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A novel self-assembled chain of water molecules in a metal-organic framework of Cu(II) with isophthalate

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Abstract

A novel coordination polymer, $\{[Cu(ip)(Him)_2(H_2O)]\cdot 3H_2O\}$ (**1**), (ip = isophthalate, Him = imidazole) was prepared under hydrothermal conditions and its structure is determined by single-crystal X-ray diffraction. X-ray structural analysis reveals that 1D zigzag metal-organic framework was connected to form a 3D metal-organic framework by a novel infinite 1D water chain constructed by five- and six-membered rings through edge-sharing. These water chains behave as glue to stabilize the 3D network. Upon removal of the water molecules by heating, the 3D structure breaks down. Thermogravimetric analysis, infrared, X-ray powder diffraction studies, elemental analysis and magnetic analysis were performed to characterize this compound.

Keywords: Isophthalate; Crystal structure; Metal-organic framework; Water chain

Investigation on water has received considerable interests because of its unusual properties and fundamental importance in many biological, chemical, and physical processes [1–3]. The exploration of structural and binding properties of "discrete" small water clusters have significantly advanced our knowledge to the first step of understanding the behaviors of bulk water, though they still remain ill-understood phenomena [4–16]. How the clusters link themselves to form a larger network, which is the bridge between clusters and bulk water, is still a challenging scientific endeavor [17–20]. In the past few years, some interesting 1D water morphologies consisting of basic water tetramer, pentamer, hexamer subunits have been reported [21–24], while the study on the polymeric water phase containing octamer subunits is very little [25–27]. Here, we report a novel infinite 1D chain with puckered $(H_2O)_8$ subunits constructed from two edge-sharing basic pentamers. The water chains assemble coordination supramolecular chains $[Cu(ip)(Him)_2(H_2O)]$ (ip = isophthalate, Him = imidazole) through water-MOF and water-water interactions to form the overall 3D metal-organic framework (MOF) structure.

Compound **1** [28] is air-stable and, once formed, insoluble in water. The X-ray crystallographic study [29] reveals that the asymmetric unit of **1** contains one ip, one Cu^{2+}, two imidazoles, one coordination water molecule and three lattice water molecules (Fig. 1a). Each Cu^{2+} ion exhibits penta-coordination with a distorted square pyramidal geometry where equatorial coordination comes from two nitrogen atoms of two different imidazoles with an average Cu–N distance of 1.979 Å and two oxygen atoms of two different ip bridges with an average Cu–O distance of 1.957(5) Å. One water molecule [Cu–Ow = 2.383(8) Å] occupies the apical coordination site. Obviously, the Cu–Ow distance is indicative for Jahn–Teller distortion due to d^9 configuration. The ip in a μ^2-way links the metal ions to form a 1D zigzag metal-organic chain. It must be mentioned that one coordinated water molecule, three crystallographically unique lattice water molecules, and their

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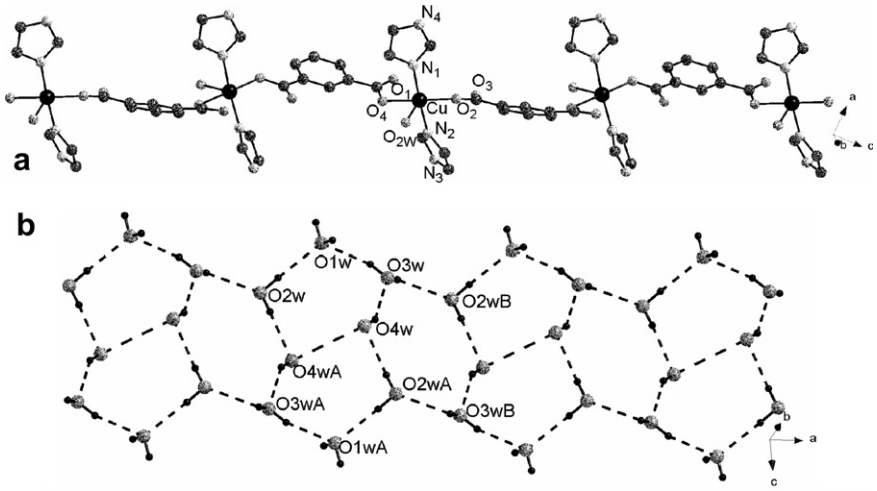

Fig. 1. (a) View of the coordination polymeric chain and (b) hydrogen-bonding motif of the self-assembled chain of water molecules.

symmetry-related ones link to each other to form a 1D water chain through hydrogen bonds.

Fig. 1b displays the coordination environments of the water chain consisting of puckered-stair-shaped $(H_2O)_8$ cluster subunits (S-Figure 1). The individual $(H_2O)_8$ unit is constructed by two edge-sharing basic pentamers. Each basic pentamer is formed by four types of water molecules, O1w, O2w, O3w and O4w. O1w serves as hydrogen bond acceptors to link O2w and O3w; O2w acts as hydrogen donors to bond with O1w and O4wA, while O3w also bonds with O1w and O4w as hydrogen donor and acceptor, respectively; O4w and its symmetry-related O4wA bond with each other, as well as O3w or O2wA, respectively. It is worth noting that the one H atom attached to O4w is not located in the difference Fourier map probably because of the result of symmetry-imposed disorder. Two cyclic water pentamer units construct the puckered-stair-shaped octamer water cluster through sharing edge O4w–O4wA. The octamers were assembled into a 1D water chain along *a* axis *via* O3w–H···O2wB and symmetry-related hydrogen bonds. This unprecedented 1D water chain consists of fused five- and six-membered rings in a ratio of 2:1. Though the distance of O3w···O2wB (3.099 Å) is slightly longer than the sum of van der Waals radii (3.04 Å), we think there still exist weak hydrogen-bonding interactions which have embodied in lots of compounds reported in literatures [30,31]. The hydrogen bonding parameters are listed in Table 1. The average O···O distance is 2.8928 Å in the water chain, which is slightly longer than those observed in liquid water (2.854 Å) [32] and octamer water clusters [10,16,25–27] reported in literatures. The average O···O···O angle is 107.83°, which is slightly smaller than the value of 109.3° in the hexagonal ice. Apparently, the octameric cluster described here is different from previously identified octameric cubane [10a], cyclic ring structures [10b], opened cube [10c], as well as other types of octameric water cluster [16,25–27].

As shown in Fig. 2, water chains serve as "glue" to reinforce the coordination polymer chains forming an overall 3D structure. As given in Table 1, O1w acts as hydrogen donors to bond with carboxylate oxygen atoms O1 and O3 from coordination chain, and O2w is coordinated to metal atom Cu(II). As a result, water chains link the coordination chains to form 3D supramolecular structure. Additionally, there exist π–π interaction between coordination chains with face-to-face distance 3.62 Å, which make the host chains stack to 3D network with channels 13 Å × 6 Å. The water chains fill in the channels, as suggests that water chains maybe influence the arrangement of the MOF host and the MOF host maybe sufficiently affects the structure of the water cluster.

Thermal analysis of the compound **1** (S-Figure 2) shows that water loss starts at about 50 °C and the loss of 15.3% corresponding to all of the water (calculated 16.5%) take place within 190 °C. The complete decomposition of the compound is reached to 475 °C. The IR spectrum (S-Figure 3) displays that a broad absorption centered at 3300 cm^{-1} attributed to the O–H stretching frequency of water cluster. This broad band vanishes after heating the

Table 1
Geometrical parameters of hydrogen bonds (Å, °) for the water chain and its association with the host in **1**

D–H···A	D–H	*d*(H···A)	*d*(D···A)	∠(DHA)
N3–H6···O3w(a)	0.785	2.015	2.787	167.52
O1w–H1w1···O3	0.885	1.830	2.713	176.01
O1w–H2w1···O1	0.824	1.950	2.766	170.33
O2w–H1w2···O1w(b)	0.842	2.028	2.870	179.66
O2w–H2w2···O4w(c)	0.820	2.082	2.902	178.42
O3w–H1w3···O1w	0.824	2.113	2.799	140.48
O3w–H2w3···O2w(d)	0.815	2.374	3.099	148.74
O4w–H1w4···O3w(e)	0.846	2.097	2.841	146.50
[a]O4w···O4w			2.922	

[a] One H atom attached to O4w could not be located in the difference Fourier map probably because of symmetry-imposed disorder. Symmetry code: (a) $x-1, y, z$; (b) $-x+1/2, y+1/2, -z+1/2$; (c) $x, y, z-1$; (d) $-x+3/2, y-1/2, -z+1/2$; (e) $x-1/2, -y+3/2, z+1/2$.