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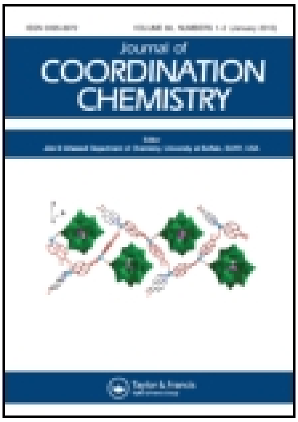

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The construction of two lanthanide coordination polymers based on 5-hydroxyisophthalate and bipyridine

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The construction of two lanthanide coordination polymers based on 5-hydroxyisophthalate and bipyridine

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Two lanthanide coordination polymers, $[Tm_2\cdot(5\text{-IPA})_4\cdot(2,2'\text{-Hbipy})_2]\cdot 3H_2O$ (**1**, 5-H_2IPA = 5-hydroxyisophthalic acid, 2,2′-bipy = 2,2′-bipyridine) and $[Er\cdot(5\text{-HIPA})_3\cdot(4,4'\text{-bipy})_3\cdot(H_2O)_2]\cdot 3H_2O$ (**2**, 4,4′-bipy = 4,4′-bipyridine), have formed by hydrothermal synthesis. Complex **1** exhibits a 2-D coordination network containing parallelepiped-shaped voids occupied by guest 2′2-bipy molecules. Complex **2** possesses a 1-D linear chain structure. The 1-D chains are linked by 4,4′-bipy molecules to form a 3-D supramolecular framework. IR spectroscopy, elemental analysis, and thermogravimetric analysis were also investigated.

Keywords: Coordination polymers; 5-hydroxyisophthalic acid; Bipyridine

1. Introduction

Construction of lanthanide coordination polymers is promising for intriguing architectures and potential application in sensing, separation, gas storage, optoelectronic devices, molecular recognition, ion exchange, and heterogeneous catalysis [1–6]. Lanthanides have high affinity for oxygen donors, so multicarboxylates are usually used to construct coordination polymers [7, 8]. Isophthalic-based acids, such as 5-aminoisophthalic acid, 5-nitroisophthalic acid, 5-methylisophthalic acid, 5-hydroxyisophthalic acid (5-H_2IPA) [9–11], etc. are excellent ligands for constructing coordination polymers with diverse structures and properties.

In our continuing work on assembly of lanthanide coordination complexes [12, 13], 5-H_2IPA was chosen to construct lanthanide-organic frameworks for the following reasons: (i) 5-H_2IPA ligand possesses two carboxylates to bond to Ln(III); (ii) the hydroxyl on the fifth position of 5-H_2IPA can display various roles in the formation of coordination polymers, coordinating directly to metal ions or acting as a typical hydrogen-bonding donor or acceptor; (iii) compared with the transition metal–organic coordination polymers, lanthanide coordination polymers based on 5-HIPA are less explored. Till now, only a

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*Corresponding authors. Email: zrh321@yahoo.com.cn (R.-H. Zeng); zhengshengrun@gmail.com (S.-R. Zheng) series of 2-D lanthanide layered structures, such as containing helical cation chains [10a] or Ln-O–C–O–Ln chains [11a], a 2-D (3,6)-connected Ho(III) complex with $(3^2.4)(3^4.4^3.5^2.6^5.7)$ network topology [11b], a complicated 3-D La(III) framework with ox ligand [11c], a 3-D **nia** network with $(4^{12}.6^3)(4^9.6^6)$ topology [11b], have been reported.

Herein, we use hydrothermal synthesis as a powerful method for preparation of coordination polymers and isolate $[Tm_2{\cdot}(5\text{-IPA})_4{\cdot}(2,2'\text{-Hbipy})_2]{\cdot}3H_2O$ (**1**) and $[Er{\cdot}(5\text{-HIPA})_3{\cdot}(4,4'\text{-bipy})_3{\cdot}(H_2O)_2]{\cdot}3H_2O$ (**2**). The structures exhibit a 2-D porous double-layer and 1-D linear chain structures, respectively. The 2,2′-bipy are guest molecules filling parallelepiped-shaped voids in **1**, while 4,4′-bipy sustain the supramolecular network via hydrogen bonds in **2**.

2. Experimental

2.1. *Chemicals and methods*

All chemicals were obtained from commercial sources and used without purification. Elemental (C, H, N) analyses were preformed on a Thermo FlashEA112 elemental analyzer. IR spectra were recorded by using a Shimadzu IR Prestige-21 spectrometer with KBr pellets from 4000 to 400 cm^{-1}. Thermogravimetric analysis (TGA) under air were carried out on a Netzsch STA409PC thermal analyzer with a heating rate of 10 °C min^{-1} from room temperature to 800 °C.

2.2. *Syntheses of 1 and 2*

2.2.1. Synthesis of $[Tm_2{\cdot}(5\text{-HIPA})_4{\cdot}(2,2'\text{-bipy})_2]{\cdot}3H_2O$ (1). A mixture of Tm_2O_3 (0.193 g, 0.5 mM), 5-HIPA (0.182 g, 1 mM), 2,2′-bipy (0.156 g, 1 mM), H_2O (10 mL), and HNO_3 (0.5 mL) was sealed in a 20 mL Teflon reactor and kept under autogenous pressure at 160 °C for 60 h, then cooled to room temperature at 10 °C h^{-1} to obtain colorless block single crystals in a yield of 38% based on Tm, $C_{52}H_{40}Tm_2N_4O_{23}$ (1426.74), Calcd (%): C 43.74, H 2.80, N 3.93; found: C 43.15, H 2.70, N 3.82. IR (KBr, cm^{-1}): 3403(*s*), 1621(*s*), 1601(*m*), 1556(*m*), 1531(*m*), 1392(*m*), 1384(*s*), 1265(*m*), 1225(*m*), 1224(*w*), 1172(*w*), 1122 (*w*), 1064(*s*), 1016(*w*), 981(*s*), 894(*s*), 798(*w*), 667(*m*), 606(*w*), 584(*w*), 540(*w*), 496(*w*).

2.2.2. Synthesis of $[Er{\cdot}(5\text{-HIPA})_3{\cdot}(4,4'\text{-bipy})_3{\cdot}(H_2O)_2]{\cdot}3H_2O$ (2). A mixture of Er_2O_3 (0.191 g, 0.5 mM), 5-HIPA (0.182 g, 1 mM), 4,4′-bipy (0.156 g, 1 mM), H_2O (10 mL), and HNO_3 (0.5 mL) was sealed in a 20 mL Teflon reactor and kept under autogenous pressure at 150 °C for 50 h, then cooled to room temperature at 10 °C h^{-1} to obtain colorless block single crystals in a yield of 45% based on Er, $C_{54}H_{49}ErN_6O_{20}$ (1269.25), Calcd (%): C 51.05, H 3.86, N 6.62; found: C 50.55, H 3.70, N 6.82. IR (KBr, cm^{-1}): 3413(*s*), 2351 (*w*), 1674(*s*), 1456(*m*), 1427(*m*), 1271(*m*), 1215(*m*), 1120(*s*), 1001(*m*), 979(*m*), 896(*w*), 833(*w*), 804(*s*), 777(*s*), 748(*w*), 717(*w*), 657(*m*), 596(*w*), 514(*w*).

2.3. *X-ray structure determination*

Diffraction data of **1** and **2** were collected on a Bruker SMART CCD APEX II diffractometer equipped with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) using scan technique at 298(2) K. Multiscan absorption corrections were applied using SADABS [14].

The structures were solved by direct methods using SHELXS97 and all nonhydrogen atoms were refined anisotropically with full-matrix least-squares methods on F^2 using SHELXL97 [15]. Hydrogens of water were located in difference Fourier maps and the other hydrogens were generated geometrically and refined as riding with isotropic thermal factors. Crystallographic data and structure determination summaries for **1** and **2** are given in table 1 and selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *IR spectra*

Infrared spectra of the complexes were determined from 400 to 4000 cm^{-1}. Owing to the symmetric and asymmetric stretching vibrations of carboxyl groups, the infrared spectra show the expected strong characteristic absorption peaks at about 1600 and 1500 cm^{-1} for **1** and **2**. The absorption peaks at 3400 cm^{-1} are ν(O–H) of coordinated and uncoordinated water.

3.2. *Crystal structures of 1 and 2*

X-ray single crystal analysis reveals that **1** crystallizes in the triclinic space group *P-1* and displays a polymeric 2-D layer which is constructed from 5-IPA^{2-} and Tm(III). The asymmetric unit consists of two Tm(III) ions, four 5-IPA^{2-}, two protonated 2,2′-bipy, and three guest waters. Each Tm(III) ion is in a bicapped trigonal prismatic coordination site surrounded by eight oxygens from five 5-IPA^{2-} with Tm···O bond lengths ranging from 2.146(1) to 2.484(1) Å and O···Tm···O bond angles ranging from 53.8(3) to 169.8(4)° (figure 1 and table 2), which are all within the range observed for other Tm(III) complexes

Table 1. Crystallographic data and structure refinement summary for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{52}H_{40}N_4O_{23}Tm_2$	$C_{54}H_{49}ErN_6O_{20}$
Formula weight	1426.74	1269.25
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a (Å)	9.941 (6)	9.987 (3)
b (Å)	12.433 (7)	15.401 (4)
c (Å)	21.299 (12)	18.105 (4)
α (°)	105.511 (7)	97.158 (3)
β (°)	90.826(7)	99.337 (3)
γ (°)	98.693 (6)	107.691 (3)
V (Å^3)	2503(3)	2572.8 (11)
Z	2	2
D_{Calcd} (g cm^{-3})	1.893	1.638
Absorption coefficient (mm^{-1})	3.615	1.719
F (0 0 0)	1404	1286
Reflections collected/unique	12,743/9441	12,924/8895
Goodness-of-fit on F^2	1.043	1.028
R_1, wR_2 [$I > 2\sigma(I)$]	0.0744, 0.1675	0.0486, 0.1160
R_1, wR_2 (all data)	0.1106, 0.1865	0.0634, 0.1263
Largest diff. peak and hole (e Å^{-3})	3.387 and −3.984	1.605 and −1.907

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

*Complex **1***			
Tm(1)–O(17)	2.177(10)	Tm(2)–O(8)#4	2.321(10)
Tm(1)–O(6)	2.189(10)	Tm(2)–O(1)	2.350(9)
Tm(1)–O(14)#1	2.330(10)	Tm(2)–O(2)	2.359(10)
Tm(1)–O(19)#2	2.346(10)	Tm(2)–O(9)#4	2.399(10)
Tm(1)–O(11)	2.346(10)	Tm(2)–O(3)#3	2.484(10)
Tm(1)–O(12)	2.387(11)	O19#2–Tm1–O18#2	53.8(3)
Tm(1)–O(18)#2	2.391(9)	O12–Tm1–O13#1	169.8(4)
Tm(1)–O(13)#1	2.451(10)	O7–Tm2–O4#3	143.3(4)
Tm(2)–O(7)	2.146(10)	O4#3–Tm2–O8#4	92.8(4)
Tm(2)–O(16)	2.177(10)	O(19)#2–Tm(1)–O(11)	126.3(4)
Tm(2)–O(4)#3	2.243(11)	O14#1–Tm1–O18#2	77.6(4)
*Complex **2***			
Er(1)–O(11)	2.230(4)	O(11)–Er(1)–O(12)#2	107.91(18)
Er(1)–O(8)#1	2.236(4)	O(8)#1–Er(1)–O(12)#2	82.90(18)
Er(1)–O(9)	2.263(4)	O(9)–Er(1)–O(12)#2	143.62(16)
Er(1)–O(12)#2	2.303(4)	O(11)–Er(1)–O(1W)	78.05(16)
Er(1)–O(2W)	2.405(5)	O(8)#1–Er(1)–O(1W)	80.67(16)
Er(1)–O(4)	2.405(4)	O(9)–Er(1)–O(1W)	141.67(16)
Er(1)–O(3)	2.558(4)	O(12)#2–Er(1)–O(1W)	74.20(16)
Er(1)–O(1W)	2.401(4)	O(1W)–Er(1)–O(3)	145.67(16)
O(11)–Er(1)–O(8)#1	152.23(18)	O(8)#1–Er(1)–O(2W)	77.6(2)
O(11)–Er(1)–O(9)	90.23(17)	O(9)–Er(1)–O(2W)	69.72(16)
O(8)#1–Er(1)–O(9)	95.58(16)	O(8)#1–Er(1)–O(2W)	146.16(19)

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

with oxygen donors [12a, 13a]. The 5-IPA^{2-} ligands display two types of coordination. In μ_2-coordination, both two carboxylates are bidendate, while in μ_3-coordination, one carboxylate is bidendate and the other is bis-monodentate.

In **1**, two Tm(III) ions are bridged by two 5-IPA^{2-} ligands resulting in a binuclear secondary building unit (SBU) with nonbonding Tm···Tm distance of 5.375 Å. Binuclear SBUs are double bridged by two μ_2-5IPA^{2-} and two μ_3-5-IPA^{2-} in *a* and *c* direction, respectively, leading to a 2-D layer (figure 2). From a network topology viewpoint, all Tm (III) ions can be considered as five-connected nodes, the μ_3-5-HIPA^{2-} can be considered as three-connected nodes, and μ_2-5-HIPA^{2-} only act as linkers. As a result, a 2-D coordination framework with (3,5)-mixed connectivity is formed, as depicted in figure 3, which has the Schläfli symbol of $(4^2\cdot6^7\cdot8)_2(4^2\cdot6)$ (figure 4). However, when considering the binuclear SBU as a node, the $(4^2\cdot6^7\cdot8)_2(4^2\cdot6)$ network can be simplified into a common (4,4) net. The parallelepiped-shaped voids are formed with size $10.660\times9.941\times5.375$ Å^3 in the 2-D layer, which are occupied by two 2,2′-bipy molecules (figure 2). Adjacent 2-D layers are connected by O–H···O hydrogen bonds involving uncoordinated water and 5-HIPA^{2-} to form a 3-D supramolecular framework with channels running along the *b* axis (table S1, Supplementary material and figure 3). The 41.7% of solvent accessible volume (1044.2 Å^3) after being activated by removing 2,2′-bipy ligands and guest waters is estimated by PLATON/Solv [16]. The potential solvent area is larger than the porosities of the other related coordination frameworks [12b, 13, 17].

X-ray single crystal analysis reveals that **2** is also crystallized in the triclinic space group *P-1* and exhibits a 1-D infinite chain that is built up by 5-HIPA$^-$ and Er(III). In the asymmetric unit, there are one Er(III) ion, three 5-HIPA$^-$, three 4,4′-bipy, two coordinated

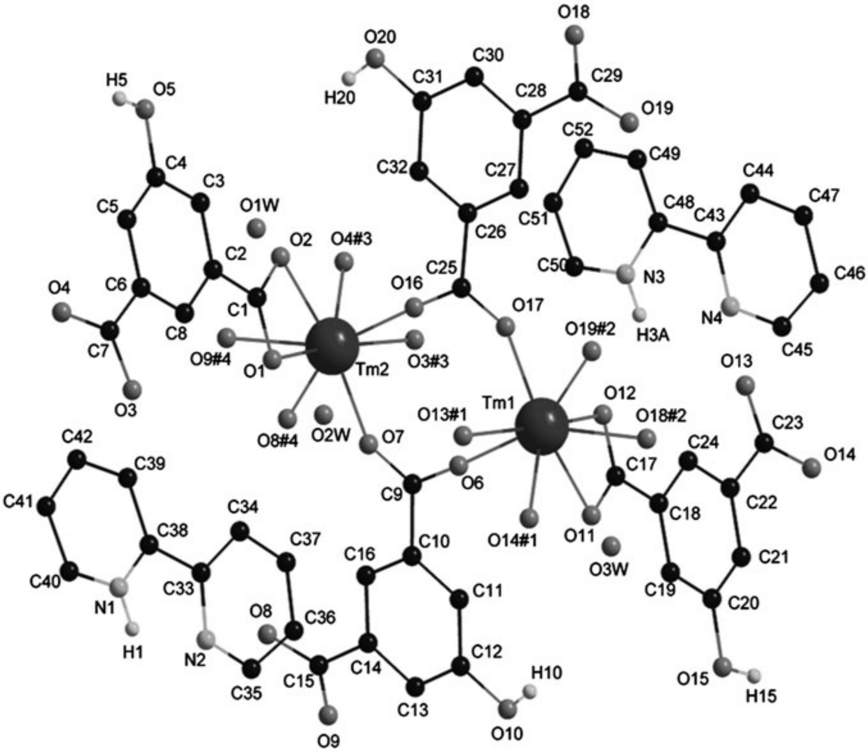

Figure 1. The coordination environment of Tm(III) in **1** (symmetry codes: #1 $-1+x$, y, $1+z$; #2 $1-x$, $1-y$, $-z$; #3 $1+x$, y, z; #4 $1-x$, $1-y$, $1-z$).

waters, and two guest waters. Each Er(III) ion is located in an eight-member coordination environment – six oxygens from carboxyl groups of five 5-HIPA$^-$ ligands and two waters (figure 5). The Er–O distances range from 2.230(4) to 2.558(4) Å and the average Er–O length is 2.350(4) Å (table 2). The 5-HIPA$^-$ ligands in **2** only use one of the two carboxylates to coordinate with Er(III), in bidendate and bis-monodentate fashion. However, the uncoordinated carboxylate is a strong hydrogen bonding site, important for the formation of the 3-D supramolecular network.

In the coordination polymer of **2**, Er(III) ion are connected by μ_2-5-HIPA$^-$ to form a linear chain (figure 6) and the other 5-HIPA$^-$ ligands bind via bidendate carboxylates. All uncoordinated carboxylates, the hydroxyl, the uncoordinated waters, and 4,4′-bipy contain strong hydrogen bonding donors or acceptors; thus a complicated hydrogen bonding framework was formed in **2** (table S2, Supplementary material). The three crystallographically independent 4,4′-bipy molecules play different roles in the molecular packing. As shown in figure 6, one of the 4,4′-bipy molecules is fixed inside the 1-D chain via two O–H···N hydrogen bonds between hydroxyl and 4,4′-bipy. The other two 4,4′-bipy molecules increase the dimensionality of the 1-D chains. The 1-D chains are further interconnected by O–H···O and O–H···N hydrogen bonds involving carboxyl oxygens of 5-HIPA$^-$, 4,4′-bipy, coordinated and uncoordinated waters and construct a 2-D supramolecular framework along the *a* axis (figure 7). The 2-D layers are further joined by O–H···O hydrogen bonds between waters and carboxyl groups to generate a 3-D supramolecular framework.

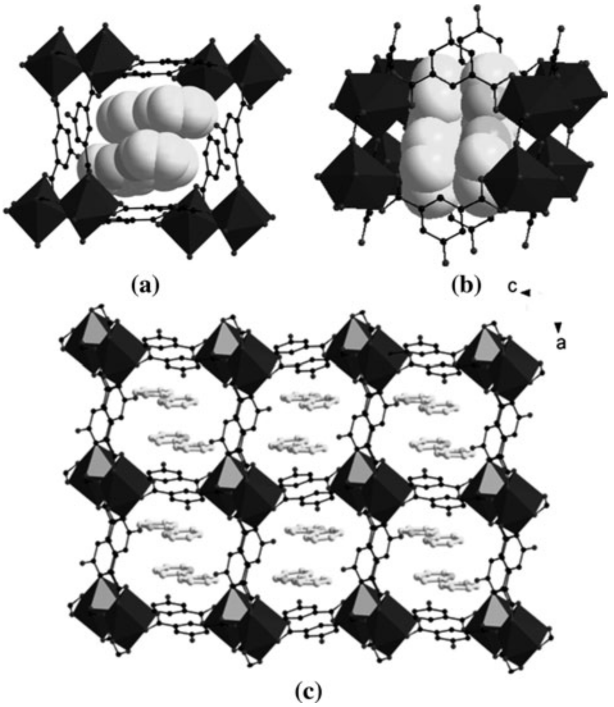

Figure 2. (a) Top view and (b) side view of parallelepiped-shaped voids in **1**, (c) view of the layer structure of **1**.

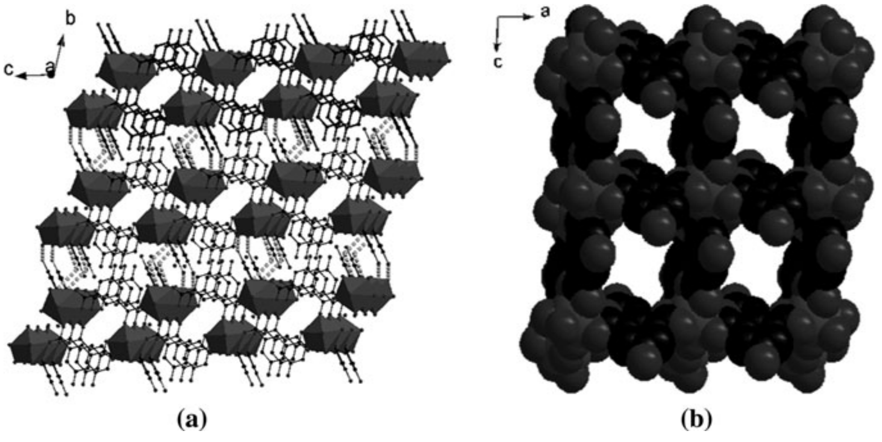

Figure 3. (a) The 3-D porous supramolecular framework of **1** (hydrogen bonds are shown in dashed lines; 2,2′-bipy and waters are omitted for clarity). (b) The 1-D channels in **1** (2,2′-bipy and waters are omitted for clarity).

From **1** and **2**, the bipyridine molecules play important roles in formation of the final frameworks. Bipyridine molecules contain two pyridines, which participate in $\pi\cdots\pi$ forces and hydrogen bonding interactions. Compared with 4′4-bipy, 2,2′-bipy is less suitable for hydrogen bond formation, since nitrogens on the 2-position have more steric hindrance

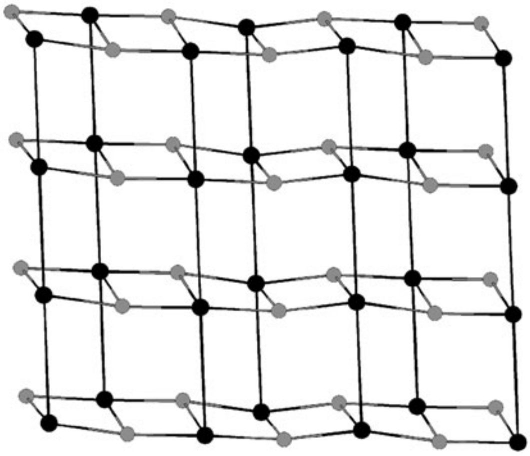

Figure 4. The 3,5-connected 2-D network of **1**.

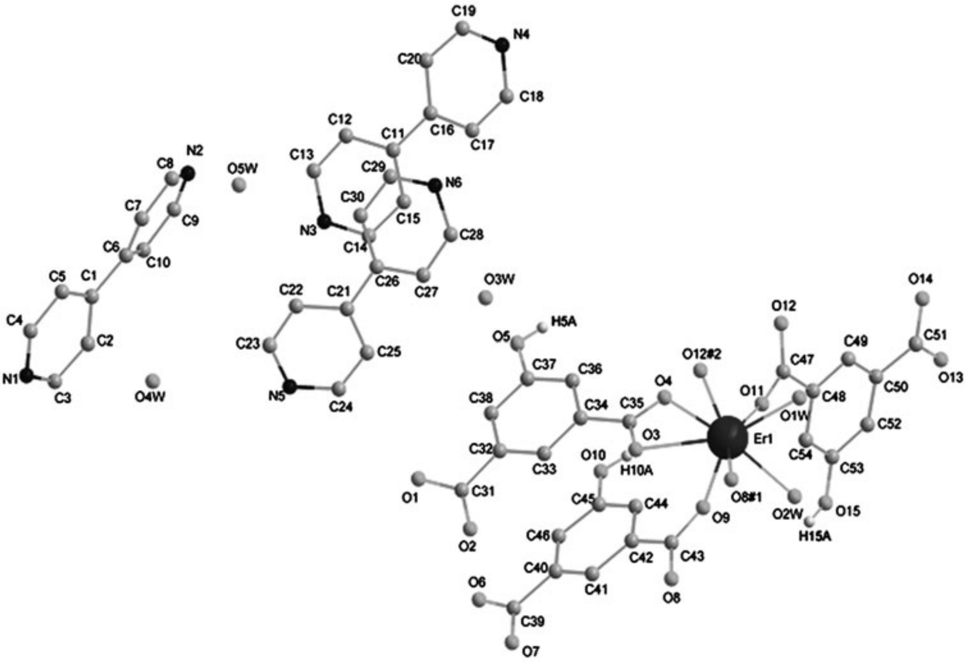

Figure 5. The coordination environment of Er(III) in **2** (symmetry codes: #1 $2-x$, $-y$, $2-z$; #2 $1-x$, $-y$, $2-z$).

than in the 4-position. Thus, 2,2′-bipy molecules in **1** are only guest molecules occupying voids created by Ln(III) ions and 5-HIPA$^-$. The 4′4-bipy molecules are effective in formation of diverse strong hydrogen bonds in **2**, increasing dimensionality (from 1-D to 3-D).

3.3. *Powder X-ray diffraction and thermal behaviors*

In order to check the purity of **1** and **2**, the isolated samples of **1** and **2** were characterized by powder X-ray diffraction at room temperature (S1–2). When compared to the simulated

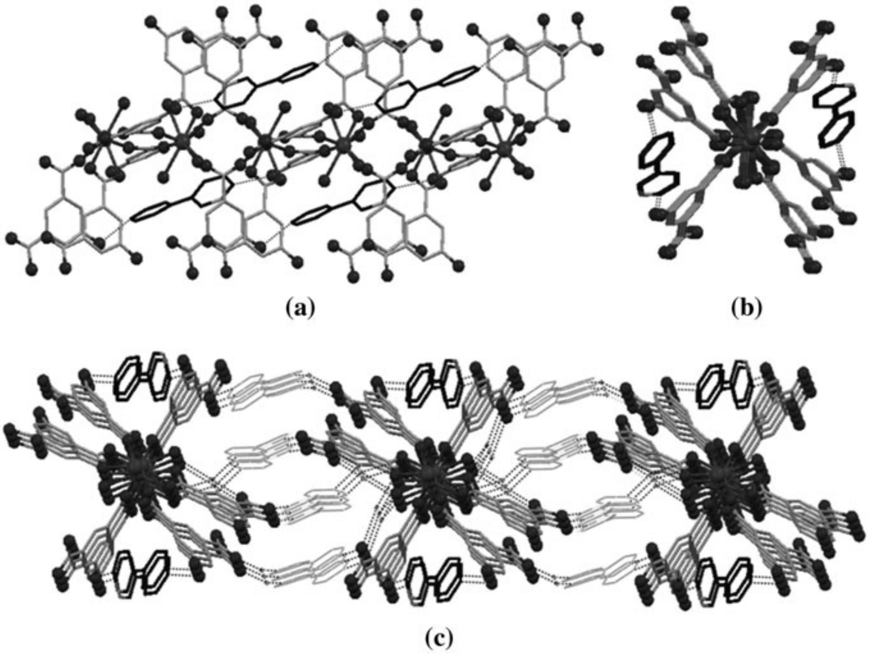

Figure 6. (a) Side view and (b) top view of the 1-D chain in **2** (4,4′-bipy molecules are shown in black). (c) the 2-D supramolecular network in **2** (4,4′-bipy molecules fixed in the 1-D chains are shown in black and 4,4′-bipy molecules between the 1-D chains are shown in light gray).

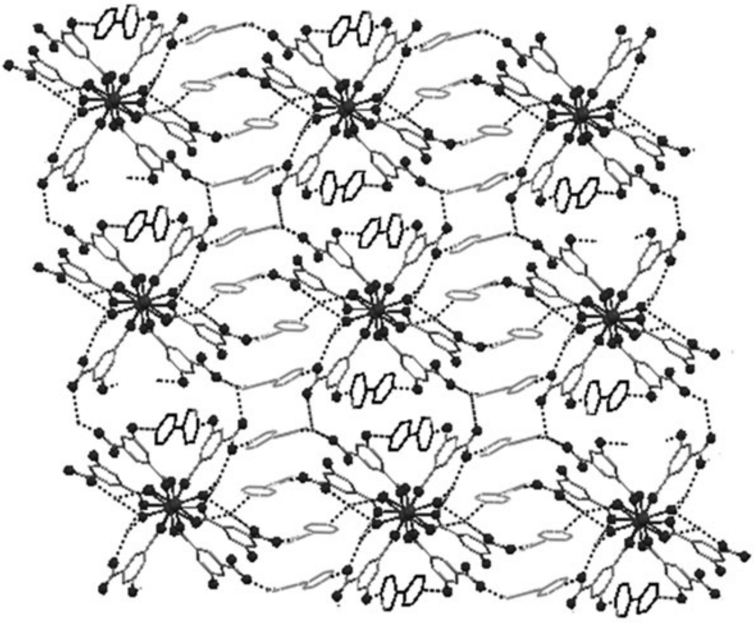

Figure 7. View of the 3-D supramolecular framework along the *a* axis of **2**.

patterns generated from single-crystal diffraction data, the measured patterns are in agreement with the calculated diffractograms, indicating that single phases of **1** and **2** are formed.

TGA of **1** and **2** were performed (figure S1, Supplementary material). The TGA curve of **1** indicates two main weight losses. The first from 40 to 127 °C corresponds to loss of three uncoordinated waters. The observed weight loss of 4.6% is in agreement with the calculated one (3.8%). When the temperature is further increased to 390 °C the organic ligands start to decompose and the framework collapses. For **2**, TGA studies showed the first weight loss (3.8%) at ca. 40–110 °C, attributed to loss of three guest waters (Calcd 4.3%). The second weight loss above 150 °C corresponds to decomposition of the coordination frameworks. The thermal behavior of **1** and **2** are different due to their different structures. The results indicate that **1** can be thermally stable at high temperature, while **2** is less stable. The relatively higher stability of **1** may be due to its higher dimension framework.

4. Conclusion

Synthesis, crystal structure, and thermal stability of new lanthanide coordination polymers prepared by utilizing 5-hydroxyisophthalic acid and bipy are reported and discussed. Compound **1** is a 2-D network containing parallelepiped-shaped voids occupied by 2,2′-bipy, while **2** is a complicated supramolecular framework composed of 1-D coordination chains and 4,4′-bipy spacers. The results show that although the bipyridine molecules are uncoordinated to Ln(III), they are important for the formation of supramolecular framework, acting as guest or spacer. The synthetic method adopted here will be used to prepare other Ln(III) coordination polymers.

Supplementary materials

CCDC 798970 and 798971 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44)1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version at doi:10.1016/j.inoche.

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References

[1] (a) T.K. Maji, G. Mostafa, R. Matsuda, S. Kitagawa. *J. Am. Chem. Soc.*, **127**, 17152 (2005); (b) H.B. Yang, A. Hawkridge, S.D. Huang, N. Das, S.D. Bunge, D.C. Muddiman, P.J. Stang. *J. Am. Chem. Soc.*, **129**, 2120 (2007).

[2] (a) M.H. Keefe, K.D. Benkstein, J.T. Hupp. *Coord. Chem. Rev.*, **205**, 201 (2000); (b) E.Q. Gao, Y.F. Yue, S.Q. Bai, Z. He, C.H. Yan. *J. Am. Chem. Soc.*, **126**, 1419 (2004).

[3] (a) B. Zhao, X.M. Chen, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang. *J. Am. Chem. Soc.*, **126**, 15394 (2004); (b) K. Hanaoka, K. Kikuchi, H. Kojima, Y. Urano, T. Nagano. *J. Am. Chem. Soc.*, **126**, 12470 (2004).

[4] (a) M. O'Keeffe, M.A. Peskov, S.J. Ramsden, O.M. Yaghi. *Acc. Chem. Res.*, **41**, 1782 (2008); (b) N. Yanai, W. Kaneko, K. Yoneda, M. Ohba, S. Kitagawa. *J. Am. Chem. Soc.*, **129**, 3496 (2007).

[5] (a) M. Nihei, L. Han, H. Oshio. *J. Am. Chem. Soc.*, **129**, 5312 (2007); (b) X.N. Chen, W.X. Zhang, X.M. Chen. *J. Am. Chem. Soc.*, **129**, 15738 (2007); (c) P.K. Thallapally, J. Tian, M.R. Kishan, C.A. Fernandez, S.J. Dalgarno, P.B. McGrail, J.E. Warren, J.L. Atwood. *J. Am. Chem. Soc.*, **130**, 16842 (2008).

[6] (a) P.K. Thallapally, R.K. Motkuri, C.A. Fernandez, P.B. McGrail. *Dalton Trans.*, **39**, 1692 (2010); (b) M.R. Kishan, J. Tian, P.K. Thallapally, C.A. Fernandez, S.J. Dalgarno, P.B. McGrail, J.E. Warren, J.L. Atwood. *Chem. Commun.*, **46**, 538 (2010).

[7] (a) H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi. *Nature*, **402**, 276 (1999); (b) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi. *Science*, **295**, 469 (2002); (c) J.J. Wang, L.P. Zhang, L. Huang, J. Chen. *J. Coord. Chem.*, **65**, 3274 (2012); (d) M. Guo, N. Chen, Y.C. Gao, H.J. Lu, G. Li. *J. Coord. Chem.*, **65**, 1724 (2012); (e) L. Wang, L. Ni. *J. Coord. Chem.*, **65**, 1475 (2012).

[8] (a) S.Y. Chui, S.M.F. Lo, J.P.H. Charmant, A.G. Orpen, I.D. Williams. *Science*, **283**, 1148 (1999); (b) J.C.G. Bünzli, C. Piguet. *Chem. Rev.*, **102**, 1897 (2002); (c) R.A.S. Ferreira, P.S. Andre, L.D. Carlos. *Opt. Mater.*, **32**, 1397 (2010); (d) O. Guillou, C. Daiguebonne, *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier B.V., Amsterdam 34 (2004). Ch. 221.

[9] (a) X.Y. Cao, Q.P. Lin, Y.Y. Qin, J. Zhang, Z.J. Li, J.K. Cheng, Y.G. Yao. *Cryst. Growth Des.*, **9**, 20 (2009); (b) R.K. Feller, A.K. Cheetham. *CrystEngComm*, **11**, 980 (2009); (c) R.K. Feller, A.K. Cheetham. *Dalton Trans.*, 2034 (2008).

[10] (a) H.T. Xu, Y.T. Li. *J. Mol. Struct.*, **690**, 137 (2004); (b) H.Y. He, Y.L. Zhou, Y. Hong, L.G. Zhu. *J. Mol. Struct.*, **737**, 97 (2005); (c) Y. Huang, B. Yan, M. Shao. *J. Mol. Struct.*, **876**, 211 (2008).

[11] (a) Y. Huang, B. Yan, M. Shao. *J. Solid State Chem.*, **181**, 2935 (2008); (b) H.Y. He, Y.L. Zhou, L.G. Zhu. *Z. Kristallogr. NCS*, **220**, 445 (2005); (c) M. Chen, C. Wang, M. Hu, C.S. Liu. *Inorg. Chem. Commun.*, **17**, 104 (2012); (d) S. Si, C. Li, R. Wang, Y. Li. *J. Coord. Chem.*, **59**, 215 (2006).

[12] (a) J.X. Mou, R.H. Zeng, Y.C. Qiu, W.G. Zhang, H. Deng, M. Zeller. *Inorg. Chem. Commun.*, **11**, 1347 (2008); (b) H.Z. Chen, J.X. Rong, J.J. Lin, X. Cai, S.L. Cai, R.H. Zeng, S.R. Zheng. *Inorg. Chem. Commun.*, **21**, 178 (2012); (c) Y.C. Qiu, H.G. Liu, Y. Ling, H. Deng, R.H. Zeng, G.Y. Zhou, M. Zeller. *Inorg. Chem. Commun.*, **10**, 1399 (2007); (d) S.R. Zheng, S.L. Cai, Q.Y. Yang, T.T. Xiao, J. Fan, W.G. Zhang. *Inorg. Chem. Commun.*, **14**, 826 (2011).

[13] (a) C.D. Huang, T.R. Qiu, Y.Y. Wu, H.H. Mo, R.H. Zeng, G. Peng, N. Wang, D.S. Lu, Z.Q. Fang. *Z. Anorg. Allg. Chem.*, **635**, 2381 (2009); (b) R.H. Zeng, G. Peng, Y.C. Qiu, S.R. Zheng, W.S. Li, W.X. Zhang, H. Deng, Y.P. Cai. *CrystEngComm*, **13**, 3910 (2011); (c) Q.Y. Lian, C.D. Huang, R.H. Zeng, Y.C. Qiu, J.X. Mou, H. Deng, M. Zeller. *Z. Anorg. Allg. Chem.*, **635**, 393 (2009); (d) Y.C. Qiu, C. Daiguebonne, J.Q. Liu, R.H. Zeng, N. Kerbellec, H. Deng, O. Guillou. *Inorg. Chim. Acta*, **360**, 3265 (2007).

[14] Bruker, *SMART and SAINT*, Bruker AXS Inc., Madison, Wisconsin (2004).

[15] G.M. Sheldrick. *SHELXS 97 and SHELXL 97, Program for X-ray Crystal Structure Solution and Refinement*, University of Göttingen, Göttingen, Germany (1997).

[16] A.L. Spek. *J. Appl. Cryst.*, **36**, 7 (2003).

[17] K.O. Kongshaug, H. Fjellvåg. *Inorg. Chem.*, **45**, 2424 (2006).