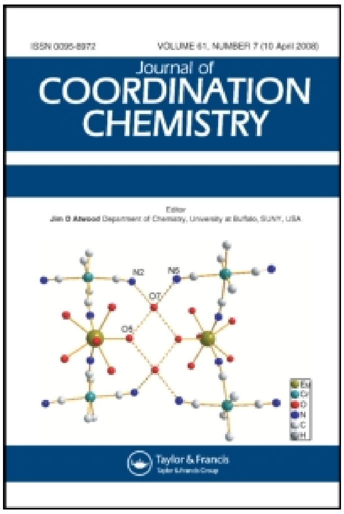

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Two 1-D europium coordination polymers: synthesis, crystal structure and fluorescence

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Two 1-D europium coordination polymers: synthesis, crystal structure and fluorescence

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Two new complexes $\{[Eu(2,4\text{-}DFBA)_3 \cdot (H_2O)_2] \cdot H_2O\}_n$ (**1**) and $[Eu(2\text{-}BrBA)_3 \cdot H_2O]_n$ (**2**) (2,4-DFBA = 2,4-difluorobenzoate, 2-BrBA = 2-bromobenzoate) have been synthesized and characterized by single crystal X-ray diffraction. **1** has a 1-D chain structure, in which Eu(III) ions are bridged by single COO^- groups and a 2-D supramolecular network is formed by hydrogen bond interactions. In **1**, each Eu(III) is eight-coordinate with six oxygens from four 2,4-DFBA ligands and two waters. **2** has a 1-D chain structure, in which Eu(III) ions are bridged by bridging-chelating-bridging COO^- groups. In **2**, each Eu(III) ion is nine-coordinate with eight oxygens from five 2-BrBA ligands and one water. The two complexes exhibit intense luminescence at room temperature. The $^5D_0 \rightarrow {}^7F_j$ ($j = 0$–4) transition emissions of Eu(III) have been observed.

Keywords: Europium; 2,4-Difluorobenzoate; 2-Bromobenzoate; Crystal structure; Fluorescence

1. Introduction

Lanthanide complexes have attracted attention of researchers for interesting structures and potential applications in luminescent materials, catalysts, and magnetic molecular materials, etc. [1–5]. Among lanthanide ions, europium(III) ion has received the most attention because of good luminescence with narrow bandwidth, large Stokes shift, and long luminescence lifetime. A large number of lanthanide carboxylate complexes have been reported [6–20] with dimeric or 1-, 2-, and 3-D polymeric structures due to variable coordination number of Ln(III) as well as coordination versatility of carboxylate. Benzoic acid and its derivatives have been widely used in preparation of lanthanide complexes because of their rigid structures and high thermal stabilities [6–16]. Benzoic acids with different substituents on the ring may lead to different structures of lanthanide complexes. A series of lanthanide complexes with benzoate-derivatives have been synthesized in our laboratory [9–12]. As a part of our studies on europium complexes with benzoate-derivatives, two new complexes $\{[Eu(2,4\text{-}DFBA)_3 \cdot (H_2O)_2] \cdot H_2O\}_n$ (**1**) and $[Eu(2\text{-}BrBA)_3 \cdot H_2O]_n$ (**2**) (2,4-DFBA = 2,4-difluorobenzoate, 2-BrBA = 2-bromobenzoate) have been synthesized and the crystal structures and luminescent properties of

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the two complexes are reported. The present structures differ from those reported for the lanthanide polymers with mono-carboxylate.

2. Experimental

2.1. *Materials and methods*

$EuCl_3 \cdot 6H_2O$ was made by the reaction of europium oxide (99.90%) and hydrochloric acid. Other analytical grade reagents and solvents were purchased commercially and used without further purification.

Elemental analyses (C, H, N) were determined on an Elementar Vario EL elemental analyzer. IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer using KBr pellets from 400–4000 cm^{-1}. UV–Vis absorption spectra were measured in DMSO solvent ($c = 1 \times 10^{-4}\,mol\,L^{-1}$) on a TU-1810 Ultraviolet-Visible spectrophotometer. Thermogravimetric analyses were performed on a WCT-1A Thermal Analyzer with a heating rate of 10°C min^{-1} from 20 to 1000°C. Excitation and emission spectra of the solids were recorded on an F-4500 fluorescence spectrophotometer at room temperature.

2.2. *Synthesis of the complexes*

2.2.1. $\{[Eu(2,4\text{-}DFBA)_3 \cdot (H_2O)_2] \cdot H_2O\}_n$ (1). 1.2 mmol 2,4-DFBA was dissolved in 25 mL ethanol, and the mixture heated under reflux with stirring while the pH was adjusted to 5 by 2 mol L^{-1} NaOH aqueous solution. Then 5 mL ethanol solution of $EuCl_3 \cdot 6H_2O$ (0.4 mmol) was dropped into the mixture. The resulting solution was filtered and colorless square single crystals suitable for X-ray structural analysis were obtained. Yield: 42%. $C_{21}H_{15}F_6O_9Eu$ (677.29), Calcd. (%): C, 37.24; H, 2.23. Found (%): C, 37.01; H, 2.18. Selected IR (KBr pellet, ν/cm^{-1}): 3407 br, 1615 vs, 1543 vs, 1437 vs, 1401 vs, 1274 vs, 1141 m, 1094 m, 850 m, 784 m, 621 m, 519 w, 441 w.

2.2.2. $[Eu(2\text{-}BrBA)_3 \cdot H_2O]_n$ (2). A mixture of $EuCl_3 \cdot 6H_2O$ (0.4 mmol), 2-BrBA (1.2 mmol) and distilled water (7 mL) was brought to pH = 5.0 with 2.0 mol L^{-1} NaOH aqueous solution. Then the mixture was placed in a 25 ml Teflon-lined stainless steel vessel, and the vessel was sealed and heated at 160°C for 3 days. After cooling to room temperature slowly, colorless crystals of **2** were isolated. Yield: 45%. $C_{21}H_{15}F_6O_9Eu$ (677.29), Calcd (%): C, 32.73; H, 1.83. Found (%): C, 32.67; H, 1.79. Selected IR (KBr pellet, ν/cm^{-1}): 3320 br, 1574 s, 1526 vs, 1501 vs, 1407 vs, 1045 m, 859 m, 761 s, 647 m, 546 w, 443 w.

2.3. *X-ray crystallographic study*

X-ray crystal data collection for the complexes were performed on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Semiempirical absorption corrections were applied using SADABS [21].

All calculations were carried out on a computer with use of SHELXS-97 and SHELXL-97 [22, 23]. The structures were solved by direct methods and refined on $|F|^2$ by full-matrix least-squares. A summary of the crystallographic data and details of the structure refinements are listed in table 1. Selected bond lengths and angles of **1** and **2** are listed in tables 2 and 3, respectively.

Table 1. Crystal data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{21}H_{15}F_6O_9Eu$	$C_{21}H_{14}Br_3O_7Eu$
Formula weight	677.29	769.99
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/n$
Unit cell dimensions (Å, °)		
a	6.3830(13)	12.530(3)
b	11.323(2)	6.9534(14)
c	15.939(3)	26.079(5)
α	92.08(3)	90
β	90.86(3)	101.65(3)
γ	93.66(3)	90
Volume (Å^3)	1148.7(4)	2225.5(8)
Z	2	4
Calculated density (Mg m^{-3})	1.958	2.298
Absorption coefficient (mm^{-1})	2.830	8.246
$F(000)$	660	1456
Crystal size (mm^3)	0.16 × 0.18 × 0.22	0.42 × 0.27 × 0.21
θ range for data collection (°)	1.80–25.50	1.69–25.30
Limiting indices	$-7 \le h \le 7$, $-11 \le k \le 13$, $-19 \le 1 \le 16$	$-15 \le h \le 14$, $-8 \le k \le 8$, $-31 \le 1 \le 31$
Reflections collected/unique	6082/4151 [$R_{(\mathrm{int})} = 0.0196$]	11494/4058 [$R_{(\mathrm{int})} = 0.0380$]
Data/restraints/parameters	4151/12/322	4058/3/259
Goodness-of-fit on F^2	1.057	1.006
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0331$, $wR_2 = 0.0832$	$R_1 = 0.0528$, $wR_2 = 0.1612$
R indices (all data)	$R_1 = 0.0377$, $wR_2 = 0.0865$	$R_1 = 0.0717$, $wR_2 = 0.1772$
Largest diff. peak and hole (e Å^{-3})	1.830 and −1.447	1.467 and −2.487

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

Eu(1)–O(1)	2.507(4)	Eu(1)–O(2)	2.432(4)
Eu(1)–O(3)	2.452(3)	Eu(1)–O(4)	2.523(3)
Eu(1)–O(5)	2.350(3)	Eu(1)–O(6)#1	2.287(3)
Eu(1)–O(7)	2.395(3)	Eu(1)–O(8)	2.385(4)
O(1)–Eu(1)–O(4)	121.32(12)	O(2)–Eu(1)–O(1)	52.51(12)
O(2)–Eu(1)–O(3)	135.18(12)	O(2)–Eu(1)–O(4)	151.55(13)
O(3)–Eu(1)–O(1)	82.75(12)	O(3)–Eu(1)–O(4)	52.15(11)
O(5)–Eu(1)–O(1)	73.28(13)	O(5)–Eu(1)–O(2)	84.28(12)
O(5)–Eu(1)–O(3)	79.76(12)	O(5)–Eu(1)–O(4)	122.40(12)
O(5)–Eu(1)–O(7)	72.53(12)	O(5)–Eu(1)–O(8)	140.71(13)
O(6)#1–Eu(1)–O(1)	130.61(13)	O(6)#1–Eu(1)–O(2)	84.60(12)
O(6)#1–Eu(1)–O(3)	135.74(12)	O(6)#1–Eu(1)–O(4)	83.68(12)
O(6)#1–Eu(1)–O(5)	131.78(13)	O(6)#1–Eu(1)–O(7)	77.03(13)
O(6)#1–Eu(1)–O(8)	83.51(14)	O(7)–Eu(1)–O(1)	145.65(13)
O(7)–Eu(1)–O(2)	126.25(13)	O(7)–Eu(1)–O(3)	88.04(13)
O(7)–Eu(1)–O(4)	75.81(13)	O(8)–Eu(1)–O(2)	82.62(14)
O(8)–Eu(1)–O(3)	83.92(14)	O(8)–Eu(1)–O(4)	70.35(13)

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

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

Eu(1)–O(1)	2.507(4)	Eu(1)–O(2)	2.432(4)
Eu(1)–O(3)	2.452(3)	Eu(1)–O(4)	2.390(7)
Eu(1)–O(5)	2.363(7)	Eu(1)–O(6)	2.618(6)
Eu(1)–O(6)#1	2.413(7)	Eu(1)–O(7)	2.623(6)
Eu(1)–O(7)#2	2.432(7)		
O(1)–Eu(1)–O(2)	52.6(2)	O(1)–Eu(1)–O(6)	70.8(2)
O(1)–Eu(1)–O(7)	92.4(2)	O(2)–Eu(1)–O(6)	93.7(2)
O(2)–Eu(1)–O(7)	72.3(2)	O(3)–Eu(1)–O(1)	142.2(2)
O(3)–Eu(1)–O(2)	143.4(2)	O(3)–Eu(1)–O(6)	73.8(2)
O(3)–Eu(1)–O(7)	73.7(2)	O(3)–Eu(1)–O(7)#2	80.6(2)
O(4)–Eu(1)–O(1)	124.2(2)	O(4)–Eu(1)–O(2)	124.8(3)
O(4)–Eu(1)–O(3)	78.1(2)	O(4)–Eu(1)–O(6)	140.8(2)
O(4)–Eu(1)–O(6)#1	85.9(2)	O(4)–Eu(1)–O(7)	143.2(2)
O(4)–Eu(1)–O(7)#2	82.5(2)	O(5)–Eu(1)–O(1)	76.9(3)
O(5)–Eu(1)–O(2)	75.7(3)	O(5)–Eu(1)–O(3)	132.6(2)
O(5)–Eu(1)–O(4)	54.5(2)	O(5)–Eu(1)–O(6)	145.4(3)
O(5)–Eu(1)–O(6)#1	93.7(3)	O(5)–Eu(1)–O(7)	146.0(3)
O(5)–Eu(1)–O(7)#2	93.1(3)	O(6)–Eu(1)–O(7)	49.3(2)
O(6)#1–Eu(1)–O(1)	126.6(2)	O(6)#1–Eu(1)–O(2)	74.1(2)
O(6)#1–Eu(1)–O(3)	80.5(2)	O(6)#1–Eu(1)–O(6)	115.19(16)
O(6)#1–Eu(1)–O(7)	66.7(2)	O(6)#1–Eu(1)–O(7)#2	159.5(2)
O(7)#2–Eu(1)–O(1)	73.8(2)	O(7)#2–Eu(1)–O(2)	126.4(2)
O(7)#2–Eu(1)–O(6)	66.5(2)	O(7)#2–Eu(1)–O(7)	114.99(16)

Symmetry transformations used to generate equivalent atoms. #1: $-x+3/2,\ y+1/2, -z+1/2$; #2: $-x+3/2,\ y-1/2, -z+1/2$.

3. Results and discussion

3.1. *Structural description of* $\{[Eu(2,4\text{-}DFBA)_3 \bullet (H_2O)_2] \bullet H_2O\}_n$ *(1)*

The crystal structure of **1** is shown in figure 1. Complex **1** can be regarded as a 1-D infinite chain composed of $[Eu(2,4\text{-}DFBA)_3 \cdot (H_2O)_2]$ units with free water. In the asymmetric unit of **1** there are one Eu(III) ion, three 2,4-DFBA, two coordinated waters, and one free water [figure 1(a)]. Each Eu(III) is eight-coordinate by six oxygens from four 2,4-DFBA ligands and two waters. The coordination environment of Eu(III) ion can be described as a distorted square-antiprism. The upper and lower planes are composed of O3, O4, O5 and O7 and O1, O2, O6A and O8, with mean deviation from the upper and lower planes of 0.2780 and 0.3626 Å, respectively. The dihedral angle between the two planes is 8.5°. The Eu1–O (carboxyl) bond lengths vary from 2.287(3) to 2.507(4) Å with average of 2.426 Å. The Eu1–O (water) distances are 2.395(3) and 2.385(4) Å, respectively, with average of 2.390 Å. The O–Eu1–O bond angles are in the range 52.15(11) to 151.55(13)°. The 2,4-DFBA ligands adopt bidentate-chelating and bidentate-bridging coordination modes. The O1–C1–O2 and O3–C8–O4 groups are bidentate-chelating with two O atoms coordinated to the same Eu(III) ion, and the O5–C15–O6 group is bidentate-bridging, in which two O atoms coordinate to adjacent Eu(III) ions. Eu(III) ions are connected through single bidentate-bridging COO^- to form a 1-D chain [figure 1(b)]. The 1-D chain is different from the common reported ones [6–9, 14–18]. In lanthanide complexes with carboxylates, metal ions are connected by carboxylate groups resulting in different structural architectures, however, many lanthanide complexes with mono-carboxylate show 1-D polymeric chain structures, in which the adjacent Ln(III) ions are linked through two, three, or four COO^- groups,

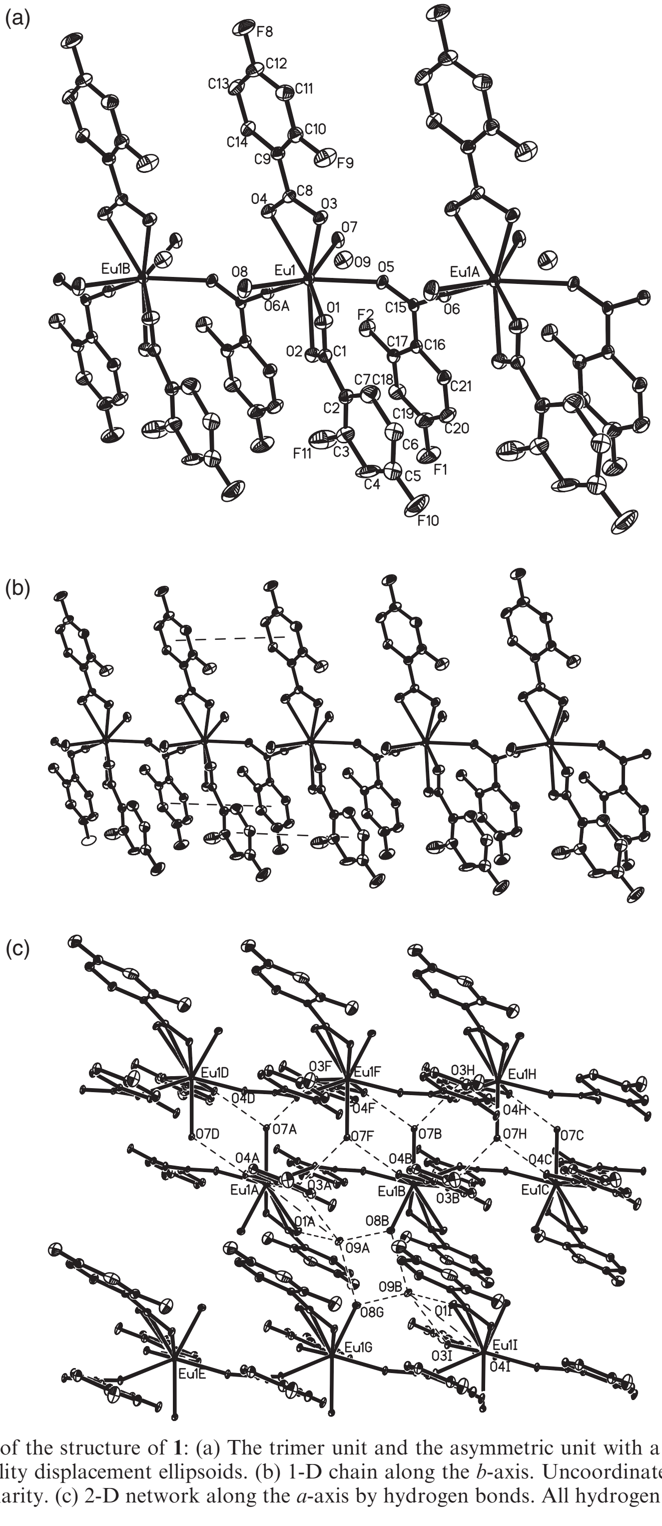
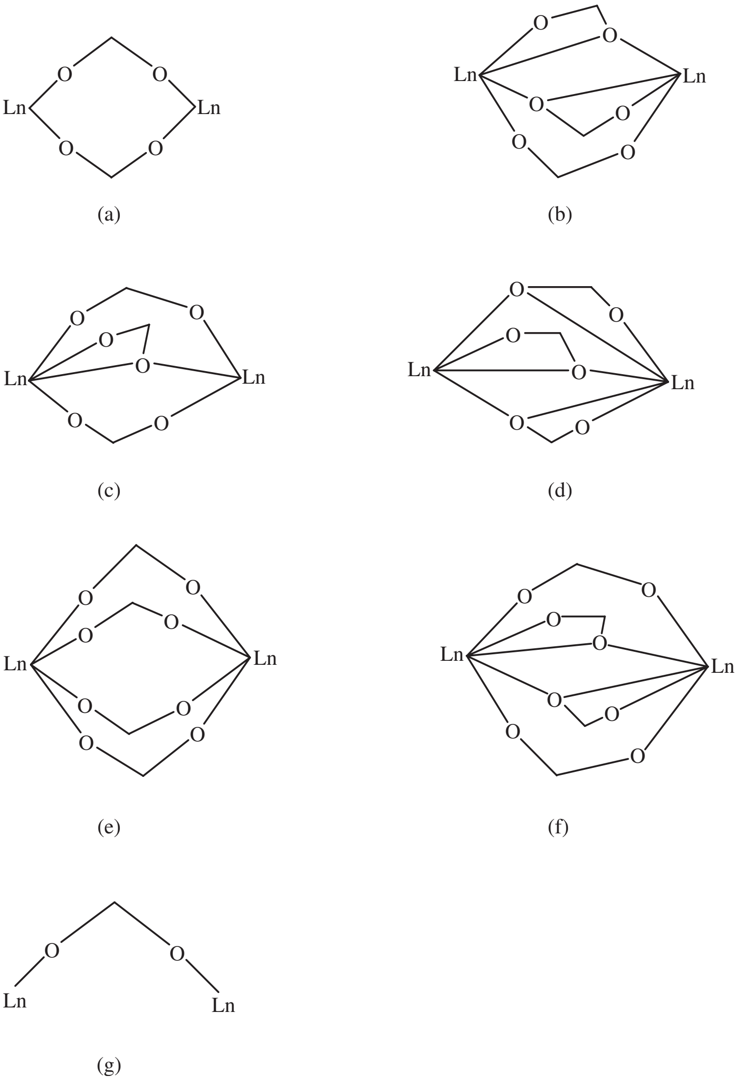


Figure 1. View of the structure of **1**: (a) The trimer unit and the asymmetric unit with a labeling scheme at the 30% probability displacement ellipsoids. (b) 1-D chain along the *b*-axis. Uncoordinated water molecules are omitted for clarity. (c) 2-D network along the *a*-axis by hydrogen bonds. All hydrogen atoms are omitted for clarity.

and these COO^- groups adopt bidentate-bridging or tridentate bridging-chelating coordination modes [scheme 1 (a–g)], such as $[\{Sm(OBz)_3(MeO)_2\}_2]_n$ (OBz = benzoate) with two bidentate-bridging COO^- groups (a) [6]; $[Eu(2,4\text{-}DMBA)_3]_n$ (2,4-DMBA = 2,4-dimethylbenzoate) with alternate one bidentate-bridging and two tridentate-bridging (b), and two bidentate-bridging and one tridentate-bridging (c) [7]; $[Eu(p\text{-}MBA)_3]_n$ (p-MBA = 4-methylbenzoate) with three bridging-chelating COO^- groups (d) [8]; $[Gd(HF_2CCOO)_3(H_2O)_2 \cdot H_2O]_n$ with four bidentate-bridging COO^- groups (e) [17]; and $[Eu(HCl_2CCOO)_3 \cdot 2H_2O]_n$ with two bidentate-bridging and two bridging-chelating COO^- groups (f) [18]. However, in **1**, the 1-D chain is formed through single COO^- groups (g) as linkers. This is rare in lanthanide complexes containing mono-carboxylate, but formation of multiple μ-COO^- bridges that join



(a) (b) (c) (d) (e) (f) (g)

Scheme 1. The coordination modes of carboxylate groups linking Ln(III) ions.

Ln^{3+} ions is very common. All Eu(III) ions lie on a straight line. The distance between adjacent Eu(III) ions is 6.383 Å, larger than Eu $\cdots$ Eu distances in other reported europium coordination polymers with mono-carboxylates [7–9].

A view of the packing of **1** shows a 2-D supramolecular network is formed by hydrogen bonds based on the 1-D chain [figure 1(c)]. Free waters (O9) form hydrogen bonds with coordinated water molecules (O8) and carboxylate oxygen atoms (O1 and O3), O8–H3W $\cdots$ O9 $[x-1, y, z]$, 2.742 Å, 173.90°; O8–H4W $\cdots$ O9 $[-x, -y+1, -z+1]$, 2.756 Å, 125.96°; O9–H6W $\cdots$ O1, 2.724 Å, 159.12°; and O9–H5W $\cdots$ O3, 2.900 Å, 110.00°. The coordinated water molecules (O7) form hydrogen bonds with carboxylate oxygen atoms (O4 and O3), O7–H1W $\cdots$ O4 $[-x-1, -y, -z+1]$, 2.694 Å, 173.40° and O7–H2W $\cdots$ O3 $[-x, -y, -z+1]$, 2.895 Å, 128.55°. These hydrogen bonds link adjacent chains to form a 2-D network structure.

3.2. *Structural description of* $[Eu(2\text{-}BrBA)_3 \cdot H_2O]_n$ *(2)*

Complex **2** crystallizes in the monoclinic system, $P2_1/n$ space group, and is different from **1** belonging to the triclinic with space group $P\bar{i}$. The crystal structure of **2** also shows a 1-D infinite chain as shown in figure 2(b). Each independent crystallographic unit of **2** comprises one Eu(III), three 2-BrBA and one water [figure 2(a)]. Each Eu(III) is nine-coordinate with eight oxygens from five 2-BrBA ligands and one water. The coordination environment of Eu(III) can be described as a distorted monocapped square-antiprism. The capping vertex of the polyhedron is occupied by O4, the upper and lower planes are O3, O7B, O5 and O6A and O6, O1, O2 and O7, respectively, the mean deviation from the upper and lower planes are 0.3237 and 0.0040 Å, respectively, and the dihedral angle between the two planes is 0.3°. The Eu1–O (carboxyl) bond lengths vary from 2.390(7) to 2.623(6) Å with the average 2.475 Å. The Eu1–O (water) distance is 2.452(3) Å. The O–Eu1–O bond angles are in the range 49.3(2) to 159.5(2)°. The 2-BrBA ligands adopt bidentate-chelating and quadridentate-bridging coordination modes. The O1–C14–O2 and O4–C21–O5 groups are bidentate-chelating with two O atoms coordinating one Eu(III). The O6–C7–O7 group is bridging-chelating-bridging with two O atoms coordinating to three Eu(III) ions to form a quadridentate-bridging. The Eu(III) ions are connected through COO^- groups of 2-BrBA via bridging-chelating-bridging coordination to form a 1-D chain [figure 2(b)]. Bidentate-bridging and tridentate-bridging modes are common in lanthanide carboxylate complexes [19, 20], as mentioned above [6–8, 17, 18], while there are a few examples of 1-D coordination chains for carboxylate adopting quadridentate-bridging.

Viewed along the *a* axis, **2** displays a 1-D double-metal chain structure [figure 2(b)]. Each metal chain is obtained through infinite extension of –Eu–O–C–O–Eu–, and the two metal chains are parallel to each other. There are two different Eu $\cdots$ Eu distances along the 1-D structure evolving along the *a* axis. The Eu1B $\cdots$ Eu1C separation of 6.953 Å is larger because of the space occupied by one –O–C–O– bridge (Eu–O–C–O–Eu), and the Eu1A $\cdots$ Eu1B or Eu1A $\cdots$ Eu1C separation of 4.216(7) Å is shorter because the space is occupied by one –O– bridge (Eu–O–Eu). The angle Eu1B $\cdots$ Eu1A $\cdots$ Eu1C is 111.1°. The benzene rings of 2-BrBA ligands are parallel to each other, located on two sides of the chain.

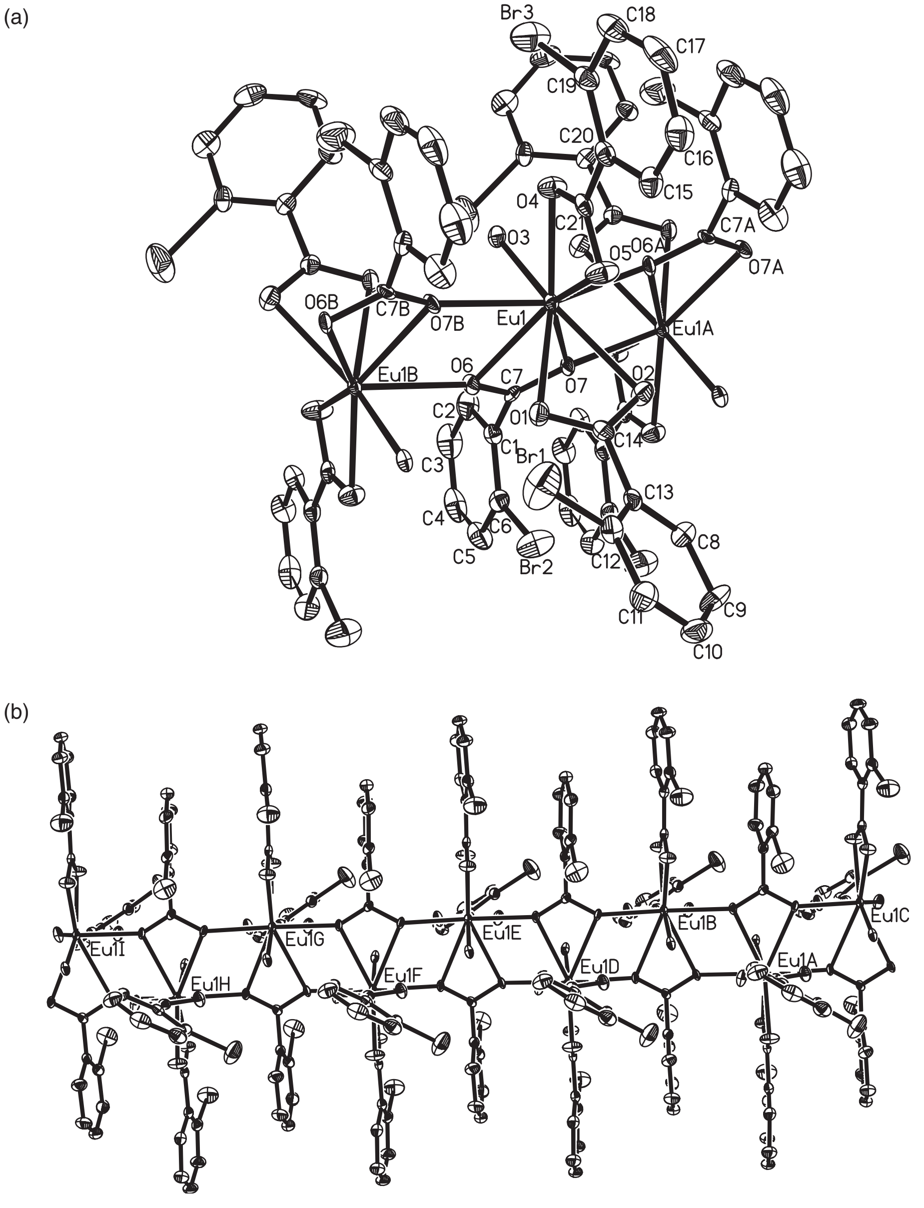


Figure 2. View of the structure of **2**: (a) The trimer unit and the coordination environment of Eu1^{3+} ion with a labeling scheme at the 30% probability displacement ellipsoids. (b) 1-D chain along the *a*-axis. All hydrogen atoms are omitted for clarity.

3.3. *Photophysical properties*

The ultraviolet absorption spectra of the complexes were measured in $1.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ DMSO solution from 200–400 nm. The broad absorption bands at 298.0 nm ($\varepsilon = 3.45 \times 10^{3}$) for **1** and 298.0 nm ($\varepsilon = 4.40 \times 10^{3}$) for **2** are attributed to π–π* electronic transition of the ligands. Both **1** and **2** emit a bright red fluorescence

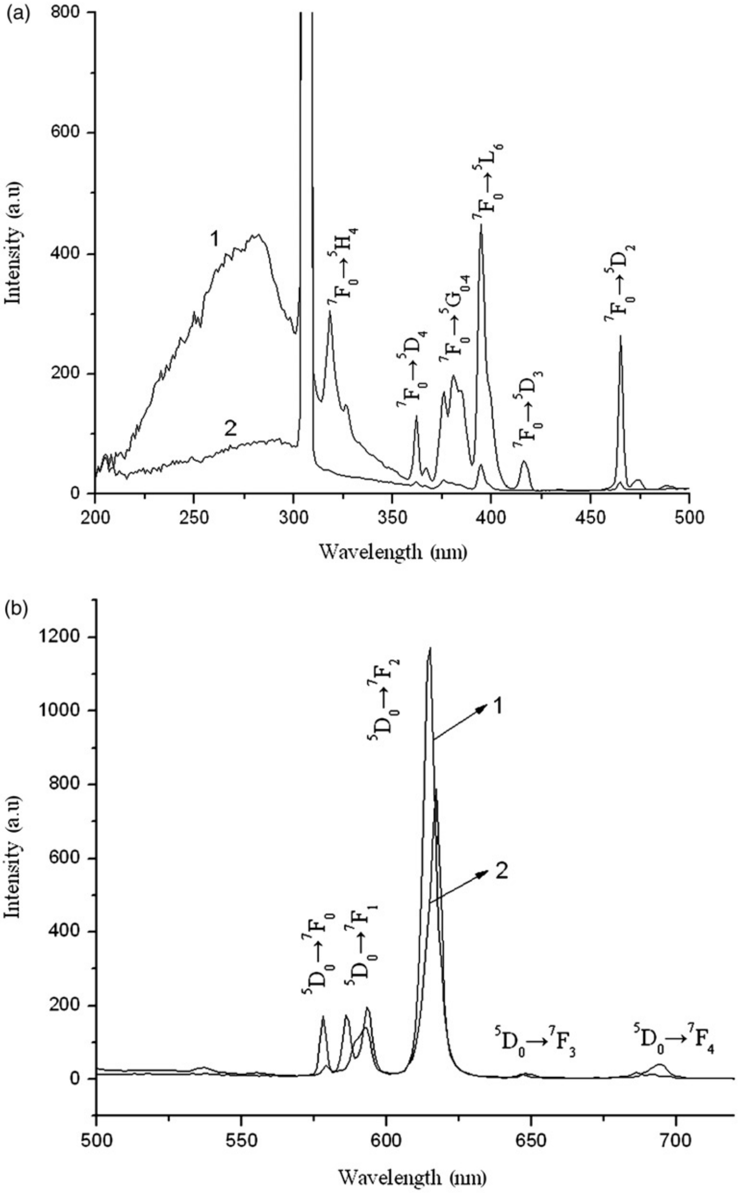


Figure 3. Luminescence spectra: (a) Excitation ($\lambda_{ex} = 612$ nm); (b) Emission ($\lambda_{em} = 395$ nm) 1 for complex **1**, 2 for complex **2**.

under ultraviolet light and the solid-state excitation and emission spectra were investigated at room temperature. The excitation and emission spectra of the two complexes are similar. The excitation spectra display a large broad band in the range 200–300 nm, which is attributed to the $S_0 \rightarrow S_1$ transition of the ligands. A series of sharp lines in the excitation spectra arise from the characteristic Eu(III) energy levels, namely, transitions from $^7F_0$ to the excited states (nm): $^5H_4$ (318), $^5D_4$ (361) $^5G_{0\text{-}4}$ (376–385), $^5L_6$ (395), $^5D_3$ (418), and $^5D_2$ (465) [figure 3(a)] [24]. The excitation bands of the ligands are much stronger than those of Eu(III), indicating efficient energy transfer from the ligands to the Eu(III) ions in the two complexes. The emission spectra of the complexes were recorded from 500–700 nm under excitation wavelength of 395 nm, as shown in figure 3(b). There are five main peaks at 579, 593, 615, 649 and 695 nm, corresponding to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5\mathrm{D}_0 \rightarrow {}^7F_4$ transitions of Eu(III) ion. The strongest emission is centered at 615 nm ($^5D_0 \rightarrow {}^7F_2$), which is responsible for the red emission; the $^5D_0 \rightarrow {}^7F_2$ transition is much more intense than the $^5D_0 \rightarrow {}^7F_1$ transition. The $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is equal to ca 8.3 for **1** and 4.3 for **2**, further confirming that Eu(III) is not located at an inversion center and symmetry of the Eu(III) is low [25].

3.4. *Thermogravimetric analysis*

The DTA-TG analyses were studied in air with a heating rate of 10°C min^{-1} from 20 to 1000°C. For **1**, the first weight loss of 8.14% occurs between 120 and 205°C, corresponding to the release of all water (calculated, 7.98%). Further weight loss occurs at 402°C, corresponding to decomposition of 2,4-DFBA. At 496°C, the complex is completely degraded into Eu_2O_3. The total weight loss of 72.64% is close to the calculated value of 74.02%. For **2**, complex starts decomposing at 211°C with weight loss of 2.52%, which corresponds to release of water (calculated, 2.34%). Further weight loss occurs in the range 477–531°C, which corresponds to decomposition of 2-BrBA. The total weight loss is 72.74%, indicating residual Eu_2O_3 (calculated 77.14%).

4. Conclusions

We obtained two new complexes $\{[\mathrm{Eu(2,4\text{-}DFBA)_3 \cdot (H_2O)_2] \cdot H_2O}\}_n$ (**1**) and $[\mathrm{Eu(2\text{-}BrBA)_3 \cdot H_2O}]_n$ (**2**). Comparing with a series of 1-D lanthanide polymers with monocarboxylate, the two complexes indicate novel structures; **1** has a 1-D chain through single COO$^-$ groups as linkers and **2** has a 1-D chain through rare quadridentate COO$^-$ groups as linkers. The two complexes display characteristic emissions of Eu(III).

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References

[1] S.K. Ghosh, J.P. Zhang, S. Kitagawa. *Angew. Chem.*, **119**, 8111 (2007).
[2] J.W. Han, C.L. Hill. *J. Am. Chem. Soc.*, **129**, 15094 (2007).
[3] A. Fratini, G. Richards. *Inorg. Chem.*, **47**, 1030 (2008).

[4] B.D. Chandler, D.T. Cramb, G.K.H. Shimizu. *J. Am. Chem. Soc.*, **128**, 10403 (2006).
[5] A. Mondry, P. Starynowicz. *Eur. J. Inorg. Chem.*, **5**, 1859 (2006).
[6] U.P. Singh, R. Kumar, S. Upreti. *J. Mol. Struct.*, **831**, 97 (2007).
[7] X. Li, Z.Y. Zhang, T.T. Zhang, Y.L. Ju. *J. Coord. Chem.*, **60**, 301 (2007).
[8] Q.H. Jin, X. Li, Y.Q. Zou, K.B. Yu. *Acta Cryst.*, **57**, 676 (2001).
[9] X. Li, Y.L. Ju, Y.Q. Zou. *J. Coord. Chem.*, **60**, 1513 (2007).
[10] X. Li, Z.Y. Zhang, Y.Q. Zou. *Eur. J. Inorg. Chem.*, **14**, 2909 (2005).
[11] X. Li, T.T. Zhang, Y.L. Ju, C.Y. Wang, Y.Q. Li, L. Zhang, Q. Zhang. *J. Coord. Chem.*, **60**, 2121 (2007).
[12] X. Li, Y.L. Ju, Y.Q. Li. *J. Coord. Chem.*, **61**, 692 (2008).
[13] S.G. Roh, M.K. Nah, J.B. Oh, N.S. Baek, K.M. Park, H.K. Kim. *Polyhedron*, **24**, 137 (2005).
[14] C. Seward, N.X. Hu, S. Wang. *J. Chem. Soc., Dalton Trans.*, **2**, 134 (2001).
[15] A.W.H. Lam, W.T. Wong, S. Gao, G.H. Wen, X.X. Zhang. *Eur. J. Inorg. Chem.*, **1**, 149 (2003).
[16] M.A.S. Goher, F.A. Mautner. *J. Mol. Struct.*, **846**, 153 (2007).
[17] A. Rohde, S.T. Hatscher, W. Urland. *J. Alloys Compd.*, **374**, 137 (2004).
[18] G. Oczko, P. Starynowicz. *J. Mol. Struct.*, **740**, 237 (2005).
[19] S. Viswanathan, A.D. Bettencourt-Dias. *Inorg Chem.*, **45**, 10138 (2006).
[20] R. Baggio, M.T. Garland, O. Peña, M. Perec. *Inorg. Chim. Acta*, **358**, 2332 (2005).
[21] G.M. Sheldrick. *SADABS, Program for Area Detector Adsorption Correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany (1996).
[22] G.M. Sheldrick. *Phase Annealing in SHELX-97*: *Direct Methods for Larger Structures*, *Acta Cryst.*, **A46**, 467 (1990).
[23] G.M. Sheldrick. *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
[24] P.I. Girginova, F.A. Almeida Paz, P.C.R. Soares-Santos, R.A. Sá Ferreira, L.D. Carlos, V.S. Amaral, J. Klinowski, H.I.S. Nogueira, T. Trindade. *Eur. J. Inorg. Chem.*, **26**, 4238 (2007).
[25] J.-C.G. Bünzli. *Lanthanide Probes in Life, Chemical and Earth Sciences, Theory and Practice*, Elsevier, Amsterdam (1989).