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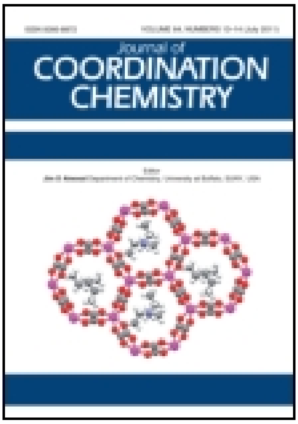

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Synthesis and characterization of two 3-D polymeric lanthanide complexes constructed from 1,2,4,5-benzenetetracarboxylic acid

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Synthesis and characterization of two 3-D polymeric lanthanide complexes constructed from 1,2,4,5-benzenetetracarboxylic acid

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Two new 3-D lanthanide coordination polymers, $[CeK(btec)(H_2O)_2]_n$ (**1**), $[Ho(btec)_{0.5}(ad)_{0.5}(H_2O)]_n$ (**2**) (H_4btec = 1,2,4,5-benzenetetracarboxylic acid, H_2ad = adipic acid), have been synthesized under hydrothermal conditions and characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction. Structural analyses reveal that both complexes crystallized in monoclinic space group $P2_1/c$ and possessed 3-D net-structures. In **1**, btec adopts two types of coordination modes: μ_{12}–η^2:η^2:η^2:η^1:η^2:η^2:η^2:η^1 bridging mode linking six Ce(III) ions and six K^+ ions and the other μ_8–η^1:η^2:η^2:η^1:η^1:η^2:η^2:η^1 bridging mode connecting four Ce(III) ions and four K^+ ions. In **2**, btec adopts a μ_6-bridging with each carboxylate group of btec ligand in a μ_2–η^1–η^2 mode, the adipate is μ_4-bridging with each carboxylate μ_2–η^1–η^1-monodentate. The topological analysis shows that **1** can be simplified to a 3-nodal net with the Schläfli symbol $\{3^2,4^8,5^3,6^2\}_4\{3^4,4^{12},5^{12}\}\{4^{38},6^{26},8^2\}$ and **2** can be simplified to a 3-nodal network with the Schläfli symbol $\{4^2,8^4\}\{4^6,6^6,8^3\}\{4^7,6^3\}_2$. The thermogravimetric analyses and the X-ray powder diffraction of **1** and **2** are discussed.

Keywords: Lanthanide coordination polymers; 1,2,4,5-Benzenetetracarboxylic acid; Adipic acid; Crystal structure; Thermogravimetric

1. Introduction

In the recent years, there has been increasing interest in metal-organic frameworks (MOF) for versatile architectures and intriguing topologies [1–8]. The construction of MOFs using polycarboxylate ligands and suitable metal salts shows that the carboxylate unit affords a favorable means for design of novel materials by acting as a linker or by imparting unique structural features owing to its functionalizability [9–14]. Many organic aromatic polycarboxylate coordination polymers with multi-dimensional networks have been extensively prepared and characterized [15–20].

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1,2,4,5-Benzenetetracarboxylic acid (H_4btec = 1,2,4,5-benzenetetracarboxylic acid) is a rigid polycarboxylate of great interest owing to its intriguing structural features [21–23]. Extensive work has been carried out using btec and co-ligands, for example 4,4′-bipyridine [24, 25], 2,2′-bipyridine [26, 27], 4,4′-azobispyridine [28], homopiperazonium [29], 4,4′-bipyridine-*N*,*N*′-dioxide [30], etc. Several lanthanide coordination polymers constructed using H_4btec and flexible ligands as mixed-linkers have been reported [31]. Our group has also synthesized and constructed a series of unique lanthanide organic frameworks with good luminescence [32, 33]. In order to further understand the synthetic regularity and various coordination modes, as well as the influence of the carboxylate group from effects of mixed ligands (rigid and flexible) on structures, we have focused our efforts to explore the family of lanthanide coordination polymers with more complicated structures for improved properties. Here, we report two coordination polymers $[\mathrm{CeK(btec)(H_2O)_2}]_n$ (**1**) and $[\mathrm{Ho(btec)_{0.5}(ad)_{0.5}(H_2O)}]_n$ (**2**). Polymer **1** exhibits an interpenetrated 3-nodal network with $\{3^2,4^8,5^3,6^2\}_4\{3^4,4^{12},5^{12}\}\{4^{38},6^{26},8^2\}$ topology and **2** exhibits an interpenetrated 3-nodal network with $\{4^2,8^4\}\{4^6,6^6,8^3\}\{4^7,6^3\}_2$ topology.

2. Experimental

2.1. *Materials and methods*

Lanthanide chlorides were prepared by dissolving lanthanide oxide in 12 molL^{-1} HCl and performing evaporation at 100°C until the crystal film formed. Lanthanide nitrate salts were prepared using the same procedure as chloride salts. All other chemicals are commercially available and used without purification. The infrared spectra were recorded on a JASCO FT/IR-480 PLUS Fourier transform spectrometer with pressed KBr pellets in the range 200–4000 cm^{-1}. The elemental analyses were carried out on a Perkin Elmer 240 C automatic analyzer. Content of lanthanide was analyzed on a Plasma-Spec(I)-AES model ICP spectrometer. Thermogravimetric analyses (TGA) were performed under N_2 atmosphere with a heating rate of 10°C min^{-1} on a Perkin Elmer Diamond TG/DTA. X-ray powder diffraction (XRD) data were collected on a Bruker Advance-D8 with Cu-Kα radiation, in the range $5° < 2\theta < 60°$, with a step size of 0.02° (2θ) and an acquisition time of 2 s per step.

2.2. *Synthesis of* $[\mathrm{CeK(btec)(H_2O)_2}]_n$ *(1)*

Complex **1** was prepared by hydrothermal reaction. $\mathrm{Ce(NO_3)_3 \cdot 6H_2O}$ (0.08 g, 0.18 mmol), 1,2,4,5-benzenetetracarboxylic acid (H_4btec, 0.05 g, 0.20 mmol), and H_2O (15 mL) were mixed in a 25 mL beaker. The pH was adjusted to 5.0 with KOH under continuous stirring. After stirring for 2 h, the mixture was sealed in a bomb and heated at 160°C for 3 days, then cooled at 10°C/3 h to 100°C, followed by slowly cooling to room temperature. Colorless block crystals suitable for X-ray diffraction analysis were obtained in *ca* 21% yield based on Ce(III). Elemental Anal. Calcd for $\mathrm{C_{10}H_6O_{10}CeK}$ ($M_r = 465.37$) (%): C, 25.81; H, 1.30; K, 8.40; Ce, 30.11. Found (%): C, 25.89; H, 1.36; K, 8.47; Ce, 30.23. IR data (KBr pellet, ν[cm^{-1}]): 3530(w), 3488(w), 1601(s), 1528(s), 1494(s), 1427(s), 1377(s), 1326(m), 1291(w), 1138(m), 950(w), 861(m), 815(s), 766(m), 660(w), 585(s), 508(s), 459(w), 356(m), 318(m).

2.3. *Synthesis of $[Ho(btec)_{0.5}(ad)_{0.5}(H_2O)]_n$ (2)*

Complex **2** was prepared by hydrothermal reaction. $HoCl_3 \cdot 6H_2O$ (0.22 g, 0.58 mmol), 1,2,4,5-benzenetetracarboxylic acid (0.06 g, 0.24 mmol), adipic acid (0.13 g, 0.89 mmol), and H_2O (15 mL) were mixed in a 25 mL beaker. The pH was adjusted to 5.0 with diisopropylamine under continuous stirring. After being stirred for 2 h, the mixture was sealed in the bomb and heated at 160°C for 3 days, then cooled at 10°C/3 h to 100°C, followed by slow cooling to room temperature. After filtration, the product was washed with distilled water and then dried at room temperature. Red block single-crystals suitable for X-ray diffraction analysis were obtained in *ca* 67% yield based on Ho(III). Elemental Anal. Calcd for $C_8H_7O_7Ho$ ($M_r = 380.07$) (%) C, 25.28; H, 1.86; Ho, 43.39. Found (%): C, 25.66; H, 1.96; Ho, 43.32. IR data (KBr pellet, $\nu[\mathrm{cm}^{-1}]$): 3441(s), 2962(w), 2923(w), 1606(s), 1574(s), 1540(m), 1497(m), 1426(s), 1385(s), 1325(m), 1148(m), 944(m), 885(m), 837(s), 780(m), 626(w), 587(m), 456(m), 326(w).

2.4. *X-ray crystallography*

Suitable single crystals of the two complexes were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature (293(2) K) on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). All absorption corrections were performed using SADABS [34]. Crystal structures were solved by the direct method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic multi-polycarboxylate ligands were fixed at calculated positions with isotropic thermal parameters, while the coordinated water molecules were located by difference Fourier map. All calculations were performed using SHELXL-97 [35]. Crystal data and details of the data collection and the structure refinement are given in table 1. Selected bond lengths of **1** and **2** are listed in tables 2 and 3, and selected bond angles of **1** and **2** are listed in tables S1 and Tables S2, respectively.

3. Results and discussion

3.1. *Synthesis*

Although various lanthanide coordination polymers with binary mixed dicarboxylate ligands have been reported, those with rigid and flexible dicarboxylate as mixed ligands remain rare. Using a hydrothermal method, we obtained **1** and **2** at 160°C for 3 days. Originally, we attempted to synthesize the complexes using KOH and adjusting the pH value but only **1** was obtained. We also attempted to synthesize the complexes using different templates to adjust the pH to 6, such as ethylenediamine, diisopropylamine, and sodium hydroxide. In the process, **2** was obtained using diisopropylamine. The mol ratio of mixed ligands in **1** ($m_{\mathrm{Ln}} : m_{\mathrm{btec}} = 1:1$) was different from that of **2**

Table 1. Crystal structure parameters for **1** and **2**.

Complex	**1**	**2**
Formula	$C_{10}H_6O_{10}CeK$	$C_8H_7O_7Ho$
Formula weight	465.37	380.07
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	8.8163(18)	7.754(3)
b	8.1249(16)	7.1798(17)
c	17.464(4)	18.788(7)
α	90	90
β	91.82(3)	112.99(3)
γ	90	90
Volume (Å^3), Z	1250.3(4), 4	962.9(6), 4
Crystal size (mm^3)	0.21 × 0.14 × 0.09	0.14 × 0.11 × 0.07
Calculated density (g cm^{-3})	2.472	2.622
Absorption coefficient (mm^{-1})	4.029	8.235
$F(000)$	892	712
θ range for data collection (°)	3.23–27.4	3.07–27.46
Reflections collected/unique (R_{int})	11,823/2863 (0.0349)	9110/2202 (0.0206)
Observed reflections ($I > 2\sigma(I)$)	2563	2132
Goodness-of-fit on F^2	1.116	1.130
Data/restraints/parameters	2863/12/202	2202/0/109
R_1,[a] wR_2[a] [$I > 2\sigma(I)$]	0.0237, 0.0529	0.0162, 0.0347
R_1,[b] wR_2[b] (all data)	0.0279, 0.0543	0.0170, 0.0350
Largest difference peak and hole (e·Å^{-3})	0.566 and −1.749	0.672 and −1.031

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2/\Sigma(w(F_o^2)^2)]^{1/2}$; [$F_o > 4\sigma(F_o)$].
[b] Based on all data.

Table 2. Selected bond distances (Å) for **1**.

Ce–O7	2.449(2)	Ce–O4	2.598(2)	K–O6#4	2.837(2)
Ce–O5	2.450(2)	Ce–O	2.625(2)	K–O8	2.841(2)
Ce–O8#1	2.477(2)	Ce–O3	2.628(2)	K–O4	2.846(3)
Ce–O1	2.525(2)	K–O7#3	2.780(2)	K–O3#5	2.941(2)
Ce–O1W	2.5639(9)	K–O1#4	2.787(2)	K–O1W#5	3.0117(15)
Ce–O6	2.571(2)	K–O2	2.794(8)		

Symmetry codes: #1, $-x+2$, $y+1/2$, $-z+1/2$; #3, $-x+2$, $y-1/2$, $-z+1/2$; #4, x, $y-1$, z; #5, $-x+1$, $y-1/2$, $-z+1/2$.

Table 3. Selected bond distances (Å) for **2**.

Ho–O5	2.3012	Ho–O3#1	2.3307	Ho–O6	2.3534
Ho–O1#1	2.3556	Ho–O1W	2.3693	Ho–O4#2	2.4289
Ho–O1	2.4578	Ho–O3#2	2.5557	Ho–O2	2.6069

Symmetry codes: #1, $2-x$, $-0.5+y$, $0.5-z$; #2, x, $-1+y$, z.

($m_{Ln} : m_{btec} : m_{ad} = 3:1:4$). The templates and the mol ratio of mixed ligands, thus, play an important role during the reaction.

3.2. *Crystal structure analysis*

The structure of **1** reveals that it is a 3-D framework, crystallizing in the monoclinic space group $P2_1/c$. The asymmetric unit [KCe(btec)(H_2O)$_2$] contains one

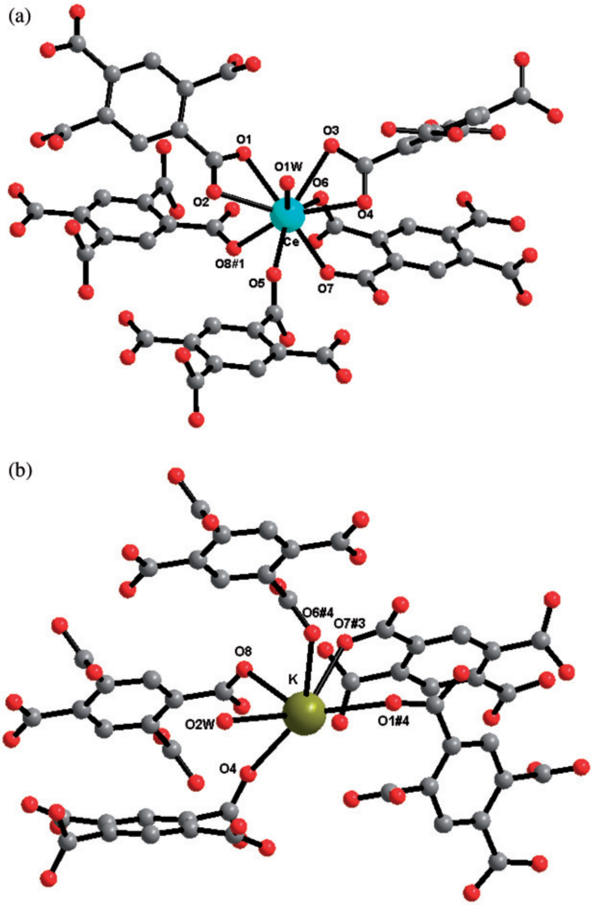


Figure 1. The coordination environment of Ce(III) (a) and K (b) ions in **1** (all hydrogen atoms are omitted for clarity). Symmetry code: #3, $-x+2$, $y-1/2$, $-z+1/2$; #4, x, $y-1$, z.

nine-coordinate cerium ion, one six-coordinate potassium ion, one 1,2,4,5-benzenetetracarboxylic acid ligand, and two coordinated water molecules. The coordination environments of cerium and potassium ions are shown in figure 1. Ce(III) is coordinated with nine oxygen atoms from two chelating bidentate carboxylates (O1, O2, O3, O4) and four dimonodentate carboxylates (O3#1, O5, O6, and O7) from 1,2,4,5-benzenetetracarboxylic acid, one coordinated water molecule (O1W) (shown as figure 1a). Six oxygen atoms coordinated with K ion are from five dimonodentate carboxylates (O1#4, O4, O6#4, O7#3, and O8) from five 1,2,4,5-benzenetetracarboxylic acid ligands, and one coordinated water molecule (O2W) (figure 1b). The distances of $\mathrm{Ce{-}O_{carboxylate}}$, $\mathrm{K{-}O_{carboxylate}}$, $\mathrm{Ce{-}O_{water}}$, and $\mathrm{K{-}O_{water}}$ are from 2.449(2)–2.628(2), 2.780(2)–2.941(2), 2.5639(9), and 3.0117(15) Å, respectively, all of which are comparable to those reported for other cerium–potassium–oxygen complexes [36–38]. In **1**, btec adopts two types of coordination: μ_{12}–η^2:η^2:η^2:η^1:η^2:η^2:η^2:η^1 bridging linking six Ce(III) ions and six K(I) ions and μ_8–η^1:η^2:η^2:η^1:η^1:η^2:η^2:η^1 bridging connecting four Ce(III) ions and four K^+ ions (figure 2a and b).

In **1**, metals (Ce and K) and the corresponding centrosymmetric atoms are linked alternatively by carboxylate groups from btec ligand to generate an infinite 1-D chain structure along the [1 0 0] direction (figure 3a). The aromatic rings of btec ligand connect these chains to form a 2-D Ce–btec sheet in the *bc* plane (figure 3b). When viewed along the [1 0 0] direction, the sheets are further cross-linked by btec ligand giving rise to a 3-D structure (figure 3c). Taking into account the coordination modes of the btec ligand, it is regarded as an 8-connected node and 12-connected node, and the metal holmium and potassium atoms are regarded as a 6-connected node. The novel topology structure with the short Schläfli symbol $\{3^2,4^8,5^3,6^2\}_4\{3^4,4^{12},5^{12}\}\{4^{38},6^{26},8^2\}$ can be seen from figure 3(d).

The structure of **2** reveals a 3-D framework, crystallizing in monoclinic space group $P2_1/c$. The asymmetric unit of $[Ho(btec)_{0.5}(ad)_{0.5}(H_2O)]$ contains one nine-coordinate holmium, half of a 1,2,4,5-benzenetetracarboxylic acid ligand, half of a adipic acid ligand, and one coordinated water molecule. The coordination environment of **2** is shown in figure 4. Each Ho ion is coordinated by six oxygen atoms (O1, O2, O3#1, O1#1, O3#2, O4#2) from three btec ligands, two oxygen atoms (O5 and O6) from two adipates and one oxygen (O1W) from water. The Ho–O$_{carboxylate}$ bond lengths are in the range 2.301(2)–2.606(9) Å and the mean Ho–O$_{carboxylate}$ bond length is 2.423(8) Å which is close to that of the reported polymer $[Ho(C_7H_6NO_2)_3(H_2O)]_n$ [39]. The Ho–O$_{water}$ bond length is 2.3693 Å, which is similar to $[Ho_2(C_4H_4O_4)_3(H_2O)_4]\cdot 6H_2O$ [40]. The coordination modes of btec and adipate in polymer **2** are depicted in figure 5. The btec ligand adopts a μ_6-bridging with each carboxylate group of btec ligand in a μ_2–η^1–η^2 mode (figure 5a). The adipate ligand is in a μ_4-bridging fashion with each carboxylate group in μ_2–η^1–η^1–monodentate mode (figure 5b).

In the framework, adjacent Ho ions are connected by bridging oxygen atoms of the carboxylate groups from btec to form an infinite 1-D Ho–O2–Ho polymeric chain structure along the [1 0 0] direction (figure 6a). The chains are further linked *via* btec ligands to give a 2-D planar layer in the *bc* plane (figure 6b). Furthermore, the 2-D layers are linked through adipates to produce a 3-D network structure (figure 6c). Taking into account the coordination modes of the ligand btec and ad, the system can be viewed as a 6-connected node and a 4-connected node, respectively, and the metal holmium(III) ion is regarded as a 5-connected node. The novel topology structure with the short Schläfli symbol $\{4^2,8^4\}\{4^6,6^6,8^3\}\{4^7,6^3\}_2$ is shown in figure 6(d).

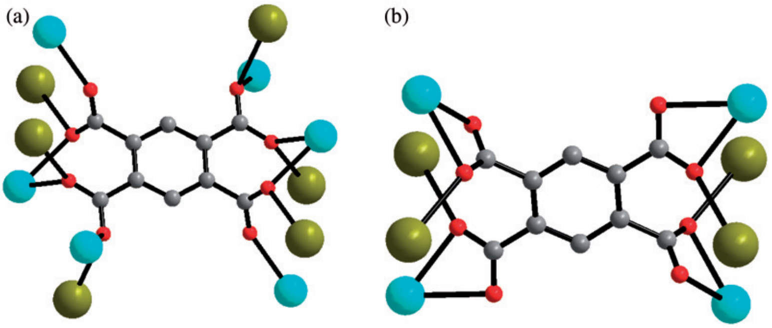


Figure 2. The coordination modes of btec ligand in the construction of **1**.

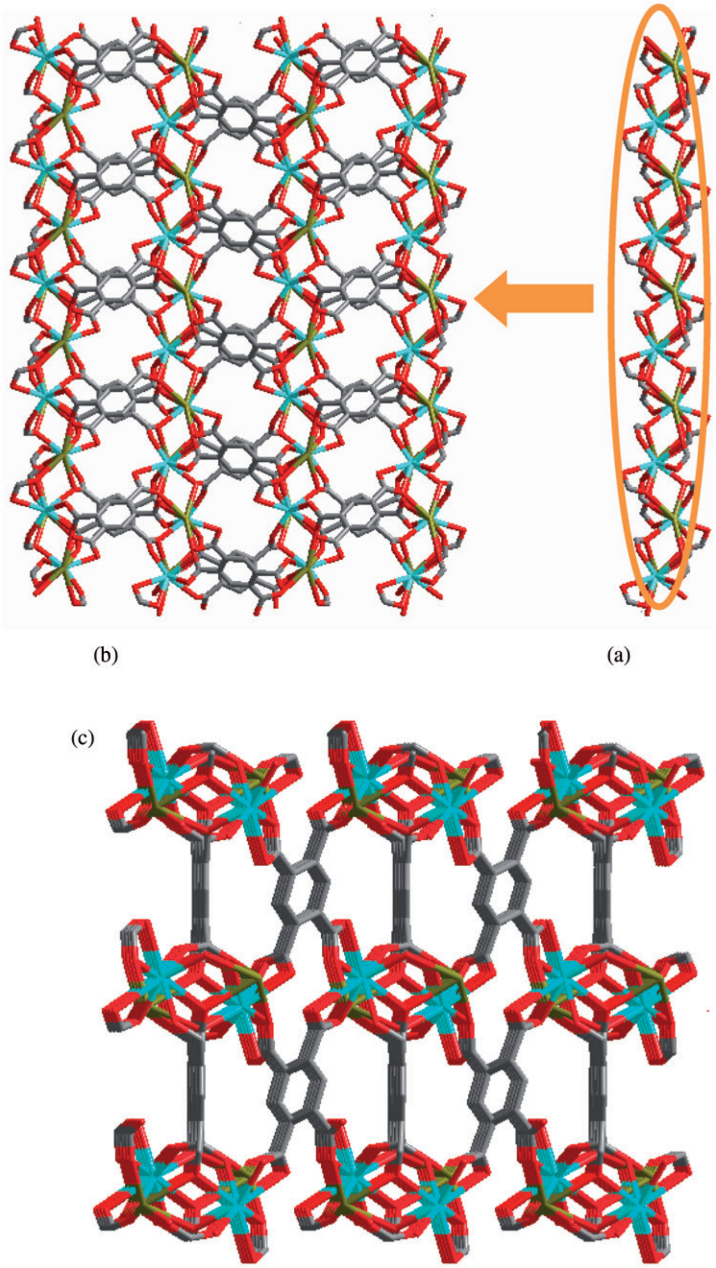
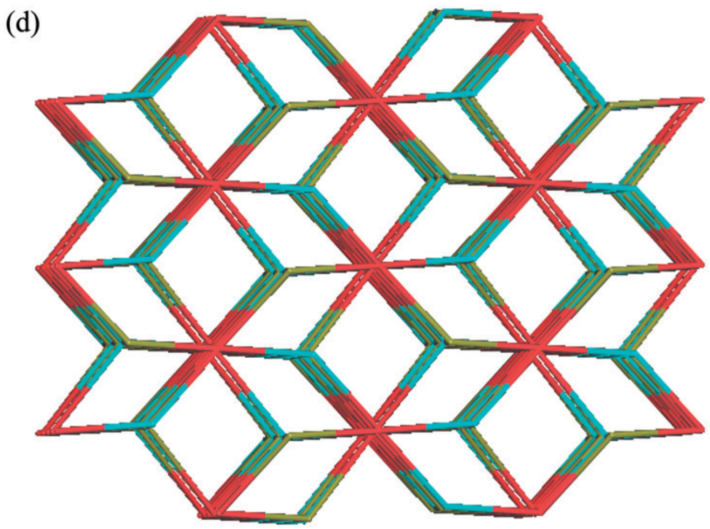


Figure 3. (a) A view of an infinite polymeric chain along the [1 0 0] direction in **1**; (b) the 2-D sheet structure formed by polymeric chain and btec ligands in the *bc* plane (the coordinated water molecules were omitted for clarity); (c) the 3-D packing framework of **1**; and (d) the 3-D topology structure of **1** (the turquoise sticks stand for Ce(III) ion, 6-connected nodes, the dark yellow sticks stand for K ion, 6-connected nodes, the red sticks for btec, 8-connected nodes and 12-connected nodes).



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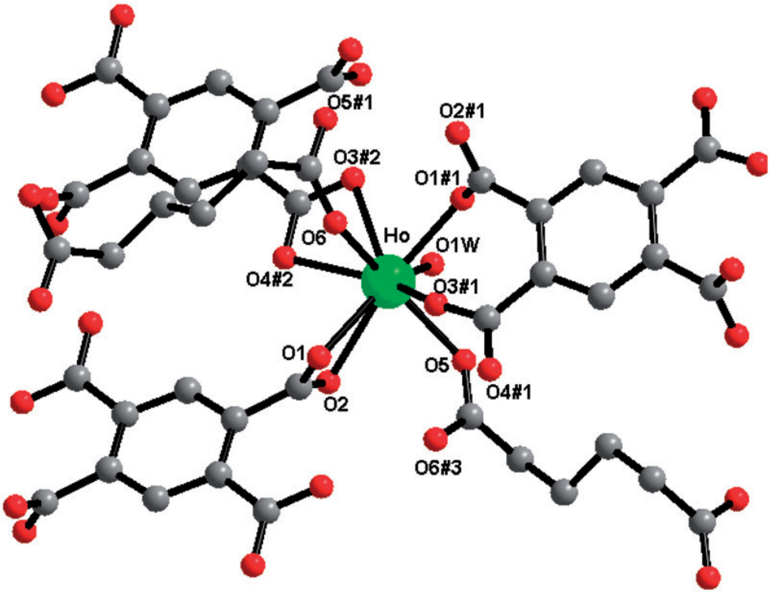

Figure 4. The coordination environment of the Ho ions in **2** (all hydrogen atoms are omitted for clarity). Symmetry codes: #1, $2-x$, $-0.5+y$, $0.5-z$; #2, x, $-1+y$, z.

3.3. *Comparison of structures*

Two lanthanide metal coordination polymers **1** and **2** with the 1,2,4,5-benzenetetracarboxylic acid and adipic acid ligands were synthesized under hydrothermal conditions. Comparing the structures of complexes, it is found that the coordination

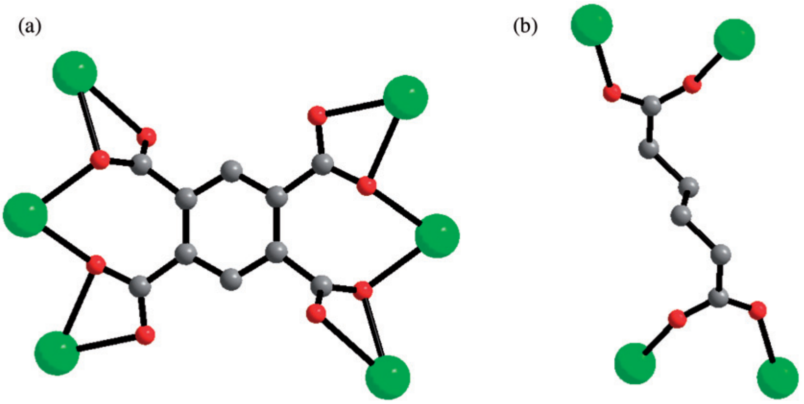

Figure 5. The coordination modes of btec (a) and adipate (b) ligand in the construction of **2**.

modes of btec and alkali metal have a significant effect on framework packings. In **1**, btec ligand adopts μ_6–η^1:η^1:η^1:η^1:η^1:η^1:η^1:η^1 and μ_4–η^1:η^1:η^1:η^1:η^1:η^1:η^1:η^1 two types of coordinated modes, while in **2**, the btec ligand adopts a μ_6-bridging with each carboxylate group of btec ligand in a μ_2–η^1–η^2 mode. Thus, different coordination modes of btec results in different framework packings.

3.4. *Infrared spectroscopy*

The coordination polymers were characterized by IR spectroscopy. For **1**, the characteristic bands of carboxyl groups are shown from 1528 to 1601 cm^{-1} for asymmetric stretching and 1377–1427 cm^{-1} for symmetric stretching. The broad band at 3429 cm^{-1} belongs to the typical band of hydroxyl group. For **2**, the characteristic bands of carboxyl groups are shown in the range 1574–1606 cm^{-1} for asymmetric stretching and 1385–1426 cm^{-1} for symmetric stretching [41]. The absence of the characteristic bands at 1730–1690 cm^{-1} indicates that full deprotonation of H_4btec and adipic acid occurs upon reaction with holmium ion [42, 43]. The splitting of COO^- bands suggests the different coordination mode of carboxylate groups from the mixed ligands [44]. The bands at 2962 and 2923 cm^{-1} are typical absorptions of the $\nu_{C–H}$ vibration modes of $-CH_2$–groups within the carbon chain of adipate. The bands with the maximum at 3441 cm^{-1} are characteristic for $\nu_{–OH}$ vibrations, which corresponds to the presence of the coordinated water molecule [45]. These results are in good agreement with the crystallographic data.

3.5. *Thermogravimetric analysis*

As shown in figure S1, the thermal decomposition of **1** can be divided into three stages. The first weight loss of 7.7% between 80°C and 456°C corresponds to release of two coordinated water molecules (7.7%, theoretical weight loss). The second weight loss of 25.1% was observed in the temperature range 456–590°C, which is attributed to the release of half btec (26.8%, theoretical weight loss). In the third stage, in the range 590–990°C, it accounts for 25.7% of weight loss, which is attributed to the release of half

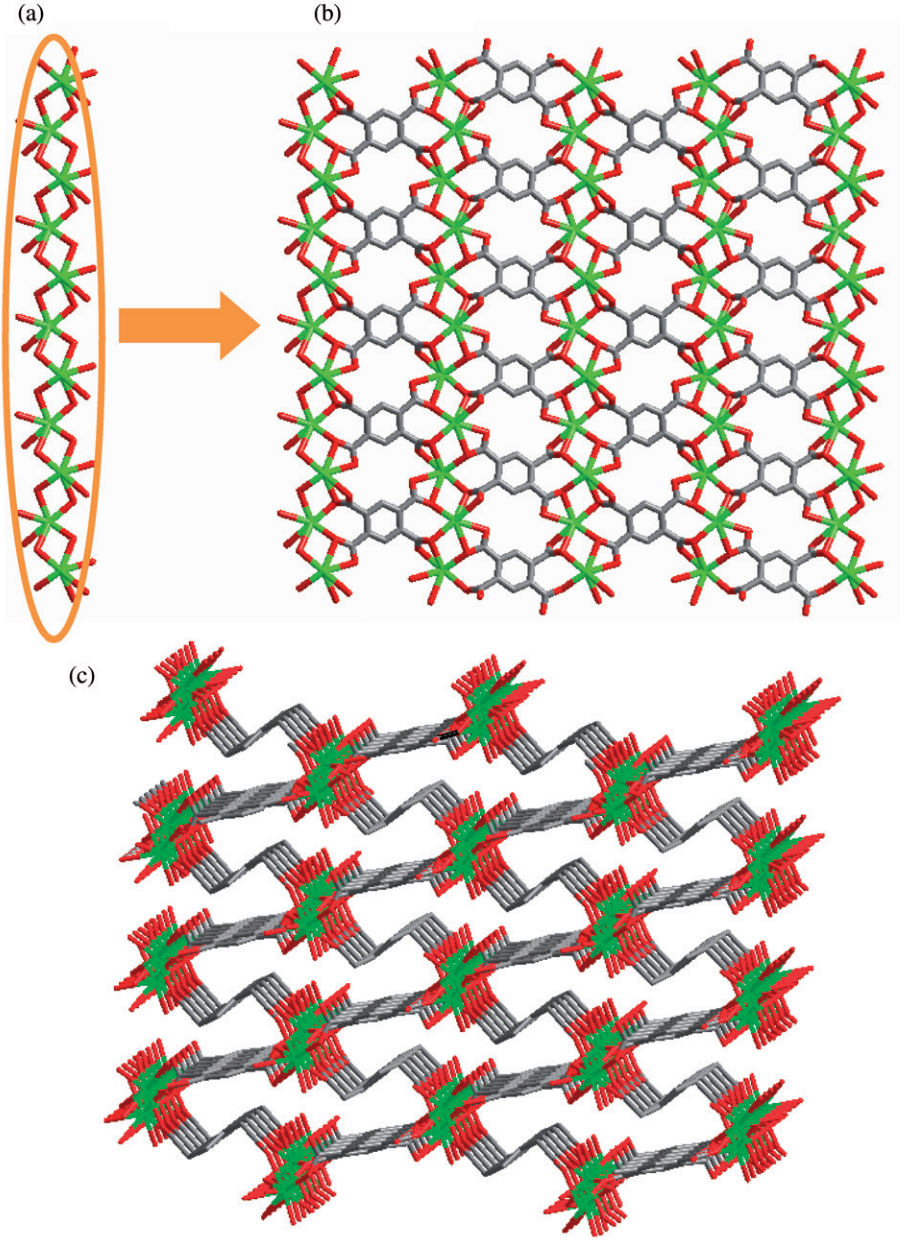

Figure 6. (a) A view of 1-D Ho–O2–Ho infinite polymeric chain of the polymer along the [1 0 0] direction; (b) the 2-D sheet structure formed by polymeric chain and btec ligands in the *bc* plane (the coordinatedion water molecules were omitted for clarity); (c) the 3-D packing framework of **2**; and (d) the 3-D topology structure of **2** (the green sticks stand for Ho atoms, 5-connected nodes, the red sticks for btec, 6-connected nodes, the pink sticks for ad, 4-connected nodes).

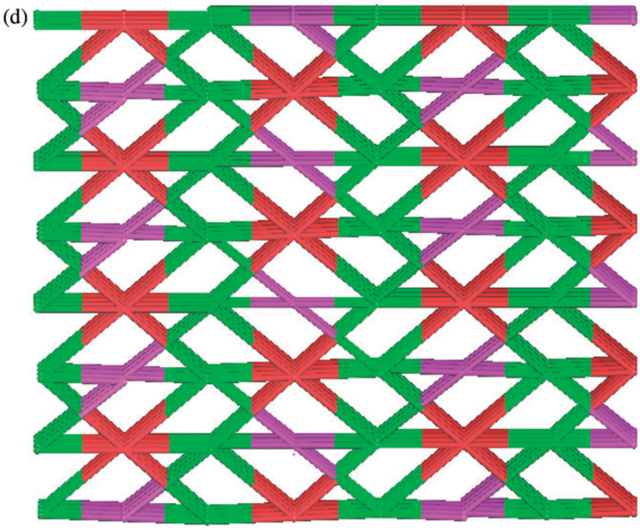

Figure 6. Continued.

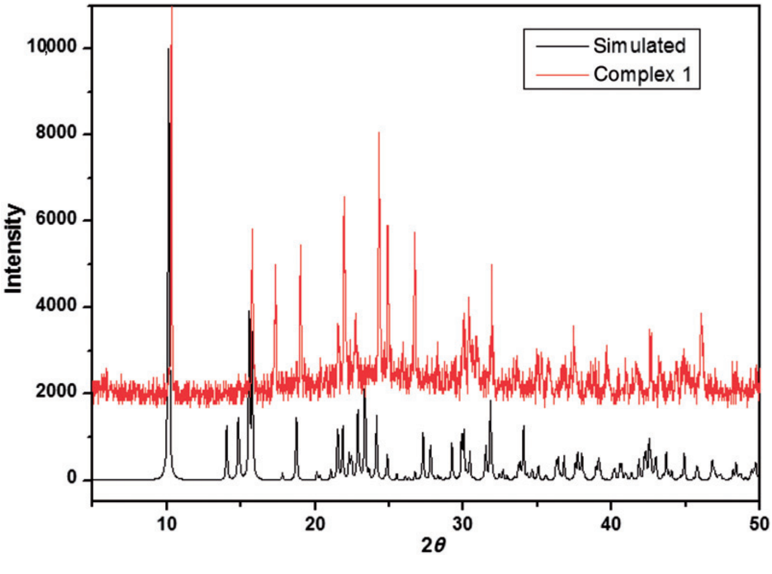

Figure 7. The experimental and simulated XRD patterns of **1**.

btec (26.8%, theoretical weight loss). As shown in figure S2, the thermal decomposition process of **2** can be divided into two stages. The first weight loss of 4.94% in the range 141–207°C corresponds to the removal of one coordinated water (4.74%, theoretical weight loss), and the second weight loss of 39.6% in the range 368–998°C can be attributed to the release of half adipate and two CO_2 molecules (42.1%, theoretical weight loss).

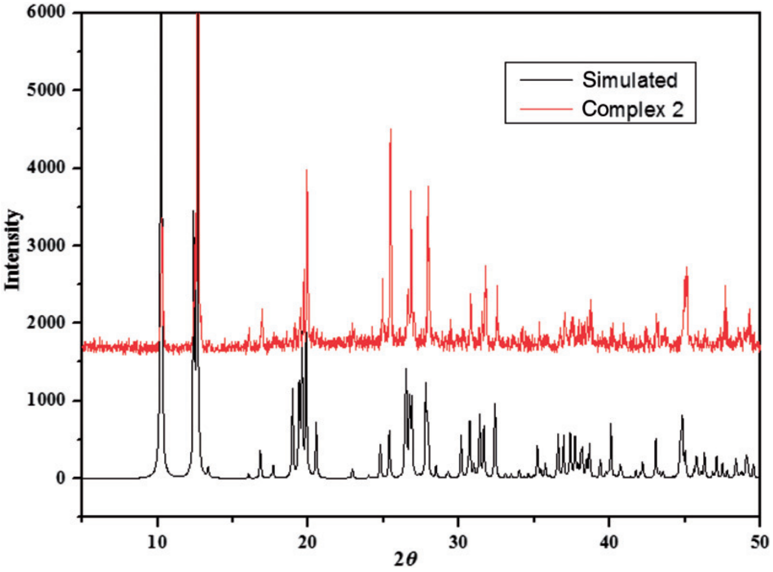

Figure 8. The experimental and simulated XRD patterns of **2**.

3.6. *Powder XRD pattern of complexes*

The XRD data of **1** and **2** were measured. The powder diffraction pattern of **1** is a bit different from that calculated from the single-crystal structure (figure 7). The differences could be a result of variations in the interplanar dimensions resulting from the presence of solvent in the powder. The XRD data of **2** are in agreement with that calculated on the basis of their structural data (figure 8), that is, complexes have been obtained successfully as pure crystalline phases.

4. Conclusion

In this study, two new 3-D lanthanide coordination polymers have been synthesized for the first time under hydrothermal conditions. The TGA of **1** and **2** were discussed. It is found that different metal ions coordinated to the ligand have an impact on the courses of thermal decomposition of complexes, so the course of thermal decomposition of complexes is appreciably different. The structure analysis indicates that the 1,2,4,5-benzenetetracarboxylic acid is a typical aromatic polycarboxylic acid which is an excellent multidentate ligand for potential coordination [46, 47]. Currently, we are pursuing the design and construction of lanthanide coordination polymers with H_4btec ligand and other flexible ligands as mixed-linkers in our laboratory.

Supplementary material

Tables S1 and S2 show the bond angles of **1** and **2**. Figures S1 and S2 denote the TG curves for polymers **1** and **2**. Tables of atomic coordinates, isotropic thermal parameters, and complete bond distances and angles have been deposited with the Cambridge Crystallographic Data Center. Copies of this information may be obtained free of charge, by quoting the publication citation and deposition numbers CCDC 830332 (**1**), 807013 (**2**) from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

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