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Crystal Structure and Fluorescence Properties of Europium Complex with 2,2′-(2,3-Naphthylenebisoxy)-bis(*N*,*N*-diisopropylacetamide)

Kewei Lei[1], **Weisheng Liu**[1,*], and **Kaibei Yu**[2]

[1] Department of Chemistry and State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, P.R. China
[2] Chengdu Center of Analysis and Measurement, Academia Sinica, Chengdu 610041, P.R. China

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Summary. Solid complex of europium nitrate with 2,2′-(2,3-naphthylenebisoxy)bis(*N*,*N*-diisopropylacetamide) (*L*) has been prepared and characterized. The X-ray crystal structure and the solvent dependent fluorescence properties of the Eu(III) complex were investigated.

Keywords. X-Ray structure; Fluorescence; Solvent effect.

Introduction

The development of luminescence chemical probes and sensors is the focus of intense research activity because such materials play considerable roles in nature and medical sciences. The probes based on europium ions are of special interest because of the particularly suitable spectroscopic properties of these ions [1, 2]. Moreover, it is essential to design the multifunctional ligand to optimize the luminescent properties of these lanthanide ions by facilitating the well-known light conversion process, the antenna effect [3], and forming highly and strongly luminescent europium ion complexes [4].

Amide-based crown ethers offer many advantages in extraction and analysis of the rare earth ions [5, 6] 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

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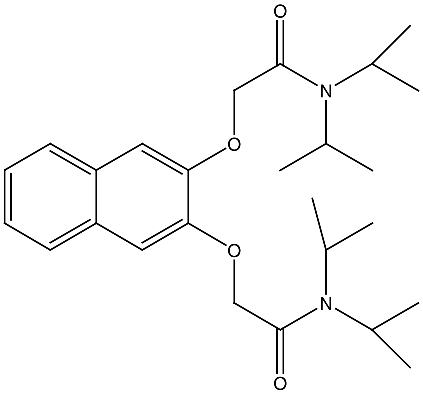
* Corresponding author. E-mail: liuws@lzu.edu.cn



Scheme

extracts of rare earth ions [7]. However, luminescent properties on open-chain crown ethers with lanthanide complexes have been rarely reported [8]. So we have designed a series of poly-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. In the present work, we designed and synthesized 2,2′-(2,3-naphthylenebisoxy)bis(*N*,*N*-diisopropylacetamide) (*L*) (Scheme) and its europium nitrate complex. We studied the crystal structure and fluorescence properties of the complex with the new ligand.

Results and Discussions

Analytical data for the complex (Table 1) conform to a 1:3:1 metal:nitrate:*L* stoichiometry. The complex is soluble in *DMSO*, *DMF*, *Me*CN, methanol, and acetone, and slightly soluble in ethanol, ethyl acetate, and chloroform. The molar conductance values of the complex in methanol (Table 1) indicate the presence of a non-electrolyte [9].

IR Spectra

The IR spectrum of free *L* shows bands at 1660 and 1174 cm^{-1} which may be assigned to O(C=O), and O(C–O–C) respectively. In the IR spectra of the lanthanide complex, these bands shift by 43 and 16 cm^{-1} toward lower wavenumbers, thus indicating that the C=O, and ether O atoms take part in coordination to the metal ion.

The absorption bands assigned to the coordinated nitrates were observed at 1483 and 1308 cm^{-1}, and 817 cm^{-1} for the complex. It indicates that coordinated

Table 1. Elemental analytical and molar conductance data for the complex

Complex	C/%	H/%	N/%	Eu/%	Λ/S $cm^2\,mol^{-1}$
$Eu(NO_3)_3L$	40.07 (40.01)	4.80 (4.91)	8.99 (8.97)	19.44 (19.47)	63.5

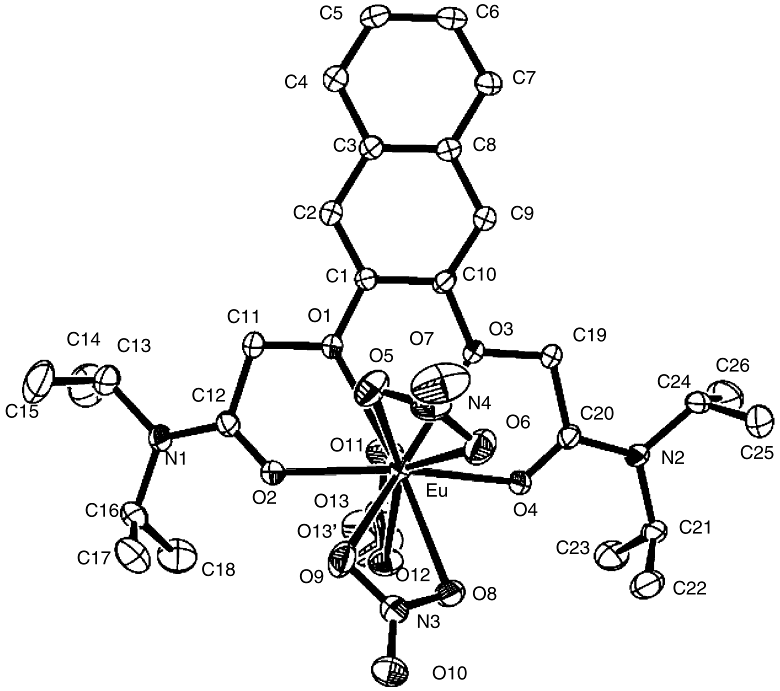


Fig. 1. Molecular structure of $[Eu(NO_3)_3L] \cdot 0.5MeCN \cdot H_2O$ with atom labeling scheme; H atoms attached to C atoms, H_2O, and *Me*CN have been omitted for clarity

nitrate groups in the complex are bidentate in agreement with the result of the conductivity experiments.

X-Ray Crystallography

Figure 1 shows the structure and the atomic numbering schemes for the Eu(III) complex. The crystal structure is composed of $[Eu(NO_3)_3L]$ and H_2O, 0.5 *Me*CN linked by *van der Waals*' forces. The Eu(III) atom is 10-coordinated by four O atoms from the tetradentate ligand *L* and three bidentate nitrates. This $EuO_4(NO_3)_3$ coordination forms a distorted bicapped dodecahedron geometry, as usually observed in the structures of Eu complexes.

The bond lengths in the complex are within normal ranges. Four O atoms of *L* are not quite coplanar. Their deviation from the plane is in the range of 0.0953–0.2489 Å. The Eu atom lies out of this plane by 0.3969 Å. The average distance between the Eu(III) ion and the coordination O atom is 2.483 Å. The Eu–O(C=O) distances (mean 2.353 Å) are significantly shorter than the Eu–O(*Ar*–O–C) distances (mean 2.615 Å). The Eu–O(C=O) bond is stronger than the Eu–O(*Ar*–O–C) bond.

Fluorescence Studies

Under identical experimental conditions, the fluorescence characteristics of the complexes in *Me*CN, *DMF*, and acetone solutions are listed in Table 2. The ligand

Table 2. Fluorescence data for the complex

Concentration / mol dm^{-3}	Solvent	λ_{ex} / nm	λ_{em} / nm	RFI[a]	Assignment
Eu(NO$_3$)L 1.0 × 10^{-3}	*Acetone*	330	617	1002	$^5D_0 - ^7F_2$
			593	222	$^5D_0 - ^7F_1$
	DMF	397	619	18	$^5D_0 - ^7F_2$
			594	14	$^5D_0 - ^7F_1$
	*Me*CN	395	620	28	$^5D_0 - ^7F_2$
			592	14	$^5D_0 - ^7F_1$

[a] Relative fluorescence intensity

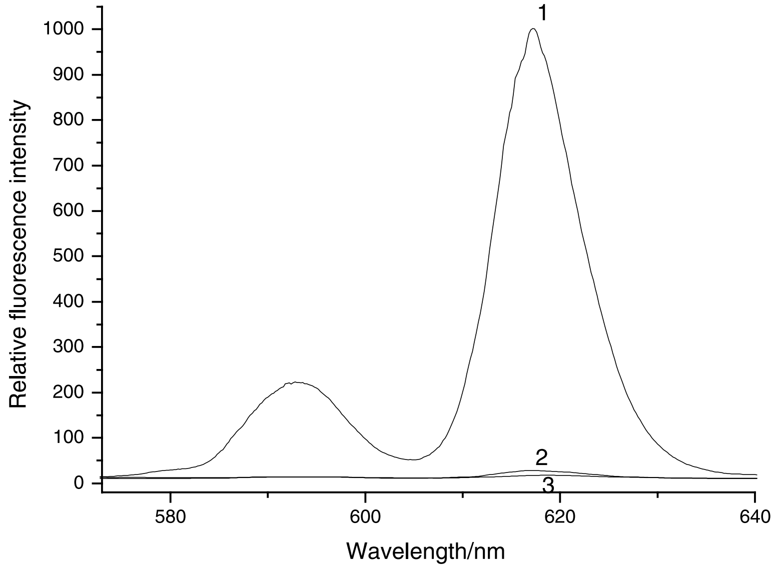


Fig. 2. Emission spectra of the europium complex in different solutions at room temperature; concentration 1.0 × 10^{-3} mol dm^{-3}; (1) λ_{ex}: 330 nm in acetone solution; (2) λ_{ex}: 395 nm in *Me*CN solution; (3) λ_{ex}: 397 nm in *DMF* solution

having aromatic rings with a rigid planar structure has a strong antenna effect. So its europium complex has very strong fluorescence. The fluorescence characteristic emission wavelengths of the europium ions were observed. In acetone solution, the europium complex has the strongest fluorescence (Fig. 2). The luminescence of Ln^{3+} chelates is related to the efficiency of the intramolecular energy transfer between the triple level of the ligand and the emitting level of the ions, which depends on the energy gap between the two levels. In organic solution, the energy gap between the ligand triple level and the emitting level of the europium ion may be in favor of the energy transfer process.

We also can see the fluorescence intensities for the europium complex become weaker from *Me*CN solution. This is due to the coordinating effects of solvents, that is solvate effect [10]. The amide-based portion of the ligand forms a caverned conformation suitable for the uptake of a lanthanide ion, but this ajar cavity could not prevent absolutely the solvent molecules from entering. Together with the raising coordination abilities of acetone, *DMF*, and *Me*CN for the lanthanide ions, the oscillatory motions of the entering molecules consume more of the energy which the ligand triple level transfers to the emitting level of the lanthanide ion. Thus, the energy transfer could not be carried out perfectly.

Quantum yield of the Eu complex in *Me*CN solution (10^{-4} *M*) is 0.5, which was measured with the standard sample of quinine sulfate in sulfate solution (10^{-4} *M*) at 25°C.

Conclusion

According to the data and discussion above, the amide-based ligand could form complex with lanthanide ion (*L*:metal = 1:1) and exhibits a caverned conformation. The complex exhibited characteristic fluorescence of europium ion. Based on those results, a series of new amide-based derivatives could be designed and synthesized to optimize the luminescent properties of these lanthanide ions.

Experimental

Materials

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

Methods

The metal ion contents were determined by *EDTA* titration using xylenol orange as an indicator. Carbon, nitrogen, and hydrogen were analysed 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 *Me*OH at 25°C. IR spectra were recorded on a Nicolet Avatar 360 FT-IR instrument using

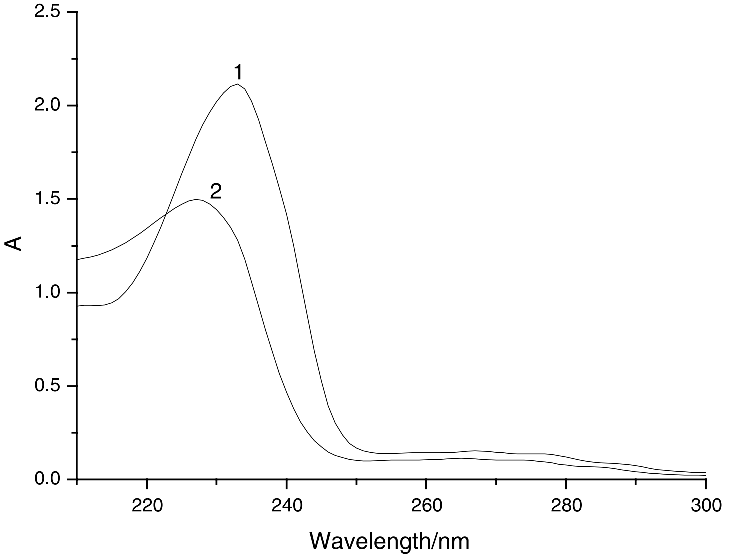


Fig. 3. Absorption spectra of the complex (2) and the ligand (1) with 10^{-4} *M* in *Me*CN solution at 25°C

KBr discs in the 4000–400 cm^{-1} region. ^{1}H NMR spectra were measured on a FT-200A spectrometer in $CDCl_3$ solution, with *TMS* as internal standard. Fluorescence measurements were made on a Shimadzu RF-540 spectrofluorophotometer equipped with quartz cuvettes of 1 cm path length at room temperature. The excitation and emission slit widths were 5 nm. Steady-state absorption spectra were recorded on a Cary 100 double beam spectrophotometer with 10^{-4} *M* in *Me*CN solution at 25°C (Fig 3). Quantum yield of the complex in *Me*CN solution (10^{-4} *M*) was measured with the standard sample of quinine sulfate in sulfate solution (10^{-4} *M*) at 25°C.

Preparation of the Ligand

Anhydrous K_2CO_3 (5.66 g, 41 mmol) was added slowly to the *DMF* solution of 2,3-dihydroxynaphthalene (3.1 g, 20 mmol) at 100°C. An hour later, a solution of *N,N*-diisopropylchloroacetamide (7.14 g, 40 mmol) in 10 cm^{3} *DMF* was added dropwise and slowly to the mixture. The reaction mixture was stirred for 10 h. Water (50 cm^{3}) was added and it was extracted by $CHCl_3$ (3×40 cm^{3}). The combined organic phase was evaporated in vacuum. The crude product was chromatographed on silica gel to afford ligand *L* as a white solid (4.8 g), yield 80%. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.29$–7.69 (m, 6H), 4.75 (s, 4H, 2O–CH_2–C(O)), 3.42 (q, 2H, 2N-CH$(R)_2$, $J = 9.6$ Hz), 1.40 (d, 12H, 2R-$(CH_2)_2$, $J = 9.9$ Hz) ppm; IR: $\bar{\nu} = 1661$(C=O), 1174 (Ar–O–C) cm^{-1}; Analytical data: calcd. for *L* C 70.85, H 8.45, N 6.38; found C 70.56, H 8.65, N 6.33.

Table 3. Crystal data and structure refinement for the single crystal $[Eu(NO_3)_3L] \cdot 0.5MeCN \cdot H_2O$

Empirical formula	$C_{27}\ H_{41.50}\ Eu\ N_{5.50}\ O_{14}$
Formula weight	819.12
Crystal description	block
Color	colorless
Temperature	285(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 15.068(3)$ Å
	$b = 17.985(4)$ Å $\beta = 99.27(2)°$
	$c = 14.477(2)$ Å
Volume, Z	3871.9(10) Å^{3}, 4
Density (calculated)	1.405 Mg/m^{3}
Absorption coefficient	1.684 mm^{-1}
$F(000)$	1668
Crystal size	$0.58 \times 0.50 \times 0.26$ mm^{3}
Theta range for data collection	1.37 to 25.25°
Reflections collected	7815
Independent reflections	7014 [R(int) = 0.0155]
Absorption correction	Empirical
Max. and min. transmission	1.0000 and 0.5928
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.914
Final R indices [$I > 2$sigma(I)]	$R1 = 0.0355$, $wR2 = 0.0865$
R indices (all data)	$R1 = 0.0542$, $wR2 = 0.0907$
Extinction coefficient	0.00065(11)
Largest diff. peak and hole	0.688 and -0.449 e.Å^{-3}

$w = 1/[\backslash s^2(Fo^2) + (0.0510P)^2 + 0.0000P]$; $P = (Fo^2 + 2Fc^2)/3$

Synthesis of the Complex

An ethyl acetate solution of $Eu(NO_3)_3 \cdot 6H_2O$ (0.1 mmol) was added dropwise to a solution of the ligand (0.1 mmol) in ethyl acetate (20 cm^3). The mixture was stirred for 4 h and a white precipitate formed. The precipitate was collected and washed three times with ethyl acetate. Further drying in vacuum afforded a pale white powder, yield 75%. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.42$–7.72 (m, 6H), 4.83(s, 4H, 2O–CH_2–C(O)), 3.46 (q, 2H, 2N-CH(R)$_2$, $J = 9.6$ Hz), 1.42 (d, 12H, 2R-(CH_2)$_2$, $J = 9.9$ Hz).

Single crystals of the solvated Eu complex $[Eu(NO_3)L] \cdot 0.5MeCN \cdot H_2O$ were grown and recrystallized from *Me*CN with slow evaporation at room temperature. About 4 h later, transparent crystals formed from the solution.

X-Ray Crystallography

X-Ray diffraction data were collected at 285(2) K on a Siemens P4 four-circle diffractometer with graphite-monochromatized Mo K_α radiation. A summary of crystallographic data and details of the structure refinements are listed in Table 3. The structure was solved by direct methods and refined by full matrix least-squares techniques with all nonhydrogen atoms treated anisotropically. All calculations were performed with the program package SHELXTL.

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 264407. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (E-mail: linstead@ccdc.cam.ac.uk, deposit@ccdc.cam.ac.uk).

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References

[1] Richardson FS (1982) Chem Rev **82**: 541

[2] Hemmilä I, Stahlberg T, Mottram P (1995) Bioanalytial Applications of Labelling Technologies, Wallac Oy, Turku

[3] Desá GF, Malta OL, de Mello Donegá C, Simas AM, Longo RL, Santa-cruz PA, da Silva EF Jr (2000) Chem Rev **196**: 165

[4] Bazzicalupi C, Bencini A, Bianchi A, Giorgi C, Fusi V, Masotti A, Valtancoli B, Roque A, Pina F (2000) Chem Commun **7**: 561

[5] Yang Y-S, Cai S-H (1984) Hua Xue Shi Ji **6**: 133

[6] Ding Y-Z, Lu J-Z, Yang Y-S (1986) Hua Xue Shi Ji **8**: 201

[7] Tan G-Z, Xu J-Z, Jiao T-Q (1986) You Ji Hua Xue **2**: 143

[8] Yang W, Teng X-L, Chem M (1998) Talanta **46**: 527

[9] Greary WJ (1971) Coord Chem Rev **7**: 81

[10] Liu HQ, Cheung TC, Che CM (1996) Chem Commun 1039