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Structure of a Discrete Hexadecameric Water Cluster in a Metal–Organic Framework Structure

Sujit K. Ghosh and Parimal K. Bharadwaj*

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

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Pyrazine-2,3,5,6-tetracarboxylic acid (pytcH$_4$) reacts with Cu(NO$_3$)$_2$·6H$_2$O in 1:2 molar ratio in the presence of pyridine (py) vapor to form blue crystals of a coordination polymer with the empirical formula $\{Cu_{2.5}(pytc)(py)_8(NO_3^-)\cdot 10H_2O\}_n$ (**1**). Four such polymeric chains gather around a hexadecameric water cluster to form an overall 3D metal–organic framework structure. Once the water molecules are removed, the 3D structure breaks down. It presents a new mode of association of water molecules not predicted theoretically or found experimentally.

Diversity of hydrogen bonding interactions among water molecules is responsible for the anomalous behavior of bulk water, cloud and ice formation, as well as structure and function of biomolecules.[1] The energetic optimization of mutual hydrogen-bonded networks involving enzyme, water, and substrate is an intrinsic part of the molecular recognition process in these biological macromolecules. In the abiological world, 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 structures. Recent years have witnessed both theoretical[2−5] and experimental[6−14] scrutiny of a number of small water clusters in different surroundings to investigate the development of properties of the condensed phase in a stepwise manner. We report here the structure of a novel hexadecameric water cluster present in the cavity of a supramolecularly built metal−organic framework. These water clusters assemble coordination polymeric chains to form the overall 3D metal−organic framework (MOF) structure.

Construction of MOFs via crystal engineering principles uses metal ions, multidentate ligands, and dative bonding to drive and direct the self-assembly processes. Syntheses of these coordination polymers with designer structures are pursued[15,16] in several laboratories with the ultimate goal(s) of having new materials with a range of applications. Success in producing such structures depends on the understanding and controlling the topological and geometric relationships between molecular modules along with the coordination characteristics of the metal ions. Water clusters can influence the final overall MOF structure via hydrogen bonding interactions with the coordination polymeric units.

The compound $\{Cu_{2.5}(pytc)(py)_8(NO_3^-)\cdot 10H_2O\}_n$ (**1**) was synthesized[17] by allowing a solution of Cu(NO$_3$)$_2$ with pyrazine-2,3,5,6-tetracarboxylic acid (pytcH$_4$) in aqueous pyridine to evaporate slowly. The compound once formed is insoluble in most solvents including water. In the solid

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* To whom correspondence should be addressed. E-mail: pkb@iitk.ac.in.

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(17) Synthesis of **1**: reaction of Cu(NO$_3$)$_2$·2.5H$_2$O (0.64 g; 2 mmol) and pyrazine-2,3,5,6-tetracarboxylic acid (0.26 g; 1 mmol) dissolved in 25 mL of aqueous pyridine (1: 1 v/v) produces a dark blue solution. This is allowed to evaporate at room temperature whereupon blue crystals of **1** appeared after 6 days in the form of rectangular parallelopipeds in 42% yield. Anal. Calcd for $C_{48}H_{60}Cu_{2.5}N_{11}O_{21}$: C, 44.84; H, 4.70; N, 11.98%. Found: C, 44.67; H, 4.62; N, 12.04%.

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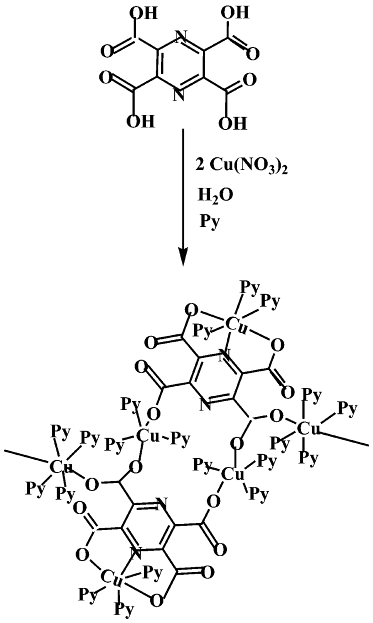
Scheme 1. Schematic Diagram Showing the Bonding Modes of the Ligand with Cu(II)



state, it exhibits a broad absorption band centered at 515 nm. The effective magnetic moment value is found to be 2.01 μ_B at 300 K which is normal for Cu(II) complexes.[18] The compound displays an EPR signal (X-band, Bruker 300E) with $g_\perp = 2.22$ and $g_\| = 2.07$ at 300 K consistent[19] with the d_{z^2} ground state of the metal ion. The signal sharpens somewhat as the temperature is lowered to 120 K without revealing any detail indicative of its stereochemistry.

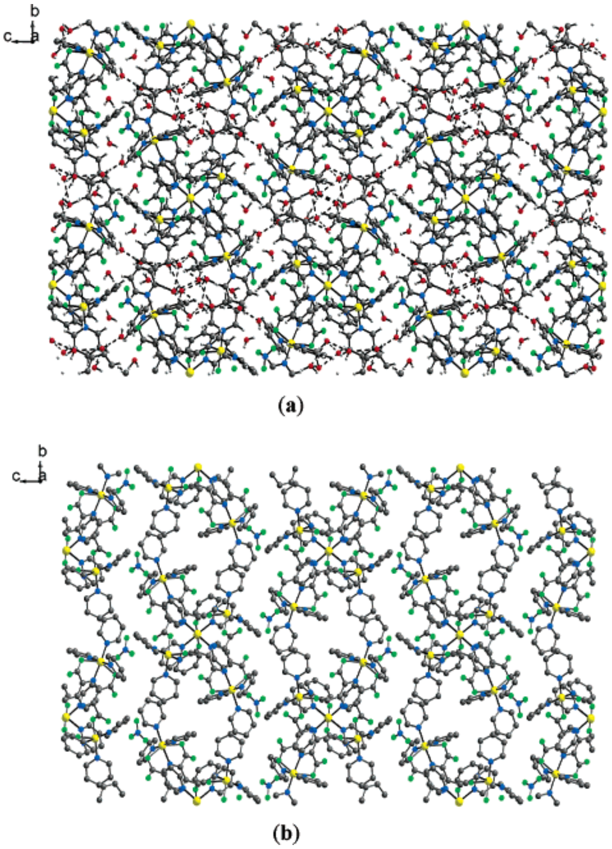


Figure 1. (a) The MOF structure of **1** viewed in the *bc* plane. The water molecules are shown in red. (b) The MOF structure of **1** viewed in the *bc* plane. The water molecules have been omitted to show the cavities.

The structure of the compound[20] can be described as a 2D coordination polymer of hexa- and pentacoordinated Cu(II) with coordination from pyrazine tetracarboxylate and pyridine. Both the carboxylate groups and the ring N on one side of the ligand bind one Cu(II) showing NO_2 coordination leaving one O atom on each carboxylate free. Three pyridine molecules bind this Cu(II) ion to complete hexacoordination. Two such metal−ligand ensembles axially coordinate two Cu(II) ions through carboxylate O atoms on the other side of the ligand where the equatorial sites on the metals are occupied by three rather than four pyridine molecules to avoid steric crowding leading to trigonal bipyramidal coordination geometry. Two more Cu(II) ions are axially bonded to this tetranuclear unit sideways via carboxylate oxygens propagating the coordination polymeric chain along the crystallographic *a* axis. These Cu(II) ions achieve hexacoordination with equatorial binding of four pyridine molecules. A view of the binding mode of the ligands to Cu(II) is illustrated in Scheme 1. The bond distances and bond angles involving the metal ions are similar to those found in other Cu(II) complexes[7d] while bond distances and bond angles in the ligand moieties are within normal statistical errors. The NO_3^- anions are not bonded to any of the metal ions. Out of the 10 water molecules present in the asymmetric unit, the group of eight forms a $(H_2O)_{16}$ cluster with a centrosymmetrically related group. Four coordination polymeric chains gather around these $(H_2O)_{16}$ clusters via hydrogen bonding to the free carboxylate O atoms and the nitrate anions leading to the 3D network structure (Figure 1a). Once the water molecules are deleted from the packing diagram, the cavities can be seen (Figure 1b).

Theoretical calculations[5] present a rich structural landscape for the $(H_2O)_{16}$ cluster showing a number of local minima. The structures associated with these minima include fused cubes derived from the D_{2d} and S_4 forms of $(H_2O)_8$ as well as structures containing various numbers of five-membered rings, two of which also contain one six-membered ring. The structures derived from fused cubes are more stable than the rest by ~1.2 kcal/mol of energy. A closer view of the $(H_2O)_{16}$ cluster in **1** (Figure 2) illustrates a new mode of supramolecular association of the water molecules that has not been predicted theorectically. Important bond distances and angles related to the $(H_2O)_{16}$ cluster collected in Table 1 also illustrate this point. A wide variation in the O···O nonbonding distances is found. These distances span the range 2.848−2.441 Å, compared[1a] to 2.759 Å in ice I_h or 2.85 Å in liquid

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(20) Crystal data for **1**: crystal dimensions 0.14 × 0.11 × 0.09 mm^3, formula $C_{48}H_{60}Cu_{2.5}N_{11}O_{21}$, fw 1285.92, monoclinic, space group $P2_1/c$, $a = 12.6380(6)$ Å, $b = 16.7017(8)$ Å, $c = 26.4479(13)$ Å, $\beta = 94.0080(10)°$, $U = 5568.9(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.534$ g cm^{-3}, $T = 100$ K, $\mu = 1.037$ mm^{-1}, R1 = 0.0350 ($I > 2\sigma(I)$), wR2 = 0.0944, $S = 1.081$. 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.

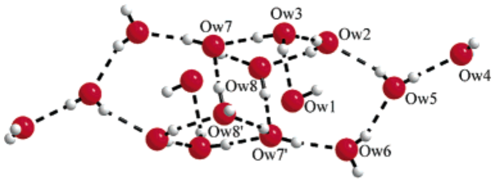

Figure 2. A perspective view of the $(H_2O)_{16}$ cluster illustrating the hydrogen bonding scheme. No connection between Ow1 and Ow7 is shown as one of the H atoms of Ow1 could not be located in the map.

Table 1. Bond Lengths and Angles for the Hexadecameric Water Cluster[a]

length (Å)		angle (deg)	
OW4···OW5	2.769(6)	OW4···H−OW5	177.6(2)
OW5···OW6	2.716(6)	OW5···H−OW6	153.9(2)
OW6···OW7	2.681(5)	OW6···H−OW7	169.0(1)
OW7···OW8	2.835(4)	OW8···H−OW7	155.4(2)
OW8···OW7′	2.757(6)	OW7′···H−OW8	159.6(1)
OW8···OW1	2.557(3)		
OW7···OW1	2.827(4)		
OW1···OW3	2.441(5)		
OW3···OW2	2.711(6)	OW3···H−OW2	177.3(1)
OW2···OW5	2.819(3)	OW2···H−OW5	148.1(2)
OW7′···OW3	2.848(5)	OW7′··· H−OW3	161.2(2)
OW2···OW8′	2.824(6)	OW8···H−OW2	170.5(1)

[a] One H atom attached to OW1 could not be located in the difference Fourier map.

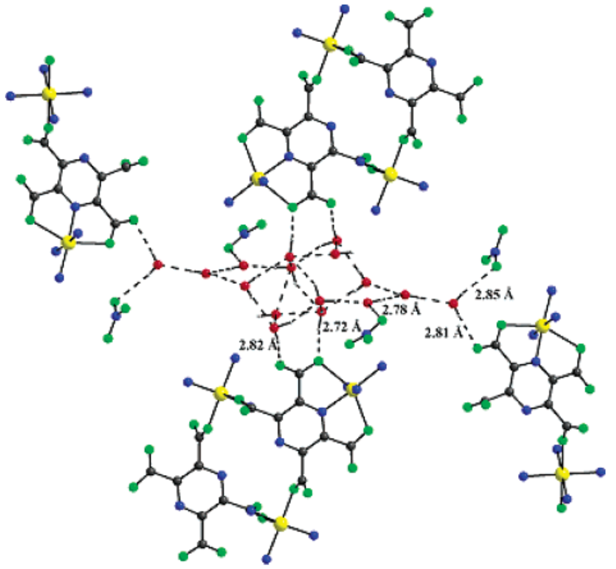

Figure 3. An view showing how water molecules are bound to the MOF. The lone blue spheres are pyridine N atoms. The entire pyridine molecule is not shown for clarity.

water. The O···O···O angles also vary widely (range 151−81°) with an average of 117° deviating considerably from the corresponding value of 109.3° in hexagonal ice. Not every O atom in the cluster shows four-coordination just like water molecules[21] at the surface of ice or liquid water. However, a majority of the nonbonding hydrogen atoms of the cluster are hydrogen-bonded to the available O atoms of the carboxylate and nitrate groups that are present nearby (Figure 3). As can be seen from Figure 1a,b, the shape of the cavity in the MOF closely follows the shape of the water cluster to maximize the strength as well as number of interactions with the MOF. This indicates a complementary relationship between the cluster and its surroundings in terms of occupying the voids, underlining the importance of water molecules in establishing hydrogen-bonding contributions to the total lattice energy and not just filling the voids in the 3D structure.

Thermal gravimetric analysis on a 9.85 mg sample of **1** shows onset of water loss at 30° C. Water removal takes place without showing any distinct plateau in the curve giving a total loss of 28.1% at ∼130 °C corresponding to loss of all water molecules (calculated value, 27.6%). The complete decomposition of the compound is achieved above 150° C. The FTIR spectrum of **1** shows a broad band centered around 3405 cm^{-1} which vanishes on heating the compound under vacuum (0.1 mm) at 120° C for 2 h due to escape of water from the lattice. Deliberate exposure to water vapor for 3 days does not lead to reabsorption of water into the lattice as monitored by FTIR spectroscopy. The O−H stretching vibrations of small water clusters $(H_2O)_n$ ($n = 2-10$) in the gaseous state have been investigated[22] using infrared depletion and fragment spectroscopy. The stretching vibrations are found to be size specific spreading over a wide range from 3720 to 2935 cm^{-1} with the higher nuclearity clusters showing the vibration below 3400 cm^{-1}. In comparison, the O−H stretching vibration in ice appears[1e] at 3220 cm^{-1} while in liquid it shifts[1e] to 3280 and 3490 cm^{-1}. Therefore, the O−H stretching frequency of the water cluster in **1** is more like liquid water with a slight variation attributable to its surroundings. Powder X-ray diffraction patterns of **1** before (simulated) and after water expulsion show a complete change in the pattern, suggesting breakdown of the host lattice due to the exclusion of water. This result is expected, as the water cluster acts as a “glue” to assemble the coordination polymeric chains around it leading to the 3D structure.

In conclusion, we have identified a novel discrete hexadecameric water cluster in an MOF structure. This new mode of association of water molecules has not been predicted theoretically. The water clusters here take the role of a “glue” in forming the 3D supramolecular network. The cluster exhibits wide variation in the hydrogen-bonding interactions and adopts a structure necessary for optimal attractive forces with the MOF. However, the degree of structuring of the water cluster that can be imposed by its environment and vice versa can be commented upon once a large number of similar water clusters in different environments are available. Water clusters of different sizes and shapes in diverse environments are presently being investigated in our laboratory.

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Supporting Information Available: Crystallographic data (CIF) and figures depicting the binding mode of ligand with Cu(II), binding mode of waters, IR, thermal analysis, and X-ray powder diffraction patterns for **1** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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