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Crystal structure and luminescence of a new europium coordination polymer $\{[\text{Eu}(\alpha\text{-FURA})_3 \cdot 2\text{H}_2\text{O}] \cdot \text{NO}_3(4,4'\text{-Hbpy})\}_\infty$

X. Li[a,b], X. Zheng[a], L. Jin[a,*], S. Lu[c], J. Zhang[c]

[a]Department of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China
[b]Department of Chemistry, Capital Normal University, Beijing 100037, People's Republic of China
[c]Laboratory of Excited State Processes, Chinese Academy of Sciences, Changchun 130021, People's Republic of China

Abstract

The structure of a europium complex $\{[\text{Eu}(\alpha\text{-FURA})_3 \cdot 2\text{H}_2\text{O}] \cdot \text{NO}_3(4,4'\text{-Hbpy})\}_\infty$ (α-FURA: α-furoate, 4,4′-Hbpy: protonated 4,4′-bipyridine) was determined by single crystal X-ray diffraction. Each europium is coordinated with two oxygen atoms of chelated carboxyl group, four oxygen atoms of bridging carboxyl groups and two oxygen atoms from two water molecules forming a coordination polymer with coordination number of eight. 4,4′-bipyridine is protonated and one of the bonded water molecules forms hydrogen bond with NO_3^- in the crystal. The luminescence behavior of the Eu^{3+} ion in $\{[\text{Eu}(\alpha\text{-FURA})_3 \cdot 2\text{H}_2\text{O}] \cdot \text{NO}_3(4,4'\text{-Hbpy})\}_\infty$ was observed at 77 K. Its luminescence lifetime and the emission spectra of $^5\text{D}_1 \rightarrow {}^7\text{F}_J$ ($J = 1\text{–}3$) and $^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J = 0\text{–}4$) transitions were measured. The complex displays intense luminescence and the Eu^{3+} ions in the polymer occur in the same chemical environment. And its crystal structure also shows that only one site for Eu^{3+} ion is in the europium coordination polymer. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: X-ray crystallography; Europium complex; Luminescence property

1. Introduction

Rare earth carboxylate has been widely studied due to the variety of its structure [1,2]. We have carried out quite a few studies on the structures and luminescence properties of the ternary rare earth carboxylate complexes with aromatic diamines such as 1,10-phenanthroline(phen) and 2,2′-bipyridine(2,2′-bipy) [3–11]. Especially, the ternary europium complexes of aromatic carboxylic acid with aromatic diamines, because the lowest excited triplet energy of the ligand matches the lowest emission energy level of the europium(III) ion. Such complexes generally have strong

fluorescence. We have studied the binary complex of $\text{La}(\text{NO}_3)_3$ with furancarboxylic acid, $\text{La}(\text{FURA})_3 \cdot 2\text{H}_2\text{O}$ [12], in which the carboxyl O atoms coordinate with La in chelated bidentate and bridging tridentate modes. As a part of our series of studies for the ternary rare earth carboxylate complexes, this paper presents the crystal structure and high resolution luminescence spectra of $\{[\text{Eu}(\alpha\text{-FURA})_3 \cdot 2\text{H}_2\text{O}] \cdot \text{NO}_3(4,4'\text{-Hbpy})\}_\infty$.

2. Experimental

2.1. Synthesis of $\{[\text{Eu}(\alpha\text{-FURA})_3 \cdot 2\text{H}_2\text{O}] \cdot \text{NO}_3(4,4'\text{-Hbpy})\}_\infty$

1.5 mmol α-furancarboxylic acid and 0.5 mmol 4,4′-bipyridine were dissolved in 20 ml 95% ethanol

* Corresponding author. Tel.: +86-10-6220-7838; fax: +86-10-6220-0567.
  E-mail address: lpjin@bnu.edu.cn (L. Jin).

Table 1
Crystal data for $\{[Eu(\alpha\text{-FURA})_3 \cdot 2H_2O] \cdot NO_3(4,4'\text{-Hbpy})\}_\infty$

Formula weight	740.42
Temperature	293 K
Radiation	0.71069 Å
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	$a = 9.756(1)$ Å, $b =$ 16.300(2) Å, $c = 17.417(3)$ Å
Volume	2769(1) Å^3
Z	4
Density (calculated)	1.776 g cm^{-3}
Absorption coefficient	23.4 cm^{-1}
$F(000)$	1472.00
Crystal size	$0.20 \times 0.20 \times 0.30$ mm^3
$2\theta_{max}$	55°
Index ranges	$-12 \leq h \leq 0$, $21 \leq k \leq 0$, $0 \leq 1 \leq 22$
Reflections collected	3587
Independent reflections	2196
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2196/0/257
Goodness-of-fit on F^2	1.61
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.032$, $\omega R_2 = 0.039$
Largest differential peak and hole	0.79 and $-0.87 e$Å^{-3}

and its pH was controlled in a range of 6–7 with 2 mol l^{-1} NaOH. Then 6 ml of Eu(NO$_3$)$_3 \cdot n$H$_2$O (0.5 mmol) aqueous solution was added. The mixture was heated under reflux with stirring for 6 h and filtered. The next day crystals of $\{[Eu(\alpha\text{-FURA})_3 \cdot 2H_2O] \cdot NO_3(4,4'\text{-Hbpy})\}_\infty$ were obtained from the mother liquor.

2.2. Crystal structure determination

The X-ray data collection was carried out by an automated Rigaku AFC7R diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71069$ Å). The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the Texsan [13] crystallographic software package of Molecular Structure Corporation. The crystal data and experimental details are shown in Table 1.

2.3. Excitation and emission spectral measurements

The luminescence spectra were recorded with

YAG:Nd^{3+} laser using Spex1403 double grating monochromator. High-resolution spectral recording was performed at 77 K using PLT-2000 laser (rhodamine 6G) pumped by N$_2$ laser.

3. Results and discussion

The molecular structure of $\{[Eu(\alpha\text{-FURA})_3 \cdot 2H_2O] \cdot NO_3(4,4'\text{-Hbpy})\}_\infty$ is shown in Fig. 1. The selected bond lengths and bond angles are tabulated in Tables 2 and 3. Fig. 1 shows that the Eu atoms are coordinated to eight O atoms, six of which (O1*, O2, O4, O5, O7*, O8) are from five different carboxylate groups and two O atoms (O10, O11) from two independent water molecules. None of the furyl O atoms are coordinated to the Eu^{3+} ions. The carboxylate ligands adopt two different coordination modes in the crystal: O1–C1–O2 group is in a bridging mode in which two O atoms coordinate to two different Eu^{3+} ions, O4–C6–O5 group is in a chelating mode in which two O atoms link to the same Eu^{3+} ion, forming an unstable four-membered ring. Unlike catena-diaquatris(α-furan-carboxylato)-lanthanum [12] we observed that the nitrate O atom forms hydrogen bond with the OH group of the coordinated water molecule (O11–H12···O13) in which the O11–H12 distance is 0.96 Å and H12···O13, 2.13 Å, and intermolecular hydrogen bond between the adjacent 4,4'-bpy molecules (N1–H22···N2*) is formed in which the N1–H22 distance is 0.97 Å and H22···N2*, 1.862 Å. Coordination number, average distances of Eu–O(H$_2$O) and of Eu–O(carboxylato) of the title complex are 8, 2.454 and 2.404 Å, respectively. It is reasonable that the corresponding structural data of the lanthanum complex [12] are larger than those mentioned above as the radius of the La^{3+} ion is larger than that of the Eu^{3+} ion. The calculated results of the least square planes show that the two furyl groups linked to the bridging carboxylato groups are approximately parallel. The dihedral angle is 8.21°. We observed the regular stacking of the furyl groups in the crystal as stacking of aromatic rings is commonly found [14]. However, the dihedral angle between the two pyridyl rings is 134° in the unbonded 4,4'-bpy molecules.
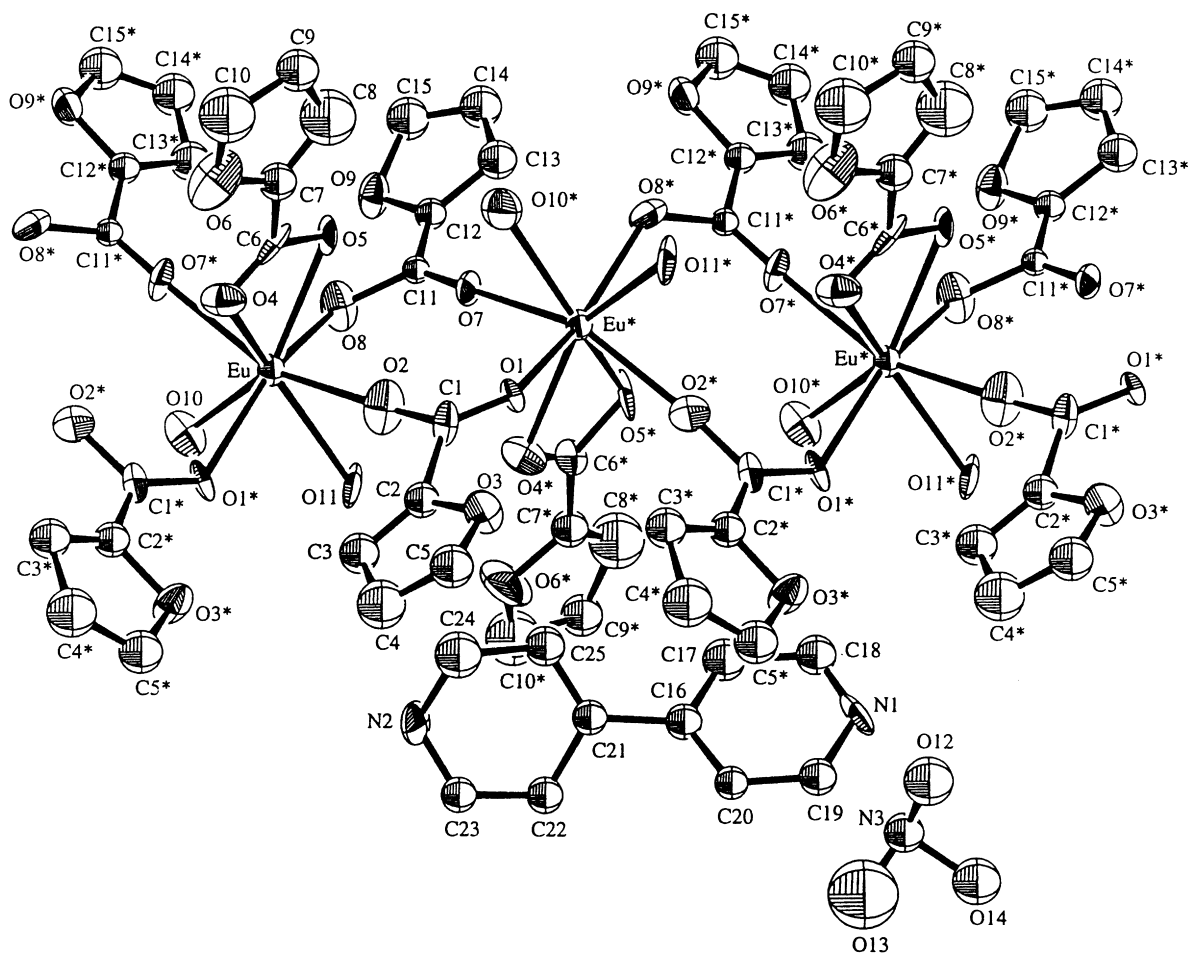
Fig. 1. Molecular structure of $\{[Eu(\alpha\text{-}FURA)_3\cdot 2H_2O]\cdot NO_3(4,4'\text{-}Hbpy)\}_\infty$.

The time-resolved spectra of the europium coordination polymer $\{[Eu(\alpha\text{-}FURA)_3\cdot 2H_2O]\cdot NO_3(4,4'\text{-}Hbpy)\}_\infty$ are shown in Fig. 2. The weak emission lines arising from $^5D_1 \rightarrow {}^7F_J$ ($J = 1, 2, 3$) were observed when delay time was 5 μs. However, $^5D_1 \rightarrow {}^7F_J$ transition bands disappear after a 30 μs

Table 2
Selected bond distances (Å)

Atom	Atom	Distance	Atom	Atom	Distance
Eu	O(1)*	2.383(8)	Eu	O(2)	2.32(1)
Eu	O(4)	2.48(1)	Eu	O(5)	2.56(1)
Eu	O(7)*	2.328(8)	Eu	O(8)	2.359(9)
Eu	O(10)	2.46(1)	Eu	O(11)	2.447(9)

Table 3
Selected bond angles (°)

| Atom	Atom	Atom	Angle	Atom	Atom	Atom	Angle
O(1)*	Eu	O(2)	82.3(3)	O(1)*	Eu	O(7)*	104.2(3)
O(1)*	Eu	O(4)	76.5(3)	O(1)*	Eu	O(10)	79.8(3)
O(1)*	Eu	O(5)	124.7(3)	O(1)*	Eu	O(8)	157.2(2)
O(1)*	Eu	O(11)	85.2(3)	O(2)	Eu	O(4)	82.0(4)
O(2)	Eu	O(5)	73.4(4)	O(2)	Eu	O(7)*	150.5(2)
O(2)	Eu	O(8)	102.7(4)	O(2)	Eu	O(10)	137.9(4)
O(2)	Eu	O(11)	69.9(4)	O(4)	Eu	O(5)	51.8(2)
O(4)	Eu	O(7)*	72.0(3)	O(4)	Eu	O(10)	129.2(3)
O(4)	Eu	O(8)	126.0(4)	O(5)	Eu	O(7)*	79.6(3)
O(4)	Eu	O(11)	148.2(3)	O(5)	Eu	O(8)	77.7(4)
O(5)	Eu	O(10)	146.3(4)	O(5)	Eu	O(11)	128.0(3)
O(7)*	Eu	O(8)	82.6(3)	O(7)*	Eu	O(10)	71.3(4)
O(7)*	Eu	O(11)	138.6(4)	O(8)	Eu	O(11)	76.0(4)
O(8)	Eu	O(10)	81.9(3)	O(10)	Eu	O(11)	70.9(2)
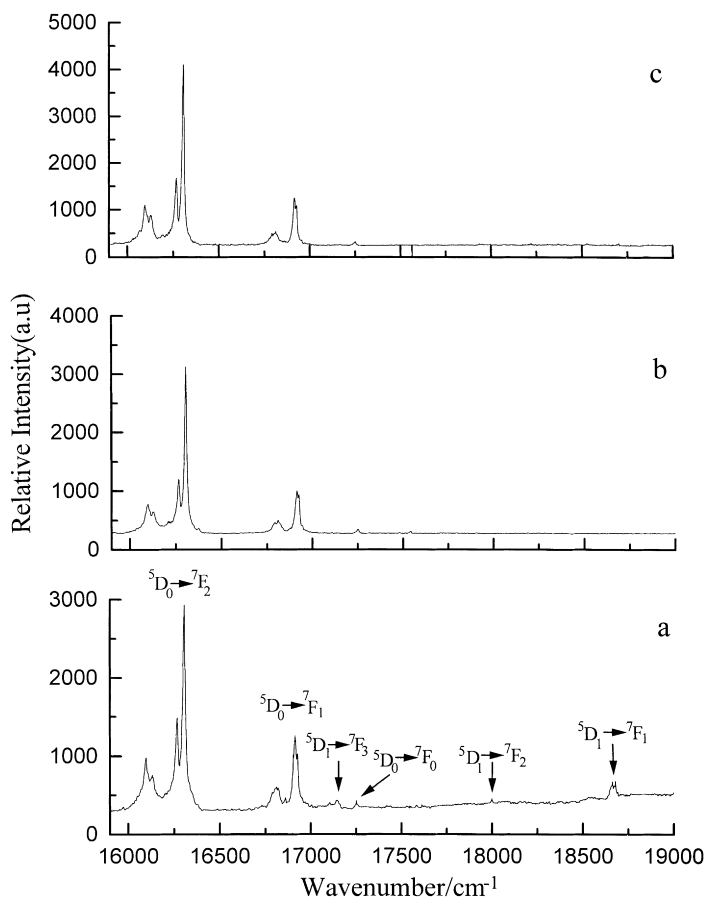
Fig. 2. Time resolved spectra of $\{[Eu(\alpha\text{-}FURA)_3\cdot 2H_2O]\cdot NO_3(4,4'\text{-}Hbpy)\}_\infty$. $\lambda_{exc} = 355$ nm, 77 K. (a) Delay time: 5 μs. (b) Delay time: 30 μs. (c) Delay time: 100 μs.

delay, while $^5D_0 \rightarrow {}^7F_J$ emission bands increase. This shows that the lifetimes of $^5D_1$ and $^5D_0$ are different. The lifetime of $^5D_1$ is much shorter than that of $^5D_0$ emitting level. This also indicates that the lowest triplet state of the ligand α-FURA is higher than the emission level $^5D_1$ of the Eu^{3+} ion and rapid process of energy transfer from $^5D_1 \rightarrow {}^5D_0$, followed by $^5D_0$ emission, and it is not exclusive that energy directly transfers from the triplet level of the ligand to $^5D_0$ level of the Eu^{3+} ion, and then $^5D_0 \rightarrow {}^7F_J$ transitions take place.

The emission line at $17\,252$ cm^{-1}, though it is weak, might easily be taken as $^5D_0 \rightarrow {}^7F_0$ transition of one Eu^{3+} ion site. The three lines at 16 927, 16 915 and 16 802 cm^{-1}, are assigned to $^5D_0 \rightarrow {}^7F_1$ transitions. Since $^7F_1$ is three-fold degenerate this splitting

leads to the three components expected to occur in a low-symmetry situation, which is in agreement with results of X-ray single crystal analysis. The intense lines in the region between 15 900 and 16 500 cm^{-1}, are attributed to $^5D_0 \rightarrow {}^7F_2$ transitions. These transitions exhibit a so-called hypersensitivity with respect to changes in the environment. Often, important vibrational satellites are found in this region due to distinct vibronic coupling. Possibly, several of these weak transitions may be assigned to vibronic lines. The intensity ratio of $^5D_0 \rightarrow {}^7F_2/^5D_0 \rightarrow {}^7F_1$ is ca. 3.7, which also confirms low-symmetry of the Eu^{3+} ion site.

Fig. 3 shows the decay curve of the $^5D_0$ emitting level of the Eu^{3+} ion, monitored at 613.3 nm under excitation of 355 nm. The measured lifetime is
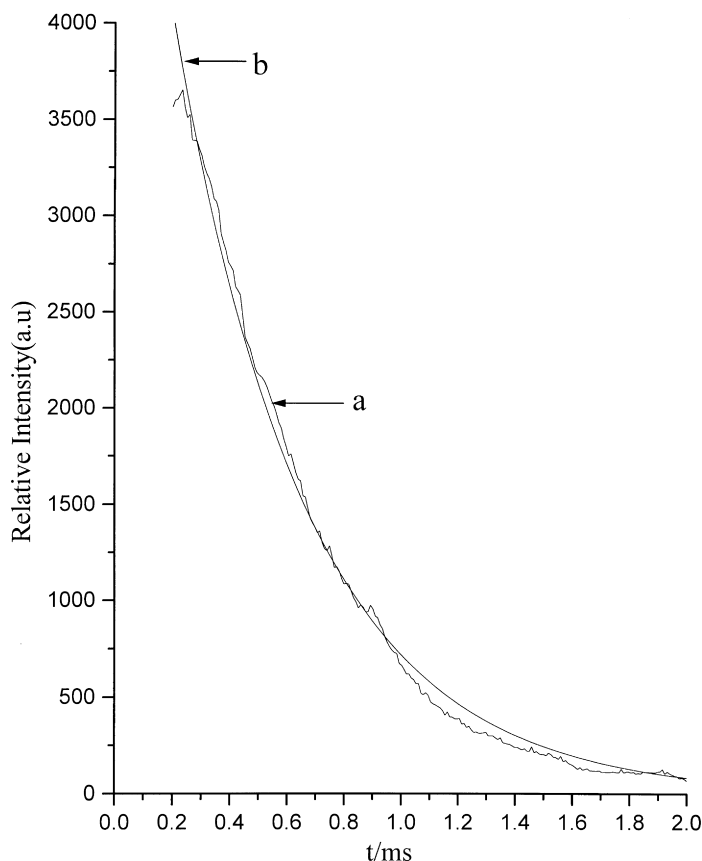
Fig. 3. Decay curve of $\{[Eu(\alpha\text{-FURA})_3 \cdot 2H_2O] \cdot NO_3(4,4'\text{-Hbpy})\}_\infty$, at 77 K. (a) Observed curve. (b) Fitting curve.

0.46 ms, which is shorter than that of the ternary europium complex which has no bonded water molecules [4]. This might be due to non-radiation transition of the water molecules bonded to the Eu^{3+} ion, which can deactivate $^5D_0$ level and thus shorten the lifetime of the Eu^{3+} emission level $^5D_0$.

Acknowledgements

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