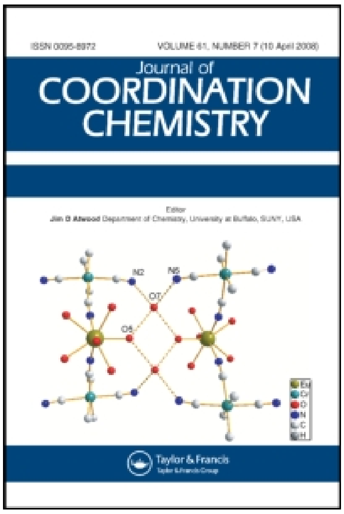

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A dimeric luminescent lanthanide complex $[Eu(PAA)_2(phen)(NO_3)]_2$: hydrothermal synthesis, crystal structure and fluorescence

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A dimeric luminescent lanthanide complex $[Eu(PAA)_2(phen)(NO_3)]_2$: hydrothermal synthesis, crystal structure and fluorescence

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A lanthanide coordination complex $[Eu(PAA)_2(phen)(NO_3)]_2$ (PAA = phenylacetic acid, phen = 1,10-phenanthroline) has been synthesized by the hydrothermal method. Single crystal X-ray diffractions show that it forms a dimeric molecular structure. The title complex crystallizes in the triclinic system, space group $P\bar{1}$, with lattice parameters $a = 8.9473(8)$ Å, $b = 13.3659(12)$ Å, $c = 13.4745(12)$ Å, $\alpha = 60.7590(10)^\circ$, $\beta = 89.5100(10)^\circ$, $\gamma = 71.9850(10)^\circ$, $V = 1317.3(2)$ Å^3, $D_c = 1.675\,\mathrm{Mg\,m^{-3}}$, $Z = 1$, $F(000) = 660$, GOF = 1.003, $R_1 = 0.0206$, $wR_2 = 0.0575$. The fluorescence excitation and emission spectra have been investigated.

Keywords: Europium(III); Hydrothermal method; Dimeric complex; Molecular structure; Fluorescence

1. Introduction

Coordination polymers with multi-dimensional structures have attracted much interest for their physical properties and potential applications as new functional materials [1–3]. Lanthanide polymers can be potentially useful as liquid crystalline, luminescent, or magnetic materials, catalysts, radiopharmaceuticals and MRI contrast agents [4–10]. Several classes of ligands have been utilized for the preparation of lanthanide complexes including calixarenes, macrocyclic ligands, β-diketone and carboxylic acid derivatives [11–14]. Carboxylate ligands are widely used in construction of lanthanide coordination polymers due to their capability to bridge in various coordination modes [15].

Hydrothermal synthesis has proved to be a powerful method for preparation of new metal-organic coordination compounds [16], applied in the syntheses of lanthanide complexes [15–20]. In the present study, we selected PPA and phen as mixed ligands to generate $[Eu(PAA)_2(phen)(NO_3)]_2$.

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2. Experimental

2.1. *Materials and measurements*

$Eu(NO_3)_3 \cdot 6H_2O$, PAA and phen were commercially available, and used without further purification. Infrared spectra were recorded on a Nicolet-460 spectrophotometer using KBr discs and sodium chloride optics. Elemental analyses were performed with a PE-2400II apparatus. The luminescence (excitation and emission) spectra were determined with Perkin–Elmer LS-55 spectrophotometer.

2.2. *Synthesis of [Eu(PAA)$_2$(phen)(NO$_3$)]$_2$*

$Eu(NO_3)_3 \cdot 6H_2O$ (0.3 mmol), PAA (0.45 mmol) and phen (0.3 mmol) were mixed in 10 mL deionized water. After stirring half an hour, the mixture was placed in a 15 mL Teflon-lined reactor and heated at 433 K in an oven for 3 days, then cooled slowly to room temperature; yellow crystals of the title complex suitable for X-ray diffraction analysis were obtained. $C_{56}H_{44}Eu_2N_6O_{14}$ (1328.89): Anal. Found: C, 50.32; H, 3.42; N, 6.51%. Calcd: C, 50.57; H, 3.31; N, 6.32%. IR spectrum exhibits a pattern of bands in the range 4000–400 cm^{-1} : 1424 cm^{-1} (ν_{sCOO-}), 1561 cm^{-1} (ν_{asCOO-}).

2.3. *X-ray crystallography*

Diffraction data for a crystal with dimensions $0.45 \times 0.40 \times 0.32\,mm^3$ for the title complex were performed by a Siemens CCD area-detector and graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K. A semi-empirical absorption correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refined against F^2 by full-matrix least squares using SHELXL-97 [21, 22]. Hydrogen atoms were placed in calculated positions. Crystal data and experimental details of the structure determinations are listed in table 1, and the selected bond distances and bond angles are listed in table 2.

3. Results and discussion

The title complex [Eu(PAA)$_2$(phen)(NO$_3$)]$_2$ is a dimer, and crystallizes in the triclinic system with space group $P\bar{1}$. Figure 1 shows the molecular structure of the title complex [Eu(PAA)$_2$(phen)(NO$_3$)]$_2$, which containing two Eu centers, four PAA ligands, two phen ligands and two nitrate ligands. Each Eu center is nine-coordinate by seven oxygens and two nitrogens, and the coordination geometry Eu can be described as a distorted monocapped square antiprism. Five of the seven oxygens are from four bridged BAA groups with a Eu–O1 distance of 2.580(2) Å, Eu–O1#1 distance of 2.3701(18) Å, Eu–O2 distance of 2.436(2) Å, a Eu–O3 distance of 2.347(2) Å and a Eu–O4# distance of 2.358(2) Å; another two are from the coordinated nitrate with a Eu–O5 distance of 2.542(2) Å, a Eu–O6 distance of 2.492(2) Å and a O5–Eu–O6 angle of 50.42(8)°. It is worthy pointing out that the Eu–O1 bond distance is much longer than Eu–O1#, due to O1# coordinated to Eu center form a quadrangular ring with

Table 1. Crystal data and structure refinement for **1**.

Complex	$[Eu(BAA)_2(phen)NO_3]_2$
Formula	$C_{56}H_{44}Eu_2N_6O_{14}$
Relative molecular weight (M)	1328.89
Color	Yellow
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Radiation	Mo-Kα
Crystal system	$P\bar{1}$
Space group	Triclinic
Unit dimensions (Å, °)	
a	8.9473(8)
b	13.3659(12)
c	13.4745(12)
α	60.7590(10)
β	89.5100(10)
γ	71.9850(10)
Volume (Å^3)	1317.3(2)
Z	1
Calculated density (Mg m^{-3})	1.675
Absorption coefficient (mm^{-1})	2.433
F(000)	660
Crystal size (mm^3)	0.45 × 0.40 × 0.32
θ range for data collection (°)	1.76–25.01
Reflections/collected/unique	6959/4586 [*R*(int) = 0.01111]
Completeness to 2θ = 25.01	98.6%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4586/0/352
Goodness-of-fit on F^2	1.003
Final *R* indices [$I > 2(I)$]	$R_1 = 0.0206$, $wR_2 = 0.0575$
Largest diff. peak and hole (e Å^{-3})	0.647 and −0.849

Table 2. Selected bond distances (Å) and bond angles (°) **1**.

Eu(1)–O(3)	2.347(2)	Eu(1)–O(5)	2.542(2)
Eu(1)–O(4)#1	2.358(2)	Eu(1)–O(1)	2.580(2)
Eu(1)–O(1)#1	2.3701(18)	Eu(1)–N(2)	2.592(2)
Eu(1)–O(2)	2.436(2)	Eu(1)–N(1)	2.609(2)
Eu(1)–O(6)	2.492(2)	Eu(1)–Eu(1)#1	3.9162(4)
O(3)–Eu(1)–O(4)#1	137.66(7)	O(2)–Eu(1)–O(1)	51.41(6)
O(3)–Eu(1)–O(1)#1	76.56(7)	O(6)–Eu(1)–O(1)	146.71(8)
O(4)#1–Eu(1)–O(1)#1	74.10(7)	O(5)–Eu(1)–O(1)	141.75(7)
O(3)–Eu(1)–O(2)	83.78(8)	O(3)–Eu(1)–N(2)	78.42(8)
O(4)#1–Eu(1)–O(2)	90.02(8)	O(4)#1–Eu(1)–N(2)	141.20(7)
O(1)#1–Eu(1)–O(2)	126.87(7)	O(1)#1–Eu(1)–N(2)	141.03(7)
O(3)–Eu(1)–O(6)	127.53(8)	O(2)–Eu(1)–N(2)	78.83(8)
O(4)#1–Eu(1)–O(6)	77.89(8)	O(6)–Eu(1)–N(2)	89.47(9)
O(1)#1–Eu(1)–O(6)	82.71(8)	O(5)–Eu(1)–N(2)	70.02(8)
O(2)–Eu(1)–O(6)	143.83(8)	O(1)–Eu(1)–N(2)	123.14(7)
O(3)–Eu(1)–O(5)	77.74(8)	O(3)–Eu(1)–N(1)	137.04(7)
O(4)#1–Eu(1)–O(5)	122.45(8)	O(4)#1–Eu(1)–N(1)	77.94(7)
O(1)#1–Eu(1)–O(5)	75.78(8)	O(1)#1–Eu(1)–N(1)	146.27(7)
O(2)–Eu(1)–O(5)	146.28(8)	O(2)–Eu(1)–N(1)	70.93(7)
O(6)–Eu(1)–O(5)	50.42(8)	O(6)–Eu(1)–N(1)	73.22(8)
O(3)–Eu(1)–O(1)	71.41(7)	O(5)–Eu(1)–N(1)	104.67(8)
O(4)#1–Eu(1)–O(1)	72.15(7)	O(1)–Eu(1)–N(1)	113.26(7)
O(1)#1–Eu(1)–O(1)	75.51(7)	N(2)–Eu(1)–N(1)	63.27(8)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2$; $-y+1$; $-z+1$.

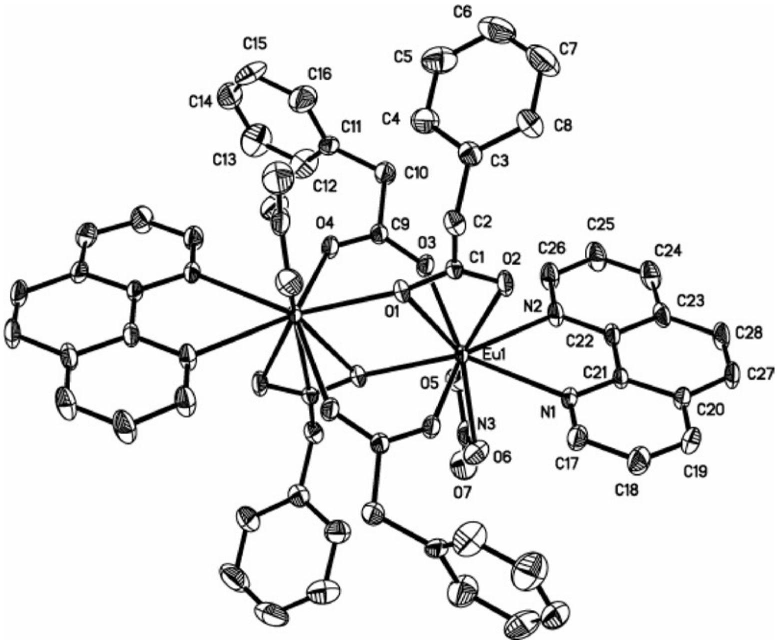

Figure 1. Molecular structure of $[Eu(PAA)_2(phen)(NO_3)]_2$.

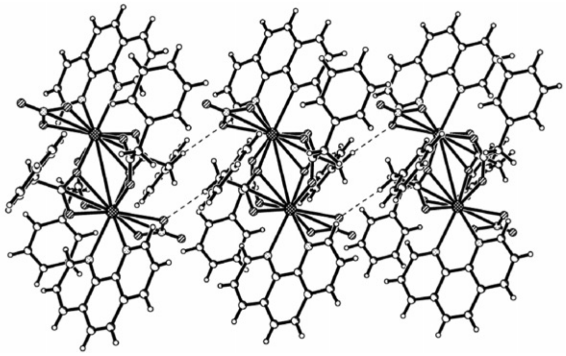

Figure 2. The supramolecular structure of $[Eu(PAA)_2(phen)(NO_3)]_2$, showing a 1D chain via C–H ··· O hydrogen bond.

oxygen 4#, enhancing the reciprocity of Eu with oxygen and shortening the Eu–O bond distance. In addition, two nitrogen atoms from the phen ligand are chelated to Eu with a Eu–N1 distance of 2.609(2) Å, a Eu–N2 distance of 2.592(2) Å and a N1–Eu–N2 angle of 63.27(8)°. Finally, the two Eu centers are linked by four PAA ligands to form a dimeric molecular structure. The four PAA ligands are of two kinds: one is bidentate bridging two Eu centers, and the other is tridentate bridging two Eu centers. The dimers are further linked by hydrogen bonds to form a 3D supramolecular architecture, weak intermolecular C–H ··· O hydrogen bonds link the molecules into chains (figure 2); hydrogen bond distances are listed in table 3.

Table 3. Hydrogen-bond geometry (Å).

D–H···A	D–H	H···A	D···A	∠D–H···A
C27–H27–O2	0.93	2.62	3.323(4)	133.1

Symmetry code: $3-x$, $2-y$, $-z$.

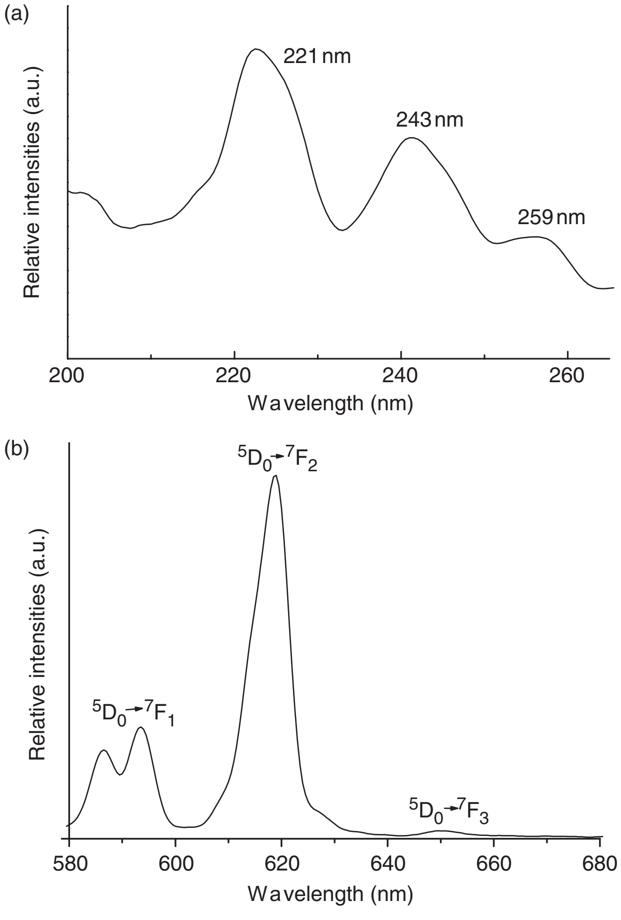

Figure 3. Emission spectrum of $[Eu(PAA)_2(phen)(NO_3)]_2$.

The excitation spectrum of complex **1**, obtained at room temperature, show excitation at 221, 243 and 259 nm (figure 3a). Under the excitation wavelength of 243 nm, the emission spectra show characteristic transitions of europium, from $^5D_0$ level of Eu^{3+} to the ^7F_j ($j=1,2,3$) manifold, as shown in figure 3(b). Among the major peaks, the one at 618 nm corresponding to $^5D_0 \rightarrow {}^7F_2$ is the strongest, so complex **1** exhibits a red photoluminescence upon radiation with UV light in the solid state at room temperature.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (No. CCDC-602770). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

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