Available online at www.sciencedirect.com

ScienceDirect

Spectrochimica Acta Part A 67 (2007) 624–627

SPECTROCHIMICA ACTA PART A

www.elsevier.com/locate/saa

Synthesis and spectroscopic properties of rare earth picrate complexes with a new biphenylamide

Yan-Ling Guo, Ya-Wen Wang, Wei-Sheng Liu*, Wei Dou, Xia Zhong

Department of Chemistry and National Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

Received 9 June 2006; accepted 15 August 2006

Abstract

The new ligand *N*-benzyl-2-{2′-[(benzyl-ethyl-carbamoyl)-methoxy]-biphenyl-2-yloxy}-*N*-ethyl-acetamide (L) and its complexes of rare earth picrates were synthesized. The complexes were characterized by elemental analysis, IR, UV–vis spectra and conductivity measurements. The fluorescence properties of the europium complex in solid state and in $CHCl_3$, ethyl acetate, acetone, acetonitrile and DMF were investigated. Under the excitation, the europium complex exhibited characteristic emissions of europium. The lowest triplet state energy level of the ligand indicates that the triplet state energy level of the ligand matches better to the resonance level of Eu(III) than Tb(III) ion.

Keywords: Biphenylamide; Rare earth picrate complexes; Spectroscopic properties

---

1. Introduction

Luminescent lanthanide complexes [1–4] are used as labels and sensors for natural and medical science [5,6] mainly due to their large Stokes shifts, narrow emission profiles, and long fluorescence lifetimes [7]. They have attracted more and more chemists to design the organized molecular architectures containing trivalent lanthanide ions (Eu^{3+}, Tb^{3+}) working as efficient light conversion devices [1,8]. So it is essential to design the multifunctional ligand to optimize the luminescent properties of these lanthanide ions by facilitating the well-known light conversion process, the antenna effect [9], and forming highly and strongly luminescent europium and terbium ion complexes [10].

Amide-based crown ethers offer many advantages in extraction and analysis of the rare earth ions because of their ring-like coordination structure and terminal group effects [11,12]. However, luminescent properties on open-chain crown ethers with lanthanide complexes have been rarely reported [13]. Due to their low luminescence, recently, we have designed a series of polyfunctional ligands having both selective ability to coordinate lanthanide ions and enhanced luminescence of lanthanide complexes, by providing proper conjugate absorption groups suitable for energy transfer.

In this work, we introduced biphenyl groups as the basic molecular frame and obtained a new open-chain crown ether ligand, *N*-benzyl-2-{2′-[(benzyl-ethyl-carbamoyl)-methoxy]-biphenyl-2-yloxy}-*N*-ethyl-acetamide (L). The fluorescent properties of the complex of europium ions with this new ligand were studied in detail. The results indicated that the organic solvent affected the fluorescence characteristics of europium ions. And the lowest triplet state energy level of the ligand which was calculated from the phosphorescence spectrum of the Gd(III) at 77 K indicates that the triplet state energy level of the ligand matches better to the resonance level of Eu(III) than Tb(III) ion.

2. Experimental

2.1. Materials

The lanthanide picrates [14] and *N*-ethyl-*N*-benzylchloroacetamide [15] were prepared according to literature method. All commercially available chemicals were of A.R. grade and all solvents used were purified by standard methods.

2.2. Methods

The metal ions were determined by EDTA titration using xylenal orange as indicator. C, H and N were determined

---

* Corresponding author. Tel.: +86 931 8912552; fax: +86 931 8912582.
E-mail address: liuws@lzu.edu.cn (W.-S. Liu).

1386-1425/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.saa.2006.08.019

Table 1
Analytical and molar conductance data for the complexes (calculated values in parentheses)

Complex	Analysis (%)				$\wedge m$ ($cm^2\ \Omega^{-1}\ mol^{-1}$)
	C	H	N	Ln	
$La(pic)_3L$	45.77 (45.92)	3.32 (3.09)	10.89 (11.33)	10.01 (10.23)	42.7
$Nd(pic)_3L$	45.57 (45.75)	3.22 (3.08)	10.91 (11.29)	10.38 (10.56)	37.0
$Eu(pic)_3L$	45.21 (45.48)	3.21 (3.06)	10.99 (11.22)	10.84 (11.08)	37.8
$Gd(pic)_3L$	45.17 (45.32)	3.14 (3.05)	10.86 (11.18)	11.17 (11.40)	48.8
$Tb(pic)_3L$	45.01 (45.25)	3.34 (3.05)	10.79 (11.17)	11.33 (11.53)	34.6
$Y(pic)_3L$	47.59 (47.67)	3.24 (3.20)	11.61 (11.76)	6.65 (6.80)	42.9

using an Elementar Vario EL. Conductivity measurements were carried out with a DDS-307 type conductivity bridge using 10^{-3} mol dm^{-3} solutions in acetone at 25 °C. IR spectra were recorded on Nicolet FT-170SX instrument using KBr discs in the 400–4000 cm^{-1} region, ^{1}H NMR spectra were measured on a Varian Mercury plus 300BB spectrometer in $CDCl_3$ solution with TMS as internal standard. Electronic spectra were recorded with a Varian Cary 100 spectrophotometer in chloroform solution. Fluorescence and phosphorescence measurements were made on a Hitachi F-4500 spectrophotometer.

2.3. *Synthesis of the ligand*

The synthetic route for the ligand is shown in Scheme 1. Anhydrous K_2CO_3 (5.6 g, 41 mmol) was added into the 15 mL DMF solution of 2,2′-dihydroxybiphenyl (1.86 g, 10 mmol) at 100 °C. After 1 h, a solution of *N*-ethyl-*N*-benzylchloroacetamide (6.35 g, 30 mmol) in 10 mL DMF was added dropwise to the mixture and maintained at 110 °C for 7 h. When cooled, 60 mL distilled water was poured and the turbid solution was extracted by 40 mL chloroform three times. Organic phase combined was washed with water and dried with anhydrous Na_2SO_4. Solvent removed, the residue was chromatographed to afford the ligand L; yield: 85%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.34–7.23(m, 9H, ArH and $C_{12}H_8$–), 7.17–6.93(m, 9H, ArH), 4.62(m, 4H, –O–CH_2–CO–), 4.51(d, 2H, –N–CH_2–), 4.35(d, 2H, –N–CH_2–), 3.29(q, 2H, –CH_2–CH_3), 3.13(q, 2H, –CH_2–CH_3), 1.14 (t, 3H,–CH_3), 0.87(t, 3H,–CH_3).

2.4. *Synthesis of the complexes*

To a solution of 0.2 mmol lanthanide picrate in 5 mL of ethanol was added dropwise the solution of 0.2 mmol L in 10 mL of ethanol. The mixture was stirred at room temperature for 5 h. The precipitated solid complex was filtered, washed with ethanol and dried in vacuo over P_2O_5 for 48 h. All the complexes were obtained as yellow powders, yield: 80–85%.

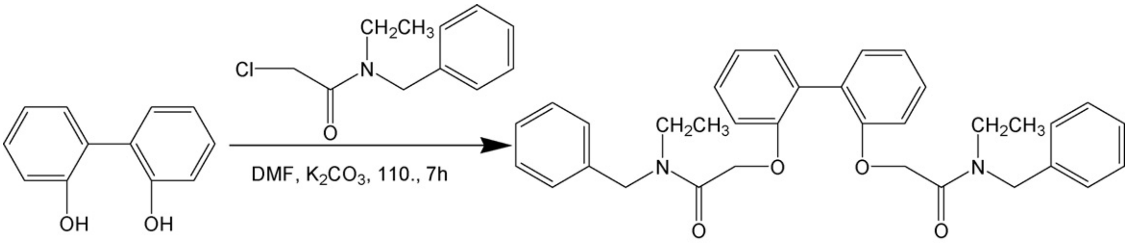
3. Results and discussion

3.1. *Properties of the discussion*

Analytical data for the complexes listed in Table 1, indicate that the complexes conform to a 1:3:1 metal-to-picrate-to-L stoichiometry $Ln(pic)_3L$. All complexes are soluble in DMF, DMSO, acetonitrile, acetone, ethyl acetate and $CHCl_3$, but slightly soluble in ethanol. The molar conductances of the complexes in acetone (see Table 1) indicate that all complexes act as nonelectrolytes [16], implying that all the picrate groups are in coordination sphere.

3.2. *IR spectra*

The main infrared bands of the ligand and its complexes are presented in Table 2. The IR spectra of the complexes are similar. The “free” ligand L exhibit two absorption bands at 1656 and 1119 cm^{-1} which are assigned to ν(C=O) and ν(C–O–C), respectively. In the complexes, the bonds shift by ca. 42 and 37 cm^{-1} towards lower wave numbers, thus indicating that the C=O and ether O-atoms take part in coordination to the metal ions. The larger shifts ν(C=O) in the spectra of the complexes suggest that the Ln–O (carbonyl) bond is stronger than the Ln–O (ether) bond. The OH out-of-plane bending vibration of the free Hpic at 1151 cm^{-1} disappears in the spectra of the complexes indicating that the H atom of the OH group is replaced by Ln(III). The vibration ν(C–O) at 1265 cm^{-1} is shifted towards



L

Scheme 1. The synthetic route for the ligand L.

Table 2
The most important IR bands (cm^{-1})

Complex	$\nu(C=O)$	ν(C–O–C)	ν(C–O)	$\nu_{as}(–NO_2)$	$\nu_s(–NO_2)$
Hpic	–	–	1265	1555	1342
L	1656	1119	–	–	–
La(pic)$_3$L	1614	1082	1273	1576, 1543	1361, 1329
Nd(pic)$_3$L	1614	1081	1273	1577, 1542	1360, 1330
Eu(pic)$_3$L	1614	1082	1274	1578, 1542	1360, 1332
Gd(pic)$_3$L	1615	1082	1274	1578, 1544	1360, 1331
Tb(pic)$_3$L	1615	1080	1271	1577, 1544	1361, 1332
Y(pic)$_3$L	1616	1082	1274	1578, 1543	1360, 1331

higher frequency by ca. 8 cm^{-1} in the complexes. This is due to the following two effects. First, the hydrogen atom of the OH group is replaced by Ln(III), increasing the π-bond character in the C–O bond. Secondly, coordination of the oxygen atom of L to Ln(III) causes the π-character to be weakened. The free Hpic has $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ at 1555 and 1342 cm^{-1}, respectively, which splits into two bands at 1577, 1543 cm^{-1} and 1360, 1331 cm^{-1} in the complexes. This indicates that some of the O-atoms in the nitro group of Pic^- take part in coordination [17]. On the basis of the similarity of their IR spectra, it may be assumed that the complexes have the similar structures.

3.3. Electronic spectra

The electronic spectra in the visible region of the Ln(III) complexes exhibit alternations in intensity and shifts in position of the absorption bands relative to the corresponding Ln(III) aquo ions. The shift has been attributed by Jorgensen to the effect on the crystal field of interelectronic repulsion between the 4f electrons, and is related to the covalent character of the metal–ligand bond, assessed by Sinha's parameter (δ), the nephelauxetic ration (β) and the bonding parameter ($b^{1/2}$) [18]. Absorption spectra of the Nd(III) complex was registered in chloroform solution at room temperature and the covalent parameters were calculated (Table 3). The values of β, which are less than unity, and positive values of δ and $b^{1/2}$ support the existence of partial covalent bonding between metal and ligand [19].

3.4. Fluorescence studies

Table 3
Covalent parameters for the neodymium complex

Complex	Frequency (cm^{-1})	Assignment	Covalent parameter
Nd(pic)$_3$L	11,160	$^4I_{9/2}$–$^4F_{3/2}$	$\beta = 0.9986$
	11,441	$^4F_{3/2}$	$\delta = 0.1402$
	12,469	$^4F_{5/2}$	$b^{1/2} = 0.02646$
	13,387	$^4F_{7/2}$	
	13,514	$^4S_{3/2}$	
	17,182	$^4G_{5/2}$	
	17,391	$^2G_{7/2}$	
	19,011	$^4G_{7/2}$	

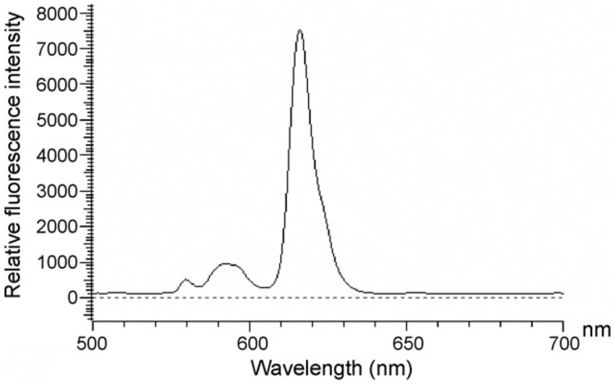


Fig. 1. The emission spectrum of the europium complex in solid state.

Monitored by the emission band at 600 nm, the europium complex exhibits broad excitation bands around 450 nm. The luminescence emission spectra of the europium complex in solid state (the excitation and emission slit widths were 2.5 nm, Fig. 1) and in solution (the excitation and emission slit widths were 10.0 nm, Fig. 2) were recorded at room temperature. The fluorescence characteristics of the europium complex in solid state and in $CHCl_3$, ethyl acetate, acetone, acetonitrile, and DMF solutions (concentration: 1.0×10^{-3} mol L^{-1}) are listed in Table 4. It can be seen that the Eu complex shows strong emission when excited with 451 nm in the solid state. This indicates that the ligand L is a comparative good organic chelator to absorb energy and transfer them to Eu ion. The most intensity ratio value η ($^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$) is 7.8, showing that the Eu(III) ion does not lie in a centro-symmetric coordination site [20]. It also could be seen that in DMF solution, the fluorescence of europium was quenched which is contributed to the decomposition of the com-

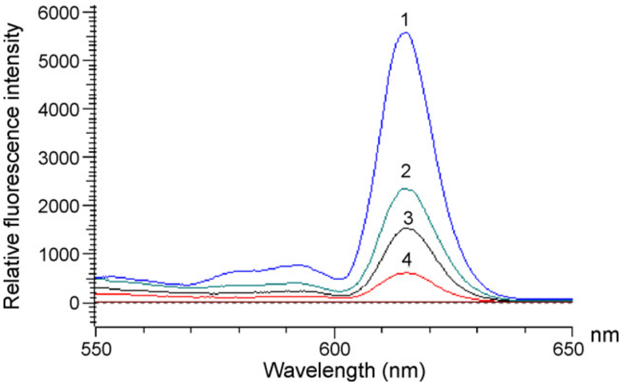


Fig. 2. The emission spectrum of the europium complex in different solutions at room temperature in: (1) $CHCl_3$, (2) ethyl acetate, (3) acetone and (4) acetonitrile.

Table 4
Fluorescence data for the europium complex

Complex	Solvent	λ_{ex} (nm)	λ_{em} (nm)	RFI	Assignment
$Eu(pic)_3L$	Solid state	451	592	967	$^5D_0 \rightarrow {}^7F_1$
			616	7524	$^5D_0 \rightarrow {}^7F_2$
	$CHCl_3$	461	592	781	$^5D_0 \rightarrow {}^7F_1$
			615	5596	$^5D_0 \rightarrow {}^7F_2$
	AcOEt	461	592	413	$^5D_0 \rightarrow {}^7F_1$
			615	2360	$^5D_0 \rightarrow {}^7F_2$
	Acetone	461	592	240	$^5D_0 \rightarrow {}^7F_1$
			615	1537	$^5D_0 \rightarrow {}^7F_2$
	Acetonitrile	461	592	131	$^5D_0 \rightarrow {}^7F_1$
			615	611	$^5D_0 \rightarrow {}^7F_2$
	DMF	–	–	–	–

plex in this solvent, and in the other four solvents, the complex has the similar excitation and emission wavelengths.

In $CHCl_3$ solution the Eu complex has the strongest luminescence, and then in ethyl acetate, acetone, acetonitrile. This is due to the coordinating effects of solvents, namely solvate effect [21]. Together with the raising coordination abilities of $CHCl_3$, ethyl acetate, acetone, acetonitrile for the lanthanide ions, the oscillatory motions of the entering molecules consume more energy which the ligand triplet level transfer to the emitting level of the lanthanide ion. Thus, the energy transfer could not be carried out perfectly.

Compared with the Eu^{3+} complex, the characteristic fluorescence of the Tb^{3+} was not determined, either in solid state or in solutions for the Tb^{3+} complex. The reason is probably that the energy gap between the triplet state levels of the ligand and the lowest resonance level of the europium favor to the energy transfer process for europium. In order to acquire the triplet excited state T_1 of the ligand L, the phosphorescence spectra of the Gd(III) picrate complex was measured at 77 K in a chloroform–methanol–ethanol mixture (v:v:v, 1:5:5). The triplet state energy levels T_1 of the ligand L, which was calculated from the shortest wavelength phosphorescence band [22] of the corresponding Gd(III) complexes, is $21{,}459\ \mathrm{cm}^{-1}$. This energy level is above the lowest excited resonance level $^5D_0$ of Eu(III) ($17{,}300\ \mathrm{cm}^{-1}$) and $^5D_4$ ($20{,}500\ \mathrm{cm}^{-1}$) of Tb(III). Thus the absorbed energy could be transferred from ligand to the Eu or Tb ions. The triplet state energy level T_1 of this ligand L matches better to the lowest resonance level of Eu(III) ($\Delta\nu = 4159\ \mathrm{cm}^{-1}$) than Tb(III) ($\Delta\nu = 959\ \mathrm{cm}^{-1}$) ion, because such small $\Delta\nu(T_1–{}^5D_4)$ could result in a back-energy transfer process from the excited resonance level $^5D_4$ of Tb(III) to the triplet state energy level T_1 of this ligand L and quench the luminescence of the Tb picrate complex [23].

4. Conclusion

According to the data and discussion above, the new ligand can form stable complexes with lanthanide picrate. From IR spectrum, the lanthanide ions were coordinated to the C=O oxygen atoms and C–O–C oxygen atoms. The europium complex exhibited characteristic fluorescence of europium ion. The different solvents may affect the fluorescence of europium ions. The lowest triplet state energy level of the ligand indicates that the triplet state energy level of the ligand matches better to the resonance level of Eu(III) than Tb(III) ion. Based on those results, a series of new ligands could be designed and synthesized to optimize the luminescent properties of these lanthanide ions.

Acknowledgements

We are grateful to the NSFC (Grants 20371022, 20431010 and 20021001), the Specialized Research Fund for the Doctoral Program of Higher Education (200307300015), and the Key Project of the Ministry of Education of China (Grant 01170) for financial support.

References

[1] N. Sabbatini, M. Guardigli, J.-M. Lehn, Coord. Chem. Rev. 123 (1993) 201.

[2] S.T. Frey, M.L. Gong, W. de, W Horrocks, Inorg. Chem. 33 (1994) 3229.

[3] N. Sato, S. Shinkai, J. Chem. Soc., Perkin Trans. 2 (1993) 621.

[4] C. Piguet, A.F. Williams, G. Bernardinelli, J.-C.G. Bünzli, Inorg. Chem. 32 (1993) 4139.

[5] F.S. Richardson, Chem. Rev. 82 (1982) 541.

[6] J.-C.G. Bünzli, in: J.-C.G. Bünzli, G.R. Choppin (Eds.), Lanthanide Probes in Life, Chemical and Earth Sciences, Elsevier, Amsterdam, 1989 (Chapter 7).

[7] B.S. Panigrahi, Spectrochim. Acta A 56 (2000) 1337.

[8] C. Piguet, J.-C.G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, J. Am. Chem. Soc. 118 (1996) 6681.

[9] G.F. Desá, O.L. Malta, C. de Mello Donegá, A.M. Simas, R.L. Longo, P.A. Santa-cruz, E.F. da Silva Jr., Chem. Rev. 196 (2000) 165.

[10] C. Bazzicalupi, A. Bencini, A. Bianchi, C. Giorgi, V. Fusi, A. Masotti, B. Valtancoli, A. Roque, F. Pina, Chem. Commun. 7 (2000) 561.

[11] Y.-H. Wen, Z. Qin, W.-S. Liu, J. Radioanal. Nucl. Chem. 250 (2001) 285.

[12] Y.-Z. Ding, J.-Z. Lu, Y.-S. Yang, Hua Xue Shi Ji 8 (1986) 201.

[13] W. Yang, X.L. Teng, M. Chem, Talanta 46 (1998) 527.

[14] Y.C. Tian, Y.Q. Liang, J.Z. Ni, Chem. J. Chin. Univ. 9 (1988) 113.

[15] L.-Y. Fan, W.-S. Liu, X.-M. Gan, N. Tang, M.-Y. Tan, W.-H. Jiang, K.-B. Yu, Polyhedron 19 (2000) 779.

[16] W.J. Gear, Coord. Chem. Rev. 7 (1971) 81.

[17] S.X. Liu, W.S. Liu, M.Y. Tan, K.B. Yu, J. Coord. Chem. 10 (1996) 391.

[18] (a) C.K. Jorgensen, Prog. Inorg. Chem. 4 (1962) 73;
(b) S.P. Sinha, Spectrochim. Acta 22 (1966) 57;
(c) D.E. Henrie, G.R. Choppin, J. Chem. Phys. 49 (1968) 477.

[19] A.K. Solanki, A.M. Bhandaka, J. Inorg. Nucl. Chem. 41 (1979) 1311.

[20] M. Albin, R.R. Wright Jr., W.D. Horrocks, Inorg. Chem. 24 (1985) 2491.

[21] H.Q. Liu, T.C. Cheung, C.M. Che, Chem. Commun. (1996) 1039.

[22] W. Dawson, J. Kropp, M. Windsor, J. Chem. Phys. 45 (1966) 2410.

[23] F. Gutierrez, C. Tedeschi, L. Maron, J.-P. Daudey, R. Poteau, J. Azema, P. Tisnes, C. Picard, J. Chem. Soc., Dalton Trans. (2004) 1334.