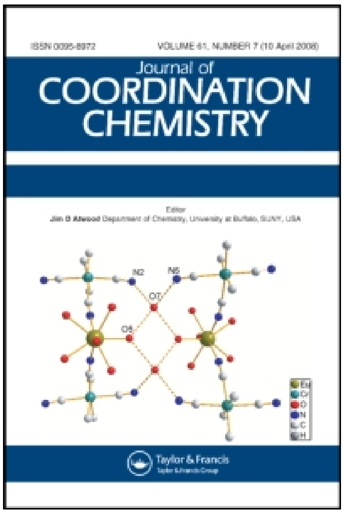

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Hydrothermal synthesis and characterizations of a novel modular europium(III) coordination polymer bridged by biphenyl-2,2'-dicarboxylate dianions and 1,10-phenanthroline

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Hydrothermal synthesis and characterizations of a novel modular europium(III) coordination polymer bridged by biphenyl-2,2′-dicarboxylate dianions and 1,10-phenanthroline

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A novel europium(III) coordination polymer, $[Eu_2(bpdc)_3(phen)_2(H_2O)_2]_n \cdot nH_2O$ (**1**) (bpdc = biphenyl-2,2′-dicarboxylate; phen = 1,10-phenanthroline), has been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction methods. Complex **1** is monoclinic, space group $C2/c$, with $a = 24.3862(6)$, $b = 12.0792(3)$, $c = 22.9120(5)$ Å, $\alpha = 90.00$, $\beta = 115.160(1)$, $\gamma = 90.00°$, $V = 6108.8(3)$ Å^3, $Z = 4$, final $R_1 = 0.0605$ and $wR_2 = 0.1760$. Each Eu(III) ion is coordinated by six oxygen atoms from three carboxylate groups of three different bpdc anions, an oxygen atom from one coordinated water molecule and two nitrogen atoms from one phen ligand to complete a deformed monocapped square antiprism. Each pair of bpdc anions acts as a tetradentate ligand to connect two adjacent Eu(III) ions through chelating carboxylate groups, resulting in a centrosymmetric binuclear unit. Each binuclear unit links two adjacent binuclear units through two terminal bpdc anions to produce a one-directional zigzag chain. Two different kinds of hydrogen-bonding interactions link the chains and the lattice water molecules to form a hydrogen-bonding network.

Keywords: Europium; Hydrogen bonds; Structure; Monocapped square antiprism

1. Introduction

Structural or framework diversity of coordination polymers is currently under intense study. The self-assembly of these materials depends on the selection of metallic centers and multifunctional ligands [1–3]. The europium(III) ion has a large radius and may exhibit coordination numbers ranging from 3 to 12, making the europium ion an excellent spacer in assembling metal–organic frameworks [4]. Multifunctional organic molecules with one or more carboxylate groups have been widely used as key building blocks because of their ability to coordinate to several metal centers in various coordination modes [4–8]. The most common coordination forms are unidentate, chelating

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bidentate (both symmetrical and asymmetrical), several bridging systems and the free carboxylate anion [7]. Although several novel coordination polymers with potential applications as functional materials assembled from biphenyl-2,2′-dicarboxylate (bpdc) dianions and transition metal ions have been reported, the lanthanide coordination polymers of bpdc dianions are very rare [9–13]. Thus, we selected the Eu–bpdc–phen (phen = 1,10-phenanthroline) system to extend this research and present here the hydrothermal synthesis and crystal structure of $[Eu_2(bpdc)_3(phen)_2(H_2O)]_n \cdot nH_2O$ (**1**).

2. Experimental

2.1. *Apparatus and reagents*

C, H and N were analyzed using a Carlo-Erba 1112 instrument. Europium was analyzed by complexometric titration with EDTA. Infrared spectra were measured on a Perkin-Elmer 2000 system in the range 4000–400 cm^{-1} as KBr disks. The crystal structure was obtained on a Bruker Smart Apex CCD diffractometer. All reagents were analar grade from commercial sources.

2.2. *Synthesis*

The title compound was synthesized by the hydrothermal method from a mixture of biphenyl-4,4′-dicarboxylic acid (1 mmol, 0.24 g), $Eu(NO_3)_3 \cdot 5H_2O$ (1 mmol, 0.43 g), 1,10-phenanthroline (4 mmol, 0.72 g) and water (20 mL) in a 30 mL teflon-lined stainless steel reactor. The solution was heated to 415 K for 5 days. The reaction system was then cooled slowly to room temperature, yellow block crystals were collected and washed with distilled water. Yield ca 65% based on Eu. The product was insoluble in water and common organic solvents. IR (KBr, ν, cm^{-1}): 3376w, 1696vs, 1548s, 1462s, 1387s, 1219s, 1158s, 1102m, 1029s, 861w, 810m, 713m, 626s, 493w. Anal. Calcd for $C_{66}H_{46}N_4O_{15}Eu_2$ (%): C, 54.78; H, 3.17; N, 4.42; Eu, 21.03. Found: C, 54.43; H, 3.46; N, 4.14; Eu, 20.78.

2.3. *Crystal structure determination*

A single crystal having dimensions of 0.30 × 0.14 × 0.10 mm was mounted on a glass fiber. All measurements were made on a Bruker Smart Apex diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation using the ω-scan technique. The data were collected at 298(2) K to a maximum θ value of 25.30°. Determinations of the lattice type, orientation matrix and cell dimensions were performed according to established procedures. Lorentz polarization and absorption corrections were applied. Absorption corrections were applied by fitting a pseudoellipsoid to the ω-scan data of selected strong reflections over a range of 2θ angles. The structure was solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically, and all of the hydrogen atoms were held stationary and included in the final stage of full-matrix least-squares refinement based on F^2 using the SHELXS-97 and SHELXL-97 programs. Crystallographic data for complex **1** are listed in table 1.

Table 1. Crystallographic data for complex **1**.

Empirical formula	$C_{66}H_{46}N_4O_{15}Eu_2$
Formula weight	1438.99
Temperature, K	298(2)
Crystal system	Monoclinic
Space group	$C2/c$
Crystal size, mm	$0.30 \times 0.14 \times 0.10$
Unit cell dimensions	
a, Å	24.3862(6)
b, Å	12.0792(3)
c, Å	22.9120(5)
α, °	90.00
β, °	115.160(1)
γ, °	90.00
Volume, $Å^3$	6108.8(3)
Z	4
ρ (Calcd), $g\,cm^{-3}$	1.565
$F(000)$	2864
Absorption coefficient, mm^{-1}	2.105
θ range for data collection, °	1.85–25.30
Reflections measured	16,083
Independent reflections	5535 [$R(\text{int}) = 0.0304$]
Limiting indices	$-29 \le h \le 25$, $-12 \le k \le 14$, $-27 \le l \le 27$
Absorption correction	Multiscan
Data/Restraints/Parameters	5535/0/397
Max. and min. transmission	0.8171 and 0.5708
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.139
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0605$, $wR_2 = 0.1760$
R indices (all data)	$R_1 = 0.0659$, $wR_2 = 0.1802$
Largest diff. peak and hole/e $Å^3$	3.068, −0.949

3. Results and discussion

The atomic coordinate and isotropic thermal parameters for non-H atoms are listed in table 2 and the selected bond lengths and bond angles are given in table 3. The coordination environment of Eu ion in **1** is depicted in figure 1. Each Eu ion coordinates to six O atoms from three carboxylate groups of three bpdc anions with a typical Eu–O (carboxylate) distance in the range 2.404(6)–2.572(6) Å [14], one water molecule with a Eu–O distance of 2.412(6) Å, and the two N atoms of one phen molecule in a chelating fashion with Eu–N distances of 2.556(7) and 2.571(7) Å. This results in a distorted monocapped square antiprism. The square plane formed by atoms O2, O7, O6 and N1, with a mean deviation of 0.4821 Å, is seriously distorted, but the mean deviation of the other square plane composed of O1, N2, O4 and O5 is only 0.2806 Å. To complete the coordination environment of the Eu center, O3 is located on the cap.

The IR spectrum of **1** shows characteristic bands of carboxylate groups at $1548\,cm^{-1}$ for asymmetric stretching and in the usual region at $1387\,cm^{-1}$ for symmetric stretching. The difference between asymmetric stretching and symmetric stretching bands of the carboxylate groups ($\Delta v = 161\,cm^{-1}$) suggests bidentate bonding [15], in agreement with the X-ray analysis results. In addition, the absence of a band in the region $1690–1730\,cm^{-1}$ (the O–H vibrations of –COOH groups) indicates the complete deprotonation of the carboxyl groups in **1**, and the typical bands (broad at 3376 and sharp at $1696\,cm^{-1}$) were found for the coordinated water molecules.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for non-H atoms.

Atom	x	y	z	U (eq)
Eu1	361(1)	6724(1)	3993(1)	28(1)
O1	775(3)	5822(5)	5027(3)	44(2)
O2	1241(3)	5406(2)	3183(1)	36(2)
O3	−569(3)	6106(2)	6807(1)	31(1)
O4	104(3)	4972(5)	3509(3)	48(2)
O5	470(3)	7307(5)	2892(3)	44(2)
O6	120(3)	8591(5)	3517(3)	42(1)
O7	873(3)	6590(6)	3297(3)	47(2)
N1	1214(3)	8052(6)	4660(4)	38(2)
N2	163(3)	7895(6)	4821(3)	35(2)
C1	1708(4)	8162(8)	4562(5)	49(2)
C2	2177(4)	8890(9)	4919(6)	58(3)
C3	2128(5)	9506(9)	5383(5)	58(3)
C4	1605(4)	9432(8)	5497(5)	47(2)
C5	1518(5)	10072(8)	5971(5)	57(3)
C6	1002(5)	9988(8)	6054(5)	57(3)
C7	539(5)	9250(7)	5680(4)	44(2)
C8	−4(5)	9139(8)	5762(5)	52(2)
C9	−428(5)	8393(8)	5388(5)	51(2)
C10	−331(4)	7790(8)	4919(5)	44(2)
C11	603(4)	8603(7)	5205(4)	36(2)
C12	1151(4)	8695(7)	5112(4)	38(2)
C13	1173(4)	5291(7)	4941(4)	34(2)
C14	1564(4)	4486(7)	5449(4)	34(2)
C15	1801(4)	3591(8)	5256(6)	51(2)
C16	2130(5)	2790(8)	5693(6)	56(3)
C17	2230(4)	2899(8)	6330(6)	54(3)
C18	2002(4)	3783(8)	6529(5)	51(2)
C19	1670(3)	4595(6)	6093(4)	34(2)
C20	−542(4)	5113(7)	3667(4)	35(2)
C21	−1017(4)	4245(6)	3504(4)	35(2)
C22	−945(5)	3277(8)	3231(4)	48(2)
C23	−1380(6)	2418(8)	3075(5)	59(3)
C24	−1861(5)	2550(9)	3221(5)	54(3)
C25	−1924(5)	3494(8)	3506(5)	50(2)
C26	−1518(4)	4377(7)	3644(4)	36(2)
C27	−310(4)	8309(6)	2997(4)	30(2)
C28	−641(4)	9181(7)	2506(4)	32(2)
C29	−1270(4)	9162(8)	2203(5)	45(2)
C30	−1586(4)	9996(8)	1795(5)	56(3)

The X-ray analysis reveals that each bpdc anion is as a tetradentate ligand connecting two adjacent Eu ions, and the two carboxylate groups of each bpdc anion are chelating. This coordination mode is different from that of $[Cu(bpdc)(phen)(H_2O)]_n$ [16], in which two carboxylate groups of each bpdc anion are monodentate. As shown in figure 2, each pair of Eu ions is bridged by two bpdc anions, forming a binuclear unit with an Eu $\cdots$ Eu ($-x$, $-y+1$, $-z+1$) separations of 6.976 Å and each of the centrosymmetric binuclear unit links two adjacent units through two terminal bpdc anions with two Eu $\cdots$ Eu ($-x$, y, $-z+1/2$) separations of 6.297 Å, extending a one-directional zigzag chain along the [−1 −1 1] direction. Because of the internal rotations about the C_2 axis, there are two different types of twists between the two aromatic rings of one bpdc, resulting in the two different separations of Eu $\cdots$ Eu. In one type, the dihedral angle between the two aromatic rings is 84.3°, while in the other,

Table 3. Selected bond lengths (Å) and angles (°) for **1**.

Eu1–O3	2.404(6)	Eu1–O1	2.405(6)
Eu1–O7	2.412(6)	Eu1–O4	2.434(6)
Eu1–O6	2.464(6)	Eu1–O2	2.513(6)
Eu1–O5	2.572(6)	Eu1–N1	2.556(7)
Eu1–N2	2.571(7)	N1–C1	1.323(12)
N1–C12	1.354(12)	N2–C10	1.324(11)
N2–C11	1.361(11)	C19–C26#1	1.493(12)
C33–C33#2	1.484(16)	O8–H8A	0.91(18)
O7–H7A	0.8205	O7–H7B	0.8200
O1–C13	1.246(10)	O2–C13	1.254(10)
O3–C20	1.255(10)	O4–C20	1.277(11)
O5–C27	1.263(10)	O6–C27	1.253(10)
O7 ··· O2	2.762(9)	O8 ··· O4#3	2.755(9)
O3–Eu1–O1	82.1(2)	O3–Eu1–O7	134.1(2)
O1–Eu1–O7	120.1(2)	O3–Eu1–O4	53.8(2)
O1–Eu1–O4	88.5(2)	O7–Eu1–O4	85.0(2)
O3–Eu1–O6	106.3(2)	O1–Eu1–O6	140.5(2)
O7–Eu1–O6	82.1(2)	O4–Eu1–O6	128.1(2)
O3–Eu1–O2	114.2(2)	O1–Eu1–O2	52.3(2)
O7–Eu1–O2	68.2(2)	O4–Eu1–O2	77.6(2)
O6–Eu1–O2	139.4(2)	O3–Eu1–N1	140.4(2)
O1–Eu1–N1	78.5(2)	O7–Eu1–N1	85.4(2)
O4–Eu1–N1	157.1(2)	O6–Eu1–N1	70.8(2)
O2–Eu1–N1	79.2(2)	O3–Eu1–N2	76.2(2)
O1–Eu1–N2	69.8(2)	O7–Eu1–N2	146.8(2)
O4–Eu1–N2	128.1(2)	O6–Eu1–N2	74.8(2)
O2–Eu1–N2	116.7(2)	N1–Eu1–N2	64.7(2)
O3–Eu(1)–O5	74.2(2)	O1–Eu1–O5	156.3(2)
O7–Eu1–O5	77.5(2)	O4–Eu1–O5	76.8(2)
O6–Eu1–O5	51.34(19)	O2–Eu1–O5	138.5(2)
N1–Eu1–O5	121.1(2)	N2–Eu1–O5	104.8(2)
O3–Eu1–H7A	131.7	O1–Eu1–H7A	105.0
O7–Eu1–H7A	16.1	O4–Eu1–H7A	78.3
O6–Eu1–H7A	97.7	O2–Eu1–H7A	52.7
N1–Eu1–H7A	86.9	N2–Eu1–H7A	151.6
O5–Eu1–H7A	90.3	O7–H7A ··· O2	110.3
O8–H8A ··· O4	167(19)	–	–

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

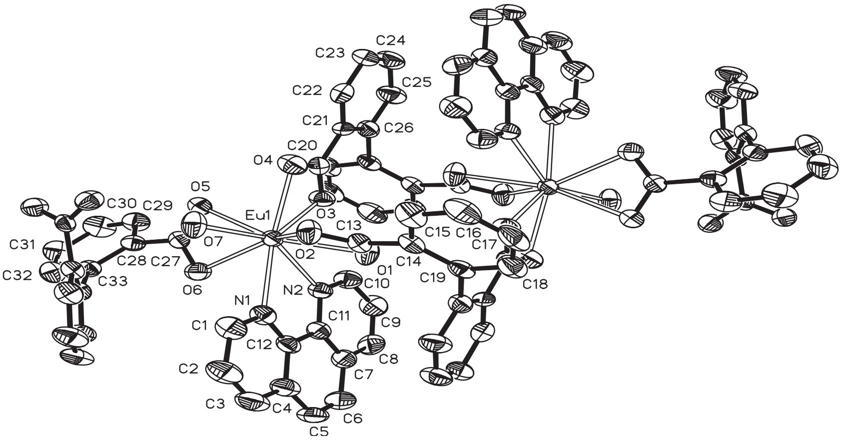

Figure 1. The coordination environment of the Eu ion in **1**.

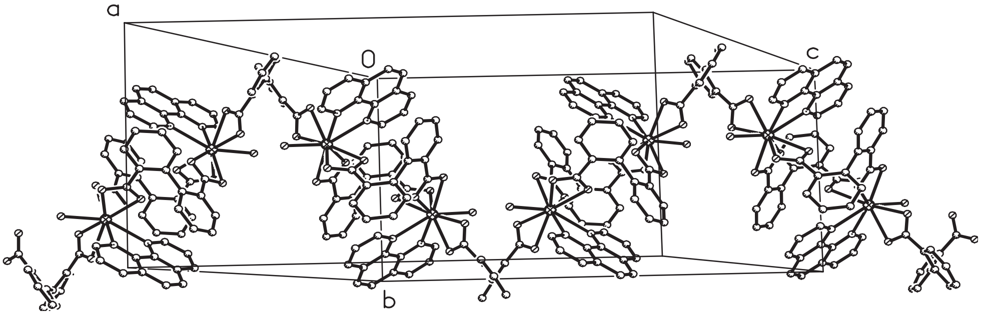

Figure 2. View of the one-directional zigzag chain along the [−1 −1 1] direction in **1**.

the dihedral angle is 61.5°. It is also noteworthy that two different kinds of O–H $\cdots$ O hydrogen-bonding interactions, with O $\cdots$ O distances 2.762(9) and 2.755(9) Å, respectively, link the chains and the lattice water molecules to form a hydrogen-bonding network.

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