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Puckered-Boat Conformation Hexameric Water Clusters Stabilized in a 2D Metal–Organic Framework Structure Built from Cu(II) and 1,2,4,5-Benzenetetracarboxylic Acid

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1,2,4,5-Benzenetetracarboxylic acid (btcH$_4$) reacts with Cu(NO$_3$)$_2$·6H$_2$O to form 2D coordination polymeric structure $\{[\mathrm{Cu_2(btc)(Py)_4}\cdot 2\mathrm{H_2O}]\cdot 4\mathrm{H_2O}\}_n$, **1**, in the presence of pyridine from water at room temperature. Puckered-boat-shaped hexameric water clusters resulting from four free water molecules and two water molecules coordinating to metal ions join these sheets to make a 3D network. These water clusters behave as pillars to join those sheets which is the key factor stabilizing the 3D network. Thermal analysis, X-ray powder diffraction, and X-ray structure analysis have been used to characterize this compound. Crystal data for **1** follow: triclinic space group $P\bar{1}$, $a = 8.905(3)$ Å, $b = 11.137(4)$ Å, $c = 17.484(2)$ Å, $\alpha = 82.342(6)°$, $\beta = 81.312(3)°$, $\gamma = 82.361(4)°$ $V = 1687.5(1)$Å^3, $Z = 2$, R1 = 0.0331, wR2 = 0.0886, S =1.066.

Hydrogen bonding interactions, their fluctuations, and their rearrangement dynamics determine the properties of liquid water, some of which are considered anomalous. A major obstacle[1] to fully comprehend its behavior is a correct description of the cooperative nature of hydrogen bonding interactions among a collection of water molecules. This diversity of hydrogen bonding interactions is very important in the biological world as it can enforce a delicate balance[2] among several possible conformations of enzymes essential for their functions. The key to testing and calibrating theoretical studies to understand this liquid is having precise structural data of hydrogen bonded small water clusters in diverse environments. The advantage of clusters is the possibility to simply vary the size and to investigate the development of properties of the condensed phase in a step by step manner. This realization has led to the upsurge[3−10] in studying small water clusters in different environments. An understanding of the properties of water is important from the perspectives of protein crystallization,[11] stabilization and functioning of biomolecules,[12] cloud and ice formation, solution chemistry, and so on. Moreover, the degree of structuring of the water cluster that can be imposed by its environment, and vice versa, can be of importance in the design of new metal−organic framework (MOF) structures.[13] Here, both water−MOF and water−water interactions can be important for the stability of the overall structure. Among the small water clusters, the hexamer is subjected to a number of experimental and theoretical studies as this cluster is the building block of ice[14] and also exhibits[15] some of the properties of bulk water. Theoretical calculations[16] have predicted five low energy isomers for this cluster that are isoenergetic. While chair,[17] boat,[18] and planar cyclic[19] forms of hexamers have been identified in crystal hydrates, the

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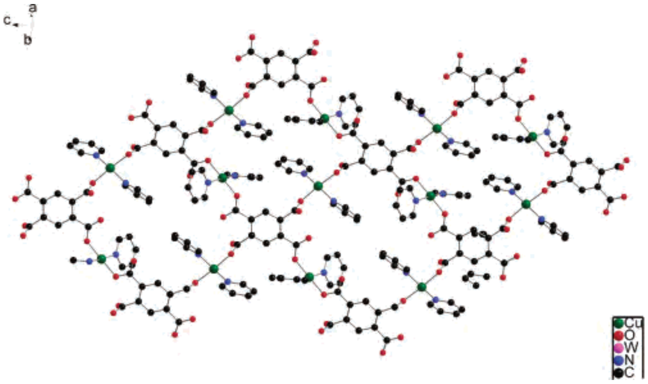

Figure 1. Perspective view of the planar sheet structure of **1**. Hydrogen atoms are omitted for clarity.

"cage" conformer predicted to be the most stable at very low temperature has been observed[20] by vibration−rotation tunneling spectroscopy. A quasiplanar cyclic hexamer had been detected[21] in a helium droplet. Herein, we describe discrete hexameric water clusters with puckered-boat conformation acting as pillars between 2D metal coordination polymers to form a stable 3D MOF.

Compound **1** was prepared[22] by evaporating at room temperature an aqueous solution containing 1,2,4,5-benzenetetracarboxylic acid (btc), $Cu(NO_3)_2{\cdot}6H_2O$, and pyridine. Blue crystals of **1**, which grew over a period of 14 days, were characterized by X-ray crystallography,[23] elemental analysis, vibrational spectroscopy, X-ray powder diffraction, and thermal analysis.

The asymmetric unit of **1** contains one btc^{4-}, two Cu^{2+}, four pyridines, and six water molecules. The MOF consists of two-dimensional sheets (Figure 1) formed by interconnecting ring structures made from four btc^{4-} units, four Cu^{2+} ions, and eight pyridines. Each metal ion is five-coordinate, having square-pyramidal geometry with equatorial coordination from two carboxylate oxygens from two different btc^{4-} units and two nitrogens from two pyridines. The axial site is occupied by a water oxygen. Two coordinated water molecules in adjacent Cu(II) ions are hydrogen-bonded to each other while another water molecule is hydrogen-bonded to an available carboxylate O atom of the same sheet. The remaining three water molecules are hydrogen-bonded to free carboxylate O atoms of another sheet leading to an overall 3D structure. Thus, the hexameric water clusters act as pillars separating two layers of coordination polymers (Figure 2). An approximate distance of 6.962 Å between the layers is maintained by these pillars.

Table 1. Geometrical Parameters of Hydrogen Bonds (Å, deg) for the Water Hexamer[a]

Ow1···Ow2	2.735	Ow1···Ow2···Ow3	99.77
Ow2···Ow3	2.923	Ow2···Ow3···Ow4	93.25
Ow3···Ow4	2.797	Ow3···Ow4···Ow5	97.20
Ow4···Ow5	2.893	Ow5···Ow6···Ow1	77.71
Ow5···Ow6	2.819	Ow6···Ow1···Ow2	107.29
Ow6···Ow1	2.906		
Ow1···O1a	2.66	Ow1−H···O1a	163.53
Ow2···O7b	2.78	Ow2−H···O7b	172.11
Ow3···O3a	2.73	Ow3−H···O3a	179.10
Ow3···O5b	2.72	Ow3−H···O5b	163.21
Ow4···O1a	2.79	Ow4−H···O1a	164.18
Ow5···O7b	2.70	Ow5−H···O7b	178.51
Cu1···Ow6	2.27		
Cu2···Ow1	2.29		
Ow1−H···Ow2	170.50	Ow2−H···Ow3	166.50
Ow4−H···Ow3	173.57	Ow5−H···Ow4	177.90
Ow6−H···Ow5	169.67	Ow6−H···Ow1	157.78

[a] Please refer to Figure 3 for atom designation.

The geometrical parameters of the water clusters are collected in Table 1. Both Ow1 and Ow6 are coordinated to adjacent Cu(II) ions from the same 2D sheet. Atom Ow1 acts as a double hydrogen bond donor while Ow4 acts as a double hydrogen bond acceptor. The remaining water molecules act as hydrogen bond donors as well as acceptors. So, every oxygen atom in the cluster does not show four-coordination. Such hydrogen bond deficient water molecules are present[24] at the surface of ice while recent X-ray absorption spectroscopy and Raman scattering studies of liquid water also point to the fact that significant numbers of O atoms show less than four-coordination in liquid water.[25] The cluster takes the shape of a puckered boat (Figure 3). The interconnected boat conformation was found[14] in hexagonal ice (I_h) and also identified[18] between the layers of an inorganic polymer constructed from $CdNi(CN)_4$ units. However, the boats are not interconnected in **1** due to the particular orientation of the btc^{4-} moieties in the structure (Figure 3). In the hexamer, the average O···O distance is found to be 2.845 Å which compares well with the distance[15] in liquid water. The bulk water exhibits a short-range O···O order in the X-ray diffraction radial distribution curve at 2.85 Å, while for the gas phase, this value is ∼0.1 Å longer.[15c] On the other hand, in I_h the average O···O distance is less at 2.74 Å. Also, the O···O···O angles in the present structure span a wide range (93.2(4)−113.2(2)°) deviating considerably from the corresponding value in ice.[14] In a recent

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(22) To an aqueous solution containing $bdcH_4$ (1 mmol) and $Cu(NO_3)_2{\cdot}6H_2O$ (2 mmol) was added pyridine (5 mmol), and the resulting dark blue solution was allowed to slowly evaporate at room temperature. After two weeks, large blue crystals in the form of rectangular parallelopipeds were collected by filtration. Crystals are stable at room temperature. Yield 40%. Anal. Calcd for $C_{30}H_{34}N_4O_{14}Cu_2$: C, 44.93; H, 4.27; N, 6.99%. Found: C, 46.12; H, 4.11, N, 6.78%.

(23) Crystal data for **1** follow: $M = 801.69$ g mol^{-1}, triclinic, space group $P\bar{1}$, $a = 8.905(5)$ Å, $b = 11.137(5)$ Å, $c = 17.484(5)$ Å, $\alpha = 82.342(5)°$, $\beta = 81.312(5)°$, $\gamma = 82.361(5)°$, $U = 1687.5(13)$ Å^3, $T = 100$ K, $Z = 4$, $D_c = 1.578$ g cm^{-3}, $\mu = 1.334$ mm^{-1}, $F(000) = 824$, crystal size = 0.18 × 0.15 × 0.13 mm^3. A total of 11333 reflections up to $\theta = 28.30°$ were collected of which 8033 unique reflections were used. The structure was solved using SHELXS-97 and refined using SHELXL-97 to R1 = 0.0331, wR2 = 0.0886, GOF = 1.067, final residual peak = +0.796 and hole = −0.462 e Å^{-3} for 7182 reflections with $I > 2\sigma(I)$ and data/parameter ratio of 14.4. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in successive difference Fourier maps, and they were treated as riding atoms using SHELXL default parameters.

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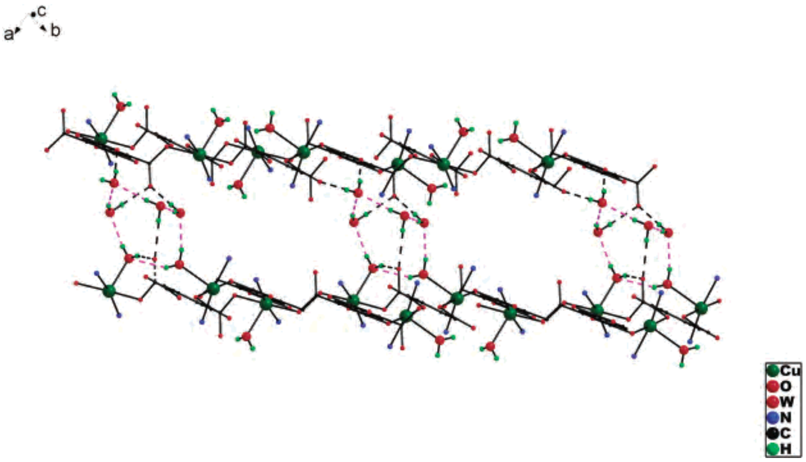

Figure 2. View of the puckered-boat-shaped hexameric water clusters between two sheets of MOF.

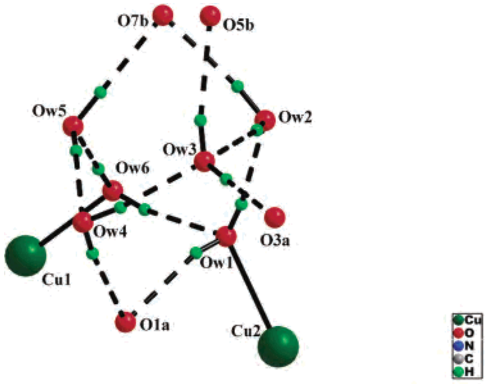

Figure 3. Perspective view of the hexameric water cluster showing hydrogen bonding interactions.

theoretical study[26] on the structure of water, an icosahedral 3D network of 280 hydrogen-bonded water molecules with an O···O distance of 2.84 Å has been proposed. This structure is based on the regular arrangement of 20 slightly flattened tetrahedral $(H_2O)_{14}$ units. Within these units, boat forms of hexamers are predicted to be present along with pentamers, and this proposed structure allows an explanation of several anomalous properties of water. Supramolecular association of water molecules to form a chair conformation and self-assembly into a 1D tape had been identified[17] in an organic host constructed from 2,4-dimethyl-5-aminobenzo-[*b*]-1,8-naphthyridine. A discrete chair conformer has recently been found[27] in the zigzag voids of an MOF constructed from pyridine-2,6-dicarboxylic acid and Ce(III) or Pr(III). The puckered-boat conformation of water molecules in **1** is enforced by the quasiplanar metal−ligand sheetlike structure. The interaction between the MOF and the water cluster is moderately strong as thermal gravimetric analysis with an 8.75 mg sample in air shows that weight loss occurs in stages beginning at 60° C and the loss of 16.24% corresponding to all of the water (calculated 16.78%) takes place above 140° C. The complete decomposition of the compound is achieved above 300 °C. The FTIR spectrum of **1** shows a broad band centered at 3415 cm^{-1} attributable to the O−H stretching frequency of the water cluster. This broad band vanishes on heating the compound under vacuum (0.1 mm) at 140° C for 2 h suggesting escape of the water molecules from the lattice. The IR spectrum of ice[15b] shows the O−H stretching at 3220 cm^{-1} while this stretching vibration in liquid water[15b] appears at 3490 and 3280 cm^{-1}. This suggests that the water cluster in **1** shows an O−H stretching vibration similar to that of liquid water. Deliberate exposure to water vapor for 3 days does not lead to reabsorption of water into the lattice as monitored by FTIR spectroscopy. Powder X-ray diffraction patterns of the compounds before and after water expulsion show major changes in peak positions as well as their intensities suggesting breakdown of the host lattice once the water molecules are expelled.

In conclusion, we have identified, for the first time, a discrete water hexamer with significantly puckered-boat conformation as suggested to be present in bulk water. These clusters act as pillars between 2D sheets of MOFs. The extent of puckering is commensurate with the MOF structure.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of compound **1**. Structural figures, IR spectra, and X-ray powder diffraction patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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