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Crystal structure and luminescence of europium 4methoxybenzoate complex with 2,2'-bipyridine $[Eu(p-MOBA)_3 bipy] \cdot 1/2C_2H_5OH$

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Abstract

Europium 4-methoxybenzoate complex with 2,2'-bipyridine, $[Eu(p-MOBA)_3bipy] \cdot 1/2C_2H_5OH$ (where *p*-MOBA=4-methoxybenzoate and bipy=2,2'-bipyridine), was obtained in the ethanol solution and the crystal structure was determined by X-ray diffraction. The crystal consists of binuclear molecules of the title compound. In the complex each Eu³⁺ ion is nine-coordinate to one bipyridine molecule, one bidentate carboxylate group and four bridging carboxylate groups in which the carboxylate groups are bonded to the europium ion in three modes: the chelating bidentate, the bridging bidentate and the bridging tridentate. Excitation and luminescence data observed at 77 K show that the Eu³⁺ ion site in the complex has low symmetry and when excited a slight change of chemical environments of the Eu³⁺ ion is observed. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Europium complex; Crystal structure; Luminescence

1. Introduction

Because of variations of the bonding forms of carboxylate anions, many different types of crystal structure of ternary lanthanide complexes with aromatic acid and nitrogen-containing ligands were obtained [1-7]. These complexes show an intensely fluorescent character and the crystals are stable in air. Such characteristics are essential to the study of the structures and luminescence of the complexes and to seeking newly fluorescent materials and applications of luminescent probes [8,9]. The Eu³⁺ ion is chosen as a probing ion because of its non-degenerate ground state of ⁷F₀ and non-overlapping $^{2}s + 1L_{J}$ multiplets. Bünzli has discussed the selection rules of electric dipole and magnetic dipole transitions for ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ transitions (J=0-6) of the Eu³⁺ ion in both centrosymmetric and non-centrosymmetric complexes [8]. We report here the results of an X-ray diffraction analysis and luminescence spectra of the title complex.

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2. Experimental

2.1. Synthesis of $[Eu(p-MOBA)_3 \cdot bipy] \cdot 1/2C_2H_5OH$

3 mmol *p*-HMOBA was dissolved in 20 ml 95% C_2H_5OH and its pH was controlled in a range of 6–7 with 1 ml⁻¹ NaOH solution, to which 1 mmol bipyridine dissolved in 10 ml 95% C_2H_5OH was added. The mixed solution was dropped into the EuCl₃ solution obtained by 1 mmol EuCl₃· 6H₂O dissolved in 10 ml 95% C_2H_5OH . The mixture was heated under reflux with stirring for 8 h. A white precipitate was formed. Single crystals were obtained from the mother liquor after 3 weeks at room temperature.

The complex obtained in a powder form was characterized by elemental analysis, IR and Raman spectra. Analysis for the complex gave the following, found (%): C, 53.42; H, 3.78; N, 3.52; calc. (%): C, 53.62; H, 3.84; N, 3.68. Characteristic bands of asymmetric and symmetric vibrations of carboxylate anions appear in the spectra of the complex: $v_{as}(COO) = 1562 \text{ cm}^{-1}$, $v_{s}(COO) =$ 1418 cm^{-1} (IR); $v_{as}(COO) = 1569 \text{ cm}^{-1}$, $v_{s}(COO) =$ 1422 cm^{-1} (Raman). Other main data are $v(C=C)_{ar} = 1607 \text{ cm}^{-1}$, 1476 cm^{-1} , 1457 cm^{-1} , 1437 cm^{-1}

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(IR); $v(C==C)_{ar} = 1603 \text{ cm}^{-1}$, 1478 cm⁻¹ (Raman), ring deformation: 1593 cm⁻¹ (IR); 1594 cm⁻¹ (Raman) and $v(OH) = 3425 \text{ cm}^{-1}$ (IR). The title complex is soluble in DMSO and DMF, slightly soluble in ethanol and THF and insoluble in water and acetone.

2.2. Crystal structure determination

The crystal system, accurate cell constants, space group and intensity data were obtained from X-ray analysis of the crystal which was mounted on a Rigaku AFCTR Xray diffractometer using graphite monochromated MoK α radiation. Data were collected by an ω -2 θ scan technique for $3 < \theta < 22.5^{\circ}$ with indices in the range of $0 \le h \le 13$, $-14 \le k \le 14$, $-12 \le l \le 11$ and were corrected for Lorentz-polarization and absorption effects. All calculations were performed using the Texsan crystallographic software package of the Molecular Structure Corporation. The structure of $[Eu(p-MOBA)_3 \cdot bipy] \cdot 1/2C_2H_5OH$ was solved by direct methods and refined with the full-matrix least-squares technique to R = 0.020 and Rw = 0.026. A summary of the crystallographic data and data collection and refinement parameters is given in Table 1.

Table 1	
Experimental	details

Chemical formula	$C_{70}H_{64}O_{19}N_4Eu_2$
Color	colorless
Crystal size (mm)	$0.20 \times 0.20 \times 0.30$
Crystal system	triclinic
Space group	ΡĪ
a (nm)	1.1482(3)
b (nm)	1.3901(2)
<i>c</i> (nm)	1.0948(2)
α (°)	103.63(1)
β (°)	92.67(2)
γ (°)	84.54(2)
$V(\text{nm}^3)$	1.6901(6)
Ζ	1
M	1569.21
$D_{\rm c} \left({\rm g}\cdot{\rm cm}^{-3}\right)$	1.54
<i>F</i> (000)	790
λ (nm) (MoK α)	0.071069
Temperature (K)	293 ± 1
θ range	3-22.5
Reflections collected	4675
Independent reflections	$4414 (R_{int} = 0.011)$
Observed reflections	$4088 [I \ge 3.000(1)]$
Number of parameters refined	443
Final <i>R</i> and <i>Rw</i>	0.020 and 0.026
Goodness-of-fit on F^2	1.56
Maximum Δ/σ	0.01
Largest diff. peak and hole $(e \mathring{A}^3)$	0.54 and 0.46

2.3. Spectral determination

The excitation and luminescence spectra of the complex were recorded as described in Ref.[10]. The conventional luminescence spectra were measured with HRG.9-5-90 N₂ laser using Spex 1403 double grating monochrometer. The high excitation and emission spectra were performed at 77 K using a PLT-2000 dye laser (rhodamine 6G) pumped by N₂ laser. IR and Raman spectra were recorded on Nicolet 71998 B FT-IR spectrometer and 910 FT-Raman spectral system, respectively.

Elemental analysis was performed by Perkin-Elmer 240-C analyzer.

3. Results and discussion

3.1. Crystal studies

The molecular structure and atomic numbering of the complex are shown in Fig. 1. The selected bond distances and angles are listed in Table 2. The two Eu^{3+} ions are linked by the four carboxylate groups through their bidentate and tridentate bridging modes, forming a dimeric unit with crystallographic inversion centre. The Eu...Eu distance is 0.40482(6) nm. Each europium ion is coordinated to nine atoms, of which five oxygen atoms are from the bridging carboxylates, two oxygen atoms from the chelating carboxylate group and two nitrogen atoms from a bipyridine molecule. Compared with ternary lanthanide complexes containing p-methylbenzoic acid and *p*-aminobenzoic acid as ligands the title complex is unlike the complexes $Eu(p-MBA)_3bpy [4] (p-MBA = p$ methylbenzoate) and Eu(p-ABA)₃bpy·2H₂O [5] (p-ABA = p-aminobenzoate) in which the Eu^{3+} ions are both eight-coordinated and there is no μ_3 -O bridge in the latter complexes. Because of formation of the μ_3 -O bridge in the $[Eu(p-MOBA)_3 \cdot bipy] \cdot 1/2C_2H_5OH$ complex the average Eu-O [Eu-O(4), Eu-O(5)* and Eu-O(2)*] bond distance formed by the bridging carboxylates is 0.2378 nm and the average Eu-O [Eu-O(1), Eu-O(2) and Eu-O(7) and Eu-O(8)] distance found in the chelating carboxylate groups is 0.2543 nm. They are a little larger than corresponding average distances 0.2369 and 0.2470 nm found in the Eu(p-MBA)₃bpy complex [4]. Average bond length of Eu-N in the title complex is 0.2629 nm which is slightly smaller than average Eu-N distance, 0.2637 nm, in the Eu(p-MBA)₃bpy complex. These indicate that interaction between the europium ion and the oxygen atom in [Eu(p-MOBA)₃bipy] $\cdot 1/2C_2H_5OH$ is weaker than that in the complex Eu(p-MBA)₃bpy and interaction between the europium ion and nitrogen atom in the title complex is stronger than that in $Eu(p-MBA)_3$ bpy. This is possibly related to electronic effect and larger steric effect of the



Fig. 1. Molecular structure of $Eu(p-MOBA)_3bpy \cdot \frac{1}{2}C_2H_5OH$.

methoxy group on the benzene ring. Calculated results show that the dihedral angle between the two pyridyls is 9.68° . The five atoms of the chelated ring containing the chelated nitrogen atoms and the europium atom are not coplanar. Bipyridine is unlike 1,10-phenanthroline in a

similar complex, $Eu(p-MOBA)_3$ phen (phen = 1,10-phenanthroline) in which phen and the chelated ring are coplanar [11]. The differences in geometry arise from fact that the free 2,2'-bipyridine is in *trans*-form while it is in *cis*-form when chelated by a metal ion. The bipyridine

Bond distances										
Atom	Atom	Distance		Atom	Atom	Distance				
Eu	O(1)	0.2426(2)		Eu	O(2)	0.2840(3)				
Eu	O(2)*	0.2372(2)		Eu	O(4)	0.2373(2)				
Eu	O(5)*	0.2387(2)		Eu	O(7)	0.2405(2)				
Eu	O(8)	0.2501(3)		Eu	N(1)	0.2599(3)				
Eu	N(2)	0.2658(3)								
Bond angles (°)										
Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle			
O(1)	Eu	O(2)	48.59(7)	O(1)	Eu	O(2)*	127.04(8)			
O(1)	Eu	O(4)	81.47(8)	O(1)	Eu	O(5)*	89.61(8)			
O(1)	Eu	O(7)	139.87(8)	O(1)	Eu	O(8)	138.54(8)			
O(1)	Eu	N(1)	71.62(9)	O(1)	Eu	N(2)	69.36(8)			
O(2)	Eu	O(2)*	78.46(8)	O(2)	Eu	O(4)	67.33(7)			
O(2)	Eu	O(5)*	73.76(7)	O(2)	Eu	O(7)	158.91(8)			
O(2)	Eu	O(8)	138.96(7)	O(2)	Eu	N(1)	114.25(8)			
O(2)	Eu	N(2)	109.58(8)	O(2)*	Eu	O(4)	77.13(8)			
O(2)*	Eu	O(5)*	73.59(8)	O(2)*	Eu	O(7)	89.78(8)			
O(2)*	Eu	O(8)	79.63(8)	O(2)*	Eu	N(1)	147.77(9)			
O(2)*	Eu	N(2)	145.16(8)	O(4)	Eu	0(5)*	134.94(8)			
O(4)	Eu	O(7)	127.33(8)	O(4)	Eu	O(8)	74.21(8)			
O(4)	Eu	N(1)	80.99(8)	O(4)	Eu	N(2)	137.64(8)			
O(5)*	Eu	O(7)	86.21(8)	O(5)*	Eu	O(8)	131.11(8)			
O(5)*	Eu	N(1)	137.38(8)	O(5)	Eu	N(2)	76.39(8)			
O(7)	Eu	O(8)	53.20(8)	O(7)	Eu	N(1)	84.93(9)			
O(7)	Eu	N(2)	70.87(8)	O(8)	Eu	N(1)	71.77(9)			
O(8)	Eu	N(2)	108.26(9)	N(1)	Eu	N(2)	61.32			

Table 2 Selected bond distances (nm) and angles (°)

molecule is flexible, however, the 1,10-phenanthroline molecule is rigid.

3.2. Excitation and luminescence spectra

The excitation spectra of the $[Eu(p-MOBA)_3]$ bipy] $\cdot 1/2C_2H_5OH$ were obtained at 77 K in a range of 578-582 nm monitored at several wavenumbers of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ components as shown in Fig. 2. The narrowing lines in all traces show that the lowest excited state ${}^{5}D_{0}$ level positions differ within 4 cm^{-1} . The highest energy position lies at 17238 cm^{-1} and the lowest one locates at 17234 cm⁻¹. Since the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition is a hypersensitive one, the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition band is very sensitive to the chemical environment of the Eu^{3+} ion in compounds. Fluorescence was observed in a range of 605–630 nm which covers the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of the europium ion. The fluorescence spectra obtained upon nonselective and site selective excitation are shown in Fig. 3. The upper trace (a) is a fluorescence spectrum excited with 337.1 nm N₂ laser emission. The lower traces (b-d) were obtained upon the selective excitation at 580.14, 580.20 and 580.25 nm, respectively. The nonselectively excited emission spectrum (a) shows relatively broad bands of 2J+1 components. However the selec-

tively excited emission bands show fine structure of Jsplitting. The b-d traces differ from each other in split band positions and band intensities. Each trace is composed of more than 2J+1 peaks which may arise from simultaneous excitation of the Eu³⁺ ions in different environments. The fact that 2J+1 components and O-O transition are observed implies that the Eu³⁺ ion site must be of low symmetry which is in agreement with the results of X-ray analysis. It can be seen from Fig. 3 that the largest difference for the a-d traces is located in a range of 16300–16260 cm⁻¹. The split sharp lines resulting from slightly different environments of the Eu(III) site are obviously observed in the selective excitation mode. The other four peaks are centred at ~16240, 16191, 16145 and 16125 cm^{-1} although there may be a few wavenumbers shifted. The results of the spectral observation show that the europium ions in the [Eu(p-MOBA)₃bipy] $\cdot 1/2C_2H_5OH$ are in slightly different chemical environments due to the conformational change of the bipyridyl which is a flexible ligand mentioned as above. The change in conformation of the complex gives a significant effect on ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition properties. This may be attributed to (1) different stacking of the molecular components of $[Eu(p-MOBA)_3bipy] \cdot 1/2C_2H_5OH$ in the crystal, (2) a transient perturbation of donor-



Fig. 2. Excitation spectra of $[Eu(p-MOBA)_3 bipy] \cdot 1/2C_2H_5OH.$ (a) Monitored at 16270 cm⁻¹; (b) monitored at 16282 cm⁻¹ and (c) monitored at 16125 cm⁻¹.

acceptor interaction caused by the rapid conversion of the complex conformation including non-planar geometry of the bipyridyl. The latter illustrates the impact of nonequilibrium molecular dynamics occurring subsequent to electronic excitation.

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Fig. 3. Luminescence spectra of $[Eu(p-MOBA)_3bipy]$ · $1/2C_2H_5OH$. (a) Excited by 337.1 nm (N₂ laser emission); (b) selectively excited by 580.14 nm; (c) selectively excited by 580.20 nm and (d) selectively excited by 580.25 nm.

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