DOI: 10.1002/anie.200701779

Water Clusters

Phase Transition Accompanied by Transformation of an Elusive Discrete Cyclic Water Heptamer to a Bicyclic $(H_2O)_7$ Cluster**

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Water is the most abundant compound on earth and also essential for living beings. It plays an important role in many biological and chemical systems and also exhibits a fascinating array of unusual physical and chemical properties in pure form and as a solvent. Theoretical and experimental studies on the structural and dynamic properties of, for example, isolated water clusters, chains, and sheets, in vapor, water, and ice have been carried out to gain further insight into the structure of bulk water, which is poorly understood.[1] The presence of water molecules in solid-state structures can play an important role in stabilizing some supramolecular structures.[2] Conversely, such supramolecular environments can also stabilize unusual morphologies of water that may not be at the global energy minimum expected from theoretical calculations. Hence, the predictability and rational design of water morphologies still remain a challenge. A number of discrete water clusters, with the number of water molecules varying from three to more than 18, have been structurally characterized in a variety of inorganic and organic crystal hosts.[3–5] Of these, the odd-numbered cyclic water heptamer seems to be unknown in protonated water among several forms.[6] A number of discrete water clusters have been found in liquid helium, but not the cyclic heptamer.[7] In the case of hydrated electrons, cyclic $e^-(H_2O)_7$ has not been reported and only linear conformers are known.[8] The electron–water heptamer represents one of the "magic" numbers in the mass spectra of electron–water clusters.[8b] Based on the infrared OH stretching vibrations in molecular beam depletion spectroscopy, Buck and co-workers have proposed to have detected only the caged heptamer.[9] Theoretical calculations have been performed on all the possible water heptamer structures.[10,11] In the discrete water clusters, the solid-state structure of cyclic water heptamer is also elusive.[3–5] Herein we report the presence of a cyclic water heptamer in the crystal structure of $[Cu_3(phen)_3(muco)_2(H_2O)_2][BF_4]_2\cdot 5H_2O$ (**1**; phen = 1,10-phenanthroline, H_2muco = *trans*,*trans*-muconic acid = *trans*,*trans*-1,3-butadiene-1,4-dicarboxylic acid).

Compound **1** was synthesized by refluxing $Cu(BF_4)_2\cdot 3H_2O$ with Na_2muco and phen in a mixture of H_2O and MeOH. Upon slowly evaporating the solution at room temperature, blue distorted octahedral-shaped crystals of **1** were obtained. X-ray crystallographic experiments at 296 K revealed that **1** belongs to the monoclinic space group *C*2/*c* with $Z = 4$. There are two independent Cu^{II} atoms present in the asymmetric unit, in which Cu1 has square-pyramidal geometry and Cu2 has square-planar geometry as shown in Figure 1 a. The asymmetric unit further contains three lattice water molecules and a $[BF_4]^-$ ion. A phen ligand and two oxygen atoms from two different muco anions occupy the equatorial positions and an aqua ligand is at the apical position. A phen ligand and two oxygen atoms from two different muco anions are bonded to Cu2 to form a plane. A carboxylate group bridges Cu1 and Cu2 through O3 and O4, respectively. There is a crystallographic twofold axis going through Cu2 and the middle of the two N atoms attached to it. The topology of the three-dimensional coordination polymer is dictated by the connectivity of these four carboxylate

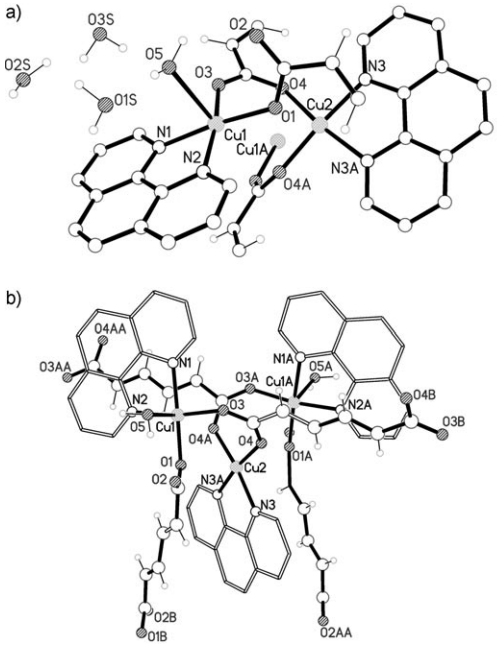

Figure 1. a) A perspective view of the structure of **1** showing the coordination geometry around Cu1 and Cu2. The H atoms attached to the phen ligand and $[BF_4]^-$ ion are not shown for clarity. The atoms with extension "A" are related by the symmetry operation $-x+1$, y, $-z+1/2$. b) A view of the selected atoms showing the orientations of the four carboxylate ligands in the repeating unit in **1**.

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[**] We thank the National University of Singapore for financial support and Ms. Geok Kheng Tang for preliminary X-ray data.

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groups from four muconate ligands from the repeating unit $[Cu_3(phen)_3(muco)_2(H_2O)_2]$ (as shown in Figure 1b).

The connectivity of muconate ligands in the 3D coordination polymeric network structure generates a diamondoid topology as shown in Figure 2a, which is ubiquitous in

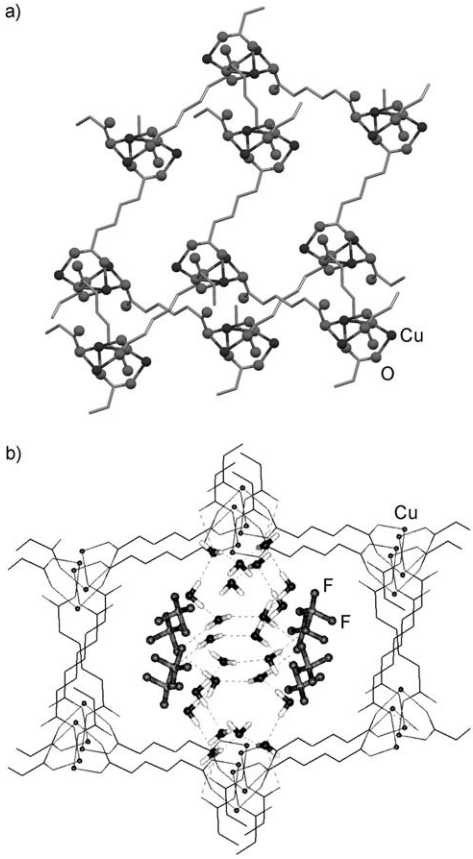

Figure 2. a) A perspective view showing the diamondoid connectivity of muconate ligands to the copper atoms; only selected atoms are shown for clarity. b) A view showing the packing of lattice water molecules and $[BF_4]^-$ ions in the channel along the *c* axis. The phen ligands, carbon-bound hydrogen atoms, and disordered F atoms in $[BF_4]^-$ are not shown for clarity.

supramolecular chemistry.[12] When viewed down from the *c* axis, the channels created by the diamondoid connectivity are found to be filled with lattice water molecules, $[BF_4]^-$ anions, and phen ligands bonded to the copper atoms. A perspective view of the packing of lattice water molecules and anions is shown in Figure 2b.

A closer look at the connectivity of coordinated and lattice water molecules reveals the presence of a discrete cyclic water heptamer, $(H_2O)_7$, as shown in Figure 3. There is a crystallographic twofold axis passing through this heptamer through O1S and the center of O2S and O2S ($-x+1, y, -z+1/2$). As a result, the hydrogen atoms of O2S are disordered. The aqua ligands bonded to Cu1 are also involved in this structure. The overall $(H_2O)_7$ cluster can be represented by $R_5^5(14)$ in the graph set notation,[13] and R7 in water cluster notation.[2] The hydrogen-bonded O···O separations in the heptamer span the range 2.768(4)–2.886(4) Å, which is

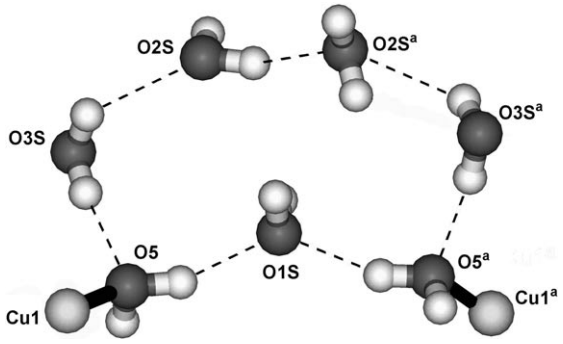

Figure 3. The structure and hydrogen-bond connectivity of $(H_2O)_7$ in **1** at 296 K. The atoms with superscript "a" are related by the symmetry operation $-x+1, y, -z+1/2$.

comparable to 2.758 Å obtained from the ab initio calculations.[12a] The heptamer has a twisted-planar structure. The O1S···O2S separation (3.428(4) Å) clearly indicates that the heptamer is a monocyclic ring. The OH···O separations vary from 1.84 Å (for H2SC···O3S) to 2.26 Å (for H2SB···O3S), and the strength of these hydrogen bonds may be considered as medium.[14] The hydrogen atoms of O2S are hydrogen-bonded to the highly disordered $[BF_4]^-$ ions.

Cell data measurements at 223 K show that the single crystal undergoes a phase transition from *C*2/*c* (room-temperature phase, **I**) to $P2_1/c$ (low-temperature phase, **II**). X-ray crystallographic analysis at 223 K reveals that the overall connectivity of the 3D coordination polymeric structure is retained. But the crystallographic twofold rotation that was going through Cu2 and the water heptamer is removed in phase **II**. The asymmetric unit contains one whole molecule, namely, $[Cu_3(phen)_3(muco)_2(H_2O)_2][BF_4]_2\cdot 5H_2O$. The $(H_2O)_7$ unit is no longer monocyclic, but has a bicyclic structure as shown in Figure 4. The bicyclic structure is composed of a water pentamer and a water tetramer, which share an edge.

This bicyclic $(H_2O)_7$ structure can be represented by the graph set notation $R_4^4(10)R_3^3(8)$.[13] The O···O separations span from 2.760(4) to 2.997(6) Å, which is higher than the value derived from the theoretical calculation (2.759 Å).[10a] The OH···O separations vary from 1.94 Å (H10A···O4S) to 2.26 Å (H1SA···O2S), and the strength of these hydrogen bonds may be considered as medium.[14] The O1S···O2S separations of

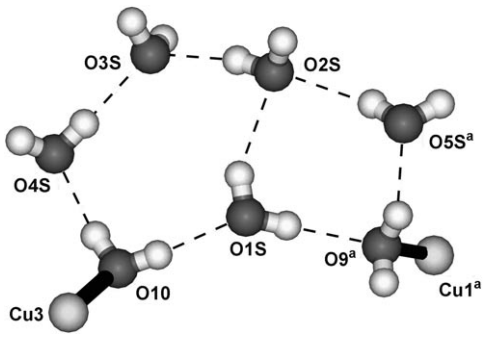

Figure 4. The structure and hydrogen-bond connectivity of $(H_2O)_7$ in **1** at 223 K. The atoms with superscript "a" are related by the symmetry operation $x-1, y, z$.

2.997(6) Å in this low-temperature form supports the presence of a bicyclic ring. The hydrogen atoms of O2S to O5S are hydrogen-bonded to the neighboring $[BF_4]^-$ ions. The bicyclic heptamer is twisted from planarity; the pentameric ring has an envelope structure while the tetrameric water ring is nonplanar.

This phase transition is reversible. When the single crystal is warmed to 296 K, the conversion from phase **II** to phase **I** is confirmed by the determination of single-crystal cell data. The differential scanning calorimetry (DSC) of the crystals of **1** shows exothermic peaks in the temperature range 290 to 270 K on cooling, indicating that the phase transition from **I** to **II** is reversible but very sluggish. Water freezes to ice below 0 °C; hence it appears that the cyclic water heptamer may exist in liquid form in the room-temperature phase **I** and as ice in the low-temperature phase **II**. A similar phase transition was observed in 2D ice sheets by Janiak and Scharamann. The neutron diffraction studies at three different temperatures of a nickel(II) complex containing 2D ice layers show stepwise freezing of a dynamic layer of pesudoliquid 2D water.[15]

Jensen, Krishnan, and Burke have predicted that the cyclic ring structure is predominant at room temperature, followed by the fused bicyclic heptamer among various structures, on the basis of the entropy and free-energy values obtained using Hartree–Fock calculations.[11] The structures of the two forms at two different temperatures indeed confirm these theoretical predications.

In summary, an elusive cyclic water heptamer has been trapped in the solid-state structure of a 3D coordination polymeric network with diamondoid topology, which provides a confined cavity for the water cluster to self-assemble along with anions. This cyclic heptamer has a twisted nonplanar conformation with crystallographic twofold rotational symmetry. Interestingly, this cyclic $(H_2O)_7$ unit undergoes structural transformation to another bicyclic water heptamer containing edge-fused pentamer and tetramer rings when the single crystal undergoes phase transition from monoclinic room-temperature phase **I** to low-temperature phase **II**. The removal of crystallographic twofold rotational symmetry in the 3D network structure as well as in the discrete water cluster appears to be responsible for the water cluster transformation. The extrapolation of the water structures reported here to gas-phase water clusters may not be logical. However, this study would certainly provide new insights into the properties and behavior of bulk water in which the water molecules interact with the surface of containers through weak interactions. Such weak interactions have been successfully mimicked in this host matrix to obtain hitherto unknown water clusters.

Experimental Section

1: $Cu(BF_4)_2{\cdot}3H_2O$ (0.5 mmol, 0.145 g), H_2muco (0.5 mmol, 0.072 g), NaOH (1.0 mmol, 0.040 g), and phen (0.5 mmol, 0.099 g) in 50% aqueous MeOH (10 mL) were heated at reflux for 60 min. The filtered solution was slowly evaporated at room temperature to obtain blue distorted octahedral-shaped crystals after a day. The crystals were washed with 50% aqueous MeOH and dried. Yield: 0.131 g, 60%. Elemental analysis (%) calcd for $C_{48}H_{36}B_2Cu_3F_8N_6O_{10}$ (dried): C 47.21, H 2.97, N 6.88; found: C 47.37, H 2.94, N 7.34. Selected IR data (KBr): $\tilde{\nu} = 3446$ (OH), 1610 (ν_{as}, OCO^-), 1335 cm^{-1} (ν_s, OCO^-). TG weight loss for the fresh sample calcd for $7H_2O$: 9.6%; found: 8.7%.

Crystal data for **I**: monoclinic, space group $C2/c$, $a = 19.0949(9)$, $b = 22.7667(11)$, $c = 13.3952(7)$ Å, $\beta = 113.1850(10)°$, $V = 5352.97$ Å^3, $Z = 4$, $\rho_{calcd} = 1.627$ g cm^{-3}, $\mu = 1.282$ mm^{-1}, $T = 296$ K, $R1 = 0.0481$, $wR2 = 0.1298$, GOF = 1.040 for $I > 2\sigma(I)$.

Crystal data for **II**: monoclinic, space group $P2_1/c$, $a = 13.3330(7)$, $b = 22.7104(12)$, $c = 18.4681(10)$ Å, $\beta = 109.127(2)°$, $V = 5283.39$ Å^3, $Z = 4$, $\rho_{calcd} = 1.648$ g cm^{-3}, $\mu = 1.298$ mm^{-1}, $T = 223$ K, $R1 = 0.0455$, $wR2 = 0.1036$, GOF = 1.018 for $I > 2\sigma(I)$. Most of the hydrogen atoms of the water molecules were located in Fourier difference. However, the distances and angles were constrained by the option DFIX. CCDC-640886 (**I**) and CCDC-640887 (**II**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: April 22, 2007
Published online: June 19, 2007

Keywords: coordination polymers · copper · phase transitions · self-assembly · water clusters

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