

Spectrochimica Acta Part A 58 (2002) 2153-2157

SPECTROCHIMICA ACTA PART A

www.elsevier.com/locate/saa

# Studies on synthesis and infrared and fluorescence spectra of new europium and terbium complexes with an amide-based open-chain crown ether

Yan-Ling Zhang, Wen-Wu Qin, Wei-Sheng Liu\*, Min-Yun Tan, Ning Tang

College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, People's Republic of China

Received 7 August 2001; received in revised form 13 November 2001; accepted 13 November 2001

# Abstract

An amide-based open-chain crown ether ligand and its complexes with europium and terbium were synthesized. The complexes were characterized by elemental analysis, infrared spectra and conductivity. The europium and terbium ions were found to coordinate to the C=O oxygen atoms and pyridine nitrogen atoms. The fluorescence properties of these complexes in DMF and CH<sub>3</sub>OH/CHCl<sub>3</sub> were studied. Under the excitation of UV light, these complexes exhibit characteristic fluorescence of europium and terbium ions. The solvent factors influencing the fluorescent intensity are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Amide-based open-chain crown ether; Complexes; Synthesis; Fluorescence properties

# 1. Introduction

The development of luminescent chemical probes and sensors is the subject of intensive research both in natural and medical science. Probes based on europium and terbium ions are of special interest because of the particularly suitable spectroscopic properties of these ions [1,2]. Moreover, chemists have realized that it is essential to design the encapsulating ligand to optimize the luminescent properties of these lanthanide ions by facilitating the well-known light conversion process, the antenna effect [3]. Recently, calixarenes and terpyridine-like ligands have attracted much attention mainly because they can form highly stable and strongly luminescent europium and terbium ion complexes [4,5].

Open-chain crown ethers offer many advantages in extraction and analysis (ion-selective electrodes) of the rare earth ions [6,7]. The open-chain crown ethers containing amide groups possess suitable molecular structure: a chain with inflexible terminal groups. Therefore, they are excellent reagents for activating ion-selective electrodes and extracts of rare earth ions [8]. However, the luminescent properties on amide-based open-chain

<sup>\*</sup> Corresponding author. Fax: +86-931-891-2582

E-mail address: liuws@lzu.edu.cn (W.-S. Liu).

crown ethers with lanthanide complexes have been rarely reported [9]. 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 the present work, we designed and synthesized a new and doubly functionalized open-chain crown ether ligand with pyridine amide terminal groups, 1,7-bis[N-(2-pridinoyl aniline)]-4-p-toluene sulfonyl-1,7-dioxa-4-azaheptane (Scheme 1), and studied the fluorescence properties of europium and terbium complexes with the new ligand. The results indicated that the organic solvent affected the fluorescence characteristics of europium and terbium ions.

# 2. Experimental

# 2.1. Materials

All solvents used were purified by standard methods.

# 2.2. Methods

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. Conductivity measurements were carried out with a DDSJ-308 type conductivity bridge using  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> solutions in dimethyl-



Scheme 1. The synthesis of ligand.

 Table 1

 Elemental analytical and molar conductance date for the complexes

Complex	C (%) found (Calc.)	H (%) found (Calc.)	N (%) found (Calc.)	Ln (%) Found (Calc.)	$\begin{array}{l} \Lambda m \\ (S \ cm^2 \ mol^{-1}) \end{array}$
L Eu(NO <sub>3</sub> ) <sub>3</sub>	64.48 (64.50) 40.51 (40.98)	4.98 (5.10) 3.55 (3.64)	10.70 (10.75) 11.07 (10.92)	15.13 (14.82)	79
$\begin{array}{l} L \cdot 2H_2O \\ Tb(NO_3)_3 \\ L \cdot 2H_2O \end{array}$	40.39 (40.71)	3.44 (3.61)	11.05 (10.85)	15.78 (15.39)	73

formamide (DMF) at 25 °C. <sup>1</sup>H NMR spectra were measured on a FT-80A spectrometer in CDCl<sub>3</sub> solution, with TMS as internal standard. Fluorescence measurements were made on a Shimadzu RF-540 spectrfluorophotometer equipped with quartz curettes of 1 cm path length. The excitation and emission slit widths were 10 nm.

#### 2.3. Synthesis of the ligand

1, 2, 3, (Scheme 1) were prepared according to the literature [10,11].

# 2.3.1. Preparation of 4

A benzene solution containing **3** (3.47 mmol) was added dropwise to another benzene solution of pyridinoyl chloride (10.4 mmol) and anhydrous pyridine (2 ml). The mixture was stirred at 50 °C for 6 h. After solvent evaporation in vacuum, the crude was chromatographed on silica gel (CHCl<sub>3</sub>/ EtOAc 5:1) to afford the ligand **4** as a pale white solid. <sup>1</sup>H NMR:  $\delta$  (CDCl<sub>3</sub>) 10.5 (s, 2H, 2NH); 8.6–7.8 (m, 8H, Py–H); 7.4–6.9 (m, 8H, Ar–H); 4.5–4.3 (q, 8H, 4CH<sub>2</sub>); 2.3 (s, 3H, CH<sub>3</sub>) IR: cm<sup>-1</sup> (KBr, pellet). *v* 3326 (m, N–H), 1685 (s, C=O), 1531 (S, C=N), 1156 (S, C–O–C),  $\delta$  619 (m, Py-ring, in-plane). Elemental analytical: (calc.) C% 64.48 (64.50), H% 4.98 (5.10), N% 10.70 (10.75).

#### 2.4. Synthesis of the complexes

An ethyl acetate solution of Ln  $(NO_3)_3 \cdot 6H_2O$ LnEu<sup>3</sup> and Tb<sup>3</sup> (0.15 mmol) was added dropwise to a solution of the ligand (0.1 mmol) in ethyl acetate (20 ml). The mixture was refluxed for 4 h, and white precipitate formed. The precipitate was collected and washed three times with ethyl acetate. Further drying in vacuum afforded a pale white powder, yield 50%.

## 3. Result and discussion

#### 3.1. Properties of the complexes

Analytical data for the complexes, presented in Table 1, conform to Eu  $(NO_3)_3L \cdot 2H_2O$  and Tb  $(NO_3)_3L \cdot 2H_2O$ .

All complexes are soluble in DMF, acetenitride, tetrahydrofuran, methanol/chloroform (1:1), but sparingly soluble in water, methanol, ethanol and acetone. Conductivity measurements for these complexes in DMF solution (Table 1) indicate that all complexes are 1:1 ionic compounds [12].

## 3.2. IR spectra

The IR spectra of the complexes are similar. Table 2 gives the characteristic bands of ligand and its complexes. The IR spectrum of the free ligand shows bands at 1685 and 1531 cm<sup>-1</sup> which may be assigned to v(C=O) and v(C=N), respectively. In the complexes, these bands for v(C=O)and v(C=N) are shifted by about 46 (from 1685 to 1639) and 21 (from 1531 to 1552) cm<sup>-1</sup>, respectively, indicating that carbonyl oxygen atoms and pyridine nitrogen atoms take part in coordination.

The absorption bands assigned to the coordinated nitrates were observed at about 1492 ( $v_{as}$ ) and 814 ( $v_s$ ) cm<sup>-1</sup> for the complexes. The  $v_3(E')$  free nitrates appear at approximately 1384 cm<sup>-1</sup> in the spectra of the complexes [13], in agreement with the results of the conductivity experiments.

Compound	v(C=O)	v(C=N)	$v_1(NO_3^-)$	$v_3(NO_3^-)$	$v_4(NO_3^-)$	$v(NO_3^-)$
L	1685	1531				
$Eu(NO_3)_3L \cdot 2H_2O$	1639	1552	1492	815	1307	1384
$Tb(NO_3)_3L \cdot 2H_2O$	1641	1553	1507	814	1295	1385

Table 2 The relevant characteristic IR bands  $(cm^{-1})$ 

#### Table 3

Fluorescence data for the ligand and complexes

	Solve	$\lambda_{\rm ex}$ (nm)	$\lambda_{\rm em}$ (nm)	RFI	Assignment
L	DMF	370	417	1126	
	CH <sub>3</sub> OH/CHCl <sub>3</sub>	380	435	242	
$Eu(NO_3)_3L\cdot 2H_2O$	DMF		591	16.3	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$
			616	23.5	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$
	CH <sub>3</sub> OH/CHCl <sub>3</sub>	395	591	8.0	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$
	5, 5		616	4.9	${}^{5}D_{0} \rightarrow {}^{7}F_{2}$
$Tb(NO_3)_3L \cdot 2H_2O$	DMF	370	488	165.2	${}^{5}D_{4} \rightarrow {}^{7}F_{6}$
( ))) 2			545	58.5	${}^{5}D_{4} \rightarrow {}^{7}F_{5}$
			590	6.6	${}^{5}D_{4} \rightarrow {}^{7}F_{4}$
	CH <sub>3</sub> OH/CHCl <sub>3</sub>	380	488	26.5	${}^{5}D_{4} \rightarrow {}^{7}F_{6}$
	5 1 5		545	9.3	${}^{5}D_{4} \rightarrow {}^{7}F_{5}$
			590	1.6	${}^{5}D_{4} \rightarrow {}^{7}F_{4}$

In addition, the separation of the two highest frequency bands  $|v_4 - v_1|$  is approximately 200 cm<sup>-1</sup>, thus the coordinated NO<sub>3</sub><sup>-</sup> ions in the complexes are bidentate ligands [14].

## 3.3. Fluorescence studies

The fluorescence characteristics of the ligand and all complexes in DMF and CH<sub>3</sub>OH/CHCl<sub>3</sub> (1:1 v/v) solutions are listed in Table 3. The ligand having multiple aromatic rings with a rigid planar structure, so it is a strong fluorescence substance. It displays a fluorescence excitation maximum at 370 nm and an emission maximum at 417 nm in DMF solvent. But in CH<sub>3</sub>OH/CHCl<sub>3</sub> solution, the excitation maximum and emission maximum of the ligand are red-shifted by approximately 10 and 18 nm compared with those in DMF solvent, respectively. From Table 3 it could be seen that the excitation and emission wavelengths of the europium complexes in organic solutions are quite different from those of the ligand, its  $\lambda_{ex}$  shift to 395 nm and  $\lambda_{em}$  to 591, 616 nm (Fig. 1). However, the excitation wavelength of terbium complex is the same as that of the ligand in DMF or in  $CH_3OH/CHCl_3$  solvent, respectively. But its emission wavelength was shifted to 488, 545 and 590 nm (Fig. 2).



Fig. 1. The emission spectrum of the europium complex. Concentration:  $5.0 \times 10^{-4}$  mol  $1^{-1}$ . One in DMF and two in CH<sub>3</sub>OH/CHCl<sub>3</sub> (1:1) solution.



Fig. 2. The emission spectrum of the terbium complex. Concentration:  $5.0 \times 10^{-4}$  mol 1<sup>-1</sup>. One in DMF and two in CH<sub>3</sub>OH/CHCl<sub>3</sub> (1:1) solution.

Due to the presence of a scattering signal near 490 nm, the peak height at 545 nm for terbium was used to measure the fluorescence intensities. From Table 3, we can see that the fluorescence intensity of terbium complex at 545 nm are stronger than those of europium complexes at 616 nm, either in DMF or in CH<sub>3</sub>OH/CHCl<sub>3</sub> solution. 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 the organic solution, probably the energy gap between the ligand triplet levels and the emitting level of the terbium favor to the energy transfer process for terbium.

We also can see the fluorescence intensities for the complexes in DMF solution are stronger than those in  $CH_3OH/CHCl_3$  solution. We consider that this is due to the O–H oscillators of  $CH_3OH$ molecules. It is well know 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  $CH_3OH/CHCl_3$  solution can be quenched easily because of the O–H oscillators.

## 4. Conclusion

According to the data and discussion above, the

amide-base open-chain crown ether could form 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 C=O oxygen atoms and pyridine nitrogen atoms. The complexes exhibited characteristic fluorescence of europium and terbium ions. Based on those results, a series of new amide-based open-chain crown ethers could be designed and synthesized to optimize the luminescent properties of these lanthanide ions.

# Acknowledgements

This work is support by the National Natural Science Foundation of China (Project 20071015) and Foundation for University Key teacher by the Ministry of Education (China).

#### References

- [1] F.S. Richardson, Chem. Rev. 82 (1982) 541.
- [2] I. Hemmilä, T. Stahlberg, P. Mottram, Bioanalytical Applications of Labelling Technologies, Wallac Oy, Turku, 1995.
- [3] 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.
- [4] N. Martin, J.-C.G. Bünzli, V. Mckee, C. Piguet, G. Hopfgartner, Inorg. Chem. 37 (1998) 577.
- [5] C. Bazzicalupi, A. Bencini, A. Bianchi, C. Giorgi, V. Fusi, A. Masotti, B. Valtancoli, A. Roque, F, Pina. Chem. Commun. 7 (2000) 561.
- [6] Y.-S. Yang, S.-H. Cai, Hua Xue Shi Ji 6 (1984) 133.
- [7] Y.-Z. Ding, J.-Z. Lu, Y.-S. Yang, Hua Xue Shi Ji 8 (1986) 201.
- [8] G.-Z. Tan, J.-Z. Xu, T.-Q. Jao, You ji Hua Xue 2 (1986) 143.
- [9] W. Yang, X.-L. Teng, M. Chen, Talanta 46 (1998) 527.
- [10] J. Dale, P.O. Krastiansen, Acta Chem. Scand. 26 (1972) 2005.
- [11] J. Zhang, Z. Tan, Z. Zhu, H.-J. He, Hecheng Huaxue 1 (1995) 36.
- [12] W.J. Greary, Coord. Chem. Rev. 7 (1971) 81.
- [13] Y. Hirashima, K. Kanetsuki, I. Yonezu, Bull. Chem.Soc. Jpn. 56 (1983) 738.
- [14] K. Nakamoto, Infrared and Raman spectra of Inorganic and Coordination Compounds, 3rd edition, John Wiley, New York. 1978, pp. 227.