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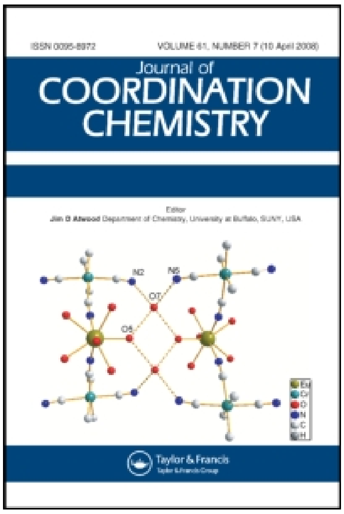

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Synthesis, structure and luminescence of three europium complexes with 2,4-dimethylbenzoic acid

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Synthesis, structure and luminescence of three europium complexes with 2,4-dimethylbenzoic acid

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Three different complexes of europium with 2,4-dimethylbenzoic acid (2,4-HDMBA), $[Eu(2,4\text{-}DMBA)_3]_n$ (**1**), $[Eu(2,4\text{-}DMBA)_3 \cdot (2,2'\text{-}bpy)]_2 \cdot 6H_2O$ (**2**) (2,2′-bipy = 2,2′-bipyridine), and $[Eu(2,4\text{-}DMBA)_3 \cdot phen]_2$ (**3**) (phen = 1,10-phenanthroline) were synthesized. Complex **1** is in an infinite one-dimensional polymer chain. Complex **2** is a dimeric unit, in which Eu(III) is nine-coordinate in a distorted monocapped square-antiprism arrangement. Complex **3** is also a dimeric unit, in which the Eu(III) ion is eight-coordinate and is in a distorted square antiprism arrangement. The three complexes displayed luminescence properties. The luminescence spectra correspond to the characteristic emission $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) transition of Eu(III).

Keywords: Europium complexes; 2,4-Dimethylbenzoic acid; Synthesis; Structure; Luminescence

1. Introduction

Lanthanide(III) carboxylate complexes have attracted attention because of their varied structures and applications including luminescent probes. Many lanthanide(III) complexes with benzoate or its derivatives have been reported [1–13]. Europium(III) aromatic carboxylate complexes showed intense fluorescence and thermal stability. Furthermore, this class of complexes form polymeric chain or dimeric structures. Luminescent intensities of the complexes are found to be strongly dependent on their organic ligands. As a part of our series of studies on europium benzoate complexes, we synthesized three europium 2,4-dimethylbenzoic acid (2,4-HDMBA) complexes, polymeric $[Eu(2,4\text{-}DMBA)_3]_n$ (**1**), dimeric units $[Eu(2,4\text{-}DMBA)_3 \cdot (2,2'\text{-}bpy)]_2 \cdot 6H_2O$ (**2**) (2,2′-bipy = 2,2′-bipyridine), and $[Eu(2,4\text{-}DMBA)_3 \cdot phen]_2$ (**3**) (phen = 1,10-phenanthroline). In the present article, the crystal structures and luminescence properties of the three synthesized complexes were reported.

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2. Experimental

2.1. *Synthesis of complexes*

For the synthesis of complex **1**, 1.5 mmol 2,4-dimethylbenzoic acid was dissolved in appropriate amounts of ethanol and the pH was controlled in a range of 6–7 by addition of a solution of 2 mol dm^{-3} NaOH. The ethanolic solution of $EuCl_3 \cdot 6H_2O$ (0.5 mmol) was dropped into the reaction solution. The mixture was then heated under reflux with stirring for 2 h. After two weeks some colorless single crystals deposited from the filtrate. Yield: 0.1529 g, 51.03%. Anal. Calcd (%): C, 53.68; H, 4.37. Found (%): C, 54.09; H, 4.54.

For the synthesis of complex **2**, 1.5 mmol 2,4-dimethylbenzoic acid was dissolved in appropriate amounts of ethanol and the pH was controlled in a range of 6–7 by addition of a solution of 2 mol dm^{-3} NaOH. Ethanolic solution of 2,2′-bipyridine (0.5 mmol) and $EuCl_3 \cdot 6H_2O$ (0.5 mmol) were successively dropped into the reaction solution. The mixture was then heated under reflux with stirring for 2 h. After one week colorless single crystals deposited from the filtrate. Yield: 0.2422 g, 59.83%. Anal. Calcd (%): C, 54.54; N, 3.65; H, 4.93. Found (%): C, 54.89; N, 3.46; H, 5.10.

The synthesis of complex **3** was similar to that of complex **2**. Yield: 0.2438 g, 62.54%. Anal. Calcd (%): C, 59.71; N, 3.24: H, 4.47. Found (%): C, 60.08; N, 3.59; H, 4.52.

2.2. *Single-crystal X-ray diffraction*

X-ray crystal data collection for the complexes is on a Bruker Smart 1000 CCD diffratometer with monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Semi-empirical absorption corrections were applied using the SADABS program. All calculations were carried out on a computer with use of SHELXS-97 and SHELXL-97 programs [14, 15]. The structures were solved by direct methods and refinement on $|F|^2$ using full-matrix least-squares. A summary of the crystallographic data and details of the structure refinements are listed in table 1. Selected bond distances and angles are in tables 2–4.

2.3. *Fluorescence spectra measurement*

Fluorescence spectra were measured on a F-4500 FL Spectrophotometer in the solid state at room temperature.

3. Results and discussion

3.1. *Structural description of complex 1*

$[Eu(2,4\text{-}DMBA)_3]_n$ (**1**) is polymeric chains built up by trimeric units of $[Eu(2,4\text{-}DBMA)_3]_3$ along the *c*-axis (figure 1a). Eu2(III) and neighboring Eu1(III) are linked by one bidentate bridging (O9–C37–O10) and two tridentate bridging (O5–C19–O6 and O3–C10–O4) group, whereas Eu2 (III) ion and another adjacent Eu1A (III) ion are

Table 1. Crystal data and structure refinement for complexes.

Complex	**1**	**2**	**3**
Empirical formula	$C_{54}H_{54}Eu_2O_{12}$	$C_{37}H_{41}EuN_2O_9$	$C_{39}H_{35}EuN_2O_6$
Formula weight	1198.89	809.68	779.65
Temperature (K)	294(2)	294(2)	294(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2(1)$	$P\bar{1}$	$C2/c$
Unit cell dimensions (Å, °)			
a	8.0988(11)	11.2196(15)	27.500(3)
b	15.595(2)	12.3639(17)	15.6784(15)
c	20.110(3)	15.945(2)	16.0249(16)
α	90.00	69.636(2)	90.00
β	96.452(2)	71.641(2)	101.176(2)
γ	90.00	83.271(2)	90.00
V (Å^3)	2523.8(6)	1968.0(5)	6778.2(12)
Z	2	2	8
D_{Calcd} (Mg m^{-3})	1.578	1.366	1.528
μ (mm^{-1})	2.524	1.645	1.901
$F(000)$	1200	824	3152
Crystal size (mm^3)	0.20 × 0.16 × 0.12	0.18 × 0.10 × 0.08	0.20 × 0.10 × 0.08
Theta range for data Collection (°)	1.02–26.38	1.43–25.01	1.50–26.30
Limiting indices	$-10 \le h \le 6$ $-18 \le k \le 19$ $-25 \le l \le 24$	$-9 \le h \le 13$ $-14 \le k \le 13$ $-18 \le l \le 18$	$-31 \le h \le 34$ $-14 \le k \le 19$ $-19 \le l \le 15$
Reflections collected/unique	14226/9333 [R(int) = 0.0484]	10030/6891 [R(int) = 0.0266]	18814/6861 [R(int) = 0.0350]
Data/restraints/parameters	7406/31/623	6891/72/529	6861/0/439
Goodness-of-fit on F^2	1.031	1.060	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0477$ $wR_2 = 0.0939$	$R_1 = 0.0414$ $wR_2 = 0.1051$	$R_1 = 0.0284$, $wR_2 = 0.0584$
R indices (all data)	$R_1 = 0.0713$ $wR_2 = 0.1054$	$R_1 = 0.0611$ $wR_2 = 0.1177$	$R_1 = 0.0462$, $wR_2 = 0.0645$
Largest diff. peak and hole (e Å^{-3})	1.248 and −1.090	1.107 and −0.565	0.891 and −0.821

linked by two bidentate bridging (O7–C28–O8 and O1A–C1A–O2A) and one tridentate bridging (O11–C46–O12) ligand to form a trimeric unit [Eu(2,4-DBMA)$_3$]$_3$. The trimeric units are then linked together to form an infinite one-dimensional polymer chain by different types and a number of bridging 2,4-DBMA groups. The distances of Eu2 $\cdots$ Eu1 and Eu2 $\cdots$ Eu1A are 3.8926(8), 4.3409(8) Å, respectively, and the angle of Eu1A $\cdots$ Eu2 $\cdots$ Eu1 is 159.2°. In the polymeric molecule, there are two crystallographically different Eu(III) ions. The Eu1(III) ion is coordinated by eight O atoms, in which O1, O8A, O9 atoms are from three bidentate bridging carboxylate groups, O3, O4, O5, O11A, O12A atoms are from three tridentate bridging carboxylate groups. Eu2(III) is surrounded by seven O atoms, in which O2A, O7, O10 atoms are from three bidentate bridging carboxylate groups, O4, O5, O6, O11 atoms are from three tridentate bridging carboxylate groups. The Eu1–O distances are in a range of 2.299(6)–2.680(6) Å with an average distance of 2.432 Å. The Eu2–O distances are in a range from 2.263(8) to 2.562(6) Å with an average distance of 2.376 Å. Obviously, the distance of Eu1–O is longer than that of Eu2–O and the difference is attributable to different coordination environments of the two Eu(III) ions. This case is similar to polymeric [Dy(4-$CH_3C_6H_4COO$)$_3$]$_n$, in which two different coordination environments

Table 2. Selected bond lengths (Å) and angles (°) for complex **1**.

Eu(1)–O(8)#1	2.299(6)	Eu(1)–O(9)	2.314(9)
Eu(1)–O(1)	2.320(7)	Eu(1)–O(5)	2.362(6)
Eu(1)–O(12)#1	2.386(6)	Eu(1)–O(3)	2.426(7)
Eu(1)–O(11)#1	2.666(6)	Eu(1)–O(4)	2.680(6)
Eu(2)–O(2)#2	2.263(8)	Eu(2)–O(7)	2.284(7)
Eu(2)–O(10)	2.332(8)	Eu(2)–O(4)	2.381(6)
Eu(2)–O(11)	2.402(6)	Eu(2)–O(6)	2.405(6)
Eu(2)–O(5)	2.562(6)		
O(8)#1–Eu(1)–O(9)	87.5(3)	O(8)#1–Eu(1)–O(1)	97.9(3)
O(9)–Eu(1)–O(1)	162.9(3)	O(8)#1–Eu(1)–O(5)	150.4(2)
O(9)–Eu(1)–O(5)	81.4(3)	O(1)–Eu(1)–O(5)	100.7(3)
O(8)#1–Eu(1)–O(12)#1	129.3(2)	O(9)–Eu(1)–O(12)#1	80.2(3)
O(1)–Eu(1)–O(12)#1	83.9(3)	O(5)–Eu(1)–O(12)#1	75.7(2)
O(8)#1–Eu(1)–O(3)	82.1(3)	O(9)–Eu(1)–O(3)	120.2(3)
O(1)–Eu(1)–O(3)	76.7(2)	O(5)–Eu(1)–O(3)	80.1(2)
O(12)#1–Eu(1)–O(3)	145.5(3)	O(8)#1–Eu(1)–O(11)#1	79.0(2)
O(9)–Eu(1)–O(11)#1	82.7(3)	O(1)–Eu(1)–O(11)#1	82.5(2)
O(5)–Eu(1)–O(11)#1	126.09(19)	O(12)#1–Eu(1)–O(11)#1	50.9(2)
O(3)–Eu(1)–O(11)#1	149.5(2)	O(8)#1–Eu(1)–O(4)	82.8(2)
O(9)–Eu(1)–O(4)	70.6(3)	O(1)–Eu(1)–O(4)	126.0(2)
O(5)–Eu(1)–O(4)	67.66(19)	O(12)#1–Eu(1)–O(4)	135.6(2)
O(3)–Eu(1)–O(4)	49.7(2)	O(11)#1–Eu(1)–O(4)	148.2(2)
O(2)#2–Eu(2)–O(7)	90.1(3)	O(2)#2–Eu(2)–O(10)	176.6(3)
O(7)–Eu(2)–O(10)	86.5(3)	O(2)#2–Eu(2)–O(4)	86.5(3)
O(7)–Eu(2)–O(4)	82.9(2)	O(10)–Eu(2)–O(4)	93.0(3)
O(2)#2–Eu(2)–O(11)	84.7(3)	O(7)–Eu(2)–O(11)	77.0(2)
O(10)–Eu(2)–O(11)	94.6(3)	O(4)–Eu(2)–O(11)	158.01(19)
O(2)#2–Eu(2)–O(6)	87.1(3)	O(7)–Eu(2)–O(6)	154.8(2)
O(10)–Eu(2)–O(6)	95.9(3)	O(4)–Eu(2)–O(6)	121.8(2)
O(11)–Eu(2)–O(6)	77.8(2)	O(2)#2–Eu(2)–O(5)	80.0(3)
O(7)–Eu(2)–O(5)	151.0(2)	O(10)–Eu(2)–O(5)	102.9(3)
O(4)–Eu(2)–O(5)	69.4(2)	O(11)–Eu(2)–O(5)	128.3(2)
O(6)–Eu(2)–O(5)	52.5(2)	O(2)#2–Eu(2)–O(9)	137.5(3)
O(7)–Eu(2)–O(9)	111.0(3)	O(10)–Eu(2)–O(9)	44.3(3)
O(4)–Eu(2)–O(9)	61.4(2)	O(11)–Eu(2)–O(9)	134.8(2)
O(6)–Eu(2)–O(9)	87.4(2)	O(5)–Eu(2)–O(9)	63.5(2)

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

Table 3. Selected bond lengths (Å) and angles (°) for complex **2**.

Eu(1)–O(1)#1	2.344(2)	Eu(1)–O(1)	2.750(2)
Eu(1)–O(3)	2.368(2)	Eu(1)–O(4)#1	2.383(2)
Eu(1)–O(6)	2.436(3)	Eu(1)–O(5)	2.458(3)
Eu(1)–O(2)	2.467(3)	Eu(1)–N(1)	2.633(3)
Eu(1)–N(2)	2.603(3)		
O(1)#1–Eu(1)–O(3)	74.06(8)	O(1)#1–Eu(1)–O(4)#1	75.15(8)
O(3)–Eu(1)–O(4)#1	134.53(7)	O(1)#1–Eu(1)–O(6)	85.10(9)
O(3)–Eu(1)–O(6)	131.13(9)	O(4)#1–Eu(1)–O(6)	77.70(8)
O(1)#1–Eu(1)–O(5)	85.98(9)	O(3)–Eu(1)–O(5)	81.41(9)
O(4)#1–Eu(1)–O(5)	128.55(9)	O(6)–Eu(1)–O(5)	52.95(8)
O(1)#1–Eu(1)–O(2)	123.73(8)	O(3)–Eu(1)–O(2)	81.54(9)
O(4)#1–Eu(1)–O(2)	88.67(9)	O(6)–Eu(1)–O(2)	143.94(9)
O(5)–Eu(1)–O(2)	139.36(8)	O(1)#1–Eu(1)–O(1)	74.83(9)
O(3)–Eu(1)–O(1)	70.73(7)	O(4)#1–Eu(1)–O(1)	69.45(7)
O(6)–Eu(1)–O(1)	144.82(7)	O(5)–Eu(1)–O(1)	149.49(8)
O(2)–Eu(1)–O(1)	49.22(7)	N(2)–Eu(1)–N(1)	62.06(9)

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

Table 4. Selected bond lengths (Å) and angles (°) for complex **3**.

Eu(1)–O(3)	2.335(2)	Eu(1)–O(5)	2.360(2)
Eu(1)–O(6)#1	2.384(2)	Eu(1)–O(4)#1	2.406(2)
Eu(1)–O(1)	2.408(2)	Eu(1)–O(2)	2.496(2)
Eu(1)–N(2)	2.601(3)	Eu(1)–N(1)	2.626(3)
O(3)–Eu(1)–O(5)	74.12(8)	O(3)–Eu(1)–O(6)#1	79.58(8)
O(5)–Eu(1)–O(6)#1	131.85(8)	O(3)–Eu(1)–O(4)#1	126.63(9)
O(5)–Eu(1)–O(4)#1	87.76(8)	O(6)#1–Eu(1)–O(4)#1	76.56(8)
O(3)–Eu(1)–O(1)	90.37(9)	O(5)–Eu(1)–O(1)	88.91(8)
O(6)#1–Eu(1)–O(1)	131.23(8)	O(4)#1–Eu(1)–O(1)	139.97(8)
O(3)–Eu(1)–O(2)	77.55(8)	O(5)–Eu(1)–O(2)	131.98(8)
O(6)#1–Eu(1)–O(2)	78.07(8)	O(4)#1–Eu(1)–O(2)	139.97(8)
O(1)–Eu(1)–O(2)	53.19(8)	O(3)–Eu(1)–O(3)#1	81.45(8)
O(5)–Eu(1)–O(3)#1	71.95(7)	O(6)#1–Eu(1)–O(3)#1	64.71(7)
O(4)#1–Eu(1)–O(3)#1	45.20(7)	O(1)–Eu(1)–O(3)#1	160.58(7)
O(2)–Eu(1)–O(3)#1	139.91(7)	N(2)–Eu(1)–N(1)	62.70(8)

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

of Dy(III) ions exist. Dy1 ion is coordinated by six O atoms, and Dy(2) ion is coordinated by eight O atoms, furthermore, the distances of Dy1–O and Dy2–O are different [1]. Complex **1** is different from a majority of lanthanide monocarboxylate complexes in structure, such as $[Eu(4\text{-}CH_3C_6H_4COO)_3]_n$ [2], $[Eu(2,3\text{-}DMOBA)_3]_n$ (2,3-DMOBA = 2,3-dimethoxybenzoate) [3], and $[Eu(3\text{-}MOBA)_3 \cdot 2H_2O]_n$ (3-MOBA = 3-methoxybenzoate) [4]. However, the coordination environments of the central ions for the above-mentioned complexes are chemically equivalent. It is obvious that the structural difference arises from different substitutents in the benzene ring. Viewing along the *a*-axis, π–π stacking interactions can be found, as shown in figure 1(b).

3.2. *Structural description of complex 2*

The molecular structure of $[Eu(2,4\text{-}DMBA)_3 \cdot (2,2'\text{-}bpy)]_2 \cdot 6H_2O$ (**2**) is shown in figure 2(a). Obviously, the molecular structure of complex **2** is different from that of complex **1** with an infinite one-dimensional polymer chain. In complex **2**, 2,2′-bipy coordinates central ion besides 2,4-DMBA ligands. Complex **2** is a centrosymmetric dimer with a center of inversion between the metal atoms, bridged by four carboxylate ligands, two of them are bidentate bridging and the other two tridentate bridging. The distance between the two central Eu(III) ions is 4.054(5) Å. In addition, each Eu(III) is also chelated by one carboxylate group and one 2,2′-bpy molecule. Eu(III) is nine-coordinate with seven O atoms of five 2,4-DMBA carboxylate ligands and by two N atoms of one 2,2′-bipy ligand. Eu(III) is in a distorted monocapped square-antiprism arrangement with O1A, O4A, O5, N2, and O1, O2, O3, N1 forming lower and upper square planes with mean deviations of 0.2293 and 0.1805 Å, respectively, with a dihedral angle between them of 8.1°; O6 caps the upper plane. The Eu1–O distances are in a range of 2.344(2)–2.750(6) Å with a mean bond length of 2.458 Å. The Eu1–N distances are 2.603(3) and 2.633(3) Å, respectively, with a mean bond length of 2.618 Å. Bond angles of O–Eu–O range from 49.22(7) to 149.49(8)°, and N–Eu–N is 62.06(9)°. Calculated results show that the dihedral angle between the two pyridines is 6.8°.

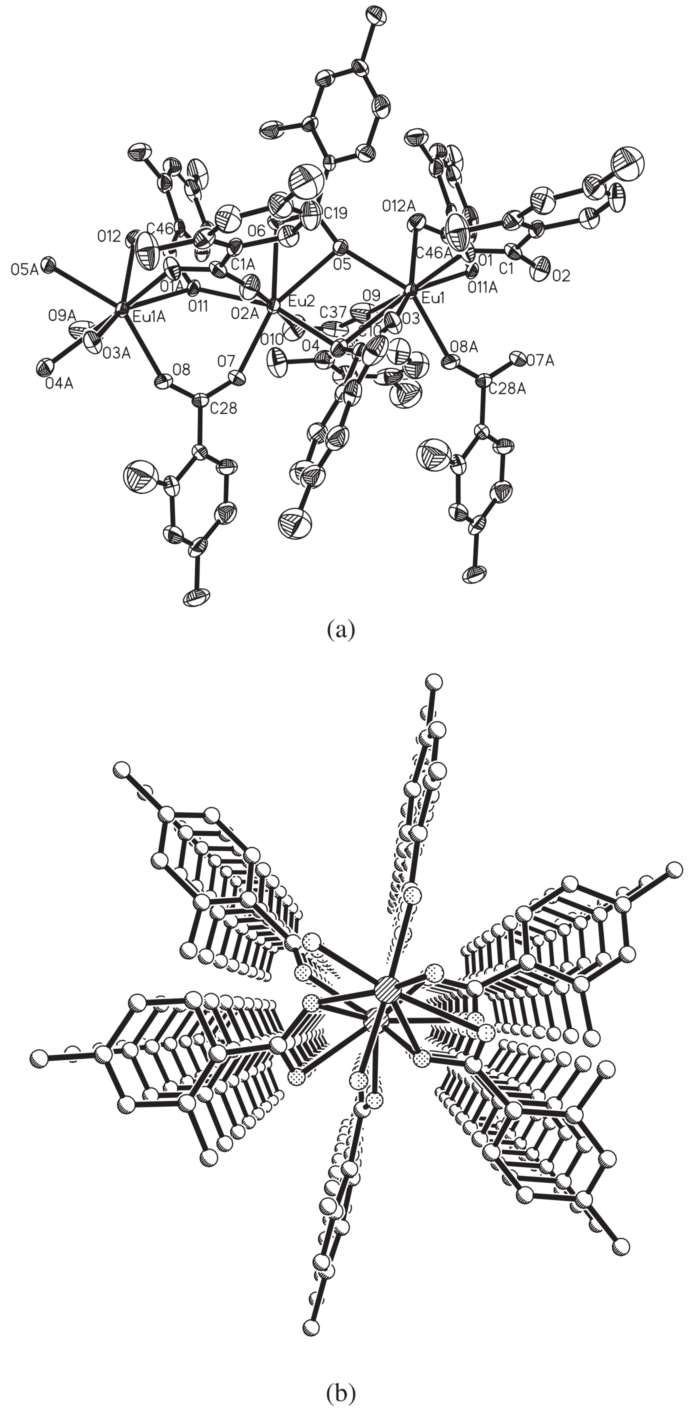
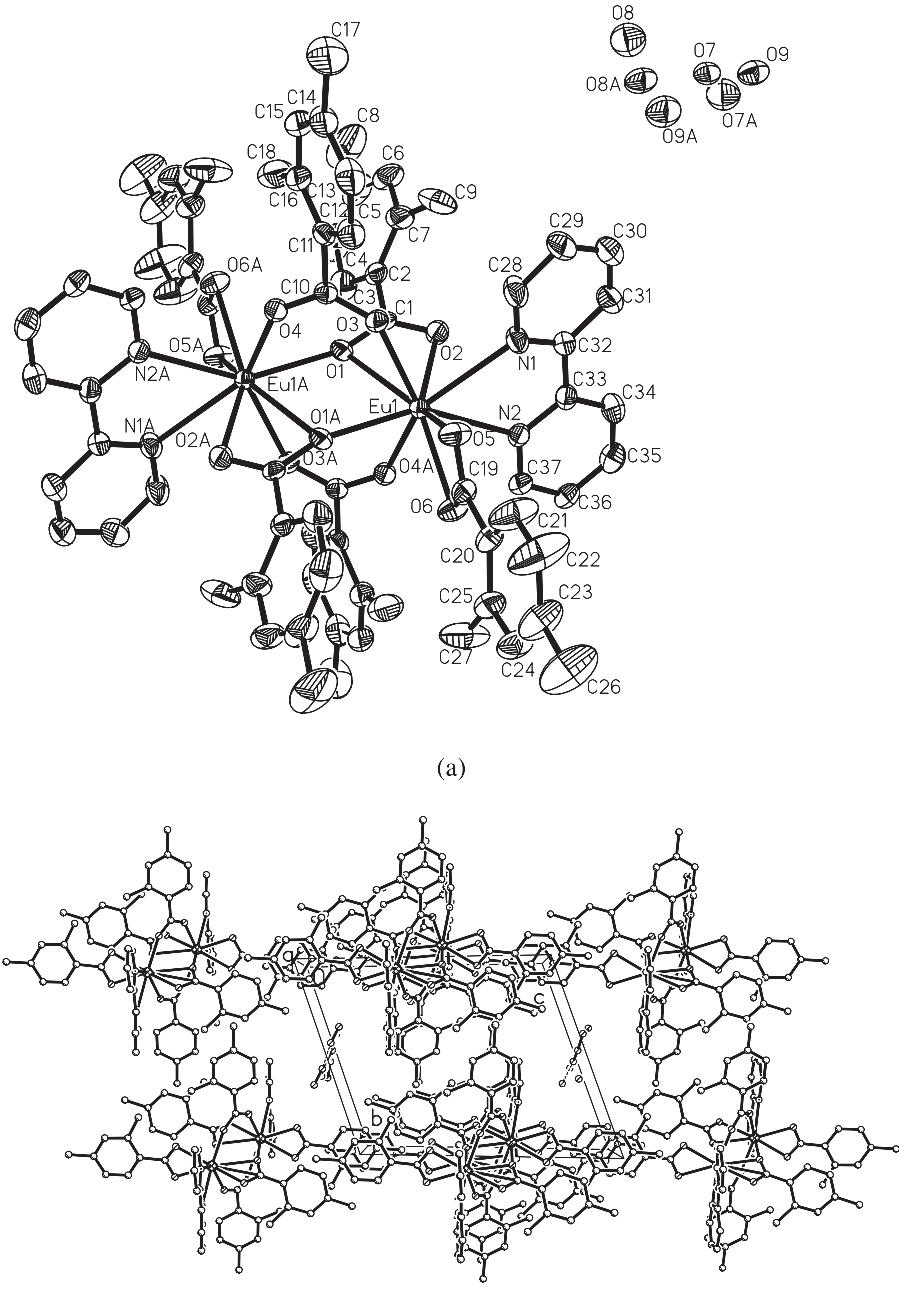


Figure 1. Polymeric structure of the complex **1**, (a) one-dimensional polymer chain structure viewed along the *c*-axis, (b) π–π stacking interaction viewed along the *a*-axis (all hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level).



(a)

(b)

Figure 2. (a) Molecular structure of the complex **2**, (b) Packing diagram of complex **2** viewed along *b*-axis. (all hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level).

The five atoms of the chelated ring containing the chelated nitrogen atoms and the europium ion atom are not coplanar. In addition, six uncoordinated water molecules exist in the asymmetric unit (figure 2b).

3.3. *Structural description of complex 3*

Unlike complex **2**, [Eu(2,4-DMBA)$_3$ · phen]$_2$ (**3**) crystallizes in the monoclinic system with space group *C*2/*c* while the anterior belongs to triclinic system with space group $P\bar{1}$. The molecular structure of the complex **3** is shown in figure 3 as a binuclear molecule with an inversion center. The distance between two central Eu(III) ions is 4.124(4) Å. The two Eu(III) ions are linked together by four bidentate bridging 2,4-DMBA ligands, with two additional 2,4-DMBA groups and two phen molecules chelated to them. Eu(III) ion is eight-coordinate by six O atoms of five 2,4-DMBA ligands and two N atoms of one phen ligand. The coordination environment of Eu(III) can be described as a distorted square antiprism; O3, O4A, O5, O6A, and O1, O2, N1, N2 form lower and upper square planes with mean deviations of 0.0507 and 0.2047 Å, respectively, with a dihedral angle of 6.9°. The Eu1–O distances are in a range of 2.335(2)–2.496(2) Å. The mean bond length is 2.398 Å. The Eu1–N distances are 2.601(3) and 2.626(3) Å, respectively, with a mean bond length of 2.613 Å. Bond angles of O–Eu–O range from 45.20(7) to 160.58(7)°, and that of N–Eu–N is 62.70(8)°.

Generally speaking, lanthanide complexes with monocarboxylic acids usually form an infinite one-dimensional polymer chain, whereas lanthanide mixed-ligand complexes

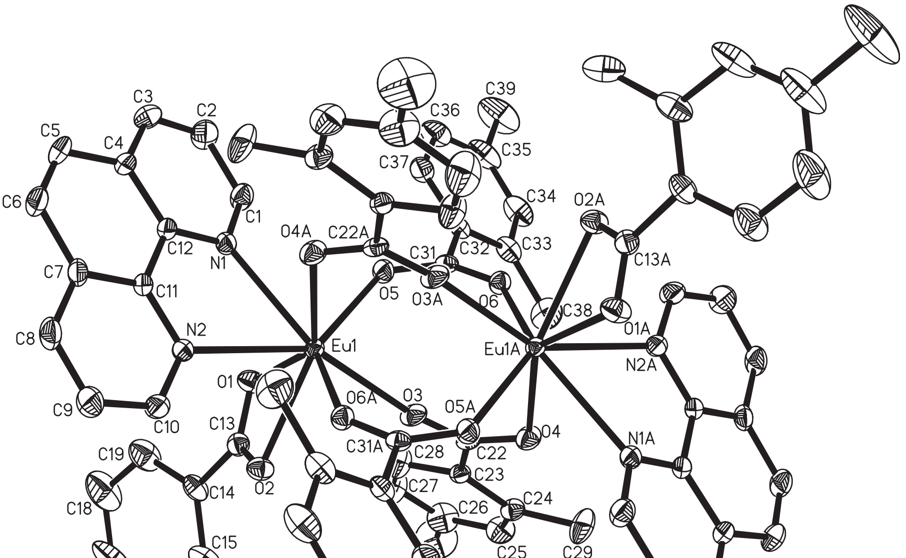


Figure 3. Molecular structure of the complex **3** (all hydrogen atoms have been omitted for clarity; the thermal ellipsoids are shown at the 30% probability level).

with monocarboxylic acids and diamines such as 2,2′-bpy and phen are commonly dimeric. For example, when 4-methylbenzoic acid was used as ligand, europium polymer complex $[Eu(4\text{-}CH_3C_6H_4COO)_3]_n$ [2], binuclear molecules $[Eu(4\text{-}CH_3C_6H_4COO)_3 \cdot phen]_2$ [5], and $[Eu(4\text{-}CH_3C_6H_4COO)_3 \cdot 2,2'\text{-}bpy]_2$ [6] were obtained. When 2,3-dimethoxybenzoic acid was used as ligand, europium polymer complex $[Eu(2,3\text{-}DMOBA)_3]_n$ [3], binuclear molecules $[Eu(2,3\text{-}DMOBA)_3 \cdot bpy]_2$ [7] and $[Eu(2,3\text{-}DMOBA)_2 \cdot NO_3 \cdot phen]_2$ [7] were obtained. Using 3-methoxybenzoic acid as ligand, europium polymer complex $[Eu(3\text{-}MOBA)_3 \cdot 2H_2O]_n$ [4], binuclear molecules $[Eu(3\text{-}MOBA)_3 \cdot 2,2'\text{-}bpy]_2$ [8], and $[Eu(3\text{-}MOBA)_2 \cdot NO_3 {\cdot} phen]_2$ [7] were obtained.

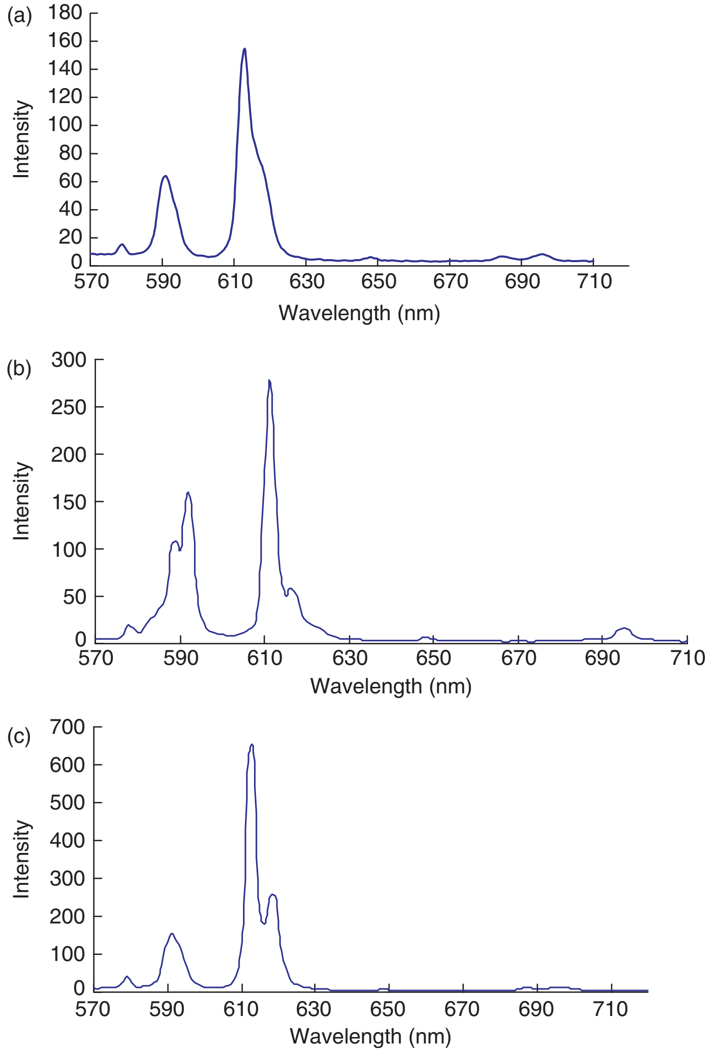


Figure 4. Fluorescence spectra of the complexes ($\lambda_{ex} = 393$ nm), (a) complex **1**, (b) complex **2**, (c) complex **3**.

3.4. *Luminescence properties*

The three complexes **1**, **2**, and **3** emit bright red light in the solid state under UV light. The fluorescence spectra of the three complexes recorded are in the range from 520 to 720 nm under excitation wavelength of 393 nm at room temperature, as shown in figure 4(a)–(c), respectively. There are five narrow bands in the luminescence spectra corresponding to the characteristic emission $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4) transition of Eu(III) ion. For the three complexes, three weak emission bands at 579, 648, and 698 nm are attributed to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ transition emission of Eu^{3+} ion, respectively. For complex **1**, emission bands corresponding to $^5D_0 \rightarrow {}^7F_1$ are at 591 nm, whereas emission bands corresponding to $^5D_0 \rightarrow {}^7F_2$ at 613 nm with a shoulder at 617 nm (figure 4a). For complex **2**, the emission bands corresponding to $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ transition at 592 nm and 611 nm, respectively, have shoulders at 589, 617 nm, respectively (figure 4b). For complex **3**, the emission at 591 nm is attributed to $^5D_0 \rightarrow {}^7F_1$ transition, whereas split emission bands corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition at 613 nm with a shoulder of 619 nm (figure 4c) were obtained. The intensity of the $^5D_0 \rightarrow {}^7F_2$ transition is most intense. The different fluorescence spectra of the three complexes indicate different chemical environments of Eu(III) ions, in agreement with the X-ray crystal structure of the three complexes.

Supplementary data

Supplementary data for the three structures are deposited with the Cambridge Crystallographic Data Center, CCDC-286723, 286724, and 2286724 for complexes **1**, **2**, and **3**, respectively. These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: + 44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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References

[1] X. Li, Z.Y. Zhang, D.Y. Wang, Y.Q. Zou. *Z. Kristallogr. NCS*, **220**, 36 (2005).
[2] Q.H. Jin, X. Li, Y.Q. Zou, K.B. Yu. *Acta Cryst.*, **C57**, 676 (2001).
[3] X. Li, Y.Q. Zou, B. Zheng, H.M. Hu. *Acta Cryst.*, **C60**, m197 (2004).
[4] X. Li, Q.H. Jin, Y.Q. Zou, K.B. Yu. *Z. Kristallogr. NCS*, **216**, 285 (2001).
[5] L.P. Jin, M.Z. Wang, G.L. Cai, S.X. Liu, J.L. Huang, R.F. Wang. *Science in China (Series B)*, **24**, 577 (1994).
[6] R.F. Wang, L.P. Jin, M.Z. Wang, S.H. Huang, X.T. Cheng. *Acta Chim. Sin. (in Chinese)*, **53**, 39 (1995).
[7] X. Li, L.P. Jin, X.J. Zheng, S.Z. Lu, J.H. Zhang. *J. Mol. Struct.*, **607**, 59 (2002).
[8] X. Li, Z.Q. Bian, L.P. Jin, S.Z. Lu, S.H. Huang. *J. Mol. Struct.*, **522**, 117 (2000).

[9] X.M. Zheng, L.P. Jin, M.Z. Wang. *J. Rare Earths (in Chinese)*, **12**, 250 (1994).
[10] L.Y. Wang, X.J. Zheng, L.P. Jin, S.Z. Lu. *Chem. J. Chin. Univ. (in Chinese)*, **20**, 1110, (1999).
[11] Y. Zhang, L.P. Jin, S.Z. Lu. *J. Chin. Rare Earth Soc.*, **16**, 5 (1998).
[12] L.P. Jin, S.X. Lu, S.Z. Lu. *Polyhedron*, **15**, 4069 (1996).
[13] S.G. Roh, M.K. Nah, J.B. Oh, N.S. Baek, K.M. Park, H.K. Kim. *Polyhedron*, **24**, 137 (2005).
[14] G.M. Sheldrick. *Acta Cryst.*, **A46**, 467 (1990).
[15] G.M. Sheldrick. *SHELXL97, Program for X-ray Crystal Structure Solution*, University of Göttingen, Germany (1997).