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Synthesis and infrared and fluorescence spectral properties of luminescent terbium and europium complexes with open-chain carboxylate crown ethers

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Abstract

Two open-chain carboxylate crown ether ligands and their terbium(III) and europium(III) complexes were synthesized and characterized. The terbium and europium ions were found to coordinate to the carboxylate oxygens. The fluorescence properties of europium complexes in the solid state and terbium complexes in the solid state and in the organic solvent were studied in detail, respectively. Under the excitation of ultraviolet light, strong green fluorescence of solid terbium complexes were observed. These observations show that the two ligands favor energy transfer to the emitting energy level of Tb^{3+} . Some factors that influencing the fluorescent intensity were also discussed.

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1. Introduction

Much attention has been paid to lanthanide complexes because of their particular luminescence properties. Especially europium(III) and terbium(III) ions have excellent luminescence properties, but their absorption coefficients are very small. In order to overcome these shortages, lanthanide ions are usually chelated with ligands that have broad intense absorption bands. Recently, podands [1,2], macrocyclic compound [3,4], carboxylic acid derivatives [5] and pyrazolone derivatives [6] have attracted much attention mainly because they can form highly stable and strongly luminescent terbium and europium ion complexes.

Open-chain crown ethers offer many advantages in separation and determination of lanthanide ions [7–9]. The basic molecular frame of ordinary open-chain crown ether molecules consists of a chain of several oxygen atoms connected by (– CH_2 –) groups. When proper conjugate absorption groups are introduced onto these (– CH_2 –), they will serve as potential luminescent reagents. In the present work, we designed and synthesized two new and doubly functionalized open-chain carboxylate crown ether ligands. They have both coordi-

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Fig. 1. Scheme of the synthesis of the ligands.

nation selective abilities to lanthanide ions and enhanced luminescence of lanthanide complexes. The fluorescence properties of europium(III) and terbium(III) complexes with new ligands were studied in detail. IR spectra show that the ethereal oxygens of the two ligands do not take park in coordination. But the length of the chains of the ethereal oxygens affects the energy transfer efficiency between ligands and rare earth ions. The role of solvents in the fluorescence intensities is also reported.

2. Experimental

2.1. Materials

All material and solvents employed in this study were analytical reagents. Absolute ethanol was dried and distilled by standard method.

2.2. Physical measurements

Carbon and hydrogen analyses were performed using a Vario EL elemental analyzer. The complexes were decomposed in stove at about 500 °C for 1 h. The residue was dissolved in HCl and then metal ions were determined by EDTA titration using xylenol orange as an indicator. Infrared (IR) spectra were obtained with a Nicolet Nesus 670 FT-IR spectrophotometer with KBr discs. Conductivity measurements were carried out with a Shanghai Instrument Factory DDSJ-308 type conductivity bridge with approximately 1.0×10^{-3} mol 1^{-1} solutions of methanol at 25 °C. ¹H NMR spectra were recorded on a Varian FT-80A spectrometer using chloroform-d as a solvent and TMS as an internal standard. Mass spectra of the ligands were recorded on a VG ZAB-HS mass spectrometer. Fluorescence measurements were made on a Shimadzu RF-540 spectrofluorophotometer equipped with quartz curettes of 1 cm path length at room temperature. The excitation and emission slit widths were 10 nm.

2.3. Preparation of ligands $(L^{I} and L^{II})$

Two ligands were prepared by the same method. Compound 1 (Fig. 1) was prepared according to the literature [10].

Metal sodium (0.30 g, 13 mmol) was slowly added to a hot anhydrous ethanol (20 ml) solution. Then ethyl salicylate (2.20 g, 13 mmol) was added. Finally 4.3 mmol of **1** was added and refluxing for 20 h. The solvent was partially removed in vacuum at about 40 °C The crude product was chromatographed on silica gel (petroleum ether/ $CH_3COOC_2H_5 5:1 v/v$) to afford **2** as white oil.

A mixture solution of **2** (2.5 mmol) and KOH (1.4 g, 25 mmol) in CH₃OH (30 ml) and H₂O (12 ml) was refluxed for 6 h. Then concentrated HCl was added and white precipitates formed. The precipitates were collected by filtration, wash with

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water and dried under in vacuo to afford $3 (L^{I} \text{ and } L^{II})$ as white powder.

2.3.1. 1,7-Bis(2'-carboxylphenyl)-1,4,7triaoxaheptane(L^{I} , n = 0)

Yield, 80%. M.p. 106–108 °C, IR (cm⁻¹, KBr), 3259 (O–H), 1734 (C=O), 1603, 1489, 1456 (phenyl C–C), 1244 (Ar–O–C), 1168 (C–O–C), 758 (phenyl subst). ¹H NMR (CDCl₃, ppm): δ 4.00 (t, 4H, 2O<u>CH</u>₂CH₂OAr), 4.41 (t, 4H, 2OCH₂ <u>CH</u>₂OAr), 7.00–8.16 (m, 8H, Ar-H). FABMS: m/z = 347 (M+1). Found: C, 62.18; H, 5.56. Anal. Calc. for C₁₈H₁₈O₇: C, 62.43; H, 5.24%.

2.3.2. 1,10-Bis(2'-carboxylphenyl)-1,4,7,10tetraoxadecane(L^{II} , n = 1)

Yield, 82%. M.p. 116–118 °C. IR (cm⁻¹, KBr), 3259 (O–H), 1716 (C=O), 1602, 1484, 1461 (phenyl C–C), 1243 (Ar–O–C), 1166 (C–O–C), 761 (phenyl subst).¹H NMR (CDCl₃, ppm): δ 3.78 (s, 4H, O<u>CH₂CH₂O</u>), 3.93 (t, 4H, 2OH₂<u>CH₂OAr</u>), 4.38 (t, 4H, 2OCH₂<u>CH₂OAr</u>), 6.99–8.15 (m, 8H, Ar-H). In this condition, the –COOH signal of the two free ligands could not be observed in the ¹H NMR spectra either, FABMS: *m*/*z* = 391 (M+1), Found: C, 61.39; H, 5.87. Anal. Calc. for C₂₀H₂₂O₈: C, 61.53; H, 5.68%.

2.4. Synthesis of complexes

To a solution of ligand L^{I} or $L^{II}(0.3 \text{ mmol})$ in 4.0 ml ethanol-water (1:1 v/v), 1:1 NH₃·H₂O was added until ligands were dissolved completely and the pH of the mixture was adjusted about 6.0. Then a 2.0 ml ethanol-water solution of Ln(NO₃)₃·6H₂O [Ln = Eu(III) or Tb(III), 0.2 mmol] was added dropwise to the solution of ligands. The mixture was refluxed for 4 h, and then a white precipitate was formed. The precipitate was collected and washed three times with ethanol-water. Further drying in vacuo afforded a white powder in about 80%.

3. Results and discussion

3.1. Properties of the complexes

Elemental analyses and molar conductance of the complexes are listed in Table 1. All complexes are soluble in methanol, DMF, DMSO and THF/ H_2O (v/v, 1:1) moderately soluble in chloroform and THF, and sparingly soluble in ethanol, acetonitrile, acetone and ethyl acetate. The elemental analyses of the complexes show that the lanthanide ions coordinate to ligand with 2:3 ratios. Conductivity measurements for these complexes in methanol solution indicate that all complexes are a partial ionization in methanol [11].

3.2. IR spectra

IR spectra of the complexes are similar to each other. The main infrared bands of the ligands and their complexes are presented in Table 2 and Figs. 2 and 3 show main infrared data of the two europium(III) complexes. The salicylic acids of both free ligands give O-H stretching band for-COOH group at 3259 cm⁻¹, disappearance of which in the complexes are caused by the replacement of hydrogen of the carboxylate group by the metal. The disappearance of carbonyl stretching frequency at 1734 (L^I) or 1716 (L^{II}) cm⁻¹ in carboxylic acid and appearance of symmetric and asymmetric vibrations for -COO group at about 1407-1411 and 1551-1561 cm⁻¹, respectively, confirms the above fact. The stretching frequency difference $(\Delta v = v_{as} - v_s)$ (140–154 cm⁻¹) of the carboxylate group is smaller in the complexes than that of the corresponding sodium salt (about 205 cm^{-1}). This indicated that the coordinated carboxylates in the complexes are bidentate [12,13].

In addition, the v(Ar–O–C) and v(C–O–C) bands of the free ligands have hardly changed compared with those of their complexes. This shows that the ethereal oxygens of the ligands have not been coordinated to the metal ion. The new bands in the 409–413 cm⁻¹ regions in the complexes may be assigned to Ln–O stretching vibration modes.

Compound	C (%) Found (Calc.)	H (%) Found (Calc.)	Ln (%) Found (Calc.)	$\Lambda m (S cm^2 mol^{-1})$
Eu ₂ L ^I ₃ ·6H ₂ O	44.65 (44.89)	4.05 (4.19)	21.33 (21.03)	65.9
Tb ₂ L ¹ ₃ ·6H ₂ O	44.51 (44.46)	4.12 (4.15)	21.51 (21.79)	65.0
$Eu_2L_3^{II} \cdot 6H_2O$	45.93 (45.69)	4.34 (4.60)	19.02 (19.27)	61.3
$Tb_2L_3^{II} \cdot 6H_2O$	45.01 (45.29)	4.87 (4.56)	19.64 (19.98)	59.7

Table 1 Analytical and molar conductance data for the complexes

3.3. Fluorescence spectra

Under identical experimental conditions, the fluorescence characteristics of the complexes in solid and in organic solvent at various concentrations (1.0-0.1 mM) are listed in Table 3. The emission spectra of the two europium complexes in solid are similar to each other (Fig. 4). They both exhibit three emission bands at about 592, 613 and 680 nm, corresponding to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transitions. The ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ emission peaks were too weak to be observed at about 645-660 nm range. Among these transitions, the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ around 613 nm is the strongest and, therefore, the peak height at 613 nm was used to measure the fluorescence intensities of an europium complex. From Table 3, we can see that terbium complexes are strongly fluorescent in the solid state and in organic solution. The emission spectra of the terbium complexes in solid and solution are similar to each other and are all characteristic emission bands of a terbium(III) ion at about 490, 545 and 585 nm. The emission peak at 545 nm is the strongest, followed by the one at 490 nm. Therefore, the peak height at 545 nm for terbium complexes was chosen to detect the fluorescence intensities of a terbium complex.

The emission spectra of the $Tb_2L_3^I \cdot 6H_2O$ complex are shown in Fig. 5.

The fluorescence intensities of the terbium complex at 545 nm are stronger than those of the europium complex at 613 nm in the solid state (see Table 3). The fluorescence intensities of $Tb_2L_3^{II}$. 6H₂O are about 100 times than those of europium complexes. The fluorescence intensities of complexes are in the order of $Tb_2L_3^{II} \cdot 6H_2O > Tb_2L_3^{I}$. $^{1}_{6H_2O} > Eu_2L_3^{I} \cdot 6H_2O > Eu_2L_3^{II} \cdot 6H_2O$. Based on the theory of antenna effect [14,15], the intensity of the luminescence of Ln^{3+} complexes is related to the efficiency of the intramolecular energy transfer between the triplet energy level of the ligand and the emitting level of the central ions, which depends on the energy gap between the two levels. In the solid state, probably the energy gap between the ligands triplet levels and the emitting level of the terbium favors the energy transfer process for terbium. This leads to the terbium complexes that show the most intense green fluorescence.

According to the results in Table 3, the relative fluorescence intensity of terbium complexes in powder is highest for ligand L^{II} . Whereas in solutions, the fluorescence intensity of terbium complexes for ligand L^{I} is stronger than that for

Table 2	
IR spectral data of the free ligands and its complexes (cm^{-1})	

Compound	ν (O-H)	v (C=O)	$v_{as} (COO^{-})$	$v_{s} \left(COO^{-} \right)$	v (Ar-O-C)	v (C-O-C)	v (Ln–O)
LI	3259	1734			1244	1168	
Eu ₂ L ^I ₃ ·6H ₂ O	3431		1553	1407	1243	1165	409
Tb ₂ L ^I ₃ ·6H ₂ O	3387		1551	1411	1243	1169	410
LII	3259	1716			1243	1166	
Eu ₂ L ^{II} ·6H ₂ O	3425		1558	1407	1245	1162	413
$Tb_2L_3^{II} \cdot 6H_2O$	3425		1561	1407	1243	1162	412



Fig. 2. The IR spectra of the $Eu_2L_3^I \cdot 6H_2O$ complex.

ligand L^{II} . Although the ethereal oxygens of the ligands do not take park in the coordination, the length of chains affects energy transfer efficiency. In the solid state the molecules are closely packed [16] so that the ligand L^{II} may has the optimum length suitable for transferring energy to the emitting level of terbium ion. However, the complex molecules are isolated in solutions. This can

result in increasing the distance between the ligand L^{II} and Tb(III) ion compared with the distance between the two in solid state. The increasing of distance between ligand L^{II} and Tb(III) ion can decrease the energy transfer efficiency from the aromatic ring of the ligand to Tb(III) ion resulting in fluorescence intensity of ligand L^{II} lower than that of ligand L^{I} . That is to say, ligand L^{I} may



Fig. 3. The IR spectra of the $Eu_2L_3^{II} \cdot 6H_2O$ complex.

Table 3				
Fluorescence	data of th	e complexes	at room	temperature

Complexes	Solve or state	Concentration (0.1 mM)	$\lambda_{ex} (nm)$	$\lambda_{em} (nm)$	RFI ^a
$Eu_2L_3^I \cdot 6H_2O$	Solid		396	613	49.0
$Eu_2L_3^{II} \cdot 6H_2O$	Solid		396	613	35.0
$Tb_2L_3^I \cdot 6H_2O$	Solid		318	545	600.0
	DMSO	10.0	305	545	453.1
		7.5			415.6
		5.0			378.1
		2.5			362.5
		1.0			306.3
	CH ₃ OH	10.0	315	545	406.3
		7.5			361.3
		5.0			315.6
		2.5			275
		1.0			243.8
	DMF	10.0	310	545	235.0
		7.5			202.5
		5.0			158.7
		2.5			116.9
		1.0			86.9
	THF/H ₂ O	10.0	310	545	111.7
	. 2.	7.5			98.8
		5.0			85.6
		2.5			75.0
		1.0			60.3
Tb₂L ^{II} .6H₂O	Solid		312	545	4400
	DMSO	10.0	308	545	362.5
	21100	7 5	200	0.10	334.4
		5.0			305.0
		2.5			266.9
		1.0			229.3
	CH-OH	10.0	308	545	316.3
	enjon	7 5	200	0.10	278.1
		5.0			221.9
		2 5			198.1
		1.0			145.6
	DMF	10.0	310	545	208.8
	DMI	7 5	510	545	171.2
		5.0			148.8
		2.5			123.4
		1.0			116.9
	THE/H.O	10.0	310	545	100.8
	1111/1120	7 5	510	545	92.5
		5.0			92.3
		2.5			63.2
		2.5			52.8
		1.0			32.8

^a RFI is relative fluorescence intensity.

have the favorable distance to transfer energy to Tb(III) ion under solution condition. The fluorescence intensities of terbium complexes in organic solution are weaker than that of powder. This may be due to the quench process of solvent molecules in the solutions.

The influence of solvent on the fluorescence intensities of two terbium complexes was investi-



Fig. 4. The fluorescence emission spectra of the $\text{Eu}_2 L_3^{\text{I}} \cdot 6\text{H}_2\text{O}$ (line 1) and $\text{Eu}_2 L_3^{\text{II}} \cdot 6\text{H}_2\text{O}$ (line 2) complexes in the solid state at room temperature.

gated. As given in Table 3, the fluorescence intensities sequence both have been shown to be DMSO > CH₃OH > DMF > THF/H₂O at the same concentration. The ε values of the four solvents are 46.7 (DMSO), 32.63 (CH₃OH), 37.6 (DMF) and 7.0 (THF). It can be see that the ε values of these solvents that contain oxygen atom are arranged in the order of 46.7 (DMSO) > 32.63 (CH₃OH) > 7.0 (THF). The order of fluorescence intensities in these solvents is in agreement with the ε values of them. This indicates that the polar of solvents effect the fluorescent intensities of these complexes.

Further investigation shows that the intensities in DMF, DMSO and CH₃OH solutions are much stronger than those in THF/H₂O solution. This may be due to the O-H oscillators of H₂O 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. Solvent molecules have strong coordination effect and can replace coordinated water. The replacement can avoid the high frequency O-H bond vibration and thus greatly decrease the energy loss through the coordination water to obtain much stronger fluorescence intensity. This indicates that environment plays an important role in determining the fluorescence intensity of the complexes [17].

In addition, the fluorescence spectra of europium complexes also provide information about the geometry of the complexes. Although there are



Fig. 5. The fluorescence emission spectra of the Tb₂L₃¹·6H₂O complex in DMSO (line 1), in CH₃OH (line 2), in DMF (line 3) and in THF/H₂O (1:1 v/v) (line 4) solution at room temperature. Concentration: 5.0×10^{-4} mol 1^{-1} .

short of the information about the number of lines resulting from the splitting of an individual transition due to the resolving power of instrument. We have a tentative conclusion a low site symmetry for the europium ions, based on the fact that ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition could not be observed [18] and the value of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}/{}^{5}D_{0} \rightarrow {}^{7}F_{1}$ (the fluorescence intensities of ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ are also strong) is about 1.05–1.10 for two europium complexes [19].

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References

- N. Sabbatini, M. Guardigli, J.-M. Lehn, Coord. Chem. Rev. 123 (1993) 201.
- [2] P.L. Jones, A.J. Amoroso, J.C. Jeffery, J.A. Mccleverty, E. Psillakis, L.H. Rees, M.D. Ward, Inorg. Chem. 36 (1997) 10.

- [3] M. Pietraszkiewicz, T. Karpiuk, A.K. Rout, Pure Appl. Chem. 65 (1993) 563.
- [4] A. Beeby, S. Faulkner, Chem. Phys. Lett. 266 (1997) 116.
- [5] G.F. De Sa, L.H.A. Nunes, Z.-M. Wang, G.R. Choppin, J. Alloys Compd. 196 (1993) 17.
- [6] D.J. Qian, W.N. Leng, Y. Zhang, Z. Chen, J. Van Houten, Spectrochim. Acta A 56 (2000) 2645.
- [7] Y.S. Yang, Y.Z. Ding, G.Z. Tan, J.Z. Xu, Z.Q. Yao, F.S. Zhang, J. Nucl. Radiochem. 6 (1984) 196.
- [8] Y.Z. Ding, J.Z. Xu, Y.S. Yang, G.Z. Tan, J.Z. Xu, Huaxue Shiji 8 (1986) 201.
- [9] G.Z. Tan, J.Z. Xu, T.Q. Jao, Youji Huaxue 2 (1986) 143.
- [10] T. Dale, P.O. Krastiansen, Acta Chem. Scand. 26 (1972) 2005.
- [11] W.J. Greary, Coord. Chem. Rev. 7 (1971) 82.
- [12] G. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.
- [13] K. Nakamoto, Infrared and Raman spectra of Inorganic and Coordination Compounds, third ed., John Wiley, New York, 1978, p. 227.
- [14] J.-M. Lehn, Angew. Chem. Int. Ed. Engl. 29 (1990) 1304.
- [15] M. Latva, H. Takalo, K. Simberg, J. Kankare, J. Chem. Soc. Perkin Trans. 2 (1995) 995.
- [16] D.J. Zhou, C.H. Huang, G.Q. Yao, J. Bai, T.K. Li, J. Alloys Compd. 235 (1996) 156.
- [17] D.J. Zhou, Q. Li, C.H. Huang, G.Q. Yao, S. Umetani, M. Matsui, L.M. Ying, A.C. Yu, X.S. Zhao, Polyhedron 16 (1997) 1381.
- [18] M.C.F. Couha, H.F. Brito, L.B. Zinner, G. Vicentini, Coord. Chem. Rev. 123 (1993) 201.
- [19] M. Albin, R.R. Wright, Jr, W.D. Horrochs, Inorg. Chem. 24 (1985) 4591.