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# Studies on synthesis, infrared and fluorescence spectra of new europium (III) and terbium (III) complexes with an β-diketonate-type ligand

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#### Abstract

A new  $\beta$ -diketonate-type ligand, *N*-(2-amino-6-methyl-pyridinyl)ketoacetamide (L) and its complexes with europium (III) and terbium (III) were synthesized. The complexes were characterized by elemental analysis, infrared spectra and conductivity. The europium (III) and terbium (III)-ions were found to coordinate to the C=O oxygen atoms and pyridine nitrogen atoms. The fluorescence properties of these complexes in solid, DMF and CH<sub>3</sub>OH were studied. The solvent factors influencing the fluorescent intensity are discussed. © 2004 Elsevier B.V. All rights reserved.

Keywords: β-Diketonate-type ligand; Europium (III) nitrate complexes; Terbium (III) nitrate complexes; Fluorescence of lanthanide complexes; IR spectra

#### 1. Introduction

Organic light-emitting devices (OLEDs) have attracted extensive attention due to their excellent performance with high brightness, low power consumption, wide viewing angle, fast response time and potentially low cost [1–5]. Since Tang and VanSlyke [1] reported a low-voltage driven electroluminescent (EL) device using tris-(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) as an emitting material and electron transport material produced strong electroluminescence in the green, the study on using metal complex as organic light-emitting material becomes more and more attention.

The europium (III) and terbium (III) complexes with  $\pi$ -conjugated ligands such as  $\beta$ -diketonato also have been studied as emitting materials for OLEDs [6–9], since the reports by Okamoto and co-workers [10]. However, the quantum efficiency of most these complexes are unfortunately still low. This may be mostly due to inefficiency of the energy transfer, particularly, triplet–triplet transfer in these complexes. Chemists have realized that it is essential to design ligands, which have better energy trans-

fer property to the lanthanide metal ion. In the present work, we designed and synthesized a new  $\beta$ -diketonatetype ligand containing pyridine terminal groups, *N*-(6-(2methyl)pyridinyl)ketoacetamide (Scheme 1), and studied the fluorescence properties of europium (III) and terbium (III) complexes with the new ligand, *N*-(2-amino-6-methylpyridinyl)ketoacetamide. The results indicated that the organic solvent affected the fluorescence characteristics of europium (III) and terbium (III) ions.

### 2. Experimental

### 2.1. Materials

2-Amino-6-methylpyridine (A.R.) was purchased from Aldrich, All other regents used were analytical grade and used without further purification. Rare earth nitrates were prepared according to the literature method [11].

# 2.2. Methods

Carbon, hydrogen and nitrogen were determined using a Elementar Vario EL elemental analyzer. Infrared spectra

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Scheme 1. The synthesis of ligand (L).

(4000–400 cm<sup>-1</sup>) were recorded with KBr optics on a Nicolet NEXUS 670 FTIR spectrophotometer. The molar conductance values were determined on a DDS-11A conductivity meter with methanol as solvent ( $10^{-3}$  mol L<sup>-1</sup> solution) at 25 °C. <sup>1</sup>H NMR and <sup>13</sup>C NMR were measured with a Bruker-300MHz nuclear magnetic resonance instrument using CDCl<sub>3</sub> as solvent and TMS as internal reference. Mass spectrum was measured using a ZAB-HS analyzer. Fluorescence measurements were made on a Hitich F-4500 spectrometer equipped with quartz curettes of 1 cm path length.

# 2.3. Synthesis of the ligand

The ligand was prepared by reaction of 2-amino-6methylpyridine with ethyl acetoacetate by a method similar to literature [12]. The ligand was obtained as a white flake solid. IR: cm<sup>-1</sup> (KBr, pellet).  $\nu$ 3240 (m, N–H), 1722 (s, CH<sub>3</sub>C=O), 1664 (s, amide C=O), 1553 (s, C=N). Elemental analytical: (calc.) C% 62.40 (62.49), H% 6.40 (6.25), N% 14.48 (14.57). MS (FAB): 193 (M + 1).

#### 2.4. Synthesis of the complexes

An ethanol solution of Ln (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Ln = Eu and Tb) (0.2 mmol) was added dropwise to a solution of the ligand (0.6 mmol) in chloroform (15 ml). The mixture was stirred for 3 h, and white precipitate formed. The precipitate was collected by filtration and washed three times with ethanol and chloroform, respectively. Further drying in vacuum afforded a white flake solid, yield ca. 80%.

Table 1						
Chemical	shifts	(nnm)	of the	ligand	(L)	i



Scheme 2. The keto and enol tautomerism of L.

#### 3. Result and discussion

# 3.1. <sup>1</sup>H NMR and <sup>13</sup>C NMR of the ligand (L)

In chloroform solution, the ligand displays keto enol tautomerism as judge by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy (Table 1, Scheme 2).

# 3.2. Properties of the complexes

Analytical data for the complexes, presented in Table 2, The results of elemental analyses indicated that the composition of the complexes conform to  $Eu(NO_3)_3L_2$  and  $Tb(NO_3)_3L_2$ , and that all the complexes conform to a 1:2 metal-to-ligand stoichiometry.

All complexes are soluble in DMF, DMSO, methanol, a little soluble in ethanol and acetone, insoluble in benzene, diethyl ether and tetrahydrofuran. The molar conductance values of the complexes measured in CH<sub>3</sub>OH solution (1 ×  $10^{-3}10^{-3}$  mol L<sup>-1</sup>) at 25 °C are 168 and 172 S cm<sup>2</sup> mol<sup>-1</sup> (Table 2), indicating 1:2 electrolytes [13] and that uncoordinated nitrates are in the complexes, which is in accordance with the results of IR spectra of the complexes.

# 3.3. IR spectra

The IR spectra of all complexes are similar, indicating that the complexes have identical structure. Table 3 gives the characteristic bands of ligand and its complexes. The IR spectrum of the free ligand shows bands at 1722 and 1664 cm<sup>-1</sup>, the former due to the CH<sub>3</sub>C=O moiety and the latter to the amide C=O. The band at 1553 cm<sup>-1</sup> in the free ligand can be assigned to  $\nu$  (C=N) of pyridine ring. In the complexes,

Chemical shifts (ppm) of the ligand (L) in CDCl <sub>3</sub>									
Tautomer	<sup>1</sup> H NMR								
	C (9) H	N (5) H	C (7) H	O (1) H	C (1) H	Py-H			
Keto	2.32		3.58						
Enol	1.97	9.12	5.03	13.5					
					2.45	6.89-7.96			
	<sup>13</sup> C NMR								
	C (6)	C (7)	C (1)	C (2)	C (3)	C (4)	C (9)		
Keto		51.6							
Enol		91.7							
	150.3		24.2	119.8	138.9	111.3	31.2		

 Table 2

 Elemental analytical and molar conductance data for the complexes

Complex	C (%) found (calc.)	H (%) found (calc.)	N (%) found (calc.)	$\Lambda_{\rm m}~({\rm S~cm^2~mol^{-1}})$
[Eu(NO <sub>3</sub> )L <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	32.98 (33.24)	3.16 (3.32)	13.76 (13.57)	168
$[Tb(NO_3)L_2](NO_3)_2$	32.68 (32.92)	3.20 (3.29)	13.60 (13.44)	172

Table 3	
The relevant characteristic IR bands (cm <sup>-1</sup> )	

Compound	ν (CH <sub>3</sub> C=O)	v (amide C=O)	ν (C=N)	$v_1$ (A <sub>1</sub> , NO <sub>3</sub> <sup>-</sup> )	$v_5 (B_2, NO_3^-)$	ν <sub>3</sub> (E', NO <sub>3</sub> <sup>-</sup> )
L	1722	1664	1553			
$[Eu(NO_3)L_2](NO_3)_2$	1654	1617	1567	1492	1306	1385
$[Tb(NO_3)L_2](NO_3)_2$	1655	1617	1567	1496	1302	1384

these bands for  $\nu$  (CH<sub>3</sub>C=O),  $\nu$  (amide C=O) and  $\nu$  (C=N) of pyridine ring are shifted by about 68 (from 1722 to 1654), 47 (from 1664 to 1617) and 14 (from 1553 to 1567) cm<sup>-1</sup>, respectively, indicating that the oxygen atoms of CH<sub>3</sub>C=O, amide C=O and pyridine nitrogen atoms take part in coordination.

The absorption bands assigned to the coordinated nitrates were observed at about 1492 ( $\nu_{as}$ ) and 814 ( $\nu_{s}$ ) cm<sup>-1</sup> for the complexes. The  $\nu$  (D<sub>3h</sub>) free nitrates appear at approximately 1385 cm<sup>-1</sup> in the spectra of the complexes, in agreement with the results of the conductivity experiments. In addition, the separation of two highest frequency bands  $|\nu_1 - \nu_4|$  is approximately 200 cm<sup>-1</sup>, thus the coordinated NO<sub>3</sub><sup>-</sup> ions in the complexes are bidentate ligands [14].

The results of elemental analysis and IR spectra indicate that the coordination only involves the keto-form of the ligand.

#### 3.4. Fluorescence studies

The fluorescence characteristics of all complexes in solid and in DMF, methanol solutions are listed in Table 4. From Table 4 it could be seen that the excitation wavelengths of the

Table 4 Fluorescence data for the complexes

	Solvent	$\lambda_{ex}$ (nm)	$\lambda_{em}$ (nm)	RFI <sup>a</sup>	Assignment
[Eu(NO <sub>3</sub> )L <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ,	Solid	308	616	3717	$^5D_0 \rightarrow {}^7F_2$
	DMF	396	591 616	16.4 32.1	${}^5D_0 \rightarrow {}^7F_1 \\ {}^5D_0 \rightarrow {}^7F_2$
	CH <sub>3</sub> OH	396	591 616	4.5 6.4	${}^5D_0 \rightarrow {}^7F_1 \\ {}^5D_0 \rightarrow {}^7F_2$
[Tb(NO <sub>3</sub> )L <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	Solid	387	495 546 588	2795 8659 179	
	DMF	337	490 545 584	896 2705 145	
	CH3OH	378	491 546 584	223 648 32	

<sup>a</sup> RFI: relative fluorescence intensity.



Fig. 1. The emission spectrum of the europium complex in solid. The excitation and emission slit widths were 2.5 nm.

europium complexes ( $\lambda_{ex} = 308$  nm) in solid and in organic solutions ( $\lambda_{ex} = 396$  nm) are quite different, and the excitation wavelengths of terbium complexes are also different between in solid and in organic solutions. The europium and terbium complexes display a fluorescence emission maximum at 616 and 546 nm in solid (Fig. 1, Fig. 3), respectively. Compared



Fig. 2. The emission spectrum of the europium complex in solution. The excitation and emission slit widths were 5 nm.



Fig. 3. The emission spectrum of the terbium complex. The excitation slit widths were 1 nm (in solid) and 2.5 nm (in solution). The excitation and emission slit widths were 2.5 nm (in solid) and 5 nm (in solution).

with those in solid, the emission maximum is identical with that in organic solutions (Fig. 2). However, from Table 4, we can see that the fluorescence intensities of all the complexes in solid are stronger than that in DMF and  $CH_3OH$  solution. This may be due to the excited state of the lanthanide ions is efficiently quenched by interactions with high-energy vibrations groups of organic solvent [15].

We also can see the fluorescence intensities of terbium (III) complex at 546 nm are stronger than those of europium complexes at 616 nm, either in solid or in organic solutions. 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. Probably the energy gap between the ligand triplet levels and the emitting level of terbium favor to the energy transfer process for terbium.

#### 4. Conclusion

According to the data and discussion above, the  $\beta$ diketonate-type ligand has formed stable complex with europium and terbium ions. Obvious IR spectrum changes were observed after the ligand formed complexes with the two ions. In the complexes, europium and terbium ions were coordinated to the oxygen atoms of CH<sub>3</sub>C=O, amide C=O and pyridine nitrogen atoms. The complexes exhibited characteristic fluorescence of europium and terbium ions. Based on those results, a series of new  $\beta$ -diketonate-type ligand could be designed and synthesized to optimize the luminescent properties of these lanthanideions.

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