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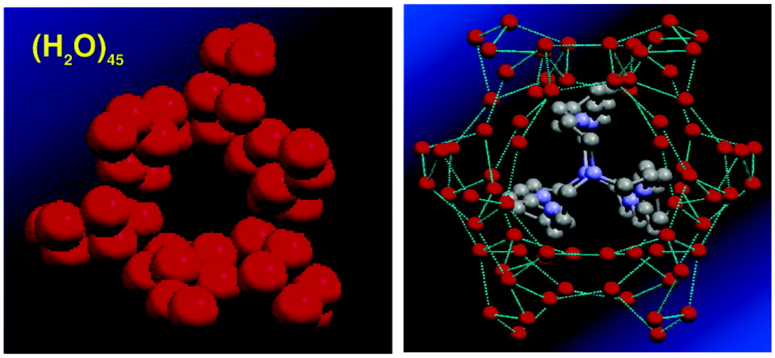

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Formation of an Infinite 2D-Layered Water of $(H_2O)_{45}$ Cluster in a Cryptand−Water Supramolecular Complex: A Template Effect

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Investigations on water have received considerable interest because of its fundamental importance.[1−3] Structural studies on “discrete” water clusters within the lattice of a crystal host have significantly advanced our knowledge toward the first step of understanding the behavior of bulk water.[4−6] Growth of larger water clusters and how the clusters link to form a large network, which is the bridge between clusters and bulk water, is still a challenging scientific endeavor.[7−9] Some interesting polymeric water phases consisting of basic water tetramer, pentamer, and hexamer subunits have been reported.[10,11] Very recently, two-dimensional (2D) water/ice layers containing large 12- or 18-membered water rings have been observed in the solid state which provide novel structural aspects of water.[9,12] Herein, we describe the formation of an unprecedented, infinite 2D layer of $(H_2O)_{45}$ clusters, each consisting of a basic cyclic eight-membered ring fused with a four-membered ring, further associated to water dimers and monomers. Hydrogen-bonding interactions between the 2D layers of water and cryptand moieties create a unique, infinite through-channel.

The homoditopic cryptand (**L**), containing eight amino nitrogen atoms, has been chosen in the present investigation.[13] **L** crystallizes from water/acetonitrile binary solvents with 15 water molecules per cryptand (**1**) revealed by X-ray crystallography.[14] **L**, having N_4 donor sets, facilitates the formation of a “*crown shape*” water structure at both ends via a hydrogen-bonding network as in biological systems (Figure 1b). Thus, the cryptand is acting as a template for the formation of channels of water layers.

The crystal structure reveals a high degree of symmetry, and the three-fold axis passes through the bridge-head nitrogen atoms of three independent cryptands, with 15 water molecules in the asymmetric unit. Out of the three independent cryptands, the phenyl rings in one show dynamic disorder. Although the data collection for the compound was carried out under liquid-nitrogen temperature conditions (100 K) most of the water hydrogens were never located; however, positions of the water molecules constituting the 2D-supramolecular architecture were determined unequivocally. The 2D layer of water is composed of a unique $(H_2O)_{45}$ cluster (Figure 2a), which is constituted by the water molecules present in the asymmetric unit possessing C_3-symmetry. The presence of **L**, generating the three-fold symmetry in the system, is obviously a template effect. The $(H_2O)_{45}$ cluster unit is basically an assembly of three $(H_2O)_{15}$ subunits (Figure 2b) which are interconnected via hydrogen bonding between (O1···O2) and (O11···O12).

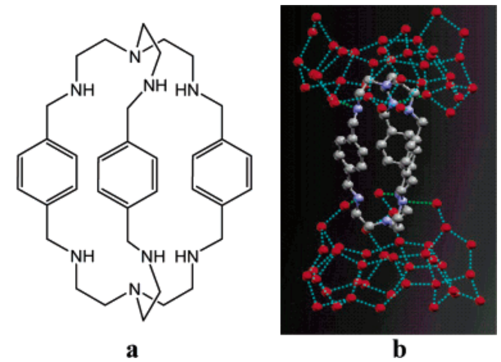

Figure 1. (a) Ligand structure **L**. (b) Depicting interaction of **L** with the water layers where N_4 units are covered by the “*water crown*” viewed down the *a*-axis; N−H···O interactions are shown in dotted green lines.

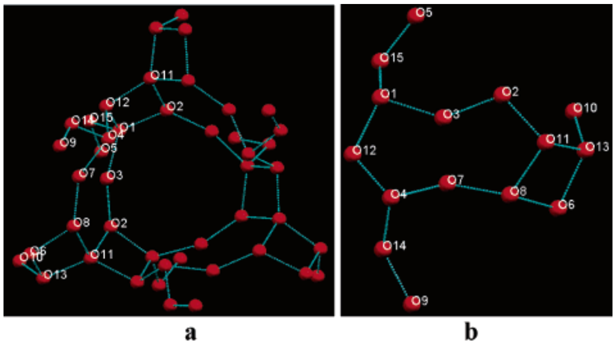

Figure 2. (a) Topology of supramolecular $(H_2O)_{45}$ cluster having C_3 symmetry. (b) Topology of $(H_2O)_{15}$ subunit in the asymmetric unit. Color code: red (water oxygen); blue (H-bonding interactions).

The subunit $(H_2O)_{15}$ has the shape of a puckered eight-membered ring (O1, O2, O3, O4, O7, O8, O11, O12) fused with a four-membered ring (O6, O8, O11, O13), and further hydrogen bonded to two water dimers (O5, O15) through O1 and (O9, O14) through O4, and one water monomer (O10) through O13 with an average O···O distance 2.746 Å which is very close to the corresponding value of 2.759 Å found in ice I_h at −90 °C.[15] In the cyclic, puckered octamer the O···O distance ranges from 2.748 to 2.824 Å, resulting in an average O···O distance of 2.765 Å, whereas the O−O−O angle ranges from 98.23° to 140.48°.[14] Blanton et al.[5a] reported the first crystallographic characterization of an octameric water cluster having an approximately cube-cage-like conformation with C_i symmetry, whereas a cyclic, puckered arrangement with $-4m2$ symmetry of the $(H_2O)_8$ cluster has been reported by Atwood et al.[4c] with the O···O distance 2.745 Å. Our observation of the puckered geometry of an eight-membered ring in a 2D layer of water may be attributed to its different modes of connectivity with the surrounding water molecules and the interactions with the cryptand. In the asymmetric unit, the water octamer ring has hydrogen-bonding interactions with a water dimer (O6, O13), forming a fused cyclic tetramer with an average O···O distance 2.790 Å where the corresponding diagonal angles of ∠O−O−O in the cyclic tetramer have similar values (85.88°, 85.33°) and (92.85°, 93.39°) and form a quasi-planar ring structure. O1 and O12 of the basic octamer water ring are further involved in hydrogen-bonding interactions with O2 and O11 water molecules from a neighboring octamer at a distance 2.764 and 2.801 Å, respectively, resulting in a quasi-planar four-membered ring with ∠O−O−O ranging from 88.33° to 90.86°. However, water

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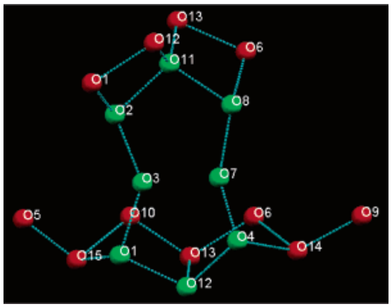

Figure 3. View depicting the puckered eight-membered ring (green balls) surrounded by other connectivity with lattice water molecules creating smaller rings.

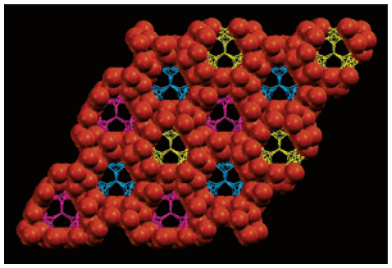

Figure 4. CPK diagram of the water structure making a through-channel down the *c*-axis.

molecules O1, O4, and O12 of the octameric ring along with O14 and O15 of the dimer, O10 of the monomer, and O6 and O13 of the fused tetramer from the asymmetric unit create two fused, cyclic, puckered five-membered rings (O1, O10, O12, O13, O15) and (O4, O6, O12, O13, O14).[14] Apart from the interactions with the surrounding cyclic rings, the O4 water molecule of the octamer has hydrogen-bonding interaction with one of the secondary nitrogens of **L**, whereas monomer O10 and dimers (O5, O15 and O9, O14) are also forming N···O short contacts with the cryptand secondary amine at a distance which ranges from 2.673 to 2.867 Å.[14] The cooperative effect of the surrounding fused four-membered and five-membered rings through O···O interactions along with NH···O interactions with **L** imposes the observed puckered geometry of the eight-membered basic ring (Figure 3).

Formation of the 2D-layer is generated by simple translation of the $(H_2O)_{45}$ cluster. The packing diagram viewed down the *c*-axis alternates arrangement of the cryptand and the 2D layer of water to generate a through-channel (Figure 4). The CPK diagram of the water structure clearly shows that the cryptand moieties are located inside the channel. The connectivity of "*water crowns*" from 2D layers with **L** forms an infinite channel along the *c*-axis.

Thermal analysis of **1** shows that onset of water loss starts at about 50 °C and complete loss of water takes place within 120 °C.[14] Total weight loss in this temperature range is 29.53%, corresponding to 14.25 molecules of water. Fifteen water molecules per cryptand are also supported from the microanalysis results of **1**.[14] Facile removal of water from **1** confirms that the 2D layer of water has weak interaction with **L**.

In FTIR spectroscopic studies of **1**, a relatively sharp band centered about 3459 cm^{-1} is attributed to the O−H stretching frequency of the water cluster.[14] The IR spectrum of the same crystals when heated for 2 h at about 100 °C under vaccum (0.1 mm) shows that disappearance of the cluster peak and spectra is virtually superimposable with the standard sample of **L**. Powdered X-ray diffraction studies on **1** before and after expulsion showed major changes in the diffraction patterns and intensities which were attributed to the complete breakdown of the host lattice on exclusion of water.[14] Deliberate immersion of dehydrated **1** in water overnight led to absorption of moisture into the lattice as indicated in the FTIR spectra. The X-ray diffraction pattern of the rehydrated sample showed a marginally different diffraction pattern and intensity compared to those of **1**, suggesting that the departure of the water layer from **1** may be a reversible process.[14]

In summary, we have characterized a novel 2D layer of the water structure composed of a unique $(H_2O)_{45}$ cluster under a confined condition. The present mode of the association of puckered cyclic eight-membered water ring, dimer, and monomer water has not been predicted theoretically nor previously reported experimentally. This new structural data definitely enhances understanding of the 2D structural aspects of water. Moreover, the observed templating effect of the cryptand on the formation of 2D-layered water that has an infinite channel is very important for correctly describing the association of water molecules in biological systems.[16]

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Supporting Information Available: Data on X-ray structure (CIF file, H-bonding distances and angles, packing diagram), NMR, elemental analysis, XRPD, FTIR, TGA for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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