Hydrothermal synthesis and structural studies of novel 2-D lanthanide coordination polymers with phthalic acid

Yonghong Wan,[a] Linpei Jin,*[a] Kezhi Wang,[a] Liping Zhang,[a] Xiangjun Zheng[a] and Shaozhe Lu[b]

[a] *Department of Chemistry, Beijing Normal University, Beijing 100875, P. R. China. E-mail: lpjin@bnu.edu.cn*

[b] *Laboratory of Excited States Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130021, P. R. China*

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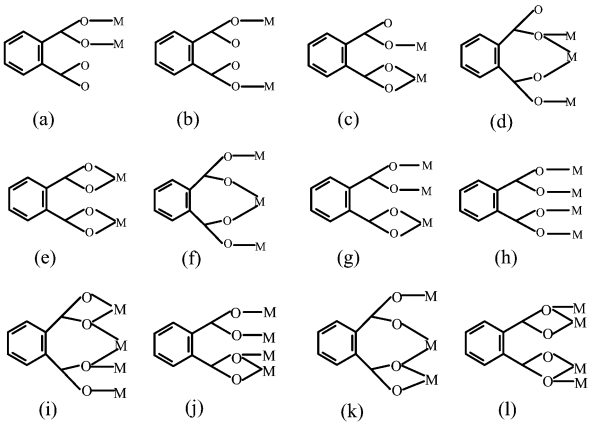
This paper presents four lanthanide coordination polymers, $[Ln_2(BDC)_3(H_2O)]_n$ (Ln = La, **1**; Ln = Eu, **2**; Ln = Tb, **3**; BDC = 1,2-benzenedicarboxylate) and $[Yb_4(BDC)_6(H_2O)_2]_n$ (**4**) prepared by the hydrothermal technique. They are all 2-D infinite structures with BDC anions connecting adjacent metal ions. In complex **1**, La(III) ions are eight- and nine-coordinated, and all La(III) ions are coplanar in the 2-D structure. In complexes **2** and **3**, Eu(III) and Tb(III) ions are also eight- and nine-coordinated, but they are distributed in a wave-like 2-D network. In complex **4**, the Yb(III) ions have four different coordination numbers (6, 7, 8 and 9), which are rarely found in one lanthanide complex. Both the coordination numbers and the arrangement of Ln atoms in these coordination polymers show the lanthanide contraction. In the four complexes, all the oxygen atoms of BDC take part in coordination with Ln(III) ions, adopting tetra-, penta- and hexadentate coordination modes for the phthalate anions. The luminescent properties of complex **2** have been investigated and the results for the explanation of the chemical environment of the Eu(III) ion are consistent with the X-ray analysis.

In recent years, metal coordination polymers have received increasing interest for their fascinating structures and potential applications in catalysis, molecular recognition and as sensors, storage devices and so on.[1] In constructing coordination polymers, multifunctional ligands such as a variety of polyacids and 4,4′-bipyridine are used as linkers, forming extended metal ion structures having pillar, brick wall, honeycomb and others geometries.[2] 1,2-Benzenedicarboxylic acid (H_2BDC) has been well studied in coordination polymers containing transition metals (such as Cu, Mn, Co and Zn), due to the versatile bonding modes of BDC anions. Some typical coordination modes for BDC anions are summarized in Scheme 1(a–h). In the transition metal phthalato complexes, the BDC anion acts as a short bridge through two,[3] three[4] or four[5] oxygen atoms from its carboxylate groups to join adjacent metals. But to the best of our knowledge, H_2BDC is seldom involved in lanthanide complexes. In particular, the structural characterization of lanthanide phthalato complexes has not been reported.

Hydrothermal syntheses, which have usually been used to prepare oxide-base materials, have been adopted in the preparation of coordination polymers.[6] It turns out that hydrothermal synthesis is an effective and powerful method in that compounds that are difficult to synthesize by conventional means may be well crystallized by using the hydrothermal technique. Recently, the hydrothermal technique has been applied to the synthesis of lanthanide carboxylate complexes and succeeded in constructing enchanting structures.[7]

We selected H_2BDC as a linker and adopted the hydrothermal technique, hoping to construct some novel lanthanide complexes with characteristic structures. Here we report syntheses and structural characteristics of four lanthanide coordination polymers with phthalic acid.



Scheme 1 Coordination modes of BDC anions in transition metal phthalato complexes (*a–h*) and in the title complexes **1–4** (g–l).

Experimental

Materials and apparatus

$LnCl_3{\cdot}nH_2O$ (Ln = La, $n = 7$; Ln = Eu, Tb and Yb, $n = 6$) were prepared by dissolving lanthanide oxide in dilute hydrochloric acid and then dried. Other commercially available solvents and chemicals were used without further purification.

CH microanalysis data were obtained using a Vario El elemental analyser and IR spectra were measured as KBr discs on a Nicolet Avatar 360 FT-IR spectrometer. Luminescence spectra of complex **2** were recorded at 77 K. The excitation light source was a YAG:Nd laser, which emitted at 1.064 μm and the excitation wavelength was 355 nm. The light was focused on the sample that was placed in a Dewar's bottle with liquid nitrogen. The luminescence was detected at right angles with a SPEX 1403 monochromator equipped with a photomultiplier tube, then averaged by a boxcar integrator and data

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were finally transferred to a computer. Time-resolved emission spectra were recorded with a YAG:Nd laser with 355 nm excitation and delay times of 5, 50 and 100 μs at 77 K.

Preparation of complexes

$LnCl_3{\cdot}nH_2O$ (0.3 mmol; La, $n = 7$, 0.111 g; Eu, $n = 6$, 0.111 g; Tb, $n = 6$, 0.113 g; Yb, $n = 6$, 0.116 g) and 0.45 mmol of H_2BDC (0.075 g) were dissolved in 10 mL deionized water and the pH value was adjusted to about 3.5 with NaOH aqueous solution. The mixture was placed in a Teflon-lined stainless steel vessel (25 mL). The vessel was sealed and heated at 170 °C for 80 h under autogeneous pressure and then cooled to room temperature. Small colorless sheetlike crystals were collected by filtration, followed by washing with water and ethanol.

$[La_2(BDC)_3(H_2O)]_n$ (**1**). Yield: 28 mg (24%). Found: C, 36.38; H, 1.55. $C_{24}H_{14}O_{13}La_2$ requires: C, 36.57; H, 1.79. IR (cm^{-1}): 3416s (br), 1609s, 1557vs, 1527vs, 1427s, 1398s, 865m, 747m, 692m, 654m, 443m.

$[Eu_2(BDC)_3(H_2O)]_n$ (**2**). Yield: 27 mg (22%). Found: C, 35.11; H, 1.22. $C_{24}H_{14}O_{13}Eu_2$ requires: C, 35.40; H, 1.73. IR (cm^{-1}): 3454s (br), 1610s, 1556vs, 1526vs, 1434s, 1417s, 1357s, 867m, 743m, 697m, 653w, 443w.

$[Tb_2(BDC)_3(H_2O)]_n$ (**3**). Yield: 62 mg (50%). Found: C, 34.79; H, 1.29. $C_{24}H_{14}O_{13}Tb_2$ requires: C, 34.80; H, 1.70. IR (cm^{-1}): 3450s (br), 1613s, 1561vs, 1526s, 1435s, 1418s, 1352s, 868m, 743s, 697m, 652w, 444w.

$[Yb_4(BDC)_6(H_2O)_2]_n$ (**4**). Yield: 49 mg (38%). Found: C, 33.87; H, 1.38. $C_{48}H_{28}O_{26}Yb_4$ requires: C, 33.66; H, 1.65. IR (cm^{-1}): 3426s (br), 1613m, 1541vs, 1447vs, 1407s, 857m, 755m, 691m, 651w, 573w, 443w.

X-Ray crystallography

The data were collected using a Bruker SMART CCD area detector diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), operating in the $\omega-2\theta$ scanning mode. Crystal parameters and details of data collection and structure refinement are summarized in Table 1. The structures were solved by direct methods using the program SHELXS 97[8] and refined by full-matrix least-squares on F^2 using SHELXL 97.[9]

CCDC reference numbers 177915 and 184845–184847. See http://www.rsc.org/suppdata/nj/b2/b206280c/ for crystallographic files in CIF or other electronic format.

Results and discussion

Single crystal X-ray diffraction studies revealed that the structures of **1**–**4** are 2-D coordination polymers. In the four coordination polymers, the H_2BDC molecules are all completely deprotonated and all the oxygen atoms from the carboxylate groups of BDC anions take part in coordination with metal ions, which is uncommon for BDC anions in transition metal phthalato complexes.[5,10] Because of the high coordination number of lanthanide ions, the BDC anions adopt multidentate coordination modes: tetra-, penta- and hexadentate. Scheme 1 summarizes the coordination modes of BDC anions in complexes **1**–**4** (g–l) and shows four new coordination modes for phthalate anions (i–l) that have never appeared in the transition metal phthalate complexes.

Structure of $[La_2(BDC)_3(H_2O)]_n$ (1)

The structure of **1** is made up of layers, stacked along the *c* axis. The asymmetric unit of **1** is depicted in Fig. 1(a) and selected bond distances are listed in Table 2. There are two crystallographically independent lanthanum ions in the asymmetric unit. The La(1) ion is eight-coordinated and surrounded by eight oxygen atoms belonging to carboxylate groups of six BDC anions; The La(2) ion is nine-coordinated and surrounded by nine oxygen atoms, eight of which are from carboxylate groups of six BDC anions while the last oxygen atom is from a water molecule. The La–O distances range from 2.422(3) to 2.702(4) Å and the distance of La(1)···La(2) is 4.464 Å.

The La(III) ions are well coplanar and have a mean deviation of ~0.087 Å from the plane. The arrangement of La atoms in a 2-D structure is shown in Fig. 1(b). In this complex, the BDC anions adopt two kinds of modes to coordinate to La ions (h and i in Scheme 1). For the three BDC anions of $La_2(BDC)_3(H_2O)$, one BDC anion adopts h coordination mode to bind four La atoms and the other two adopt the i coordination mode to connect four La ions. Due to the different coordination modes, the distances between adjacent La ions are different. When BDC anion adopts coordination mode i, one oxygen atom coordinates to two La atoms simultaneously, which brings the La atoms close to each other (La···La = 4.464, 4.434, 4.558 Å). The closer La ions form distorted infinite ladders, which are connected by BDC anions *via* coordination mode h, forming a 2-D infinite network. The

Table 1 Crystallographic data and refinement details for **1**–**4**

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{24}H_{14}O_{13}La_2$	$C_{24}H_{14}O_{13}Eu_2$	$C_{24}H_{14}O_{13}Tb_2$	$C_{48}H_{28}O_{26}Yb_4$
M	788.17	814.2	828.19	1712.86
T/K	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P*-1	*P*2(1)/*c*	*P*2(1)/*c*	*P*-1
a/Å	8.638(3)	7.998(3)	8.024(5)	12.570(4)
b/Å	10.625(3)	26.397(9)	26.656(16)	13.780(4)
c/Å	14.376(4)	11.677(4)	11.743(7)	15.869(5)
α/°	96.975(5)	90	90	75.363(4)
β/°	102.110(4)	107.226(4)	107.018(9)	69.196(5)
γ/°	104.372(4)	90	90	65.697(4)
U/Å^3	1228.6(6)	2354.6(13)	2402(3)	2323.3(12)
Z	2	4	4	2
μ/mm^{-1}	3.501	5.352	5.914	8.076
No. data collected	5014	7876	9019	9393
No. unique data	4208	3327	4038	7875
R_{int}	0.0260	0.0356	0.0961	0.0408
R_1 (all data)	0.0384	0.0337	0.1026	0.0477
wR_2 (all data)	0.0970	0.0721	0.1740	0.1158

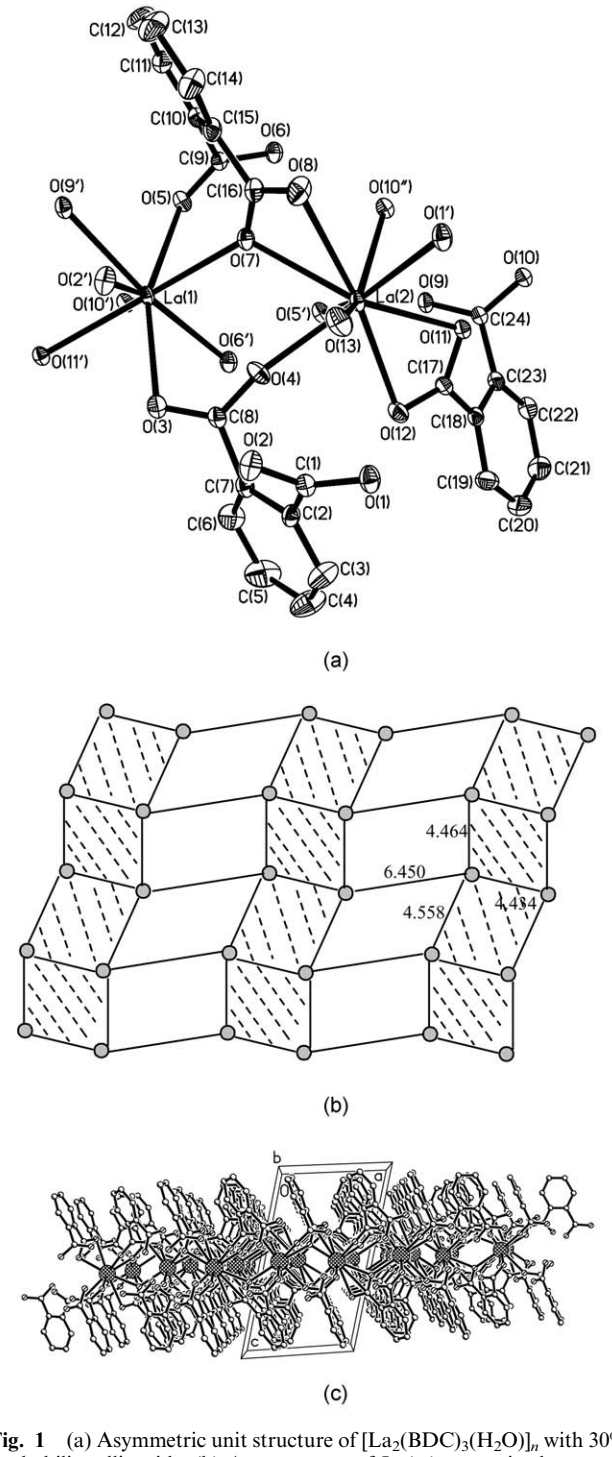


Fig. 1 (a) Asymmetric unit structure of $[La_2(BDC)_3(H_2O)]_n$ with 30% probability ellipsoids. (b) Arrangement of La(III) atoms in the crystal of $[La_2(BDC)_3(H_2O)]_n$ viewed along the *c* axis (C, H, O atoms are omitted for clarity). (c) Packing diagram of $[La_2(BDC)_3(H_2O)]_n$.

distance between two ladders is about 6.450 Å (La···La). The adjacent sheets are stacked at a interplane distance of ~14.4 Å.

Worth noting here is that the benzene rings of the BDC groups lie in both flanks of the La ion plane, which forms a "sandwich" structure [Fig. 1(c)].

Structures of $[Ln_2(BDC)_3(H_2O)]_n$ (Ln = Eu, 2; Ln = Tb, 3)

The crystal structures of **2** and **3** are 2-D structures extending in the *ac* plane. Complexes **2** and **3** are isomorphous. The asymmetric unit of **2** is shown in Fig. 2(a). Selected bond distances for **2** and **3** are listed in Tables 3 and 4, respectively. There are two types of metal ion environments in the asymmetric unit. As shown in Fig. 2(a), Eu(1) [or Tb(1)] is eight-coordinated and thus surrounded by eight oxygen atoms, seven of which come from carboxylate groups of five BDC anions and the other one from a water molecule; Eu(2) [or Tb(2)] is nine-coordinated and coordinates to nine oxygen atoms from carboxylate groups of six BDC anions. The Eu(1)···Eu(2) and Tb(1)···Tb(2) distances are 3.786 and 3.785 Å, respectively.

Table 2 Selected bond distances (Å) for **1**[a]

La(1)–O(2)#1	2.422(3)	La(2)–O(1)#4	2.482(4)
La(1)–O(6)#2	2.465(3)	La(2)–O(10)#5	2.546(3)
La(1)–O(7)	2.485(3)	La(2)–O(13)	2.600(4)
La(1)–O(9)#2	2.497(4)	La(2)–O(11)	2.603(3)
La(1)–O(11)#3	2.530(3)	La(2)–O(7)	2.607(3)
La(1)–O(3)	2.546(3)	La(2)–O(5)#2	2.617(3)
La(1)–O(10)#3	2.624(3)	La(2)–O(12)	2.647(4)
La(1)–O(5)	2.642(3)	La(2)–O(8)	2.702(4)
La(2)–O(4)	2.443(4)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+2$, $-y+1$, $-z+1$; #2 $-x+2$, $-y+2$, $-z+1$; #3 $x+1$, y, z; #4 $-x+1$, $-y+1$, $-z+1$; #5 $-x+1$, $-y+2$, $-z+1$.

In the two complexes, the BDC anions adopt three coordination modes (i, j and k in Scheme 1) to connect Ln atoms into 2-D structures. It is noteworthy that the 2-D structures for **2** and **3** are much different from that for **1**. All the Eu and Tb atoms in each coordination polymer are non-coplanar. From Fig. 2(b), we can see that all the Eu (or Tb atoms) form a wave-like plane in which there are two types of inclined planes and the angle between the planes (dihedral angle) is 55.8° in **2** and 55.0° in **3**. In this wave-like plane, all the Eu(2) [or Tb(2)] atoms occupy the wave crests and troughs while all the Eu(1) [or Tb(1)] atoms lie in the inclined planes between the crests and troughs. The 2-D layers stack "face-to-face" along the *a* axis [Fig. 2(b)] with the shortest Eu···Eu distance being about 10.3 Å (Tb···Tb, 10.4 Å) and the longest about 16.1 Å (Tb···Tb, 16.2 Å) for the two adjacent layers. In the 2-D structure, the carboxylate groups of BDC anions connect the Ln(1) and Ln(2) atoms by oxygen atoms resulting in a nonplanar honeycomb network in which the Eu···Eu distances are 3.786, 4.440, and 5.277 Å, as shown in Fig. 2(c) (Tb···Tb distances are 3.785, 4.469 and 5.314 Å). When the carboxylate groups of BDC adopt bidentate coordination modes the Ln···Ln distance is the longest repetition, while the carboxylate groups of BDC chelat Ln ions in the tridentate bridging mode between the two nearer Ln ions (Ln = Eu, 3.786 and 4.440 Å; Ln = Tb, 3.785 and 4.469 Å). There is a series of seven-membered channels arranged along the wave-like plane because the BDC anions adopt coordination modes i or k in which two oxygen atoms of the two carboxylates of one BDC anion coordinate to one Ln ion, thus forming a seven-membered ring (1Ln, 2O and 4C). Similarly to **1**, the benzene rings arranged on in both sides of the Ln(III) ion plane form a rippled "sandwich".

Structure of $[Yb_4(BDC)_6(H_2O)_2]_n$ (4)

The structure of **4** consists of 2-D layers, and the asymmetric unit of **4** is shown in Fig. 3(a). Selected bond distances are listed in Table 5. It is interesting to note that there are four types of metal ion environments in this crystal. The Yb ions are surrounded by six, seven, eight or nine oxygen atoms. Yb(1) binds eight oxygen atoms from carboxylate groups of five BDC anions; Yb(2) coordinates to six oxygen atoms belonging to carboxylate groups of six BDC anions; Yb(3) is surrounded by nine oxygen atoms of carboxylate groups of six BDC anions, and Yb(4) by seven oxygen atoms, five of which are from carboxylate groups of five BDC and the other two from two coordinated water molecules. It is rare that the

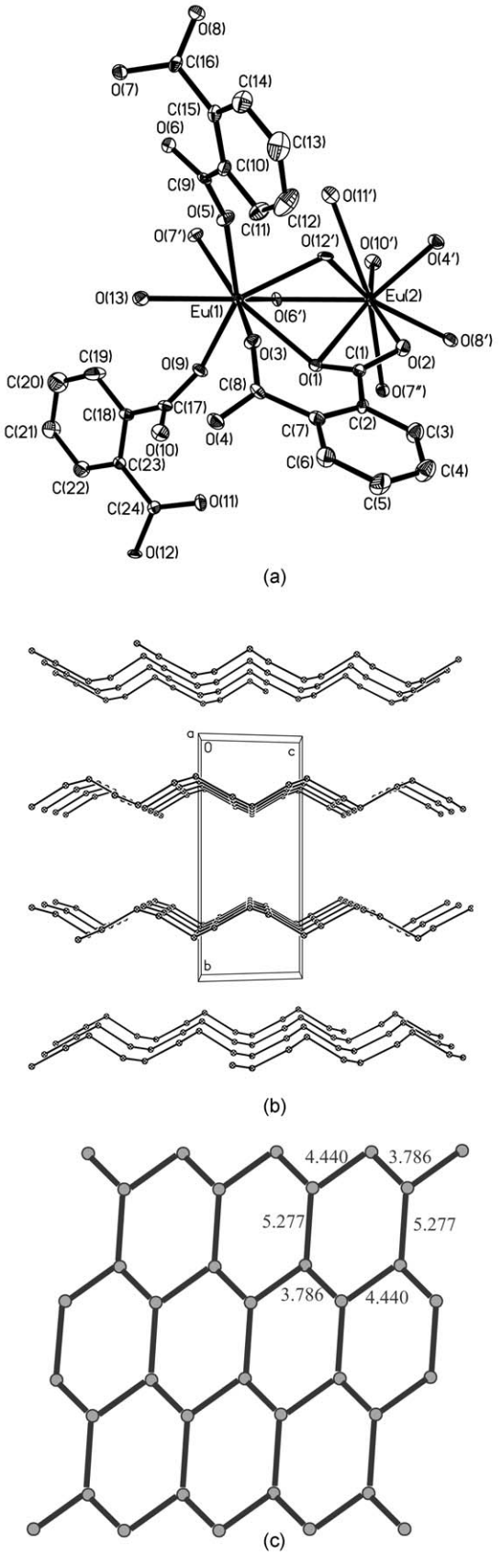


Fig. 2 (a) Asymmetric unit of $[Eu_2(BDC)_3(H_2O)]_n$. (b) Arrangement of Eu(III) atoms of two adjacent planes in the crystal of $[Eu_2(BDC)_3(H_2O)]_n$ viewed along the *a* axis (C, H, O atoms are omitted for clarity). (c) Projection of Eu(III) atoms in a 2-D structure along the *b* axis.

Table 3 Selected bond distances (Å) for **2**[a]

Eu(1)–O(3)	2.293(4)	Eu(2)–O(4)#3	2.296(4)
Eu(1)–O(9)	2.313(4)	Eu(2)–O(6)#2	2.421(4)
Eu(1)–O(5)	2.354(4)	Eu(2)–O(2)	2.436(4)
Eu(1)–O(12)#1	2.405(4)	Eu(2)–O(12)#1	2.447(4)
Eu(1)–O(7)#2	2.414(4)	Eu(2)–O(8)#4	2.461(4)
Eu(1)–O(13)	2.411(4)	Eu(2)–O(7)#4	2.536(4)
Eu(1)–O(6)#2	2.470(4)	Eu(2)–O(1)	2.700(4)
Eu(1)–O(1)	2.532(4)	Eu(2)–O(11)#1	2.872(4)
Eu(2)–O(10)#3	2.265(5)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $x-1$, $-y+1/2$, $z-1/2$; #2 x, $-y+1/2$, $z+1/2$; #3 $x-1$, y, z; #4 x, y, $z+1$.

same metal ion has four different coordination numbers in one complex. Corresponding to the four coordination numbers, there are four types of coordination polyhedra, which can be described as octahedron (CN = 6), capped trigonal prism (CN = 7), bicapped trigonal prism (CN = 8) and capped square antiprism (CN = 9). Moreover, the four kinds of coordination polyhedra connect into infinite chains by vertices connection (shared oxygen atoms of two adjacent Yb ions) [Fig. 3(b)].

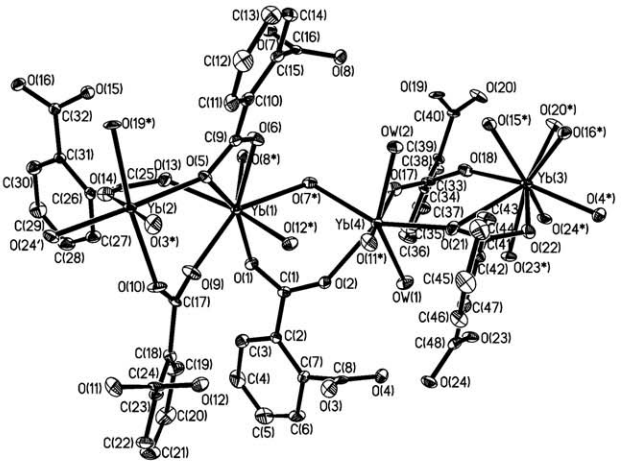
Yb atoms in this complex are not coplanar, distributing in a wave-like plane because of the steric hindrance of ligands. The arrangement of Yb ions is shown in Fig. 3(c). It can be seen that there are two kinds of infinite chains. Each chain is composed of four repeated Yb ions in the asymmetric unit. The chains arrange in the order: abab... The Yb···Yb distances in one chain are: Yb(1)···Yb(2) = 4.296, Yb(1)···Yb(4) = 4.218, Yb(3)···Yb(4) = 4.633, Yb(2*)···Yb(3) = 4.402 Å. The Yb···Yb distances between the a and b chains are: Yb(1)···Yb(1′) = 6.330, Yb(4)···Yb(2′) = 6.691, Yb(3)···Yb(3″) = 7.052 Å. The six independent BDC anions adopt three kinds of coordination modes to connect Yb ions (g, h and l in Scheme 1). One of the six BDC anions adopts the g coordination mode to connect three Yb ions with one carboxylate group bridging two Yb ions in one chain and the other carboxylate group chelating one Yb ion in a neighbouring chain; two adopt the l coordination mode with each carboxylate group binding two Yb ions in a tridentate fashion while the other three adopt the h coordination mode with each carboxylate group binding two Yb ions in a bidentate fashion. Interestingly, each phthalate anion bridges two adjacent chains with the two carboxylate groups. Similar to complexes **2** and **3**, the plane of Yb(III) ions locates between the benzene rings, which also form a rippled ''sandwich''.

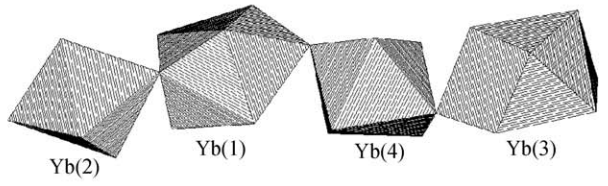
Comparing the title complexes with lanthanide 1,4-benzenedicarboxylate (1,4-BDC) complexes,[7c,d,11] we can see that the benzenedicarboxylic acids are all completely deprotonated and all the oxygen atoms coordinate to the Ln ions into extended structures. But owing to the different positions

Table 4 Selected bond distances (Å) for **3**[a]

Tb(1)–O(3)	2.277(11)	Tb(2)–O(4)#3	2.286(12)
Tb(1)–O(9)	2.300(12)	Tb(2)–O(6)#1	2.405(12)
Tb(1)–O(5)	2.342(13)	Tb(2)–O(2)	2.412(13)
Tb(1)–O(7)#1	2.405(12)	Tb(2)–O(12)#2	2.455(12)
Tb(1)–O(13)	2.394(15)	Tb(2)–O(8)#4	2.468(13)
Tb(1)–O(12)#2	2.405(12)	Tb(2)–O(7)#4	2.548(11)
Tb(1)–O(6)#1	2.495(12)	Tb(2)–O(1)	2.672(12)
Tb(1)–O(1)	2.538(13)	Tb(2)–O(11)#2	2.917(14)
Tb(2)–O(10)#3	2.246(14)		

[a] Symmetry transformations used to generate equivalent atoms: #1 x, $-y+1/2$, $z+1/2$; #2 $x-1$, $-y+1/2$, $z-1/2$; #3 $x-1$, y, z; #4 x, y, $z+1$.





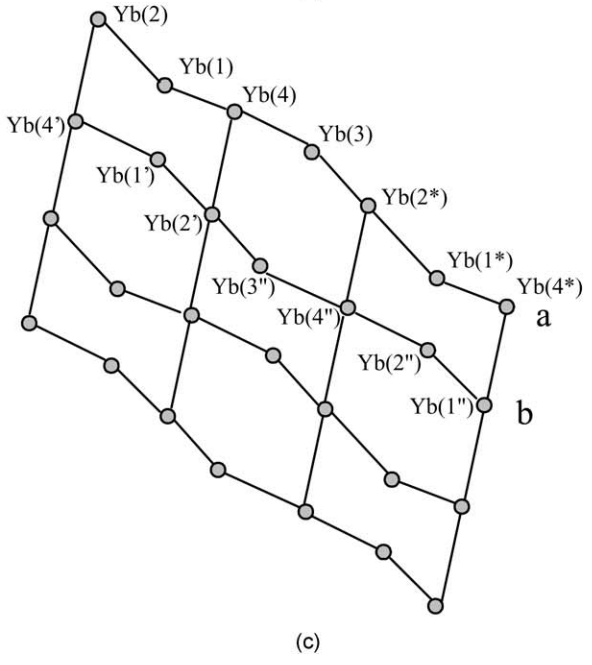


Fig. 3 (a) Asymmetric unit of $[Yb_4(BDC)_6(H_2O)_2]_n$. (b) The chain of coordination polyhedra with connecting vertices. (c) Arrangement of Yb(III) atoms in the crystal of $[Yb_4(BDC)_6(H_2O)_2]_n$ viewed along the *b* axis (C, H, O atoms are omitted for clarity. Symmetry code: * $x-1, y, z+1$; ′ $-x+1, -y, -z+1$; ″ $-x, -y, -z+2$).

of two carboxylate groups (ortho and para positions), the coordination modes are obviously different. 1,4-BDC usually adopts the tetradentate coordination mode (similar to h) to connect four metal ions, while the coordination modes of 1,2-BDC are more abundant and versatile. Especially, 1,2-BDC can adopt i or k modes in which two oxygen atoms belonging to two carboxylate groups of one 1,2-BDC bind one metal ion and form a seven-membered ring. For 1,4-BDC, the two carboxylate groups are isolated by the benzene ring and are in para position, which makes 1,4-BDC a good spacer to connect metal ions into higher dimensional structures with channels liable to be formed owing to the long distance

Table 5 Selected bond distances (Å) for **4**[a]

Yb(1)–O(12)#1	2.206(5)	Yb(3)–O(4)#4	2.295(5)
Yb(1)–O(9)	2.215(5)	Yb(3)–O(22)	2.306(5)
Yb(1)–O(13)	2.233(5)	Yb(3)–O(15)#2	2.375(5)
Yb(1)–O(1)	2.264(5)	Yb(3)–O(23)#4	2.393(5)
Yb(1)–O(6)	2.288(5)	Yb(3)–O(16)#2	2.418(6)
Yb(1)–O(8)#2	2.369(5)	Yb(3)–O(24)#4	2.850(6)
Yb(1)–O(7)#2	2.544(5)	Yb(3)–O(21)	2.889(5)
Yb(1)–O(5)	2.814(6)	Yb(3)–O(20)#3	2.202(5)
Yb(2)–O(19)#2	2.205(5)	Yb(4)–O(11)#1	2.210(5)
Yb(2)–O(10)	2.224(5)	Yb(4)–O(21)	2.243(6)
Yb(2)–O(24)#1	2.232(5)	Yb(4)–O(7)#2	2.272(5)
Yb(2)–O(5)	2.234(5)	Yb(4)–O(2)	2.277(5)
Yb(2)–O(14)	2.241(6)	Yb(4)–Ow(1)	2.320(5)
Yb(2)–O(3)#1	2.247(6)	Yb(4)–Ow(2)	2.340(6)
Yb(3)–O(18)	2.183(6)	Yb(4)–O(17)	2.198(5)

[a] Symmetry transformations used to generate equivalent atoms: #1 $-x+2, -y, -z+1$; #2 $-x+1, -y, -z+1$; #3 $-x, -y, -z+2$; #4 $-x+1, -y, -z+2$.

between the two carboxylate groups. For 1,2-BDC, the two carboxylate groups are in ortho position, which may impede the formation of higher dimensional networks with the benzene rings, resulting in "sandwich" structures when the carboxylate groups coordinate with the metal ions. Compared to reported binary transition metal phthalato complexes,[12] we find that all the carboxyl oxygen atoms of the deprotonated phthalato anions are liable to form coordination bonds in the title complexes. Furthermore, coordination modes for the transition metal phthalato complexes are simpler than those of the lanthanide phthalato complexes due to the large ionic radii and high coordination numbers of lanthanide ions. In the lanthanide complexes, the BDC anions adopt six fold coordination modes to connect Ln ions, and each BDC anion connects three or four Ln ions in tetradentate, pentadentate or hexadentate coordination fashion.

Photophysical properties

Complex **2** shows intense red photoluminescence and the characteristic luminescence spectrum of the trivalent europium ion. Fig. 4 shows the luminescence spectrum of complex **2** excited with 355 nm radiation at 77 K. The intensity ratio $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$ is equal to *ca.* 5.2, which shows that the Eu(III) ion is not at an inversion center.[13] The $^5D_0 \rightarrow {}^7F_1$ transition comprises more than three components, which shows that the Eu(III) ions are not in the same chemical environments. The $^5D_0 \rightarrow {}^7F_0$ transition is particularly weak but asymmetric (see Fig. 4, inserted spectrum) and was consequently studied by selective excitation techniques.

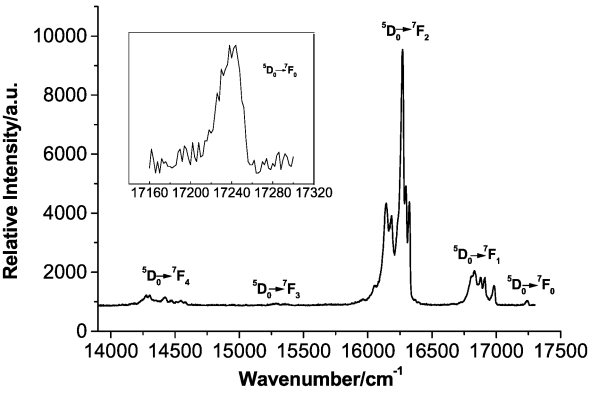


Fig. 4 High-resolution spectrum of complex **2** corresponding to the $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions at 77 K ($\lambda_{exc} = 355$ nm).

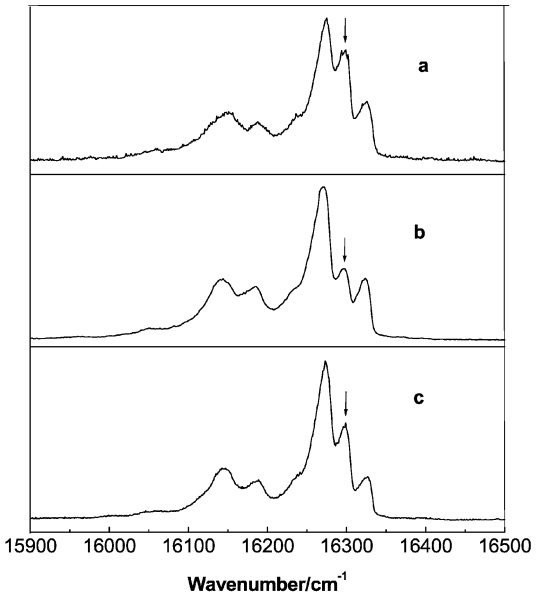


Fig. 5 Time-resolved spectra of complex **2** in the range of 15 900–16 500 cm^{-1} at 77 K ($\lambda_{exc} = 355$ nm), delay time: a, 5 μs; b, 50 μs; c, 100 μs.

Among the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–6) transitions, the $^5D_0 \rightarrow {}^7F_2$ transition induced by the electric dipole moment is hypersensitive to the coordination environment, while the intensity of the $^5D_0 \rightarrow {}^7F_1$ transition allowed by the magnetic dipole moment is almost independent of the environment. So, the time-resolved spectra were recorded in the range of 15 900 to 16 500 cm^{-1} ($^5D_0 \rightarrow {}^7F_2$ transition) for studying the chemical environment of the Eu(III) ions. From Fig. 5 we find that the relative intensity of the emission peaks change, especially the peak marked with an arrow varies in comparison with the others when the delay time differs, which indicates that there are different Eu(III) ion sites with distinct lifetimes.

For the europium ion, $^5D_0$ and $^7F_0$ are non-degenerate so there should be only one line for the $^5D_0 \leftarrow {}^7F_0$ transition if europium ions are in the same chemical environment.[14] We recorded the excitation spectrum for $^5D_0 \leftarrow {}^7F_0$ (Fig. 6) by monitoring at 16 310 and 16 275 cm^{-1}. It can be seen from Fig. 6 that there are two obvious components with peak positions of 579.60 and 579.82 nm. This means that there are two kinds of chemical environments for the europium ions. This is in good agreement with the crystal structure. However, in the two Eu(III) chemical environments, there may be slightly different environments in each group, as broad $^5D_0 \leftarrow {}^7F_0$ excitation bands are observed in Fig. 6. But we failed to obtain finely developed emission spectra by selective excitation techniques. This is a common phenomenon for europium coordination polymers.[15]

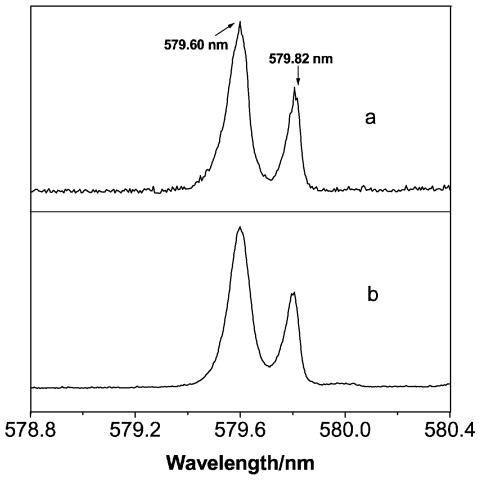


Fig. 6 Excitation spectra of complex **2** at 77 K ($\lambda_{exc} = 355$ nm), analyzing wavenumber: a, 16 310 cm^{-1}; b, 16 275 cm^{-1}.

Conclusion

First examples of lanthanide phthalato complexes with 2-D layer structure have been obtained and characterized by X-ray crystallography. All compounds have polymeric structures with phthalato ligands locating on both sides of the Ln(III) ions to form "sandwich" structures. Both the average Ln–O bond distance and coordination number of the Ln(III) ions show lanthanide contraction in the series. In addition, IR spectra (νOH: 3450–3410 cm^{-1}; ν_{as}COO: 1610–1550 cm^{-1} and ν_sCOO: 1450–1440 cm^{-1}) support the results of the X-ray analysis.

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