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两个具一维水链的镧系配位聚合物的合成与晶体结构

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摘要:以 Ln_2O_3(Ln=Nd 和 La),2,2′-联吡啶-3,3′-二羧酸(bpdc),4,4′-联吡啶(bpy)为原料,采用溶剂热法合成了 2 个具有二维骨架结构的无机–有机杂化材料$[Nd_2(bpdc)_3(H_2O)_2]\cdot bpy\cdot 4H_2O$ (**1**)和$[La_2(bpdc)_3(H_2O)_4]\cdot 4H_2O$ (**2**),通过 IR 和 X-射线单晶衍射分析等手段对其结构进行了表征。晶体 **1** 属于单斜晶系,*C*2/*c* 空间群,晶胞参数 *a*=3.310 4(7) nm,*b*=0.748 12(15) nm,c=1.984 8(4) nm,β=104.75(3)°。晶体 **2** 属于单斜晶系,*C*2/*c* 空间群,晶胞参数 *a*=2.674 9(5) nm,*b*=0.711 65(14) nm,*c*=2.054 2(4) nm,*β*=92.70(3)°。在这 2 个配位聚合物中,晶体中的结晶水沿着 *b* 轴呈现一维无限有序排列,将化合物中二维的金属有机骨架通过氢键相连进而形成了三维超分子结构。

关键词:镧系金属;水热合成;晶体结构;超分子;水链
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Hydrothermal Synthesis and Crystal Structure of Two Novel Lanthanide MOF Compounds with One-Dimensional Water Chains

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Abstract: Two new lanthanide MOF compounds, $[Nd_2(bpdc)_3(H_2O)_2]\cdot bpy\cdot 4H_2O$ (**1**) and $[La_2(bpdc)_3(H_2O)_4]\cdot 4H_2O$ (**2**) (bpdc=2,2′-bipyridine-3,3′-dicarboxylate, bpy=4,4′-bipyridine) have been synthesized under hydrothermal conditions. The crystal structure analysis indicates that both compounds crystallize in monoclinic system, space group *C*2/*c*. the crystal cell parameters for compound **1** are *a*=3.310 4(7) nm, *b*=0.748 12(15) nm, *c*=1.984 8(4) nm, *β*=104.75(3)°, and for compound **2** are *a*=2.674 9(5) nm, *b*=0.711 65(14) nm, *c*=2.054 2(4) nm, *β*=92.70(3)°. In compound **1**, the Nd(Ⅲ) ions are bridged by bpdc ligands with two coordination modes to form a two-dimensional neodymium MOF layer. The layers are connected by one-dimensional water chains and bpy molecules through rich hydrogen-bonding interactions to build up a three-dimensional supramolecular structure. The crystal structure of **2** is constructed by the layered lanthanum MOFs and the interlayer water chains through hydrogen bonding interactions. CCDC: 660394, **1**; 662044, **2**.

Key words: rare earth; hydrothermal synthesis; crystal structure; supramolecular; water chain

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0 Introduction

The metal-organic frameworks (MOFs) are built up by lanthanide metal atoms and polyfunctional organic ligands through coordination bonds to form one-dimensional chain, two-dimensional sheet or three-dimensional network[1]. The interest toward MOFs is not only at getting intriguing structures but also probing its possible usages in hydrogen storage[2], catalysis[3], magnetism[4], fluorescence[5], gas separation[6] and nano material precursors[7]. Many multidentate ligands containing N- or O-donors, such as 2,2′-bipyridine-3,3′-dicarboxylate and 2,2′-bipyridine-4,4′-dicarboxylate would be expected to be good organic ligands in constructing lanthanide-organic frameworks, due to the inherent negative charge of carboxylate groups compensate for the charge induced by metal cations and can mitigate the counterion effect, and the diverse coordination modes of bpdc provide the potential for the formation of metal-organic bridging units, which help enhance the robustness of the resulting network architecture.

The lanthanide and transition metal compounds constructed from 2,2′-bipyridine-3,3′-dicarboxylate were widely studied[8-14]. With this communication, we employed lanthanide ions, with large radii and high coordination numbers, multi-dentate organic ligand containing N- and O-donors, 2,2′-bipyridine-3,3′-dicarboxylate acid (H_2bpdc) and typical bis-dentate ligand 4,4′-bipyridine, to hydrothermally synthesize MOF compounds of the more interesting topologic structures. Herein, we report two novel lanthanide MOF compounds with one dimensional water chains, $[Nd_2(bpdc)_3(H_2O)_2]\cdot bpy\cdot 4H_2O$ (**1**) and $[La_2(bpdc)_3(H_2O)_4]\cdot 4H_2O$ (**2**). To the best of our knowledge, experimental investigations on large hydrogen bonding network of water molecules are very limited[15], and one dimensional water chains in two dimensional MOF compounds have not been reported yet.

1 Experimental

1.1 Chemicals and general methods

H_2bpdc was prepared according to the reported method[16]. All the other chemicals and solvents used in the syntheses were of reagent grade without further purification. Elemental analysis for the title compound was performed by Elementar Vario EL analyzer. Infrared (IR) spectra, in the region (600~4 000 cm^{-1}), were recorded on Nicolet Avatar 360 FTIR spectrometer.

1.2 Syntheses

$[Nd_2(bpdc)_3(H_2O)_2]\cdot bpy\cdot 4H_2O$ (**1**). A mixture of Nd_2O_3 (0.5 mmol, 0.168 2 g), H_2bpdc (0.5 mmol, 0.122 0 g) and bpy(0.5 mmol, 0.096 2 g) in 1∶1∶1 molar ratio was sealed in a 25 mL Teflon-lined stainless steel Parr bomb containing H_2O (14 mL), heated at 423 K for 24 h, and then cooled down to room temperature. Purple sheet crystals were isolated and washed with deionized water and ethanol. Anal. Calcd. for **1**, $Nd_2C_{46}N_8O_{18}H_{38}$: C, 43.19; N, 8.75; H, 2.99. Found: C, 43.32; N, 8.69; H, 3.07. IR (KBr)/cm^{-1}: 3 384(m), 1 614(vs), 1 590(s), 1 556(s), 1 494(w), 1 450(m), 1 402(s), 1 168(w), 1 074(w), 866(w), 776(m), 748(w), 696(w).

$[La_2(bpdc)_3(H_2O)_4]\cdot 4H_2O$ (**2**). Colorless sheet crystals of 2 were synthesized from a mixture of La_2O_3 (0.162 9 g, 0.5 mmol), H_2bpdc (0.5 mmol, 0.122 0 g) in 1∶1 molar ratio under the same conditions as above. Anal. Calcd. for **2**, $La_2C_{36}N_6O_{20}H_{34}$: C, 37.65; N, 7.32; H, 2.98. Found: C, 37.59; N, 7.37; H, 2.93. IR (KBr)/cm^{-1}: 3 476(m), 3 383(m), 1 653(w), 1 613(vs), 1 590(s), 1 557(s), 1 445(m), 1 435(m), 1 401(s), 1 168(w), 1 059(w), 848(w), 776(m), 748(w), 696(w).

1.3 X-ray crystallographic study

Single crystal diffraction data of **1** and **2** were, respectively, collected on a Bruker SMART APEX-CCD diffractometer equipped with graphite-monochromatic Mo $K\alpha$ radiation (0.071 073 nm) at room temperature. The SMART software[17] was used for data collection and the SAINT[18] software for data extraction. Absorption corrections were performed with SADABS[19]. The structures were solved by direct methods and refined by full matrix least squares on F^2 using SHELX-97 programs[20]. All the non-hydrogen atoms were refined anisotropically. The crystallographic data and details of the refinements for the compounds are summarized in Table 1.

CCDC: 660394, **1**; 662044, **2**, respectively. Structures are available from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/

Table 1　Crystal data for complexes 1 and 2

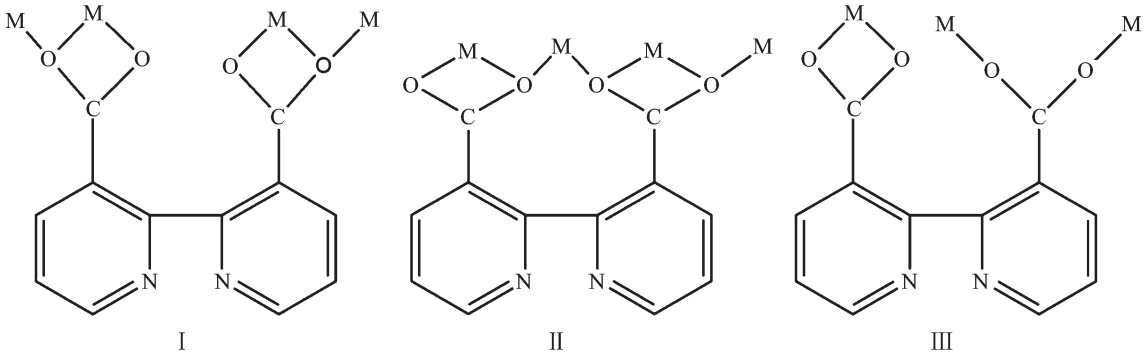
	1·Nd	**2**·La
Formula	$Nd_2C_{46}N_8O_{18}H_{38}$	$La_2C_{36}N_6O_{20}H_{34}$
Formula weight	1 279.32	1 148.5
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a / nm	3.310 4(7)	2.674 9(5)
b / nm	0.748 12(15)	0.711 65(14)
c / nm	1.984 8(4)	2.054 2(4)
β / (°)	104.75(3)	92.70(3)
Z	4	4
λ (Mo $K\alpha$) / nm	0.071 073	0.071 073
V / nm^3	4.753 6(17)	3.906 1(13)
D_c / ($g\cdot cm^{-3}$)	1.788	1.953
Temperature / K	293(2)	293(2)
μ / mm^{-1}	0.224 6	0.225 3
Reflections collected	12 631	16 646
Total independent reflections	4 171	7 201
R_{int}	0.029 9	0.036 3
R_1, wR_2 [$I>2\sigma(I)$]	0.024 4, 0.068 6	0.031 8, 0.086 7

data_request/cif (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 IEZ, UK; fax: (internat.) +44 1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

2　Results and discussion

2.1　Synthesis

We utilized the more active carboxylic groups of bpdc ligand to coordinate with the Ln(Ⅲ) ions to construct new lanthanide metal-organic coordination frameworks. The bpdc is a multi-dentate and flexible ligand. Any one of four carboxyl oxygen atoms and two pyridyl nitrogen atoms of bpdc may be coordinating atom. The two carboxylic groups of bpdc can be *cis*- or *trans*-form, which can rotate freely to lead to the most adaptable conformation to coordinate to the center metal ion. The bpdc ligand has various coordination modes as shown in Scheme 1.The mode Ⅰ and Ⅱ exist in compound **1**, while mode Ⅰ and Ⅲ can be found in compound **2**.

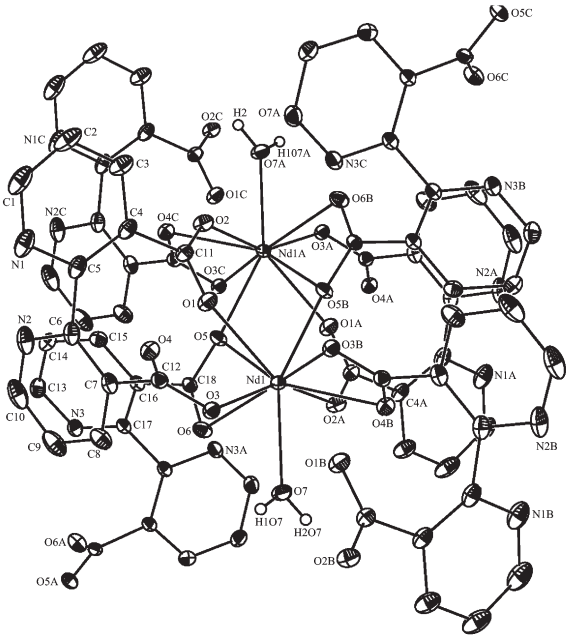


Scheme 1　Coordination mode of 2,2′-bipyridine-3,3′-dicarboxylate(bpdc) in complex **1** and **2**: mode Ⅰ, bis(chelating-bridging bidentate); mode Ⅱ, chelating-bridging bidentate and chelating/bridging tridentate; mode Ⅲ, chelating bidentate and bridging bidentate

2.2　Crystal structure analysis of 1

The X-ray crystallographic study reveals that the asymmetric unit of **1** contains one Nd(Ⅲ) ion, one and half bpdc moieties, half a 4,4′-bipy moiety, one aqua

ligand and two crystalline water molecules. Fig.1 shows the coordination environment of Nd(Ⅲ) in **1**. The Nd(Ⅲ) is located in a distorted tricapped trigonal prism geometry, and coordinated by nine oxygen atoms, of which, eight are from carboxylic groups of five different bpdc ligands and one is from the coordination water molecule. The Nd-O bond length ranges from 0.238 60 to 0.266 24 nm, comparable to other related Nd-O distances[21]. The carboxylic groups of H_2bpdc molecule are all deprotonated.

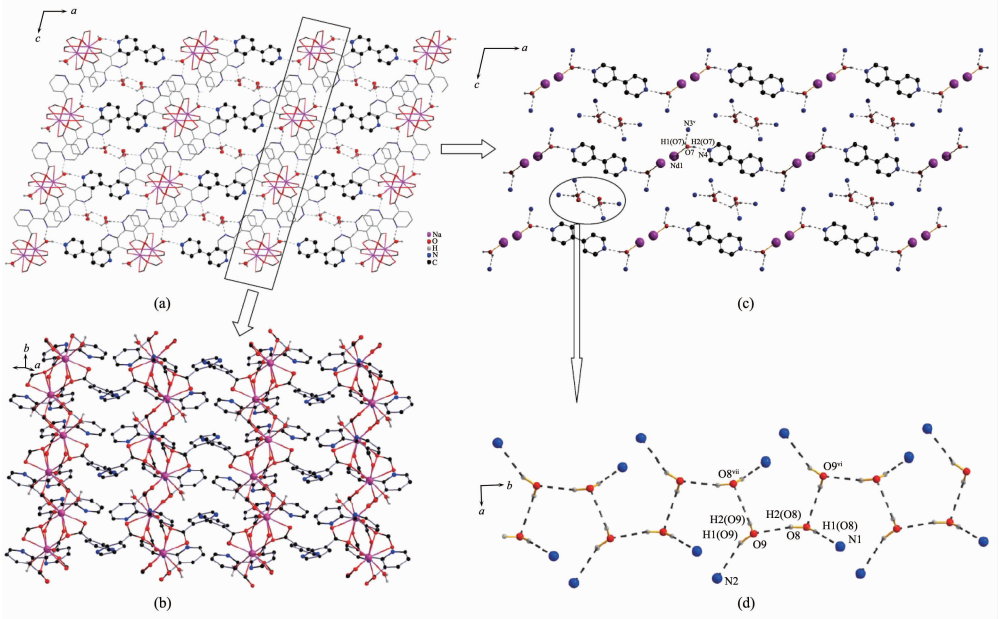


Symmetry code A: $-x$, $-y+2$, $-z+1$; B: $-x$, $-y+1$, $-z+1$; C: $-x$, y, $-z+1/2$

Fig.1 An ORTEP plot of the Nd(Ⅲ) coordination environment in **1**, all hydrogen atoms except those hydrogen bonding H are omitted for clarity, with displacement ellipsoids drawn at the 30% probability level

In compound **1**, the bpdc ligand adopts coordination mode Ⅰ and Ⅱ (Scheme 1); the dihedral angle between two pyridyl rings of the ligand in mode Ⅰ is about 134.923°, and approximately 64.207° in mode Ⅱ. The Nd(Ⅲ) ions are connected into chains along [001] direction by the ligand in mode Ⅰ, and those 1D chains are further connected along [010] direction by the ligands in mode Ⅱ to form a 2D coordination framework in [100] plane (Fig.2(a) and (b)).

It′s most interesting to note that the supramolecular structure of **1** is architected by the uncoordinated bpy and water molecules through strong hydrogen bonds (Table 2). Between the 2D Nd(III) MOF sheets, the two independent crystalline water molecules of asymmetry units are arrayed by repeating the structural unit, [H2(O8)⋯O9–H2(O9)⋯O8], to generate one-dimensional infinite water chain along the [100] direction. The side hydrogen atoms of the water chain, H1(O8) and H1(O9) link to N1 and N2 of the bpdc



(a) 3D supramolecular structure of complex **1**; (b) 2D metal organic layer structure of complex **1**; (c) Hydrogen network of complex **1** (v x, $y-1$, $z+1/2$); (d) 1D infinite water chains in complex **1** (vi x, $y-1$, z; vii $x1/2$, $y+1/2$, $z+1/2$)

Fig.2 Crystal structure of **1**

Table 2　Hydrogen-bonding geometry in 1

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠D–H···A / (°)
O7-H1(O7)-N3^{v}	0.085 00	0.240 00	0.316 3(2)	149.700
O7-H2(O7)-N4	0.085 00	0.191 00	0.274 4(2)	166.400
O8-H1(O8)-N1	0.085 00	0.214 00	0.298 8(3)	171.400
O8-H2(O8)-O9^{vi}	0.085 00	0.201 00	0.284 2(5)	167.600
O9-H1(O9)-N2	0.085 00	0.223 00	0.303 7(4)	158.700
O9-H2(O9)-O8^{vii}	0.085 00	0.230 00	0.284 7(5)	124.300

Symmetry codes: ^{i} *x*, *y*+2, *z*+1; ^{ii} *x*, *y*+1, *z*+1; ^{iii} *x*, *y*, *z*+1/2; ^{iv} *x*+1/2, *y*+3/2, *z*+1; ^{v} *x*, *y*−1, *z*+1/2; ^{vi} *x*, *y*−1, *z*; ^{vii} *x*−1/2, *y*+1/2, *z*+1/2.

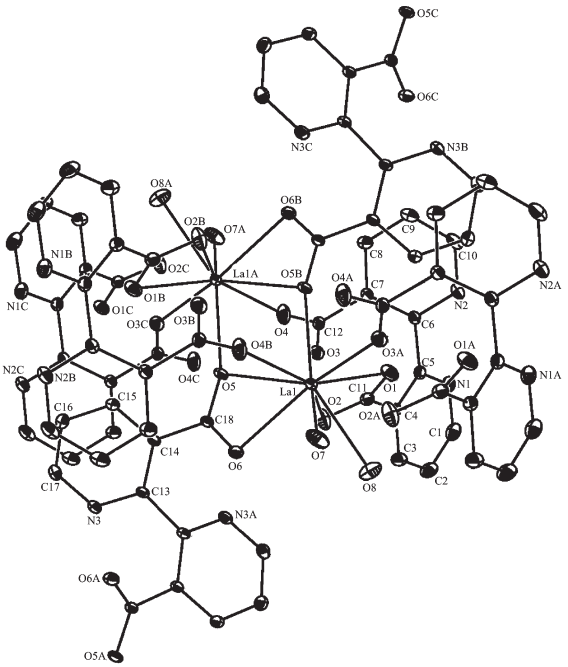
ligand of mode Ⅱ to bridge the adjacent two neodymium MOF layers by hydrogen bonds to stabilize both of the host MOF sheets and water chains(Fig.2(d)). Furthermore, bpy ligand also form hydrogen bondings via its two pyrindyl N atoms, O7–H2(O7)···N(4), with the MOF layers. While the bpdc ligand of mode Ⅰ form hydrogen bonds only in MOF layer involved in its pyridyl N(3) atoms and the coordination water molecules. In compound **1**, the 2D lanthanide metal organic framework sandwiches are braced by the water chains and bpy moieties through hydrogen-bonding interactions, as illustrated in Fig.2(c).

Researches toward states of aggregation of water molecules in MOF are dominant in recent years [22-25]. Two or three-dimensional MOFs compounds containing 1D water chains are rarely reported and the two-dimensional lanthanide MOF compound with 1D water chains have not yet been presented[26-27].

2.3　Crystal structure analysis of 2

The X-ray crystallographic study indicates that the asymmetric unit of compound **2** contains one La(Ⅲ) ion, one and half bpdc moieties, two aqua ligands and two crystalline water molecules. La(Ⅲ) is coordinated by nine oxygen atoms in a distorted tricapped trigonal prism geometry, as shown in Fig.3, of which seven oxygen atoms are from the carboxylic groups of different bpdc ligands and two oxygen atoms are from the two aqua ligands. The La-O bond distance ranges from 0.243 28 to 0.270 60 nm, comparable to other related La-O distances[28].

In compound **2**, the two deprotonated carboxylic groups of bpdc ligand distribute two types of coordination modes, Ⅰ and Ⅲ, with the dihedral angles of 133.689° and 51.912° between the two pyridyl rings,

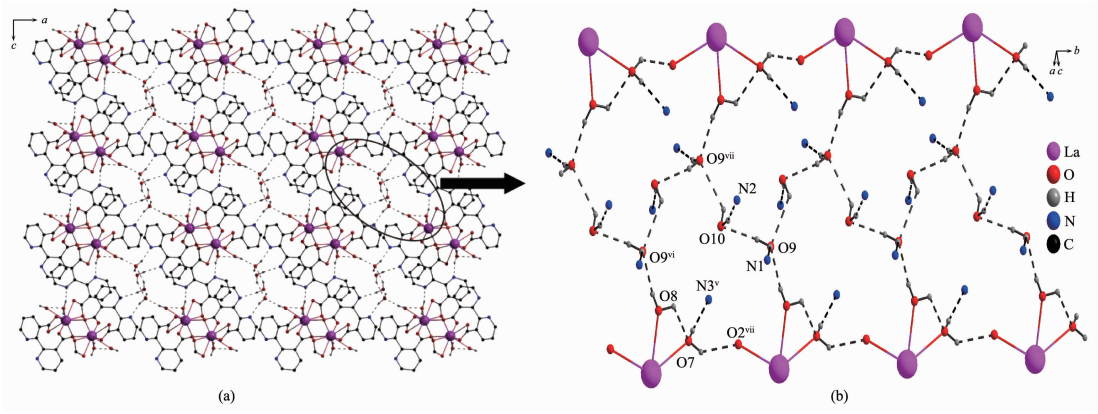


Symmetry code A: −*x*, −*y*+1, −*z*; B: *x*, *y*+1, *z*; C: *x*, *y*−1, *z*

Fig.3　An ORTEP plot of the La coordination environment of complex **2**, all hydrogen atoms are omitted for clarity, with displacement ellipsoids drawn at the 30% probability level

respectively. The arrangement of two-dimensional metal coordination framework (MOF) in **2** is similar with that in **1** (Fig.4(a)).

Extensive hydrogen-bonding interactions also exist in **2**, as shown in Fig.4(b). The geometrical parameters of the hydrogen bonds are collected in Table 3. A notable structure feature in the compound is the presence of one-dimensional water chain. Two lattice water molecules, O(9) and O(10), are arranged in an ABAB fashion along [010] direction to construct the one dimensional water chains. O(9) and O(10) water molecules also act as hydrogen bond acceptors to form H-



(a) 3D supramolecular structure connected by hydrogen bonds; (b) 1D infinite water chains trapped between 2D coordination frameworks ([ii] x, y+1, z; [v] −x, y+1, −z+1/2; [vi] −x+1/2, −y+1/2, −z; [vii] −x+1/2, y+1/2, −z−1/2)

Fig.4 Crystal structure depictions for **2**

Table 3 Hydrogen-bonding geometry in 2

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠D–H···A / (°)
O(7)–H(1O7)···N(3)[v]	0.085	0.198	0.280 5(2)	162.9
O(7)–H(2O7)···O(2)[ii]	0.085	0.210	0.28 09(2)	140.4
O(8)–H(1O8)···O(9)[vi]	0.085	0.191	0.275 0(3)	169.4
O(8)–H(2O8)···O(7)	0.085	0.229	0.270 7(3)	110.7
O(9)–H(1O9)···N(1)	0.85	0.196	0.278 8(3)	165.9
O(9)–H(2O9)···O(10)	0.085	0.205	0.283 0(5)	152.1
O(10)–H(2O)···N(2)	0.085	0.203	0.286 2(3)	165.6
O(10)–H(1O)···O(9)[vii]	0.085	0.233	0.290 3(4)	125.6

Symmetry codes: [i] −x, −y+1, −z; [ii] x, y+1, z; [iii] x, y−1, z; [iv] −x, y, −z+1/2; [v] −x, y+1, −z+1/2; [vi] −x+1/2, −y+1/2, −z; [vii] −x+1/2, y+1/2, −z−1/2.

bonds, with N(1) and N(2) atoms from different bpdc ligands in mode Ⅲ, respectively. These hydrogen bonding interactions between the water chains and the MOF sheet are not only construct a supramolecular framework for compound **2**, but also further stabilize the water chains.

In the IR spectra of **1** and **2**, the broad band center around 3 400 cm^{-1}, which is comparable to the O-H stretching vibration of water clusters in other MOF (3 400~3 500 cm^{-1}). It had come into our notice that the most of MOF compounds containing derivatives of bipyridine are absent from water chains[5,29-30]. The compounds **1** and **2** are two new lanthanide MOF compounds involving the infinite water chains.

3 Conclusions

Two new lanthanide MOF compounds **1** and **2** had been synthesized hydrothermally and characterized structurally, which reveals that both these compounds are composed of two-dimensional metal-organic frameworks connected by one-dimensional infinite water chains to construct a three-dimensional supermolecular structure. The bpdc ligand may be expected to be suitable for constructions of lanthanide MOF compounds containing water chains. The structural information may be helpful for understanding the cooperation between water aggregate and crystal host, stabilities and functions of the biological assemblies, as well as the anomalous properties of water.

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