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Synthesis, Crystal Structure, and Luminescence Properties of a One-Dimensional Europium(III) Polymer[1]

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Abstract—In the title complex, $[Eu_2(C_8H_7O_3)_6(C_{12}H_8N_2)_2]_n$, which has an inversion center midway between two Eu(III) atoms of the structural unit, forms a one-dimensional polymer bridged by two mondentate, two bidentate, and two tridentate carboxylate groups with an Eu–Eu separation of 4.1853(7) Å. Each Eu atom is nine-coordinated by two N atoms of a 1,10-phenanthroline (phen) ligand and seven O atoms from six phenoxyacetate ligands, to form a distorted tricapped trigonal prismatic. The luminescence spectrum of the polymer indicates that the intensity of the emission wavelength at 619 nm is the strongest among all emission wavelengths and the second phen ligand shows an enhancement effect on the luminescence of the complex.

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INTRODUCTION

As is well known, owing to the lanthanides exhibiting large radii, high coordination numbers, and special luminescence properties, growing attention has been paid to the investigation of lanthanide coordination polymers [1–5]. Ligands coordinating with lanthanides play an important role during emission processes, so, in recent years, many ligands containing bi- or multidentate oxygen, nitrogen, or sulfur donors have been used to build lanthanide coordination polymers [6–8]. Among the ligand systems, one ligand containing carboxylate groups is popularly used in synthetic systems for the construction of polymeric structures because of their various coordination modes to metal cations, such as monodentate, chelating bidentate, bridging bidentate, and bridging tridentate [9]. This proved that lanthanide(III) aromatic carboxylates display good luminescence properties owing to the high efficiency of light conversion of aromatic carboxylic groups [10], and another bidentate chelating ligand like 1,10-phenanthroline or dipyridine with symmetric and conjugated structure can not only result in the effective intramolecular energy transfers from the excited state of the ligands to the emitting level of the lanthanide ions, but also prevent the coordination of water molecules with O–H vibration to quench the luminescence of lanthanide ions [11–12]. However, most of the reported lanthanide coordination polymers are hydrated and/or contain inner coordinated water molecules [13–15]. Eu(III) has more excellent luminescence properties in their ternary complexes with aromatic acids and ligands containing nitrogen than their carboxylate hydrates. The aim of this work is to prepare and study the luminescence properties of the anhydrous mixed lanthanides complexes with phenoxyacetate and 1,10-phenanthroline. Herein, we report the solvothermal synthesis, structural features, and luminescence properties of a novel lanthanide coordination polymer $[Eu_2(C_8H_7O_3)_6(C_{12}H_8N_2)_2]_n$ (**I**).

EXPERIMENTAL

Apparatus and reagents. All the reagents and solvents from commercial sources were of AR grade purity. Element analysis of carbon, hydrogen, and nitrogen was performed with a Flash-EA1112 elemental analyzer. The emission and excitation spectra of the samples were obtained using a PerkinElmer LS 55 luminescence spectrometer with a Xe flash lamp at room temperature. The excitation and emission slits were set at 2.5 nm. The excitation spectra were automatically corrected for the variation in the lamp intensity by a second photomultiplier and a beam splitter. The emission spectra were corrected by dividing the measured emission intensity by the ratio of the observed spectrum of a calibrated W lamp and its known spectrum from 300 to 900 nm. All of the spectra were measured with a scan speed of 1000 nm/min.

X-Ray diffraction analysis. A yellow single crystal with dimensions of 0.32 × 0.13 × 0.08 mm was selected for diffraction analysis. Data collection was performed on a Bruker APEX-II CCD area-detector diffractometer equipped with a graphite-monochromatized MoK_α

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[1] The text was submitted by the authors in English.

radiation ($\lambda = 0.71073$ Å) at 273(2) K. A total of 26 800 reflections were collected by using an ω–2θ scan mode, of which 7358 were unique with $R_{\text{int}} = 0.0426$ and used in the succeeding structure calculations. Data intensity was corrected by the Lorentz polarization factors and empirical absorption. The non-hydrogen atoms were solved by direct methods and subsequent difference Fourier synthesis. The hydrogen atoms were calculated in ideal positions and refined with a riding model. The final cycle of full-matrix least-squares refinement was based on 4933 observed reflections ($I > 2\sigma(I)$) and 403 variable parameters and converged with weighed agreement factors. The final refinement including hydrogen atoms converged to 0.0478 and $wR = 0.1371$ ($w = 1/[\sigma^2(F_0^2) + (0.0939P)^2 + 0.7782P]$, where $P = (F_0^2 + 2F_c^2)/3$), $S = 0.999$, $(\Delta/\sigma)_{\max} = 0.002$, $(\Delta\rho)_{\max} = 0.002$, and $(\Delta\rho)_{\min} = -0.867$ e Å^{-3}. All calculations were performed with SHELXTL-97 program package [16].

Synthesis of the complex. Crystals of the title complex were synthesized using the solvothermal method in a 23-ml teflon-lined Parr bomb, which was then sealed. Anhydrous europium(III) chloride (258.5 mg, 1 mmol), Phen (198.2 mg, 1 mmol), phenoxyacetate (302.2 mg, 2 mmol), and tetrahydrofuran (10 ml) were placed into the bomb and sealed. The bomb was then heated under autogenous pressure up to 413 K over the course of 7 days and allowed to cool at room temperature for 24 h. Upon opening the bomb, a clear colorless solution was decanted from small yellow crystals. These crystals were washed with ethanol and allowed to air-drying at room temperature. The yield, as calculated with respect to the europium chloride, was 45.3%.

For $C_{72}H_{58}Eu_2N_4O_{18}$

anal. calcd, %:	C, 54.99;	H, 3.69;	N, 3.56.
Found, %:	C, 55.06;	H, 3.72;	N, 3.59.

RESULTS AND DISCUSSION

Complex I crystallizes in monoclinic crystal system, space group $P2_1/n$ with $a = 19.8127(11)$, $b = 8.4405(16)$, $c = 21.0036(14)$ Å, $\beta = 108.017(3)°$, $V = 3340.2(7)$ Å^3, $C_{72}H_{58}Eu_2N_4O_{18}$, $M_r = 1571.14$, $Z = 2$, $\rho_{\text{calcd}} = 1.562$ g/cm^3, $\mu = 1.936$ mm^{-1}, $F(000) = 1576$. The molecule of complex I features a dinuclear structure and the Eu atoms are bridged by two tridentate, two bidentate, and four monodentate carboxylate groups with an inversion center between the two Eu^3 ions. Eu(1) is coordinated by one phen ligand via N(1) and N(2) atoms; two bridging bidentate phenoxyacetate ligands via O(1) and O(2)$^{\text{i}}$; two bridging tridentate phenoxyacetate ligands via O(7), O(8), and O(8)$^{\text{i}}$; and two chelating mondentate phenoxyacetate ligands via O(4) and O(5)$^{\text{ii}}$ with a distorted tricapped trigonal prism geometry (Fig. 1). The quadrangular faces are defined by two nitrogen atoms from the chelating phen ligand, one carboxylate oxygen atom from the bidentate phenoxyacetate ligand, and the other carboxylate oxygen atom from the tridentate phenoxyacetate ligand (O(2)$^{\text{i}}$, O(8)$^{\text{i}}$, N(1), and N(2)) with a mean deviation of 0.2752 Å from the least-squares plane. The two N atoms and two C atoms of phen and one Eu atom make up a five-membered ring with Eu–N bond distances of 2.694(4) and 2.701(5) Å and an NEuN angle of 61.26(15)° (Table 1), which is one of the most stable structures and helps to stabilize the whole structure of the complex. The average Eu–N bonds of complex I (2.697 Å) are slightly longer than those of [Eu(p-MOBA)$_3$(Phen)] (2.624 Å) and [Eu(DBM)$_3$(Phen)] (2.656 Å) [17, 18]. The Eu–O distances are in the range of 2.389(4)–2.802(4) Å, which could indicate that the carboxylate groups are bound to the Eu^{3+} ions in three different coordination fashions. This shows that there is a different degree of electron delocalization in the area of O–C–O atoms. The average of the bridging bidentate Eu–O bonds (2.525(8) Å) is slightly shorter than that of the bridging tridentate Eu–O bonds (2.575(3) Å), which in turn is longer than the average of the chelating mondentate Eu–O bonds (2.472(8) Å). The Eu–O bonds in complex I are longer than the equivalent bonds in the reported coordination compound [19] but are similar to the La(III) complexes [20], which could be the reason that these complexes have the same coordination number and coordination modes. Also, the non bonding Eu(1)···Eu(1)$^{\text{i}}$ separation is 4.1853(7) Å. It is more interesting that two Eu^{3+} ions, as well as O and/or C atoms of bridging phenoxyacetate ligands, form the dinuclear structure of an eight-membered ring [Eu(1)O(1)C(13)O(2)Eu(1)$^{\text{i}}$O(1)$^{\text{i}}$C(13)$^{\text{i}}$O(2)$^{\text{i}}$], as well as a four-membered ring [Eu(1)O(8)Eu(1)$^{\text{i}}$O(8)$^{\text{i}}$], and then generate a 1D infinite chain (Fig. 2). There are nonclassical C–H···O hydrogen bonding interactions between adjacent $[Eu_2(C_8H_7O_3)_6(C_{12}H_8N_2)_2]_n$ chains (C(1)···O(2)$^{\text{i}}$ 3.071(7) Å, C(12)···O(5)$^{\text{ii}}$ 3.007(7) Å, C(10)···O(7)$^{\text{iii}}$ 3.204(7) Å, and C(30)···O(4)$^{\text{iv}}$ 3.330(7) Å) (Table 2), which indicates that stronger C–H···O hydrogen bonds play an important role in generating a layered hydrogen bonding network. Therefore, through the nonclassical hydrogen bonding interactions, the one-dimensional chains are further linked into a supramolecular network structure (Fig. 3).

As is well known, owing to the shielding function of the electrons in the inner shell, the 4f electrons are not sensitive to the lattice environment, but the 5d electron may couple strongly to the lattice. Therefore, the rare-earth luminophor can be separated into two types: broadband emitting owing to the transition between the 5d and 4f (Eu^{2+}, Ce^{3+}) or narrow line emitting owing to the transition of the 4f levels (Eu^{3+}, Tb^{3+}, Sm^{3+}). As shown in Fig. 4, the excitation spectrum of the solid sample I demonstrates that the Eu^{3+} ion can be well excited in a relatively broad wavelength range at room temperature, and the emission spectrum excited under the wavelength of 305 nm displays four narrow line emission peaks at 590, 619, 653, and 690 nm, which correspond to $^5D_0 \longleftarrow {}^7F_1$, $^5D_0 \longleftarrow {}^7F_2$, $^5D_0 \longleftarrow {}^7F_3$,

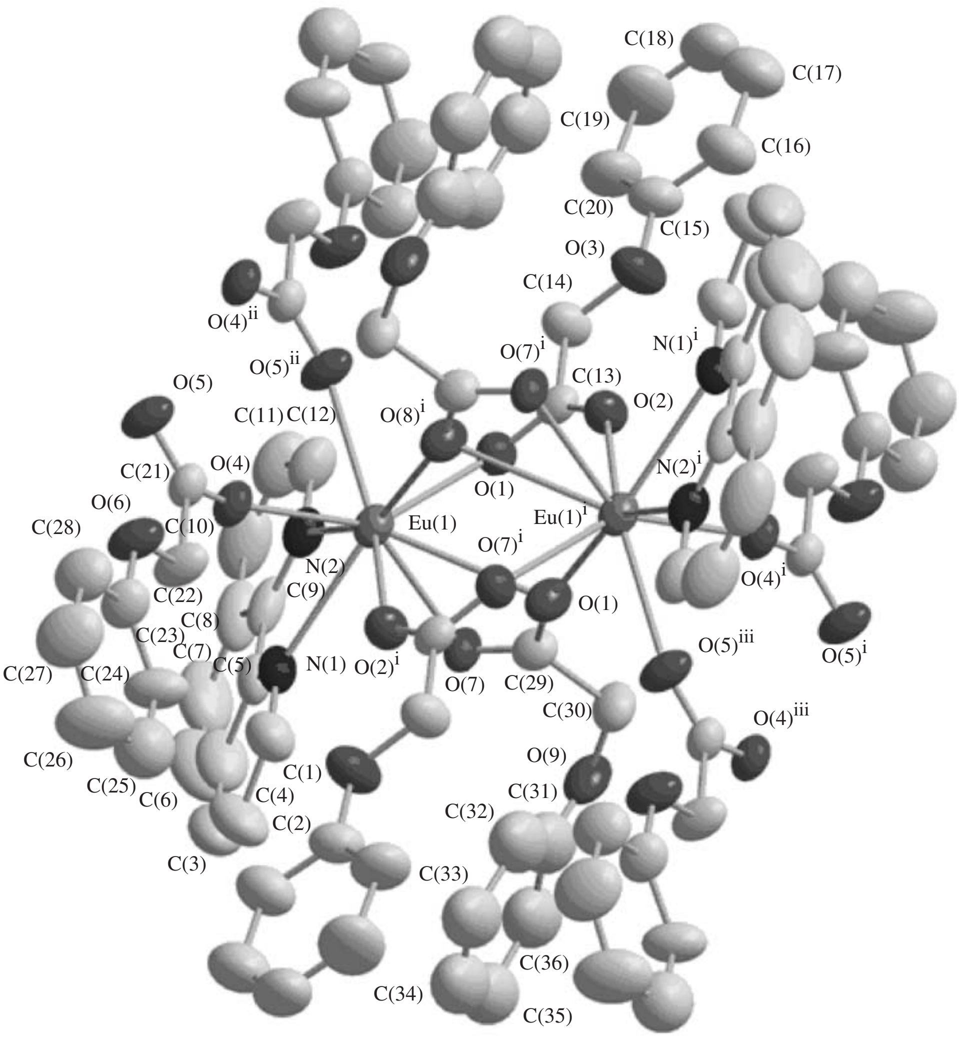

Fig. 1. Molecular structure of complex I with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level (symmetry codes: (i) $-x + 2, -y, -z + 2$; (ii) $-x + 2, -y + 1, -z + 2$; (iii) $x, y - 1, z$). All H atoms are omitted for clarity.

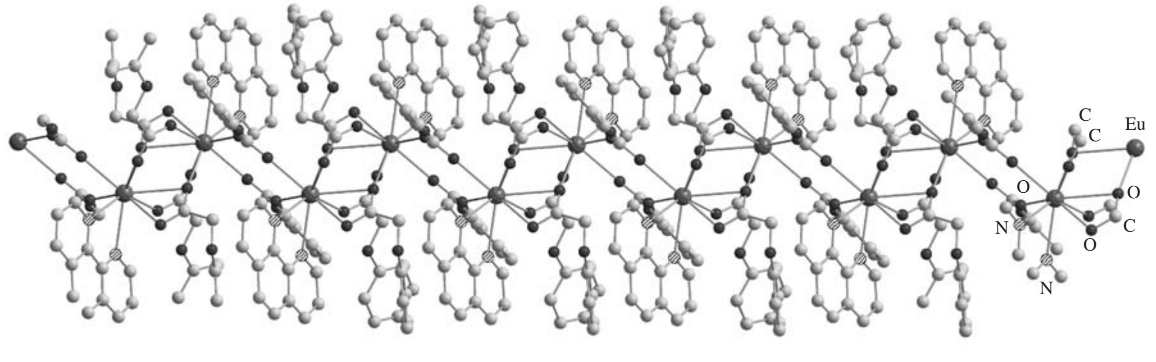

Fig. 2. One-dimensional infinite chain in I.

Table 1. Selected bond lengths (Å) and bond angles (deg) in I*

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Eu(1)–O(1)	2.497(3)	Eu(1)–O(2)^{i}	2.554(3)	Eu(1)–O(4)	2.408(3)
Eu(1)–O(5)^{ii}	2.537(4)	Eu(1)–O(7)	2.533(3)	Eu(1)–O(8)	2.802(4)
Eu(1)–O(8)^{i}	2.389(4)	Eu(1)–N(1)	2.701(5)	Eu(1)–N(2)	2.701(5)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)Eu(1)O(4)	146.00(12)	O(1)Eu(1)O(7)	73.40(12)	O(1)Eu(1)O(8)	65.74(11)
O(4)Eu(1)O(7)	138.94(12)	O(4)Eu(1)O(8)	139.13(11)	O(7)Eu(1)O(8)	47.78(10)
O(1)Eu(1)N(1)	127.86(12)	O(4)Eu(1)N(1)	76.50(13)	O(7)Eu(1)N(1)	64.21(12)
O(8)Eu(1)N(1)	102.26(13)	O(1)Eu(1)N(2)	79.81(13)	O(4)Eu(1)N(2)	97.28(12)
O(7)Eu(1)N(2)	74.65(12)	O(8)Eu(1)N(2)	118.24(11)	N(1)Eu(1)N(2)	61.26(15)
O(1)Eu(1)O(2)^{i}	129.29(12)	O(1)Eu(1)O(5)^{ii}	68.68(12)	O(2)Eu(1)O(8)^{i}	65.54(11)
O(4)Eu(1)O(2)^{i}	74.83(11)	O(4)Eu(1)O(5)^{ii}	78.17(12)	O(5)^{ii}Eu(1)O(2)^{i}	142.28(12)
O(5)^{ii}Eu(1)O(8)	129.73(12)	O(7)Eu(1)O(2)^{i}	84.25(12)	O(7)Eu(1)O(5)^{ii}	132.73(11)
O(8)^{i}Eu(1)O(1)	78.64(12)	O(8)^{i}Eu(1)O(2)^{i}	74.56(12)	O(8)^{i}Eu(1)O(4)	87.84(13)
O(8)^{i}Eu(1)O(5)^{ii}	78.61(13)	O(8)^{i}Eu(1)O(7)	120.35(13)	O(8)^{i}Eu(1)O(8)	72.81(14)
O(2)^{i}Eu(1)N(1)	76.04(13)	O(5)^{ii}Eu(1)N(1)	122.26(14)	O(8)^{i}Eu(1)N(1)	149.41(13)
O(2)^{i}Eu(1)N(2)	137.14(14)	O(5)^{ii}Eu(1)N(2)	71.82(14)	O(8)^{i}Eu(1)N(2)	148.15(14)

* Symmetry codes: ^{i} $-x + 2, -y, -z + 2$; ^{ii} $-x + 2, -y + 1, -z + 2$; ^{iii} $-x + 3/2, y + 1/2, -z + 3/2$; ^{iv} $x, y - 1, z$ (see in Table 2 too).

and $^5D_0 \longleftarrow {}^7F_4$ transitions of the Eu^{3+} ion, respectively [21]. Moreover, the intensity of the emission wavelength at 619 nm is much stronger than that of the emission wavelength at 590 nm, which implies that the electric dipole transition probability is larger than the magnetic dipole transition probability. Meanwhile, the introduction of the second ligand Phen increases the transition probability and enhances luminescence properties compared with the lanthanide coordination polymers containing O–H vibration [13–15]. The emission spectra shows a result of highly efficient intramolecular energy transfer from the ligand triplet state to the

Table 2. Hydrogen bond lengths (Å) and bond angles (deg) in I

D–H···A	*d*, Å			Angle DHA, deg
	D–H	H···A	D···A	
C(1)–H(1)···O(2)^{i}	0.93	2.38	3.071(7)	131
C(12)–H(12)···O(5)^{ii}	0.93	2.42	3.007(7)	151
C(10)–H(10)···O(7)^{iii}	0.93	2.34	3.204(7)	125
C(30)–H(30*B*)···O(4)^{iv}	0.97	2.38	3.330(7)	165

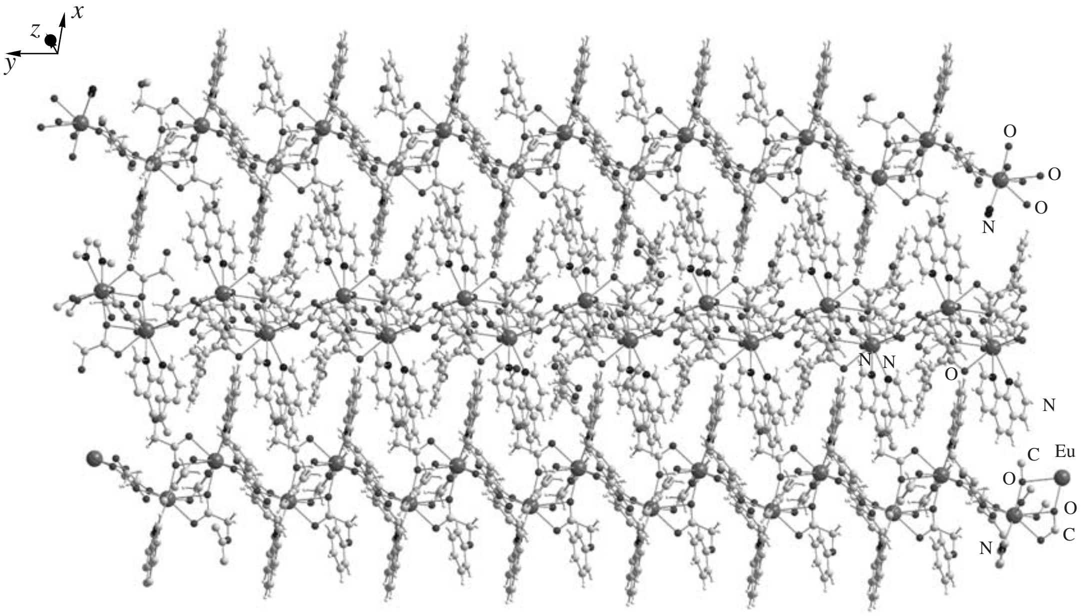

Fig. 3. Packing diagram of I linked by hydrogen bonding.

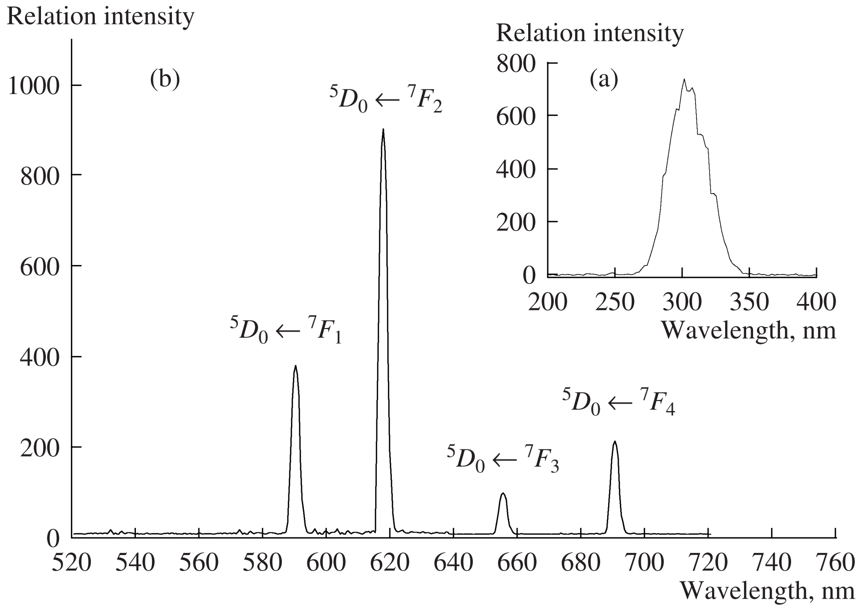

Fig. 4. Excitation (a) and emission (b) spectra of complex I at room temperature.

excited state of the Eu^{3+} ion, $^5D_0$, which then relaxes to the ^7F_j ($j = 1$–4) states.

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