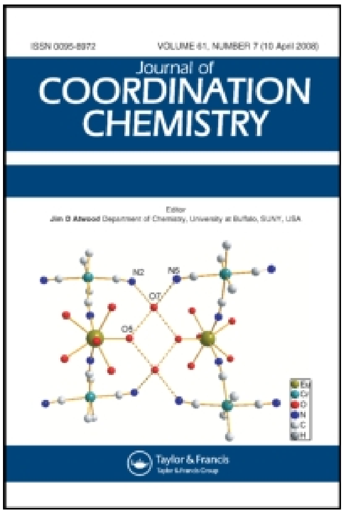

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Li Tian[a]; Liang-cai Yu[a]; Lin Chen[a]; Wei-qiang Xia[a]
[a] Institute of chemistry and chemical engineering, Xiangtan 411201, P.R. China

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Synthesis, crystal structure, and luminescence of a quaternary binuclear europium complex $[Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4]$

LI TIAN*, LIANG-CAI YU, LIN CHEN and WEI-QIANG XIA

Institute of chemistry and chemical engineering, Hunan University of Science and Technology, Xiangtan 411201, P. R. China

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A quaternary binuclear europium complex $[Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4]$ (H_2phth = phthalic acid, phen = 1,10-phenanthroline) has been synthesized. The structure was determined by X-ray crystallography which reveals that it is binuclear with each europium nine-coordinate. Intermolecular hydrogen bonds link the complex units to form a 3D supermolecular network. Its properties have been studied by means of luminescence spectrum and thermal analysis. Fluorescence spectra show that the complex exhibits strong red emission.

Keywords: Synthesis; Crystal structure; Europium(III) complex; Luminescence

1. Introduction

Lanthanide complexes have attracted attention for their interesting photophysical properties, their potential application as light-conversion molecular devices and as luminescence probes for chemical or biological macromolecules [1–4]. Considerable studies have focused on the design and assembly of lanthanide complexes with ligands such as nitrogen-containing ligands, aromatic carboxylic acids and their derivatives. Yan *et al*. reported the synthesis and crystal structure of a terbium complex with phthalate ion and 1,10-phenanthroline *via* the hydrothermal method [5]. Lanthanide complexes with aromatic carboxylic acids readily form binuclear or infinite chain polymeric structures and have higher thermal and luminescent stabilities for practical applications than other lanthanide systems [6–9]. In this article, we describe the synthesis, crystal structure and luminescence of a new europium phthalate coordination complex $[Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4]$ with an unexpected asymmetrical binuclear structure based on two coordination modes for H_2phth and intermolecular hydrogen bonds such as O···H–C.

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*Corresponding author. Tel.: +86-732-8291861. Fax: +86-732-8291770. Email: tianli_cl@163.com

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2. Experimental

2.1. *Materials and apparatus*

$Eu(NO_3)_3 \cdot 6H_2O$ was prepared by dissolving europium oxide in dense nitric acid and then dried. Other reagents were commercially available and used without further purification.

Elemental analyses (C, H, N) were determined on a Perkin–Elmer 2400 Elemental Analyzer. An IR spectrum was recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Perkin–Elmer 1710 spectrophotometer. A T4-1 different thermal analysis balance was used to carry out the TG and DTA analyses in air with a heating rate of $10^{\circ}C\,min^{-1}$. Luminescence spectra for the solid sample of the title complex were measured with a Perkin–Elmer LS-55 model spectrophotometer at room temperature.

2.2. *Synthesis of [$Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4$]*

A mixture of phthalic acid (1.5 mmol), 1,10-phenanthroline (1.0 mmol), $Eu(NO_3)_3 \cdot 6H_2O$ (1.0 mmol), H_2O and alcohol ($V:V=1:1$, 20 mL) was stirred for 6 h at pH = 7.0. The resulting solution was allowed to stand at room temperature without further disturbing for four weeks to give pink crystals. Anal. Calcd (%) for $C_{56}H_{42}\,Eu_2N_4O_{20}$: C, 48.63; H, 3.08; N, 4.13. Found (%): C, 48.22; H, 3.04; N, 4.02. IR(KBr): 3403(s), 3063(w), 2342(w), 1958(m), 1588(m), 1538(s), 1519(m), 1449(m), 1423(m), 1385(s), 1169(s), 1038(m), 851(s), 752(s), 729(s), 590(m).

2.3. *X-ray crystallography of [$Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4$]*

X-ray single-crystal diffraction data for the complex were collected on a computer-controlled Siemens P4 diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω-2θ scan technique at 273(±2) K. A pink single crystal of dimensions $0.30 \times 0.27 \times 0.25\,nm^3$ was used. The structure was solved by direct methods and refined by full-matrix least squares against F^2 using SHELXTL-97 [10]. The non-hydrogen atoms were determined with theoretical calculation. Crystal data and structure refinement parameters are listed in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Description of crystal structure*

The ORTEP diagram of [$Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4$] is presented in figure 1, showing a binuclear structure in which each central ion is nine-coordinate to form a distorted square monoantiprism geometry. Four oxygen atoms are from two bridged phth groups, one oxygen is from chelated Hphth, two oxygen atoms are from two water molecules, and two nitrogen atoms from one phen. The Eu1–Eu2 distance in the binuclear unit is 4.568 Å. The bond distances between the Eu1 ion and oxygen atoms (O5, O6 from one bridged phth and O9, O10 from the other bridged phth) are in the

Table 1. Crystal data and structure refinement parameters for the complex.

Complex	$[Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4]$
Deposition number	CCDC 613407
Empirical formula	$C_{56}H_{42}Eu_2N_4O_{20}$
Formula weight	1394.89
Crystal size (mm^3)	0.30 × 0.27 × 0.25
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	10.105(6)
b	10.676(7)
c	11.927(8)
α	90.188(3)
β	99.526(2)
γ	100.981(2)
Volume ($Å^3$)	1244.79(14)
Z	1
Density (calculated) ($Mg\,m^{-3}$)	1.850
Absorption coefficient (mm^{-1})	2.586
$F(000)$	684
$\theta_{max}, \theta_{min}$(°)	3.76, 28.23
No. of Reflections collected	9575
No. of Independent reflections	7069 [R(int) = 0.0192]
No. of variables	741
Max. and min. transmission	0.5641 and 0.5109
GOF	1.090
R	0.0302
wR_2	0.0769
Extinction coefficient	0.0086(16)
The largest peak and hole ($e\,nm^{-3}$)	1.882 and -2.536×10^{-4}

range 2.395–2.515 Å, while the bond distances between Eu2 and oxygen atoms (O11, O12 from one bridged phth and O15, O16 from the other bridged phth) are 2.385–2.469 Å. The bond distances of Eu–O from Hphth are shorter, 2.324(9) Å for Eu1–O4 and 2.346(11) Å for Eu2–O17, respectively. Phen is a terminal ligand with a typically Eu–N distance of 2.538 Å (Eu1–N1, 2.517(13) Å; Eu1–N2, 2.493(12) Å; Eu2–N3, 2.544(10) Å; Eu2–N4, 2.599(10) Å). The bond angle is 64.3(4)° for N2–Eu1–N1 and 65.4(4)° for N3–Eu2–N4. The title complex is asymmetrical and different from the dimeric structure of $[Tb_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4]$ [5].

There are two types of coordination mode of H_2phth in the molecular structure. The H_2phth molecules are completely deprotonated to form phth anions and all the oxygen atoms (O5 and O6, O9 and O10, O11 and O12, O15 and O16) take part in the coordination to the two central Eu ions (Eu1 and Eu2) connected into a binuclear structure by bidentate coordination. The average bond distances between Eu–O is 2.433 Å; the bond angle of Eu and O ranges from 52.2(3)–55.5(4)°. Some H_2phth molecules lose one proton to form Hphth anions and coordinate Eu by monodentate chelation.

Two types of intermolecular hydrogen bonds exist in the molecule structure as shown in figure 2. One is the O … H–O intermolecular hydrogen bonds between the oxygen atoms (O1D and O2D) of the Hphth ligands and the oxygen atoms (O7B, O8B) of the coordinated water molecules in the adjacent molecular unit; the other is the O … H–C between the oxygen atoms (O3D) of Hphth and the carbon atoms (C11B) of coordinated phen in an adjacent molecular unit. The complex units are linked together

Table 2. Selected bond lengths (Å) and bond angles (°) of the complex.

Eu1–O7	2.309(10)	Eu2–O14	2.325(8)
Eu1–O4	2.324(9)	Eu2–O17	2.346(11)
Eu1–O8	2.360(9)	Eu2–O11	2.385(11)
Eu1–O6	2.395(11)	Eu2–O15	2.412(9)
Eu1–O9	2.397(7)	Eu2–O12	2.461(11)
Eu1–O5	2.428(13)	Eu2–O16	2.469(12)
Eu1–N2	2.493(12)	Eu2–O13	2.469(10)
Eu1–O10	2.515(11)	Eu2–N3	2.544(10)
Eu1–N1	2.517(13)	Eu2–N4	2.599(10)
O7–Eu1–O4	85.0(4)	O14–Eu2–O17	82.8(4)
O7–Eu1–O8	73.8(3)	O14–Eu2–O11	130.7(3)
O4–Eu1–O8	136.6(4)	O17–Eu2–O11	87.7(4)
O7–Eu1–O6	131.6(4)	O14–Eu2–O15	131.5(3)
O4–Eu1–O6	142.6(4)	O17–Eu2–O15	144.3(4)
O8–Eu1–O6	72.1(3)	O11–Eu2–O15	76.3(3)
O7–Eu1–O9	130.1(4)	O14–Eu2–O12	77.9(3)
O4–Eu1–O9	87.1(4)	O17–Eu2–O12	68.8(3)
O8–Eu1–O9	79.1(4)	O11–Eu2–O12	53.8(3)
O6–Eu1–O9	74.5(4)	O15–Eu2–O12	121.2(3)
O7–Eu1–O5	83.0(4)	O14–Eu2–O16	85.1(4)
O4–Eu1–O5	140.7(4)	O17–Eu2–O16	141.2(4)
O8–Eu1–O5	74.4(5)	O11–Eu2–O16	127.0(3)
O6–Eu1–O5	55.5(4)	O15–Eu2–O16	52.2(3)
O9–Eu1–O5	128.4(4)	O12–Eu2–O16	143.2(4)
O7–Eu1–N2	140.9(4)	O14–Eu2–O13	76.3(3)
O4–Eu1–N2	72.0(4)	O17–Eu2–O13	138.4(4)
O8–Eu1–N2	143.3(3)	O11–Eu2–O13	79.7(4)
O6–Eu1–N2	73.1(4)	O15–Eu2–O13	70.3(3)
O9–Eu1–N2	81.0(4)	O12–Eu2–O13	71.9(4)
O5–Eu1–N2	94.9(4)	O16–Eu2–O13	72.5(5)
O7–Eu1–O10	78.5(4)	O14–Eu2–N3	139.4(4)
O4–Eu1–O10	68.9(4)	O17–Eu2–N3	72.1(4)
O8–Eu1–O10	70.0(4)	O11–Eu2–N3	80.5(4)
O6–Eu1–O10	119.0(4)	O15–Eu2–N3	73.9(3)
O9–Eu1–O10	52.9(3)	O12–Eu2–N3	119.2(4)
O5–Eu1–O10	143.2(3)	O16–Eu2–N3	94.8(5)
N2–Eu1–O10	119.3(4)	O13–Eu2–N3	142.2(4)
O7–Eu1–N1	78.6(4)	O14–Eu2–N4	76.7(4)
O4–Eu1–N1	71.1(4)	O17–Eu2–N4	71.4(4)
O8–Eu1–N1	136.9(4)	O11–Eu2–N4	144.0(4)
O6–Eu1–N1	105.0(4)	O15–Eu2–N4	103.6(3)
O9–Eu1–N1	143.1(3)	O12–Eu2–N4	134.8(4)
O5–Eu1–N1	69.9(4)	O16–Eu2–N4	69.9(4)
N2–Eu1–N1	64.3(4)	O13–Eu2–N4	135.0(4)
O10–Eu1–N1	135.1(4)	N3–Eu2–N4	65.4(4)

via such intermolecular hydrogen bonds to form a three dimensional supramolecular network structure shown in figure 3.

3.2. *Thermogravimetric analysis*

Figure 4 shows the TG-DTA curve of the title complex. The thermal analysis data indicate that thermal decomposition of the europium complex $[Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4]$ has four stages. The 1st weight loss of 4.3% (Calcd 5.2%) occurs at

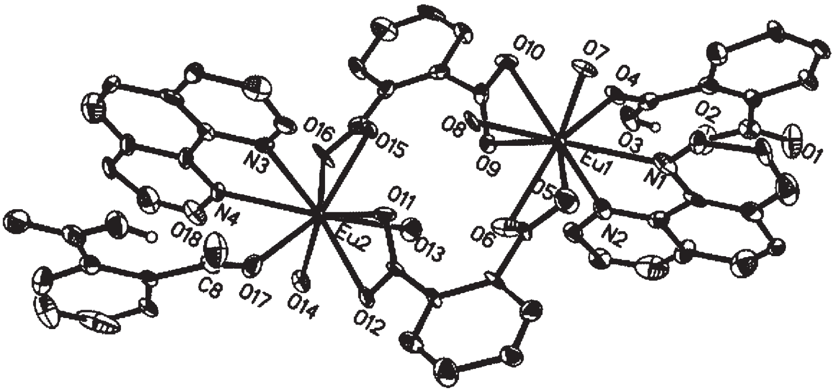

Figure 1. The ORTEP drawing for $[Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4]$.

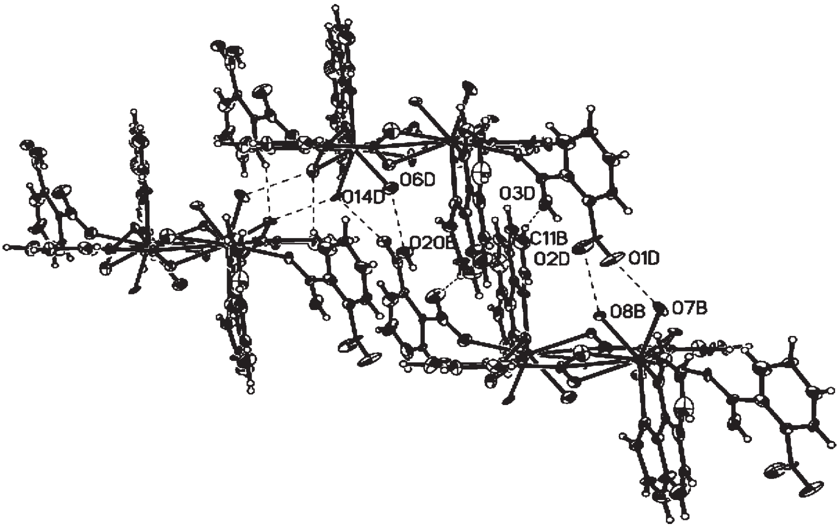

Figure 2. The hydrogen bonds diagram for $[Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4]$.

ca 120–160°C and corresponds to dehydration of coordinated water molecules. The 2nd weight loss of 21.8% (Calcd 23.5%) in the range of 230–280°C is identified as the removal of terminal phth ligands followed by a small endothermic peak; the 3rd step with the mass loss of 22.9% (Calcd 23.8%) around 360°C is considered as breaking of Eu–O bonds between Eu and bridged phth ligands. The last strikingly clean weight loss of 23.7% (Calcd 25.8%) around 480°C is the release of phen followed by the sharp exothermic peak for the explosion. On further heating, the complex does not lose any more weight at a temperature higher than 700°C.

3.3. *Luminescence*

The photoluminescence of the title complex was studied in the solid state. Figure 5 gives the emission spectrum of $[Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4]$ under excitation of 250 nm at room temperature and the strong red luminescence with three emission

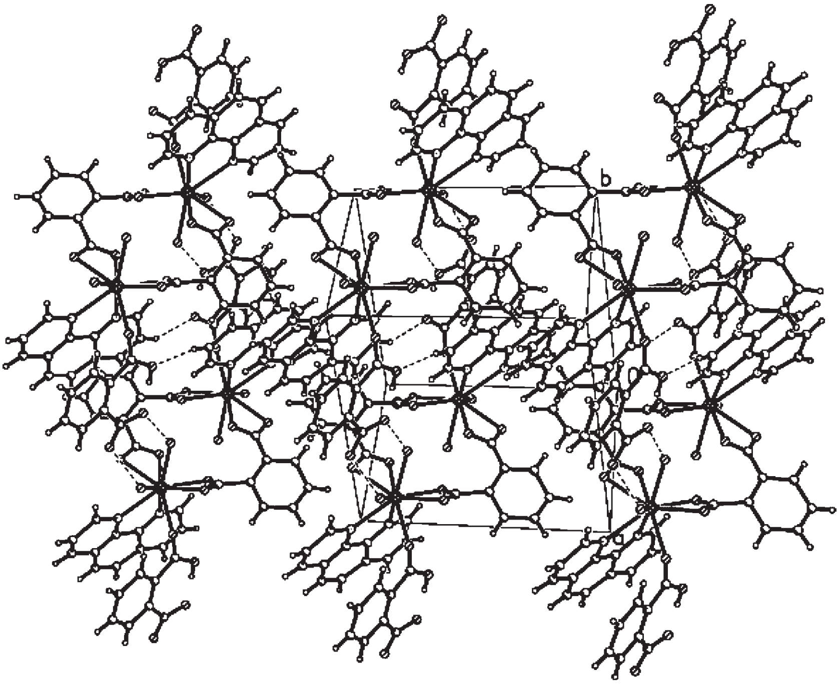

Figure 3. The three-dimensional packing structure of [$Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4$].

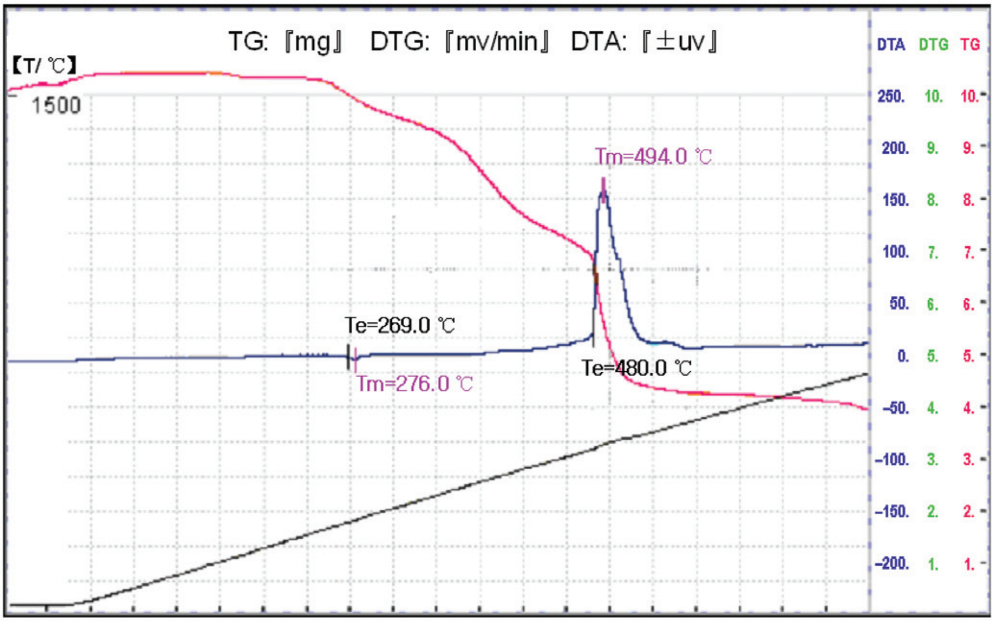

Figure 4. The DTA-TG culve for [$Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4$].

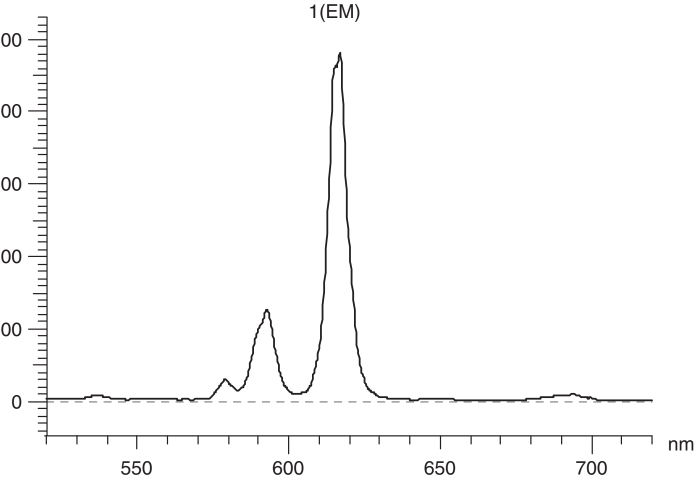

Figure 5. Th photoluminescence spectra of solid complex $[Eu_2(phth)_2(Hphth)_2(phen)_2(H_2O)_4]$.

bands at 577, 591 and 615 nm, respectively, corresponding to the characteristic emission from the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} ion. The electric dipole transition $^5D_0 \rightarrow {}^7F_2$ exhibits the strongest red emission with relative intensity of 4630 and the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ shows the second strongest orange emission with relative intensity of 1136. The intensity specific value of electric dipole transition and magnetic dipole transition is about 4 implying that the central Eu is in an asymmetrical environment [11].

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 613407. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk).

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