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Terminal group effects on the fluorescence spectra of europium(III) nitrate complexes with a family of amide-based 2,3-dihydroxynaphthalene derivatives

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Abstract

Three ligands 2,2'-[2,3-naphthylenebis(oxy)]-bis(N,N-diethyl(acetamide)) (L^a), 2,2'-[2,3-naphthylenebis(oxy)]-bis(N,N-diisopropyl(acetamide)) (L^b) and 2,2'-[2,3-naphthylenebis(oxy)]-bis(N,N-dibutyl(acetamide)) (L^c) and their europium(III) nitrate complexes were synthesized. The complexes were characterized by elemental analysis, IR, fluorescence spectroscopy and conductivity. The europium atoms are coordinated by O-atoms from C=O, Ar–O–C. With the difference of the ligands, the solid fluorescent intensities of the Eu complexes vary regularly. Some factors that influencing the fluorescent intensity were discussed.

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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]. The main advantages of lanthanide chelates in fluorescence spectrometry are their large stokes shifts, narrow emission profiles and long fluorescence lifetimes [5]. 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 [2]. And these properties have also been used to improve the sensitivity for lanthanide estimation by conventional spectrofluorimetry and laser-induced spectrofluorimetry [5].

Amide-based open-chain crown ethers offer many advantages in extraction and analysis of the rare earth ions [6,7] because of their ring-like coordination structure and terminal group effects [7,8]. So we have designed a series of multi-

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functional ligands having selective ability to coordinate lanthanides ions. The luminescence of these lanthanide complexes were enhanced by providing some of proper conjugate absorption groups suitable for energy transfer, i.e. naphthalene, and the other coordinating groups with cavities for lanthanide ions, i.e. amide-based open-chain crown ethers. In the present work, we designed and synthesized three ligands and their Eu(III) nitrate complexes. The effects of the terminal groups on the fluorescence properties of the solid complexes were investigated.

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 xylenol orange as an indicator. Carbon, nitrogen and hydrogen analyses were determined using a Vario EL elemental analyzer. Conductivity measurements were carried out with a DDSJ-308 type conductivity bridge using 1.0×10^{-3} mol dm⁻³ solution in

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MeOH at 25 °C. IR spectra were recorded on a Nicolet Avatar 360 FT-IR instrument using KBr discs in the 400–4000 cm⁻¹ region. ¹H NMR spectra were measured on a FT-80A or FT-200A spectrometer in CDC1₃ 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

2.3.1. General procedure for ligand synthesis

The three ligands were prepared by the same procedure. Anhydrous K_2CO_3 (4.0 g) was added slowly to the DMF solution of 2,3-dihydroxynaphthalene (1) (6.04 mmol) at 110 °C. An hour later, a DMF solution containing 2 (L^a: *N*,*N*diethylchloroacetamide; L^b: *N*,*N*-diisopropylchloroacetamide; L^c: *N*,*N*-dibutylchloroacetamide) (13.0 mmol) was added dropwise and slowly to the mixture. The reaction mixture was stirred for 24 h. Fifty milliliters of water were poured into the cooled mixture. Then the crude product was extracted by CHCl₃ (3 × 40 ml). The combined organic phases were dried in vacuum. The crude product was dissolved in EtOAc and then purified by chromatography on silica gel until **3** was received as white solid.

2.3.2. 2,2'-[2,3-naphthylenebis(oxy)]bis(N,N-diethyl(acetamide)) (L^a)

Yield, 80%. ¹H NMR spectrum (80 MHz, CDC1₃): δ 7.27–7.74 (m, 6H); 4.84 (s, 4H; 2O–CH₂–C(O)); 3.41 (q, 8H; 4N–CH₂–R), 1.20 (t, 12H; 4R–CH₃). IR: ν 1640(C=O), 1166 (Ar–O–C). Analytical data, Calc. for L^a: C, 66.30; H, 8.29; N, 7.73. Found: C, 66.10%; H, 9.21%; N, 7.20%.

2.3.3. 2,2'-[2,3-naphthylenebis(oxy)]-bis(N,Ndiisopropyl(acetamide)) (L^b)

Yield, 80%. ¹H NMR (200 MHz, CDC1₃): δ 7.29–7.69 (m, 6H); 4.75 (s, 4H; 2O–CH₂–C(O)); 3.42 (q, 2H; 2N–CH(R)₂); 1.40 (d, 12H; 2R–(CH₂)₂) IR: ν 1661(C=O), 1174 (Ar–O–C). Analytical data, Calc. for L: C, 70.85; H, 8.45; N, 6.38. Found: C, 70.56%; H, 8.65%; N, 6.33%.

2.3.4. 2,2'-[2,3-naphthylenebis(oxy)]-

$bis(N,N-dibutyl(acetamide))(L^{c})$

Yield, 78%. ¹H NMR (200 MHz, CDC1₃): δ 7.26–7.68 (m, 6H); 4.85 (s, 4H; 2O–CH₂–C(O)); 3.35 (t, 8H; 2N–(CH₂–R)₂); 1.52 (m, 8H; 2N–(R–CH₂–R)₂) 1.30 (m, 8H; 2N–(R–CH₂–R)₂) 0.92 (t, 12H; 4R–CH₃) IR: ν 1646(C=O), 1172 (Ar–O–C). Analytical data, Calc. for L: C, 72.35; H, 9.24; N, 5.68. Found: C, 72.25%; H, 9.30%; N, 5.62%.

2.4. Synthesis of complexes

A solution of Eu(NO₃)₃· $6H_2O$ (0.1 mmol) in ethyl acetate was added slowly to 20 ml of a solution of the ligand (0.1 mmol). The mixture was stirred for 5 h and white precipitate formed. The precipitate was collected and washed three times with ethyl acetate. Further drying in vacuum resulted in a pale white powder, yield: 80% Fig. 1.

3. Result and discussion

3.1. Properties of the complexes

Analytical data for the complexes are listed in Table 1, conformed to $[Eu(NO_3)_3L]$. All complexes are soluble in DMF, DMSO, acetonitrile, THF, methanol and acetone, but little soluble in chloroform and ethyl acetate. Conductivity measurement for these complexes in methanol solution (Table 1) indicate the presence of a non-dissociated compound [9].

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. The IR spectrum of the free ligands show a strong band in the region $1640-1661 \text{ cm}^{-1}$, which can assigned to the stretch vibration of the carbonyl group. The peak at



 L^b : $R_1 = R_2 = isopropyl$

 $L^c: R_1 = R_2 = butyl$

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

Table 1	
Elemental analytical and molar conductance data for the complexe	es

Complexes	Found (calc. %)		$\Lambda_{\rm m}~({\rm s~cm^2~mol^{-1}})$		
	C	Н	Ν	Eu	
[Eu(NO ₃) ₃ L ^a]	37.36 (38.02)	4.50 (4.35)	9.47 (9.56)	20.55 (21.06)	68.2
$[Eu(NO_3)_3L^b]$	40.76 (39.86)	5.19 (5.24)	8.80 (8.75)	19.10 (19.26)	63.5
$[Eu(NO_3)_3L^c]$	43.72 (44.21)	5.80 (5.84)	8.22 (8.36)	17.84 (18.26)	58.6

Table 2

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

Compound	v(C=O)	v(Ar–O)	$v_1(NO_3^-)$	v ₄ (NO ₃ ⁻)
La	1640	1166		
[Eu(NO ₃) ₃ L ^a]	1623	1159	1482	1303
L ^b	1661	1174		
$[Eu(NO_3)_3L^b]$	1618	1158	1483	1308
L ^c	1646	1172		
$[Eu(NO_3)_3L^c]$	1620	1161	1489	1316

1166–1174 cm⁻¹, is attributed to the ν of the Ar–O bond. In the IR spectra of the Eu complexes, the ν (C=O) and ν (Ar–O) are shifted by 20–40 and 6–14 cm⁻¹, respectively.

The absorption bands assigned to the coordinated nitrates were observed as two bands at about 1483 cm^{-1} (ν_1) and 1308 cm^{-1} (ν_4), 817 cm^{-1} for the complexes. This indicates that coordinated nitrate groups in the complex are bidentate in agreement with the results of the conductivity measurements.

3.3. Fluorescence studies

Under identical experimental conditions, the fluorescence characteristics of the solid complexes at room temperature were studied. They are summarized in Table 3. The maximum of excitation was observed at a wavelength of 466 nm for all complexes. As shown in Fig. 2, the emission spectra of the three complexes at room temperature are similar to each other and show characteristic emission bands of Eu(III) ion at about 593, 617 nm, assigned to ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$, ${}^5D_0 \rightarrow {}^7F_3$, emission peaks are too weak to be observed at about 645–660 nm range [2]. The emission at 619 nm from ${}^5D_0 \rightarrow {}^7F_2$, electronic dipole transition is the strongest, suggesting low symmetry around the Eu(III) ion [10]. Therefore, the peak height at 619 nm is used to measure the fluorescence intensities of three europium complexes. As shown in Fig. 2, the fluorescence intensities of 5D_0 to 7F_2 .

Table 3				
Fluorescence	data for	the c	complexes	\$

Complex	λ_{ex} (nm)	$\lambda_{em} (nm)$	RFI	Assignment
[Eu(NO ₃) ₃ L ^a]	466	616	590	${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$
		593	127	${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{1}$
[Eu(NO ₃) ₃ L ^b]	466	617	904	${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$
		592	229	${}^{5}\mathrm{D}_{0} \rightarrow {}^{7}\mathrm{F}_{1}$
$[Eu(NO_3)_3L^c]$	466	618	1252	${}^{5}\mathrm{D}_{0} \rightarrow {}^{7}\mathrm{F}_{2}$
		591	273	$^5D_0 \rightarrow {}^7F_2$



Fig. 2. Emission spectra of the solid europium complexes and Eu nitrate at room temperature: (1) $[Eu(NO_3)_3L^a] \lambda_{ex} = 466 \text{ nm}$; (2) $[Eu(NO_3)_3L^b] \lambda_{ex} = 466 \text{ nm}$; (3) $[Eu(NO_3)_3L^c] \lambda_{ex} = 466 \text{ nm}$; (4) $Eu(NO_3)_3 \cdot 6H_2O \lambda_{ex} = 466 \text{ nm}$.

(619 nm) decrease continuously with the decrease of the terminal groups, i.e. in the series dibutylamide, diisopropylamide, diethylamide. We can also see the fluorescence intensity of $Eu(NO_3)_3 \cdot 6H_2O$ is weaker than that of the complexes. The formation of complex is helpful to enhance fluorescence intensity of Eu ion. Based on antenna effect [11,12], the intensity of the luminescence of Ln³⁺ 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 ion, which depends on the gap between the two levels. We consider that the group having a positive effect to the fluorescence intensity of the Eu(III)—complexes is mainly the naphthalene group, as can be deduced by the excited wave numbers. The terminal group has a negative effect to the fluorescence intensity of the Eu(III) complex. The ligand with the shorter alkyl terminal group increases the ability of O-atoms of the C=O and Ar-O-C to coordinate to lanthanide ions and decreases the fluorescence intensity of the Eu(III)-complexes.

4. Conclusion

According to the data and discussion above, obvious changes in IR spectra were observed, after formation of complexes between the ligands and Eu(III). In the complexes, Eu ions were coordinated to the C=O oxygen atoms and ether oxygen atoms. The complexes emitted the characteristic fluorescence of Eu(III) ions. The terminal group may affect the fluorescence of Eu ions. A series of new amide based 2,3-dihydroxynaphtahlene derivates was synthesized to optimize the luminescence properties of lanthanide ions.

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