Available online at www.sciencedirect.com

ScienceDirect

Spectrochimica Acta Part A 69 (2008) 513–516

SPECTROCHIMICA
ACTA
PART A

www.elsevier.com/locate/saa

Investigations into the synthesis and fluorescence properties of Eu(III), Tb(III), Sm(III) and Gd(III) complexes of a novel bis-β-diketone-type ligand

Yi-Ming Luo*, Zhe Chen, Rui-Ren Tang, Lin-Xiang Xiao, Hong-Jian Peng

School of Chemistry and Chemical Engineering, Central South University, Hunan 410083, PR China

Received 21 January 2007; received in revised form 29 March 2007; accepted 6 April 2007

Abstract

A novel bis-β-diketon ligand, 1,1′-(2,6-bispyridyl)bis-3-phenyl-1,3-propane-dione (L), was designed and synthesized and its complexes with Eu(III), Tb(III), Sm(III) and Gd(III) ions were successfully prepared. The ligand and the corresponding metal complexes were characterized by elemental analysis, and infrared, mass and proton nuclear magnetic resonance spectroscopy. Analysis of the IR spectra suggested that each of the lanthanide metal ions coordinated to the ligand via the carbonyl oxygen atoms and the nitrogen atom of the pyridine ring. The fluorescence properties of these complexes in solid state were investigated and it was discovered that all of the lanthanide ions could be sensitized by the ligand (L) to some extent. In particular, the Tb(III) complex was an excellent green-emitter and would be a potential candidate material for applications in organic light-emitting devices (OLEDs) and medical diagnosis.

Keywords: 1,1′-(2,6-Bispyridyl)bis-3-phenyl-1,3-propanedione; Bis-β-diketone; Synthesis fluorescence of lanthanide complexes; IR spectra

1. Introduction

Since a brightly photoluminescent europium complex was first reported by Weissman in 1942 [1], the properties of lanthanide organic complexes have been extensively studied. Complexes of lanthanide ions with organic ligands have been doped in polymers for optical amplification [2,3], and luminescent lanthanide complexes have been used in medical diagnosis where they are used to detect small amounts of biomolecules that reveal information about the physical state of a patient [4,5]. More recently, organic electroluminescence (OEL) has been investigated at length for applications because of its low drive voltage, suitability for integrated circuit and potential application for large flat panel display [6,7]. Several lanthanide complexes have been utilized in the fabrication of OEL devices (OLEDs), and significant progress has been made in improving the brightness and electroluminescence efficiencies of OELDs with Eu(III), Tb(III), Sm(III)and Gd(III) organic complexes as luminescent centers [8].

The complexes of Eu(III), Tb(III), Sm(III) and Gd(III) ions with π-conjugated ligands such as β-diketones have also been examined as emitting materials for OLEDs [9–12] following the reports by Okamoto and his coworkers [13]. However, in most cases the quantum efficiency of most of these complexes is still low, possibly due to inefficiency of triplet–triplet energy transfer in these complexes. To combat this difficulty, chemists have sought to design ligands that allow for improved energy transfer to the lanthanide metal ion.

In the present work, we have designed and synthesized a novel, pyridine-containing, bis-β-diketone-type ligand, 1,1′-(2,6-bispyridyl)bis-3-phenyl-1,3-propanedione (Scheme 1), and studied the fluorescence properties of its Eu(III), Tb(III), Sm(III) and Gd(III) complexes in the solid state.

2. Experimental

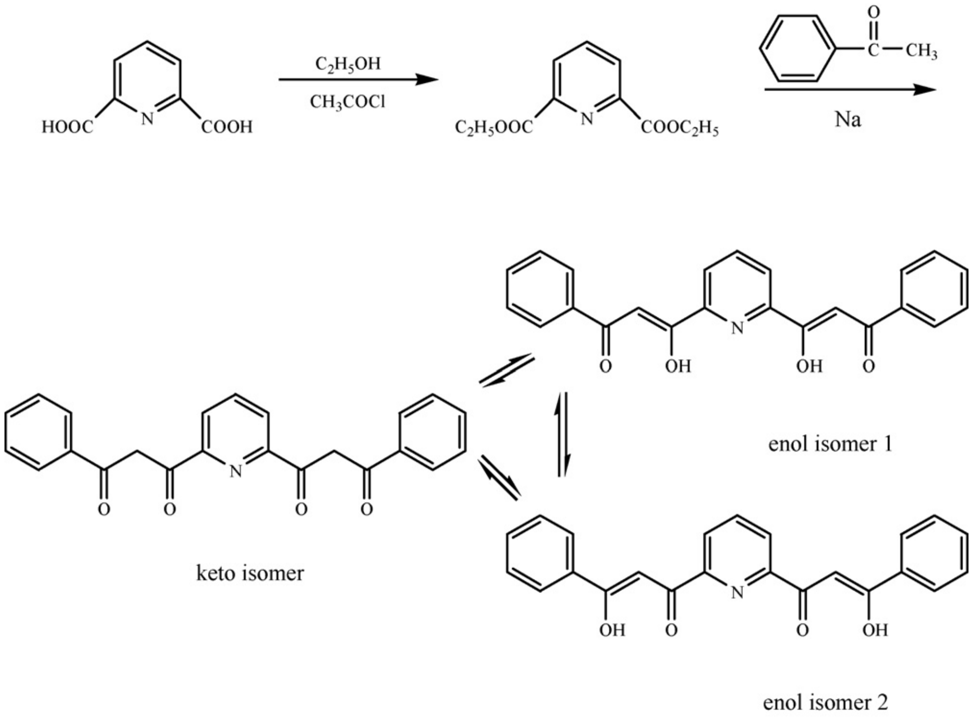
2.1. Materials

Pyridine-2,6-dicarboxylic acid and other reagents used were purchased and used as analytical grade. Rare earth chlorides were prepared according to the literature method [14,15].

---

* Corresponding author. Fax: +86 731 8879616.
E-mail address: ymluo@mail.csu.edu.cn (Y.-M. Luo).

1386-1425/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2007.04.029



Scheme 1. Synthesis of the ligand (L).

2.1.1. Methods

Contents of carbon, hydrogen and nitrogen were determined using an Elementar vario EL elemental analyzer. Content of Ln(III) was determined by EDTA titration. Infrared spectra (4000–400 cm^{-1}) were recorded with samples as KBr discs using a Nicolet NEXUS 670 FTIR spectrophotometer. ^{1}H-NMR spectra were measured using a Bruker-400 MHz nuclear magnetic resonance spectrometer with $CDCl_3$ as solvent and TMS as internal reference. Mass spectra were measured using a ZAB-HS analyzer. Fluorescence measurements were made on a Hitich F-4500 spectrometer.

2.2. Synthesis of the ligand (L)

2.2.1. Synthesis of 1,1′-(2,6-bispyridyl)bis-3-phenyl-1,3-propanedione (L)

To a suspension of freshly cut sodium (1.0 g, 44 mmol) and diethyl 2,6-pyridinedicarboxylate (4.90 g, 22 mmol) in dry benzene (50 ml) was placed in a three-necked, round-bottom flask, fitted with a condenser. The mixture in the flask was stirred, while a solution of acetophenone (5.28 g, 44 mmol) in benzene (25 ml) was added dropwise. The reaction mixture was incubated and stirred at room temperature for about 30 min until the yellow sodium salt had precipitated. The resulting suspension was heated to 45 °C and incubated for about 2 h. The sodium salt was collected by filtration, washed thoroughly with petroleum ether and dried. The dried solid was added to dilute hydrochloric acid (2 M, 50 ml) and the resulting precipitate was collected by filtration. The crude products were recrystallized from methanol to give the ligand (L) (5.89 g, 72%).

Physical properties of 1,1′-(2,6-bispyridyl)bis-3-phenyl-1,3-propanedione (L): The ^{1}H-NMR spectrum shows the presence of several keto-enol tautomers. In this paper, we describe only the major tautomer, the bis(keto-enol) system, which formed yellow microcrystals from methanol, m.p. 176–178 °C; IR (KBr): $\nu_{max}(cm^{-1})$; 3422 (C=C–OH), 2924 (CH_2), 1616 (C=O), 1560 (C=N); ^{1}H-NMR (400 MHz, $CDCl_3$): δ16.5 (d, 2H, OH), 8.04–8.32(m, 3H, C_5H_3N), 7.25–7.75(m, 10H, C_6H_5); MS, *m/z*: 371(M^+), 294, 266, 252, 224, 105, 77. Elemental analytical (calc.) C% 74.26 (74.38), H% 4.78 (4.61), N% 3.90 (3.77).

2.3. Synthesis of the complexes

A solution of $LnCl_3 \cdot 6H_2O$ (Ln = Eu, Tb, Sm, Gd) (0.2 mmol) in ethanol (5 ml) was added dropwise to a solution of the ligand (0.6 mmol) in ethanol (15 ml) and the mixture stirred at 60 °C for 3 h. The resulting precipitate was collected by filtration, washed three times each with ethanol and chloroform and dried in vacuo to give a flaky solid (typically about 80% yield).

3. Results and discussion

3.1. Properties of the complexes

The results of elemental analysis (see Table 1) indicated that the composition of the complexes conforms to $Eu_2L_3 \cdot 6H_2O$, $Tb_2L_3 \cdot 4H_2O$, $Sm_2L_3 \cdot 6H_2O$ and $Gd_2L_3 \cdot 8H_2O$, respectively. All complexes were found to be soluble in H_2O, DMF, DMSO, slightly soluble in ethanol and acetone, and insoluble in benzene, diethyl ether and tetrahydrofuran.

Table 1
Elemental analytical data for the complexes

Complex	M (%) found (calc.)	C (%) found (calc.)	H (%) found (calc.)	N (%) found (calc.)
Eu2L3·6H2O	19.23 (19.92)	54.08 (54.30)	2.83 (2.75)	4.08 (4.16)
Tb2L3·4H2O	21.15 (21.13)	55.60 (55.10)	2.86 (2.79)	4.02 (3.95)
Sm2L3·6H2O	19.86 (19.75)	54.51 (54.41)	4.36 (4.17)	2.87 (2.76)
Gd2L3·8H2O	20.05 (20.00)	53.00 (52.70)	4.21 (4.30)	2.89 (2.67)

Table 2
Characteristic IR bands (cm^{-1}) of the ligand and its complexes

Compounds	C—OH	C=O	C=N	Eu—N	Eu—O
L	3422	1616	1560		
$Eu_2L_3·6H_2O$	3401	1608	1572	526	431
$Tb_2L_3·4H_2O$	3396	1611	1574	529	436
$Sm_2L_3·6H_2O$	3376	1610	1571	525	432
$Gd_2L_3·8H_2O$	3393	1611	1573	525	434

3.2. IR spectra

The IR spectra of all four complexes are similar, indicating that they are structurally alike. Table 2 summarises the characteristic bands observed for the ligand and its metal complexes. The IR spectrum of the free ligand shows bands at 3422, 1616 and 1560 cm^{-1}, which can be assigned as (C–OH), ν(C=O) and ν(C=N) of the ligand, respectively. In the complexes, these bands are shifted upfield by 21–46 cm^{-1} for ν(C–OH) and 5–8 cm^{-1} for ν(C=O) and downfield by 11–14 cm^{-1} for ν(C=N). In each case, the shifts suggested that the relevant oxygen and nitrogen atoms of the ligand were involved in coordination to the metal centre. The absorption bands assigned to the Ln–O and Ln–N stretching frequencies of the complex were observed at 431–436 cm^{-1} and 525–529 cm^{-1}, respectively. The results of elemental analysis and IR spectroscopy indicate that coordination only involves the enol-forms of the ligand.

3.3. Fluorescence studies

The fluorescence data for each of the complexes in the solid state is listed in Table 3. The maximum excitation wavelengths (λ_{ex}) of the Eu(III), Tb(III), Sm(III) and Gd(III) complexes were 276 281, 272 and 274 nm, respectively (Table 3). Fluorescent spectra for the Eu(III), Sm(III) and Gd(III) complexes were measured at two different drive voltages, 400 V (Fig. 1) and 700 V (Figs. 2–4). At 400 V, the fluorescent intensity observed from Eu(III), Sm(III) and Gd(III) complexes were very weak (spectra not shown), while very strong fluorescence was observed from the Tb(III) complex (Fig. 1) under the same experimental condi-

Table 3
Fluorescence data for the complexes

Complexes	λ_{ex} (nm)	λ_{em} (nm)	RFI	Assignment
$Eu_2L_3·6H_2O$	276	593	746	$^5D_0$-$^7F_1$
		616	2616	$^5D_0$-$^7F_2$
$Tb_2L_3·4H_2O$	281	493	2208	$^5D_4$-$^7F_6$
		545	3896	$^5D_4$-$^7F_5$
		584	385	$^5D_4$-$^7F_4$
$Sm_2L_3·6H_2O$	272	487	2985	$^4I_{9/2}$
		532	439	$^4F_{3/2}$
		545	3780	$^4G_{5/2}$
		584	549	$^4G_{5/2}$
		648	44	$^4G_{5/2}$
$Gd_2L_3·8H_2O$	274	493	1238	$^4I_{9/2}$
		545	939	$^4G_{5/2}$
		586	214	$^4G_{5/2}$

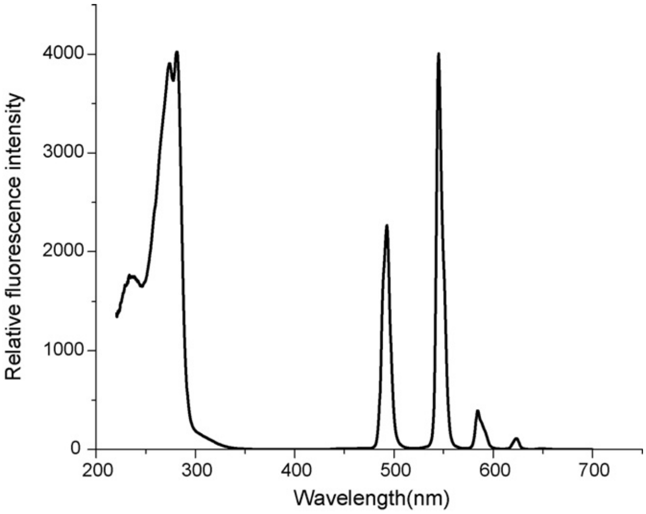


Fig. 1. The excitation and emission spectrum of the Tb(III)complex. The excitation and emission slit widths were 2.5 nm in solid state and the drive voltage was 400 V.

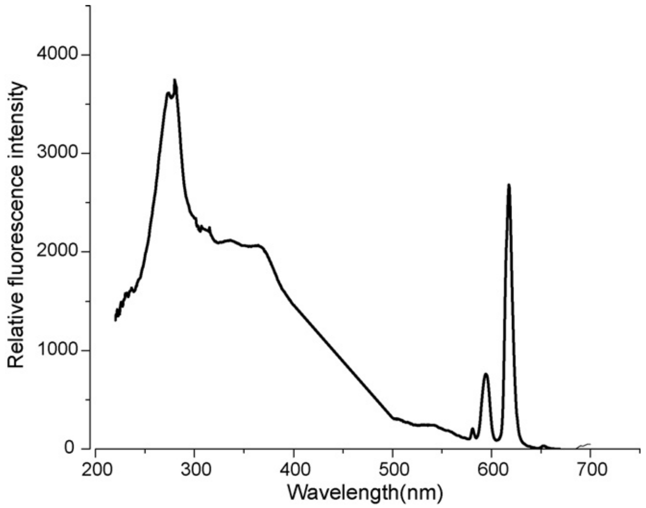


Fig. 2. The excitation and emission spectrum of the Eu(III) complex. The excitation and emission slit widths were 2.5 nm in solid state and the drive voltage was 700 V.

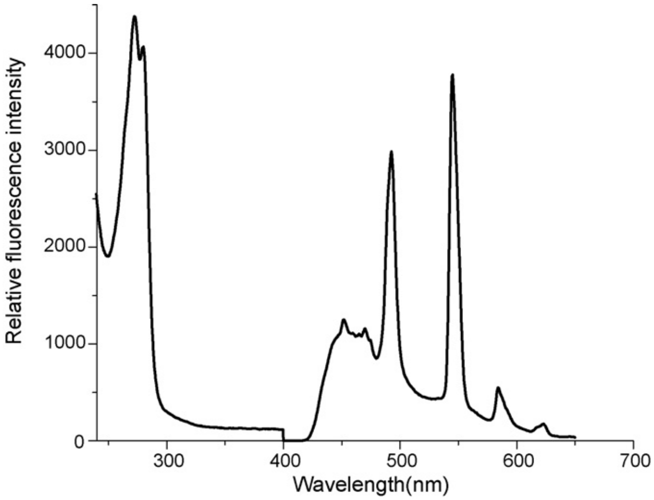


Fig. 3. The excitation and emission spectrum of the Sm(III) complex. The excitation and emission slit widths were 2.5 nm in solid state and the drive voltage was 700 V.

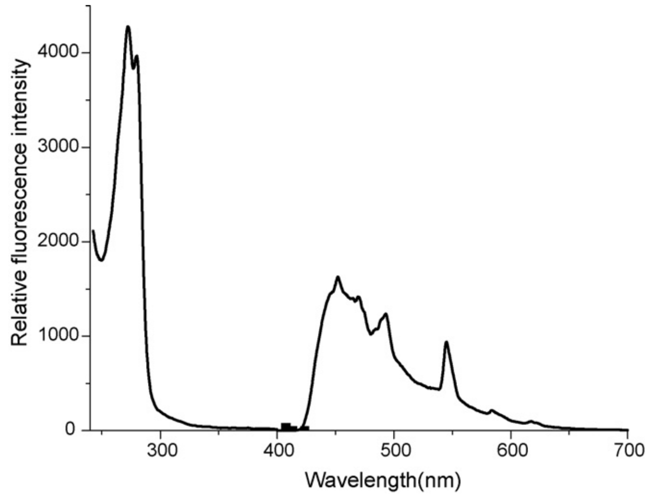


Fig. 4. The excitation and emission spectrum of the Gd(III) complex. The excitation and emission slit widths were 2.5 nm in solid state and the drive voltage was 700 V.

tions. It appears that the energy-transfer from the organic ligand (L) to the central Tb(III) ions is much more effective compared to other Ln(III) ions we have studied. It is thought that the strong emission observed is due to the $^5D_4$-$^7F_5$ transitions of the 4f electrons of the Tb(III) ions.

The luminescence of Ln(III) complexes is related to the efficiency of the intra-molecular energy transfer between the triplet energy states of the ligand and the emitting energy states of the metal ions. One factor that can contribute to the observed fluorescence intensity is the energy gap between the two energy states involved. Since the fluorescence intensity of the Tb(III) complex at 545 nm was much stronger than that of the Eu(III), Sm(III) and Gd(III) complexes, it can be inferred that the energy difference between the ligand triplet states and the emitting energy state of Tb(III) is more favorable for energy transfer than those of the other three rare earth ions.

4. Conclusion

We have successfully synthesized a novel bis-β-diketo-type ligand and shown that it can form stable complexes with Eu(III), Tb(III), Sm(III) and Gd(III) ions. Differences in the IR spectra of the free ligand and the metal complexes indicated that coordination of each of the four rare earth ions to the ligand was occurring at the oxygen atoms of the carbonyl and enol groups and the nitrogen atom of the pyridine ring. The complexes each exhibited characteristic fluorescence, with the Tb(III) complex being an excellent green luminescent material that could be considered as a candidate material for applications in organic light-emitting devices (OLEDs) and medical diagnosis. Based on our results, a series of novel bis-β-diketo-type ligands could be synthesized and screened to optimize the luminescent properties of these lanthanide ions complexes.

Acknowledgement

This work is supported by Science Foundation of Hunan Province.

References

[1] S.I. Weissman, J. Chem. Phys. 10 (1942) 214.
[2] L.H. Slooff, A. Polman, S.I. Klink, G.A. Hebbink, L. Grave, F.C.J.M. van Veggel, D.N. Reinhoudt, J.W. Hofstraat, Opt. Mater. 14 (2000) 101.
[3] D. An, Z. Yue, R.T. Chen, Appl. Phys. Lett. 72 (1998) 2806.
[4] I.J. Hemmil, Alloys Compd. 225 (1995) 480.
[5] J. Moynagh, H. Schimmel, Nature 400 (1999) 105.
[6] P.K.H. Ho, D.S. Thomas, R.H. Friend, N. Tessler, Science 285 (1999) 233.
[7] R.H. Friend, R.W. Gymer, A.B. Homes, J.H. Buroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A. Dos Santos, J.L. Brédas, M. LöDylund, W.R. Salaneck, Nature 397 (1999) 121.
[8] J. Kido, Y. Okamoto, Chem. Rev. 102 (2002) 2357.
[9] J. Kido, K. Nagai, Y. Okamoto, Chem. Lett. (1991) 1267.
[10] K. Kido, Y. Nagai, J. Okamoto, Alloys Compd. 30 (1993) 192.
[11] N. Takada, T. Tsutsui, S. Saito, J. Jpn, Appl. Phys. 33 (1994) 863.
[12] L. Huang, K.Z. Wang, C.H. Huang, F.Y. Li, Y.Y.J. Huang, Mater. Chem. 11 (2001) 790.
[13] J. Kido, K. Nagai, Y. Okamoto, Chem. Lett. (1990) 657.
[14] A.J. Chandrasekhar, Imaging Technol. 16 (1990) 158–161.
[15] R.R. Tang, Z.E. Yan, C.C. Guo, Chem. J. Chin. Universities 27 (2006) 472–477.