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Anion effects on the fluorescence spectra of europium and terbium complexes with a family of ether-amide type multipodal ligands

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Abstract

Three multipodal ligands: 3,3,7,7-tetra[*N*-methyl-*N*-phenyl(acetamide)-2-oxymethyl]-5-oxanonane (L^a), 3,3,7,7-tetra[*N*-ethyl-*N*-phenyl(acetamide)-2-oxymethyl]-5-oxanonane (L^c) and their europium and terbium nitrate and perchlorate complexes were synthesized. The 12 complexes were characterized by elemental analysis, IR, fluorescence spectroscopy and conductivity. The lanthanide atoms are coordinated by O atoms from C=O, C–O–C. With the difference of the anion, the fluorescence properties of anion effect for the complexes were investigated. Some factors that influencing the fluorescent intensity were discussed.

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Keywords: Ether-amide type multipodal ligand; Lanthanide; Fluorescence; Nitrate; Perchlorate; Anion effect

1. Introduction

The development of luminescent probes and sensors [1] is the subject of intensive research both in natural and medical science [2,3]. Probes based on europium and terbium ions are of special interest because of the particularly suitable spectroscopic properties of these ions [2,4,5]. The main advantages of lanthanide chelates in fluorescence spectrometry are their large stokes shifts, narrow emission profiles and long fluorescence lifetimes [6]. These have led to use lanthanides as fluorescent probes for highly sensitive time-resolved fluorimetric immunoassays, metal ion coordination in proteins and structural studies of biological macromolecule [7]. And these properties have also been used to improve the sensitivity for lanthanide estimation by conventional spectrofluorimetry and laser induced spectrofluorimetry [8].

Amide-based crown ethers offer many advantages in extraction and analysis of the rare earth ions [9,10] because of their ring-like coordination structure and terminal group effects. 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 [11]. However, luminescent properties on open-chain crown ethers with lanthanide complexes have been rarely reported [12]. So we have designed a series of multi-functional ligands having both selective ability to enhance luminescence of lanthanide complexes by providing some of proper conjugate absorption groups suitable for energy transfer, i.e. the coordinating groups with cavities for lanthanide ions and amide-based crown ethers. With several suitably designed arms, the multipodal ligands could shield the encapsulated lanthanide ions from interaction with the surroundings, and by deliberate incorporation of appropriate multiple absorption groups suitable for energy transfer, they could be used to develop strong luminescent lanthanide complexes (Scheme 1).

In the recent work, we designed and synthesized a family of open-chain crown ether ligands, 3,3,7,7-tetra[*N*-methyl-*N*phenyl(acetamide)-2-oxymethyl]-5-oxanonane (L^a), 3,3,7,7tetra[*N*-ethyl-*N*-phenyl(acetamide)-2-oxymethyl]-5-oxanonane (L^b), 3,3,7,7-tetra[*N*-benzyl-*N*-phenyl(acetamide)-2-oxymethyl]-5-oxanonane (L^c) and 12 europium and terbium nitrate and perchlorate complexes. The anion effects on fluorescence properties of the complexes were investigated.

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Scheme 1. The ligands.

2. Experimental

2.1. Materials

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 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, ¹H NMR spectra were measured on a Varian Mercury plus 300 M spectrometer in CDCl₃ solution with TMS as internal standard. Fluorescence measurements were made on a Hitachi F-4500 spectrophotometer equipped with quartz curettes of 1 cm path length at room temperature. The excitation and emission slit widths were 2.5 nm.

2.3. Synthesis of the ligand

A solution of 3,3,7,7-tetrahydroxymethyl-5-oxanonane (2.5 g, 10 mmol) in THF was added dropwise into a THF solution that was suspended with NaH (1.6 g, 60%, 40 mmol), and the mixture was stirred under nitrogen at room temperature until no gas appeared. Then a solution of *N*-ethyl-*N*-phenylchloroacetamide (8.7 g, 44 mmol) (*N*-methyl-*N*-phenylchloroacetamide for L^a , *N*-benzyl-*N*-phenylchloroacetamide for L^c) in THF was added dropwise into the mixture. After the mixture was refluxed for 6 h, the THF was evaporated and the

residue was washed by column chromatography (silica gel, 2:1 CHCl₃/CH₃CO₂Et) and evaporated in vacuum resulted a yellow oil (4.3 g). Yield: 50%. L^a, ¹H NMR spectrum (300 M, CDCl₃): δ = 7.13–7.38 (m, 20H); 3.73(s, 8H; 4O–CH₂–C(O)); 3.22(s, 12H; 4N–CH₃); 3.21(s, 8H; 4C–CH₂–O); 2.98(s, 4H; 2C–CH₂–O); 1.23 (q, 4H; 2R–CH₂–C); 0.70(t, 6H; 2CH₃–R–C). IR: ν 1674s (C=O), 1112s (Ar–O–C). Formula weight of L^a: 839.45. Analytical data, C 68.67(Calc. 68.71); H 7.39(7.45); N 6.56(6.68) %.

L^b, ¹H NMR spectrum (300 M, CDCl₃): δ = 7.06–7.36 (m, 20H); 3.66(s, 8H; 4O–CH₂–C(O)); 3.65(q, 8H; 4N–CH₂–R); 3.17(s, 8H; 4C–CH₂–O); 3.02(s, 4H; 2C–CH₂–O); 1.21 (q, 4H; 2R–CH₂–C); 1.04(t, 12H; 4CH₃–R–N); 0.70(t, 6H; 2CH₃–R–C). IR: ν 1674s (C=O), 1122s (Ar–O–C). Formula weight of L^b: 895.13. Analytical data, C 69.77(Calc. 69.53); H 7.88(7.97); N 6.26(6.42) %.

L^c, ¹H NMR spectrum (300 M, CDCl₃): $\delta = 6.92-7.26$ (m, 40H); 4.84(s, 8H; 4N–CH₂–R); 3.75(s, 8H; 4O–CH₂–C(O)); 3.23(s, 8H; 4C–CH₂–O); 3.11(s, 4H; 2C–CH₂–O); 1.27 (q, 4H; 2R–CH₂–C); 0.76(t, 6H; 2CH₃–R–C). IR: ν 1675s (C=O), 1108s (Ar–O–C). Formula weight of L^c: 1142.58. Analytical data, C 75.77(Calc. 75.63); H 7.02(6.88); N 5.06(4.90) %.

2.4. Synthesis of complexes

An ethyl acetate solution of $Ln(NO_3)_3 \cdot 6H_2O$ [Ln = Eu(III), Tb(III), 0.2 mmol], $Ln(CIO_4)_3 \cdot 6H_2O$ [Ln = Eu(III), Tb(III), 0.1 mmol], was added dropwise to a solution of the ligand L (0.1 mmol) in the ethyl acetate (30 ml). The mixture was stirred for 4 h and white precipitate formed. The precipitate was collected and washed three times with ethyl acetate. Further drying in vacuum afforded pale white powder, yield: 75–80%.

3. Result and discussion

3.1. Properties of the complexes

Analytical data for the complexes listed in Table 1 conform to an 2:6:1 metal-to-nitrate-to-L stoichiometry $[LnL] \cdot [Ln(NO_3)_5] \cdot (NO_3)$, 1:3:1 metal-to-perchlorate-to-L stoichiometry $[LnL] \cdot (ClO_4)_3$. All complexes are soluble in DMF, acetonitrile, THF, MeOH, acetone, dioxane and CHCl₃, but sparingly soluble in water and ethyl acetate. The molar conductances of the complexes in MeOH (see Table 1) indicate that all nitrate complexes act as 1:2 electrolytes, and all perchlorate complexes act as 1:3 electrolytes [13].

3.2. IR spectra

The main infrared bands of the ligand and its complexes are presented in Table 2. The IR spectrum of free ligand shows bands at 1674–1675 and 1122–1108 cm⁻¹, which may be assigned to ν (C=O) and ν (C–O–C), respectively. In the IR spectra of all the lanthanide complexes, these bands shift by about 50 and 25 cm⁻¹ toward lower wavenumbers, thus indicating that the carbonyl and ethereal oxygen atoms take part in coordination to the metal ion. Table 1

Complexes	С	Н	Ν	Ln	$\Lambda_{\rm m}~({\rm s~cm^2~mol^{-1}})$
$\overline{[EuL^{a}]\cdot[Eu(NO_{3})_{5}]\cdot(NO_{3})}$	38.14(38.05)	4.23(4.12)	9.16(9.25)	20.89(20.06)	180
$[TbL^{a}] \cdot [Tb(NO_{3})_{5}] \cdot (NO_{3})$	38.12(37.71)	4.12(4.09)	9.08(9.16)	20.65(20.79)	176
$[EuL^b] \cdot [Eu(NO_3)_5] \cdot (NO_3)$	39.85(39.75)	4.55(4.49)	8.85(8.92)	19.28(19.35)	193
$[TbL^{b}] \cdot [Tb(NO_{3})_{5}] \cdot (NO_{3})$	39.51(39.40)	4.37(4.45)	8.89(8.84)	19.98(20.05)	185
$[EuL^{c}] \cdot [Eu(NO_{3})_{5}] \cdot (NO_{3})$	48.01(47.53)	4.39(4.32)	7.85(7.70)	16.58(16.71)	167
$[TbL^{c}] \cdot [Tb(NO_{3})_{5}] \cdot (NO_{3})$	47.06(47.17)	4.20(4.29)	7.52(7.64)	17.69(17.34)	171
$[EuL^{a}] \cdot (ClO_{4})_{3}$	44.85(44.71)	4.72(4.83)	4.24(4.35)	11.26(11.79)	321
$[TbL^{a}] \cdot (ClO_{4})_{3}$	44.41(44.47)	4.80(4.82)	4.50(4.32)	12.31(12.26)	342
$[EuL^b] \cdot (ClO_4)_3$	46.48(46.42)	5.28(5.24)	4.20(4.16)	11.24(11.29)	332
[TbL ^b]·(ClO ₄) ₃	46.12(46.18)	5.28(5.22)	4.18(4.14)	11.85(11.75)	348
$[EuL^{c}] \cdot (ClO_{4})_{3}$	54.19(54.26)	4.89(4.93)	3.57(3.52)	9.57(9.54)	336
$[TbL^{c}] \cdot (ClO_{4})_{3}$	54.12(54.02)	4.22(4.91)	3.54(3.50)	9.87(9.93)	327

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The absorption bands assigned to the coordinated nitrates were observed at about 1493 cm^{-1} (ν_1), 1311 cm^{-1} (ν_4) and $816 \text{ cm}^{-1}(\nu_3)$ for the complexes, respectively, implying that coordinated nitrate groups in the complexes are bidentate ligands [14]. The absorption band of about 1384 cm^{-1} suggests that there is free nitrate in the complexes, which is in agreement with the results of the conductivity experiments.

3.3. Fluorescence studies

Under identical experimental, the fluorescence characteristics of the solid complexes are listed in Table 3. The ligands have strong antenna effect. So its terbium and europium complexes have strong fluorescence. The fluorescence characteristic emission wavelengths of the terbium and europium ions were observed (Fig. 1). As shown in Fig. 1, the emission spectra of the six Eu complexes at room temperature are similar to each other and show characteristic emission bands of Eu (III) ion at about 594 and 616 nm, assigned to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$. The ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ emission peaks are too weak to be observed at about 645–660 nm range [2]. The emission at

Table 2	
IR spectral data of the free ligands and their complexes (cm ⁻¹

about 616 nm from ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ electronic dipole transition is the strongest, suggesting low symmetry around the Eu(III) ion [15]. Therefore, the peak height at 619 nm is used to measure the fluorescence intensities of europium complexes. We also see characteristic emission bands of Tb(III) ion at about 492, 546 and 586 nm, assigned to ${}^{5}D_{4}-{}^{7}F_{6}$, ${}^{5}D_{4}-{}^{7}F_{5}$ and ${}^{5}D_{4}-{}^{7}F_{4}$. The peak height of the strongest emission at about 546 nm from ${}^{5}D_{4}-{}^{7}F_{5}$ electronic dipole is used to measure the fluorescence intensities of Tb complexes. We can notice solid luminescence intensity of each Eu perchlorate complex is stronger than that of Eu nitrate complex with the same ligand, the case is the same with the Tb complexes (Fig. 1). This is due to the anion effect [16]. In the studied examples, perchlorate anion distinctly increase the Ln(III) luminescence intensity. We know that the complexes conform to $[LnL] \cdot [Ln(NO_3)_5] \cdot (NO_3)$ (nitrate complexes) and [LnL]·(ClO₄)₃ (perchlorate complexes). In every complex, a ligand chelates a Ln ion with nine O atoms, but the counter-anions are different: $[Ln(NO_3)_5]^{2-}$ and $(NO_3)^{-}$ in nitrate complexes, (ClO₄)₃ in perchlorate complexes. Based on antenna effect [17,18], the intensity of the luminescence of Ln³⁺ complexes is related to the efficiency of the intramolecular

Compound	ν (C=O)	v (C–O–C)	$v_1 (NO_3^-)$	v ₃ (NO ₃ ⁻)	v ₄ (NO ₃ ⁻)	v (free)	v ₃ (ClO ₄ ⁻)	v ₄ (ClO ₄ ⁻)
La	1675	1112						
$[EuL^{a}] \cdot [Ln(NO_{3})_{5}] \cdot (NO_{3})$	1623	1090	1490	816	1309	1384		
$[TbL^{a}] \cdot [Ln(NO_{3})_{5}] \cdot (NO_{3})$	1624	1091	1492	816	1310	1384		
$[EuL^{a}] \cdot (ClO_{4})_{3}$	1623	1096					1097	942
$[TbL^{a}] \cdot (ClO_{4})_{3}$	1624	1097					1098	946
L ^b	1675	1122						
$[EuL^b] \cdot [Ln(NO_3)_5] \cdot (NO_3)$	1618	1095	1488	813	1308	1384		
$[TbL^{b}] \cdot [Ln(NO_{3})_{5}] \cdot (NO_{3})$	1920	1095	1493	815	1310	1384		
$[EuL^b] \cdot (ClO_4)_3$	1618	1098					1099	962
$[TbL^b] \cdot (ClO_4)_3$	1619	1099					1100	962
L ^c	1676	1108						
$[EuL^{c}] \cdot [Ln(NO_{3})_{5}] \cdot (NO_{3})$	1616	1093	1492	816	1310	1384		
$[TbL^{c}] \cdot [Ln(NO_{3})_{5}] \cdot (NO_{3})$	621	1076	1495	826	1306	1384		
$[EuL^{c}] \cdot (ClO_{4})_{3}$	1619	1094					1095	926
$[TbL^c] \cdot (ClO_4)_3$	1620	1096					1098	922



Fig. 1. (a) Emission spectra of the solid $[EuL^a] \cdot (ClO_4)_3$ (1) ($\lambda_{ex} = 398 \text{ nm}$) and $[EuL^a] \cdot [Eu(NO_3)_5] \cdot (NO_3)$ (2) complex ($\lambda_{ex} = 399 \text{ nm}$) at room temperature. (b) Emission spectra of the solid $[TbL^a] \cdot (ClO_4)_3$ (1) ($\lambda_{ex} = 309 \text{ nm}$) and $[TbL^a] \cdot [Tb(NO_3)_5] \cdot (NO_3)$ (2) complex ($\lambda_{ex} = 319 \text{ nm}$) at room temperature. (c) Emission spectra of the solid $[EuL^b] \cdot (ClO_4)_3$ (1) ($\lambda_{ex} = 397 \text{ nm}$) and $[EuL^b] \cdot [Eu(NO_3)_5] \cdot (NO_3)$ (2) complex ($\lambda_{ex} = 399 \text{ nm}$) at room temperature. (d) Emission spectra of the solid $[TbL^b] \cdot (ClO_4)_3$ (1) ($\lambda_{ex} = 306 \text{ nm}$) and $[TbL^b] \cdot [Tb(NO_3)_5] \cdot (NO_3)$ (2) complex ($\lambda_{ex} = 321 \text{ nm}$) at room temperature. (e) Emission spectra of the solid $[EuL^c] \cdot (ClO_4)_3$ (1) ($\lambda_{ex} = 397 \text{ nm}$) and $[EuL^c] \cdot (FOO_3)_5] \cdot (NO_3)$ (2) complex ($\lambda_{ex} = 399 \text{ nm}$) at room temperature. (f) Emission spectra of the solid $[TbL^c] \cdot (ClO_4)_3$ (1) ($\lambda_{ex} = 377 \text{ nm}$) and $[EuL^c] \cdot (Eu(NO_3)_5] \cdot (NO_3)$ (2) complex ($\lambda_{ex} = 399 \text{ nm}$) at room temperature. (f) Emission spectra of the solid $[TbL^c] \cdot (ClO_4)_3$ (1) ($\lambda_{ex} = 354 \text{ nm}$) and $[TbL^c] \cdot (Tb(NO_3)_5] \cdot (NO_3)$ (2) complex ($\lambda_{ex} = 320 \text{ nm}$) at room temperature.

Table 3

Fluorescence data for the complexes

Complexes	$\lambda_{ex} (nm)$	$\lambda_{em} \ (nm)$	RFI	Assignment
$\overline{[EuL^a]\cdot [Eu(NO_3)_5]\cdot (NO_3)}$	399	595 617	34 121	
$[EuL^a] \cdot (ClO_4)_3$	398	594 616	285 865	${}^5D_0 \rightarrow {}^7F_1 \\ {}^5D_0 \rightarrow {}^7F_2$
$[TbLa] \cdot [Tb(NO3)5] \cdot (NO3)$	319	493 546 586	1179 2252 189	
[TbLa]·(ClO4)3	309	492 546 585	4807 7998 822	
[EuLb]·[Eu(NO3)5]·(NO3)	399	595 618	35 131	${}^5D_0 \rightarrow {}^7F_1 \\ {}^5D_0 \rightarrow {}^7F_2$
[EuLb]·(ClO4)3	397	594 617	105 298	${}^5D_0 \rightarrow {}^7F_1$ ${}^5D_0 \rightarrow {}^7F_2$
[TbLb]·[Tb(NO3)5]·(NO3)	321	492 547 586	413 848 82	
[TbLb]·(ClO4)3	306	492	1385	$^5D_4 \rightarrow {}^7F_6$
[EuLc]·[Eu(NO3)5]·(NO3)		546 586	2574 310	${}^5D_4 \rightarrow {}^7F_5 \\ {}^5D_4 \rightarrow {}^7F_4$
[EuLc]·(ClO4)3	399 397	595 618 593	26 102 302	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$
[TbLc]·[Tb(NO3)5]·(NO3)	320	618 491 546 586	352 854 1506 171	
$[TbL^{c}] \cdot (ClO_{4})_{3}$	354	492 546 586	433 1041 81	

RFI is relative fluorescence intensity.

energy transfer between the triplet energy level of the ligand and the emitting level of the central ion, which depends on the gap between the two levels. As we know luminescence intensity of solid Ln (Ln = Eu, Tb) nitrate is quite weak, we consider that efficiency of energy transfer from NO₃ to Ln in [Ln(NO₃)₅] is very poor, which results in incomplete energy transfer in the whole nitrate complex molecule though that from L to Ln is efficient. The [Ln(NO₃)₅] group is negatively effective to the fluorescence intensity of the nitrate complexes.

4. Conclusion

According to the data and discussion above, the amide-based multipodal ligand could form complexes with lanthanide ions and exhibit a caverned conformation. The complexes exhibited characteristic fluorescence of europium and terbium ion, respectively. The different anions may affect the fluorescence of europium and terbium ions. Based on those results, a series of new amide-based multipodal derivatives could be designed and synthesized to optimize the luminescent properties of these lanthanide ions.

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