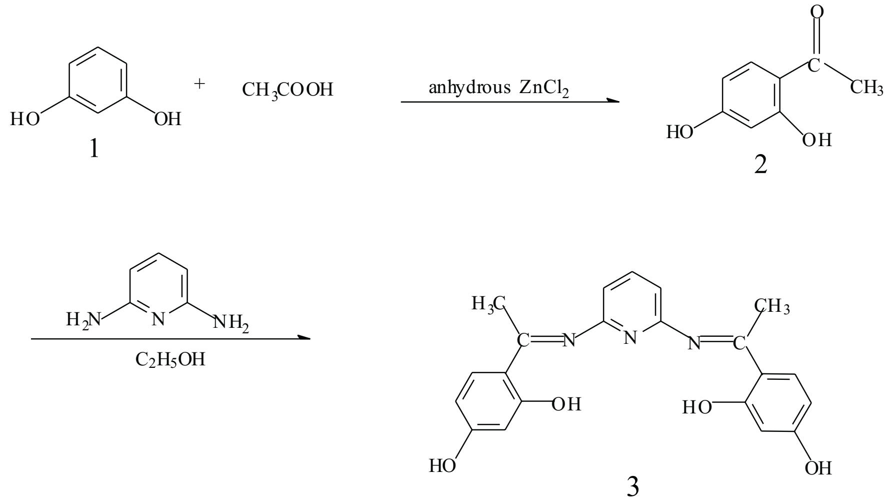
anhydrous ethanol. 1.0 mmol $Eu(NO_3)_3 \cdot 6H_2O$ in 10 mL ethanol was added dropwise to the solution of H_4L (1.0 mmol) in 10 mL ethanol. After stirring for 3 h at room temperature the product formed was then collected by filtration, washed several times with ethanol and dried in a vacuum. The terbium complex was also synthesized by this method.

The molar conductivities (Λ_m) [9] of europium and terbium complexes indicate that they are non-electrolytes in DMF [10]. The results of elemental analyses [9] give the formula of the complexes as $Ln(H_2L)(NO_3) \cdot 3H_2O$ (where Ln = Eu, Tb), which indicates that all these complexes conform to 1:1 metal-to-ligand stoichiometry.



Scheme 1. The synthesis of ligand.

The IR spectra [9] of the europium and terbium complexes indicate that Schiff base nitrogen atoms and the pyridyl nitrogen atoms take part in coordination to rare earth ions [11]. The mass spectral data [9] for Eu and Tb complexes are consistent with deprotonation of two hydroxyl groups among the four hydroxyl groups of the ligand, which indicate that two phenolic hydroxyl oxygen atoms are coordinated to metal ions. This conclusion is also supported by conductivity measurement for both complexes in DMF solution. In addition, there are no bands at 1360–1400 cm^{-1}, indicating that the complexes do not contain free nitrates [12], which is in accordance with the molar conductivities of the complexes. The separation of the two highest frequency bands $|\nu_4 - \nu_1|$ is 171 cm^{-1} (for europium complex) and 169 cm^{-1} (for terbium complex), thus, the coordinated NO_3^- ions in the complexes are bidentate ligands [12].

The results of thermal analysis indicate, that one lattice water molecule and two coordinated water molecules are in the complex.

The fluorescence characteristics of the ligand (H_4L), europium and terbium complex in DMSO, DMSO/CH_3OH (1:1 v/v) solutions were investigated. The ligand

(H_4L) is a strong fluorescence substance, because of its multiple aromatic rings with a rigid planar structure. It displays a fluorescence excitation maximum at 470 nm and an emission maximum at 510 nm in DMSO solution. But in DMSO/CH_3OH (1:1 v/v) solution, the excitation maximum and emission maximum of the ligand are blue-shifted about 7 and 13 nm, respectively, compared with those in DMSO solution.

From the emission spectra in Fig. 1 and Fig. 2, it could be seen that the europium and terbium complexes with H_4L can emit intrinsic spectrum of Eu^{3+} and Tb^{3+} ions under excitation of ultraviolet light. Due to the presence of a scattering signal near 490 nm (for terbium) and 590 nm (for europium), the peak height at 545 nm (for terbium) and 615 nm (for europium) was used as a measure of the fluorescence intensities. From Fig. 1 and Fig. 2, we can see that the fluorescence intensities of terbium complexes at 545 nm are stronger than those of europium complexes at 615 nm, both in DMSO and in DMSO/CH_3OH solution, which shows that terbium ions exhibit an excellent luminescence characteristics when the native luminescence is enhanced by H_4L. So, trivalent terbium ion potentially may be used 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 DMSO, the energy gap between the ligand triplet levels and the emitting levels of the terbium is more favorable for the energy transfer process than in europium.

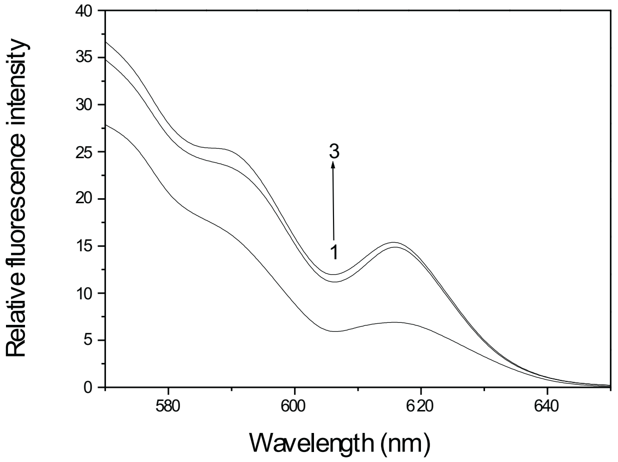


Figure 1. The emission spectrum of the europium complex. Concentration: 1.0×10^{-4} mol· L^{-1}. 1 in DMSO/CH_3OH (1:1) solution, 2 in DMSO solution, and 3 in DMSO solution with EDTA used as a secondary ligand.

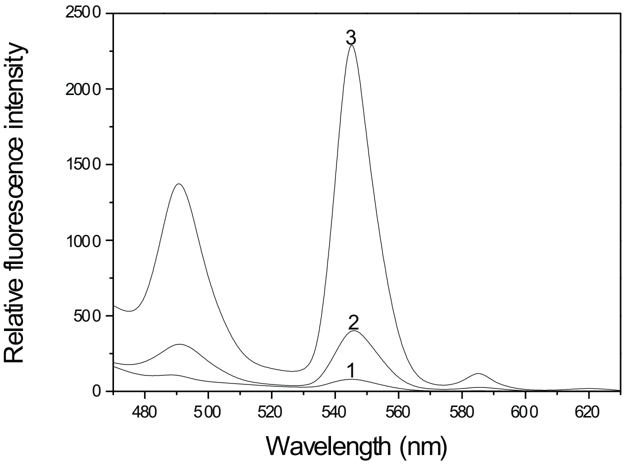


Figure 2. The emission spectrum of the terbium complex. Concentration: 1.0×10^{-4} mol· L^{-1}. 1 in DMSO/CH_3OH (1:1) solution, 2 in DMSO solution, and 3 in DMSO solution with EDTA used as a secondary ligand.

From Fig. 1 and Fig. 2, we can see that EDTA could strongly enhance the luminescence of terbium complex with H_4L, but almost did not enhance the luminescence of europium complex with H_4L. Although EDTA was used as a secondary ligand in fluorescence enhancement [13], it has not been reported that EDTA also could strongly enhance the luminescence of terbium complex with Schiff base ligand. So this is a novel spectral phenomenon. We think that intramolecular energy transfer plays a key role in fluorescence enhancement. That is to say, after absorbing radiation, the EDTA transfers energy to the H_4L, and subsequent energy transfer from H_4L to the emission levels of the Tb^{3+} ion causes a dramatic increase of luminescence intensity. H_4L simultaneously serves as the energy donor and acceptor.

We also can see that the fluorescence intensities for both complexes in DMSO are stronger than those in DMSO / CH_3OH solution. We assume 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.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (Grants 20071015, 20371022 and QT Project), University Doctoral Foundation of the Ministry of Education (Grant 200307300015) and Key project of the Ministry of Education of China (Grant 01170).

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8. Ligand H_4L: Yield, 79%. m.p. 121–123℃. Anal. Calcd. for $C_{21}H_{19}N_3O_4$: C, 66.84; H, 5.04; N, 11.14. Found: C, 67.02; H, 4.97; N, 11.23. IR (KBr, cm^{-1}): 1631 (C=N), 1549 (C=C + C=N of pyridine ring).
9. The europium complex: Yield, 72%. Anal. Calcd. for $C_{21}H_{23}N_4O_{10}Eu$: C, 39.19; H, 3.58; N, 8.71; Eu, 23.64. Found: C, 38.87; H, 3.64; N, 8.56; Eu, 23.42. MS: m/z = 644 (M+1). Λ_m: 9.6 $S \cdot cm^2 \cdot mol^{-1}$ (DMF solution, 1×10^{-3} $mol \cdot L^{-1}$). IR (KBr, cm^{-1}): 1614 (C=N), 1467 (ν_1 NO_3^-), 812 (ν_3 NO_3^-), 1296 (ν_4 NO_3^-), 427 (Eu-O), 543 (Eu-N), 1542, 1557 (C=C + C=N). The terbium complex: Yield, 67%. Anal. Calcd. for $C_{21}H_{23}N_4O_{10}Tb$: C, 38.77; H, 3.54; N, 8.62; Tb, 24.46. Found: C, 38.53; H, 3.38; N, 8.95; Tb, 24.81. MS: m/z = 651 (M+1). Λ_m: 8.2 $S \cdot cm^2 \cdot mol^{-1}$ (DMF solution, 1×10^{-3} $mol \cdot L^{-1}$). IR (KBr, cm^{-1}): 1615 (C=N), 1471 (ν_1 NO_3^-), 798 (ν_3 NO_3^-), 1302 (ν_4 NO_3^-), 432 (Tb-O), 547 (Tb-N), 1542, 1557 (C=C + C=N).
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