

Terminal group effects on the fluorescence spectra of Eu(III) nitrate complexes with a family of amide-based 1,10-phenanthroline derivatives

Su-Wen Chen, Yu-Liang Zhang, Wei Dou, Ya-Wen Wang, Wei-Sheng Liu*

Department of Chemistry and State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

Received 29 January 2005; received in revised form 23 March 2005; accepted 23 March 2005

Abstract

Four ligands 1,10-phenanthroline-5,6-bis(*N,N*-dibenzyl-1'-oxopropylamide) (L^a), 1,10-phenanthroline-5,6-bis(*N*-methyl-*N*-benzyl-1'-oxopropylamide) (L^b), 1,10-phenanthroline-5,6-bis(*N*-benzyl-1'-oxopropylamide) (L^c) and 1,10-phenanthroline-5,6-bis(*N,N*-diethyl-1'-oxopropylamide) (L^d), and their lanthanide(III) (La and Eu) complexes were synthesized. The complexes were characterized by elemental analysis, IR, fluorescence spectroscopy and conductivity. The lanthanide atoms are coordinated by O atoms from C=O, Ar–O–C and N atoms from phen. With the difference of the ligands, the fluorescent intensities of the Eu(III) complexes vary regularly in the THF solution. Some factors that influence the fluorescent intensity were discussed.

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Keywords: Amide-based 1,10-phenanthroline derivative; Synthesis; Complexes; Fluorescent property

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 the 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 the 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-functional ligands having selective ability to coordinate more than one lanthanides ions. The luminescence of these lanthanide complexes were enhanced by providing some of the proper conjugate absorption groups suitable for energy transfer, i.e. phen, 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 four ligands and their europium(III) nitrate complexes. The terminal group effects on fluorescence properties of the complexes were investigated.

2. Experimental

2.1. Materials

All commercially available chemicals were of A.R. grade and all the solvents used were purified by standard methods.

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

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 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 spectrometer in CDCl $_3$ solution, with TMS as the internal standard. Fluorescence measurements were made on a Hitachi F-4500 spectrophotometer equipped with quartz cuvettes of 1 cm path length at room temperature. The excitation and emission slit widths were 10 nm.

2.3. Synthesis of the ligand

Compounds 1, 2 and 3 (Fig. 1) were prepared according to the literature methods [9–12].

2.3.1. General procedure for ligand synthesis

The four ligands were prepared by the same procedure.

Anhydrous K $_2$ CO $_3$ (4.0 g) was added slowly to the DMF solution of 2 (1.5 g, 6.04 mmol) at 110 °C. An hour later, a DMF solution containing 3 (18.0 mmol) was added dropwise and slowly to the mixture. The reaction mixture was stirred for 24 h. Fifty milliliters water was poured and extracted by CHCl $_3$ (3 \times 40 ml). Organic phase combined was evaporated in vacuum. The crude product was chromatographed on silica gel (EtOAc/MeOH, 95:5) to afford 4 as pale yellow solids.

2.3.2. 1,10-Phenanthroline-5,6-bis(*N,N*-dibenzyl-1'-oxopropylamide) (*L*^a, *R*₁ = *R*₂ = benzyl)

Yield, 85%. IR (cm $^{-1}$, KBr): 1663 (C=O), 1613 (phen, C=N), 1116 (Ar–O), 1495 (phen ring). ^1H NMR (CDCl $_3$,

ppm): δ 8.99–8.97 (m, 2H; phen: 2H and 9H); 8.69–8.65 (m, 2H; phen: 4H and 7H); 7.76–7.68 (m, 2H; phen: 3H and 8H); 7.19–7.16 (s, 20H; 2Ar H); 5.14 (s, 4H; 2O–CH $_2$ –C(O)); 4.42 (s, 8H; 4N–CH $_2$ –Ar).

2.3.3. 1,10-Phenanthroline-5,6-bis(*N*-methyl-*N*-benzyl-1'-oxopropylamide) (*L*^b, *R*₁ = methyl, *R*₂ = benzyl)

Yield, 80%. IR (cm $^{-1}$, KBr): 1662 (C=O), 1613 (phen, C=N), 1114 (Ar–O), 1492 (phen ring). ^1H NMR (CDCl $_3$, ppm): δ 9.15–9.11 (m, 2H; phen: 2H and 9H); 8.87–8.70 (m, 2H; phen: 4H and 7H); 7.73–7.58 (m, 2H; phen: 3H and 8H); 7.30 (s, 10H; 2Ar H); 5.11 (s, 4H; 2CH $_2$); 4.65–4.48 (s, 4H; 2O–CH $_2$ –C(O)); 3.00–2.86 (s, 6H; 2CH $_3$).

2.3.4. 1,10-Phenanthroline-5,6-bis(*N*-benzyl-1'-oxopropylamide) (*L*^c, *R*₁ = H, *R*₂ = benzyl)

Yield, 78%. IR (cm $^{-1}$, KBr): 1667 (C=O), 1616 (phen, C=N), 1117 (Ar–O), 1497 (phen ring). ^1H NMR (CDCl $_3$, ppm): δ 9.14–9.12 (m, 2H; phen: 2H and 9H); 8.41–8.38 (m, 2H; phen: 4H and 7H); 7.65–7.61 (m, 2H; phen: 3H and 8H); 7.36–7.32 (m, 10H; 2Ar H); 7.31–7.29 (m, 2H; 2C(O)–N–H); 4.73 (s, 4H; 2O–CH $_2$ –C(O)); 4.59–4.52 (m, 4H; 2CH $_2$).

2.3.5. 1,10-Phenanthroline-5,6-bis(*N,N*-diethyl-1'-oxopropylamide) (*L*^d, *R*₁ = *R*₂ = ethyl)

Yield, 70%. IR (cm $^{-1}$, KBr): 1657 (C=O), 1614 (phen, C=N), 1117 (Ar–O), 1492 (phen ring). ^1H NMR (CDCl $_3$, ppm): δ 9.13–9.09 (m, 2H; phen: 2H and 9H); 8.34–8.30 (m, 2H; phen: 4H and 7H); 7.67–7.62 (m, 2H; phen: 3H and 8H); 7.35 (m, 10H; 2Ar H); 3.73 (s, 4H; 2O–CH $_2$ –C(O)); 3.43–3.41 (m, 8H; 4CH $_2$); 1.25–1.13 (m, 12H; CH $_3$).

2.4. Synthesis of complexes

An ethyl acetate solution of Ln(NO $_3$) $_3$ ·6H $_2$ O [Ln = Eu(III) or La(III), 0.15 mmol] was added dropwise to a solution of ligand L (0.1 mmol) in the ethyl acetate (20 ml). The mixture was stirred for 24 h and white precipitate was formed.

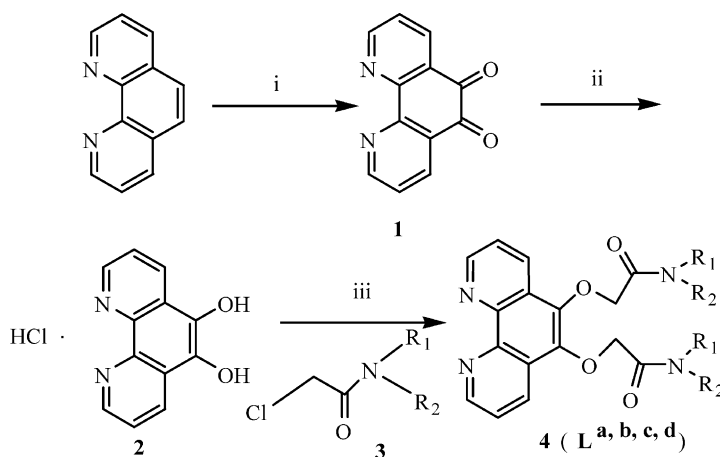


Fig. 1. Scheme of the synthesis of the ligands. (i) KBr, H $_2$ SO $_4$, HNO $_3$, –15 °C; (ii) NH $_2$ NH $_2$ ·HCl, 100 °C; (iii) K $_2$ CO $_3$, DMF, 110 °C (*L*^a: *R*₁ = benzyl, *R*₂ = benzyl; *L*^b: *R*₁ = methyl, *R*₂ = benzyl; *L*^c: *R*₁ = H, *R*₂ = benzyl; *L*^d: *R*₁ = ethyl, *R*₂ = ethyl).

The precipitate was collected and washed three times with ethyl acetate. Further drying in vacuum afforded a pale white powder, yield: 80%.

3. Results and discussion

3.1. Properties of the complexes

Analytical data for the complexes are listed in Table 1, conformed to $[\text{Eu}_4(\text{NO}_3)_{10}\text{L}_3] \cdot (\text{NO}_3)_2$ and $[\text{La}_4(\text{NO}_3)_{10}\text{L}_3] \cdot (\text{NO}_3)_2$.

All complexes are soluble in DMF, acetonitrile, THF, methanol and ethanol, but sparingly soluble in water and ethyl acetate. Conductivity measurement for these complexes in methanol solution (in Table 1) indicates that both complexes are 2:1 ionic complexes [13].

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. Table 2 shows main infrared data of the four Eu(III) and La(III) complexes. The IR spectrum of the free ligands show strong band at $1657\text{--}1667\text{ cm}^{-1}$, which is attributable to stretch vibrations of the carbonyl group of amide ($\nu(\text{C}=\text{O})$). The peak at $1613\text{--}1617\text{ cm}^{-1}$ can be assigned to $\nu(\text{C}=\text{N})$, and the peak at $1114\text{--}1117\text{ cm}^{-1}$ to $\nu(\text{Ar}-\text{O})$ [14]. In the IR spectra of the lanthanum complexes, the $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{Ar}-\text{O})$ shift by 8–30, 6–12

and $6\text{--}27\text{ cm}^{-1}$, respectively; thus indicating that carbonyl, ethereal oxygen atom and phen nitrogen atom take part in coordination to the metal ion.

The absorption bands assigned to the coordinated nitrates were observed as two bands at about 1470 cm^{-1} (ν_1) and 1310 cm^{-1} (ν_4), for the complexes, respectively. The differences between the strongest absorption band ν_1 and ν_4 of nitrate group lie in $182\text{--}189\text{ cm}^{-1}$ and $115\text{--}122\text{ cm}^{-1}$, indicating that coordinated nitrate groups in the complexes are bidentate and unidentate ligands [15], respectively. The ν_3 (E) of free nitrate group appears at approximately 1384 cm^{-1} in the spectra of the complexes [16], in agreement with the results of the conductivity experiments.

3.3. Fluorescence studies

Under identical experimental, the fluorescence characteristics of the complexes in THF, dioxane, MeCN and DMF solution are studied. In THF solution, the europium complexes have the strongest fluorescence [17]. The fluorescence characteristics of the europium complexes in THF solution are listed in Table 3 (concentration: 5.5×10^{-4}). The maximum excitation wave lengths of the THF solution are observed at 366, 351, 350 and 314 nm for $[\text{Eu}_4(\text{NO}_3)_{10}\text{L}^{\text{a}}_3] \cdot (\text{NO}_3)_2$, $[\text{Eu}_4(\text{NO}_3)_{10}\text{L}^{\text{b}}_3] \cdot (\text{NO}_3)_2$, $[\text{Eu}_4(\text{NO}_3)_{10}\text{L}^{\text{c}}_3] \cdot (\text{NO}_3)_2$ and $[\text{Eu}_4(\text{NO}_3)_{10}\text{L}^{\text{d}}_3] \cdot (\text{NO}_3)_2$, respectively. As shown in Fig. 2, The emission spectra of the four complexes at the room temperature in THF solution are similar to each other, and show characteristic emission bands of an Eu(III) ion at about 595 and 619 nm, assigned

Table 1
Elemental analytical and molar conductance data for the complexes

Complexes	C (%) found (calc.)	H (%) found (calc.)	N (%) found (calc.)	Ln (%) found (calc.)	Δm ($\text{s cm}^2 \text{ mol}^{-1}$)
$[\text{Eu}_4(\text{NO}_3)_{10}\text{L}^{\text{a}}_3] \cdot (\text{NO}_3)_2$	46.52 (46.46)	3.49 (3.37)	9.39 (9.85)	17.90 (17.60)	202
$[\text{La}_4(\text{NO}_3)_{10}\text{L}^{\text{a}}_3] \cdot (\text{NO}_3)_2$	47.31 (47.18)	3.36 (3.12)	9.69 (10.00)	16.71 (16.54)	208
$[\text{Eu}_4(\text{NO}_3)_{10}\text{L}^{\text{b}}_3] \cdot (\text{NO}_3)_2$	39.44 (39.01)	2.59 (3.07)	11.25 (11.37)	20.45 (20.57)	200
$[\text{La}_4(\text{NO}_3)_{10}\text{L}^{\text{b}}_3] \cdot (\text{NO}_3)_2$	37.93 (39.71)	2.85 (3.12)	11.19 (11.58)	19.00 (19.14)	196
$[\text{Eu}_4(\text{NO}_3)_{10}\text{L}^{\text{c}}_3] \cdot (\text{NO}_3)_2$	38.09 (37.64)	2.56 (2.74)	11.55 (11.71)	20.81 (21.17)	200
$[\text{La}_4(\text{NO}_3)_{10}\text{L}^{\text{c}}_3] \cdot (\text{NO}_3)_2$	38.52 (38.34)	2.34 (2.79)	11.57 (11.92)	19.28 (19.71)	201
$[\text{Eu}_4(\text{NO}_3)_{10}\text{L}^{\text{d}}_3] \cdot (\text{NO}_3)_2$	34.20 (34.42)	3.05 (3.40)	12.28 (12.60)	22.67 (22.79)	207
$[\text{La}_4(\text{NO}_3)_{10}\text{L}^{\text{d}}_3] \cdot (\text{NO}_3)_2$	32.83 (33.07)	3.04 (3.47)	12.35 (12.85)	21.03 (21.25)	204

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

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{Ar}-\text{O})$	$\nu(\text{C}=\text{N})$	$\nu_1(\text{NO}_3^-)$	$\nu_4(\text{NO}_3^-)$	$\nu_3(\text{NO}_3^-)$
L^{a}	1663	1116	1613			
$[\text{Eu}_4(\text{NO}_3)_{10}\text{L}^{\text{a}}_3] \cdot (\text{NO}_3)_2$	1655	1127	1620	1482, 1430	1300, 1314	1384
$[\text{La}_4(\text{NO}_3)_{10}\text{L}^{\text{a}}_3] \cdot (\text{NO}_3)_2$	1653	1126	1619	1495, 1454	1300, 1308	1384
L^{b}	1662	1114	1613			
$[\text{Eu}_4(\text{NO}_3)_{10}\text{L}^{\text{b}}_3] \cdot (\text{NO}_3)_2$	1645	1120	1619	1470, 1429	1286, 1307	1384
$[\text{La}_4(\text{NO}_3)_{10}\text{L}^{\text{b}}_3] \cdot (\text{NO}_3)_2$	1651	1121	1623	1461, 1432	1302, 1319	1384
L^{c}	1667	1117	1616			
$[\text{Eu}_4(\text{NO}_3)_{10}\text{L}^{\text{c}}_3] \cdot (\text{NO}_3)_2$	1637	1130	1626	1489, 1429	1300, 1314	1384
$[\text{La}_4(\text{NO}_3)_{10}\text{L}^{\text{c}}_3] \cdot (\text{NO}_3)_2$	1637	1127	1625	1470, 1428	1300, 1317	1384
L^{d}	1657	1117	1614			
$[\text{Eu}_4(\text{NO}_3)_{10}\text{L}^{\text{d}}_3] \cdot (\text{NO}_3)_2$	1630	1129	1626	1496, 1431	1310, 1302	1384
$[\text{La}_4(\text{NO}_3)_{10}\text{L}^{\text{d}}_3] \cdot (\text{NO}_3)_2$	1630	1144	1624	1477, 1422	1300, 1294	1384

Table 3
Fluorescence data for the complexes

Complex	Concentration (mol dm ⁻³)	Solve	λ_{ex} (nm)	λ_{em} (nm)	RFI	Assignment
[Eu ₄ (NO ₃) ₁₀ L ^a ₃](NO ₃) ₂	5.5×10^{-4}	THF	366	619 595	7130 1750	⁵ D ₀ → ⁷ F ₂ ⁵ D ₀ → ⁷ F ₁
[Eu ₄ (NO ₃) ₁₀ L ^b ₃](NO ₃) ₂	5.5×10^{-4}	THF	351	619 595	4330 1312	⁵ D ₀ → ⁷ F ₂ ⁵ D ₀ → ⁷ F ₁
[Eu ₄ (NO ₃) ₁₀ L ^c ₃](NO ₃) ₂	5.5×10^{-4}	THF	350	619 595	2658 746	⁵ D ₀ → ⁷ F ₂ ⁵ D ₀ → ⁷ F ₁
[Eu ₄ (NO ₃) ₁₀ L ^d ₃](NO ₃) ₂	5.5×10^{-4}	THF	314	619 595	1475 42	⁵ D ₀ → ⁷ F ₂ ⁵ D ₀ → ⁷ F ₁

to D₀ → ⁷F₁, and ⁵D₀ → ⁷F₂. The ⁵D₀ → ⁷F₃ emission peaks are too weak to be observed at about 645–660 nm range [2]. The emission at 619 nm from ⁵D₀ → ⁷F₂ electronic dipole transition is the strongest, suggesting low symmetry around the Eu(III) ion [18]. Therefore, the peak height at 619 nm is used to measure the fluorescence intensities of four europium complexes. From Fig. 2, the biggest fluorescence intensities of ⁵D₀ → ⁷F₂ continually fall along with the sterically hindered decrease of the terminal groups (from dibenzylamide to *N*-methylbenzylamide, benzylamide and diethylamide). Based on the antenna effect [19,20], 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 positively effective group to the fluorescence intensities of the Eu(III) complexes is mainly the phen, as can be deduced by the excited wave numbers. And the terminal group is negatively effective to the fluorescence intensity of the Eu(III) complex. The bridging ligand with the smaller terminal group increases the coordinated ability of O atoms of the C=O and Ar–O–C to lanthanide ions and decreases the fluorescence intensity of the Eu(III) complexes, respectively.

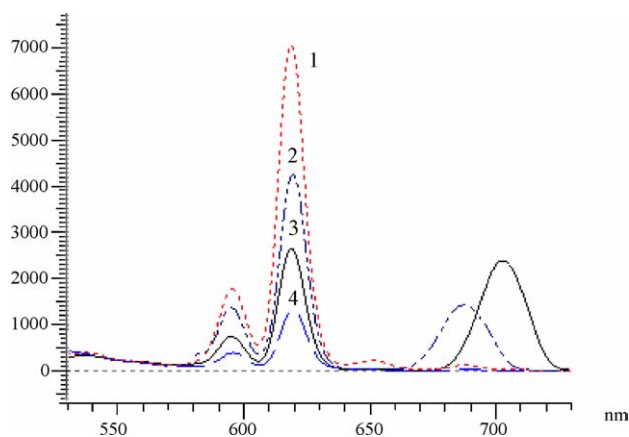


Fig. 2. Emission spectra of the europium complexes at room temperature in THF solution concentration: 5.5×10^{-4} mol dm⁻³. (1) [Eu₄(NO₃)₁₀L^a₃](NO₃)₂ λ_{ex} = 366 nm; (2) [Eu₄(NO₃)₁₀L^b₃](NO₃)₂ λ_{ex} = 351 nm; (3) [Eu₄(NO₃)₁₀L^c₃](NO₃)₂ λ_{ex} = 350 nm; (4) [Eu₄(NO₃)₁₀L^d₃](NO₃)₂ λ_{ex} = 314 nm.

4. Conclusion

According to the data and discussion above, obvious changes in IR spectra were observed, after the ligands formed complexes with Eu(III) and La(III) ions. In the complexes, europium ions were coordinated to the C=O oxygen atoms and phen nitrogen atoms. The complexes exhibited characteristic fluorescence of europium ions. The terminal group may affect the fluorescence of europium ions. Based on those results, a series of new amide-based phenanthroline derivatives could be 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.

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