7192 *J. Am. Chem. Soc.* **2001,** *123,* 7192−7193

A Well-Resolved Ice-like $(H_2O)_8$ Cluster in an Organic Supramolecular Complex

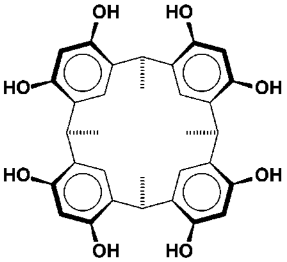
Jerry L. Atwood,*,† Leonard J. Barbour,† Timothy J. Ness,‡
Colin L. Raston,‡ and Paul L. Raston†

Department of Chemistry, University of Missouri-Columbia
Columbia, Missouri 65211
Department of Chemistry, Monash University
Clayton, Melbourne, Victoria 3168, Australia

Received March 5, 2001
Revised Manuscript Received May 11, 2001

Recently we reported the crystal structure of a supramolecular copper coordination complex that is stabilized by an $(H_2O)_{10}$ cluster with an ice I*c*-like arrangement of the water molecules.[1] Subsequently, we were able to show that the introduction of subtle changes to the system (i.e. substitution of Co for Jahn−Teller distorted Cu, as well as changes in ligand orientation) does not disrupt the overall geometry of the water cluster.[2] In these reports we addressed the importance of the study of water clusters in “small-molecule” solid-state supramolecular complexes. In summary, such model systems afford precise structural information and may thus yield a better understanding of the anomalous properties of water as well as its exact role in the stabilization of biopolymers. These topics continue to generate considerable interest among both theoretical and experimental chemists[3] and a recent report[3c] by Blanton et al. describes the first crystallographic characterization of an octameric water cluster within the lattice of a cobalt coordination complex. The cluster adopts an approximately cubic cage-like conformation with C_i symmetry, where all eight water molecules are positioned at the corners of the cube. In that report, the authors note that predictions of the structure of $(H_2O)_8$ in the gas phase suggest the most favorable conformation also to be cubic and cage-like, but with S_4 symmetry. Although higher in energy, the experimentally observed cube-like octamer is stabilized by the formation of four hydrogen bonds to the surrounding lattice. In this context, we now report the observation of an ice-like, *cyclic* $(H_2O)_8$ cluster in the solid-state structure of an organic supramolecular complex.

1 =



Single crystals suitable for X-ray diffraction analysis[4] were grown by slow evaporation of a solution of **1** in acetone. No precautions were taken to exclude adventitious water. The crystal structure possesses a high degree of symmetry: the asymmetric unit consists of a quarter of a molecule of **1** and two-quarter-occupancy acetone molecules, all situated on positions of 2*mm* site symmetry. Furthermore, there are two water molecules, each situated on a 2-fold rotation axis, as well as one water molecule on a mirror plane. The bowl-shaped *C*-methylcalix[4]resorcinarene molecules assume a C_{2v} conformation and pack in two-dimensional bilayers as shown in Figure 1.

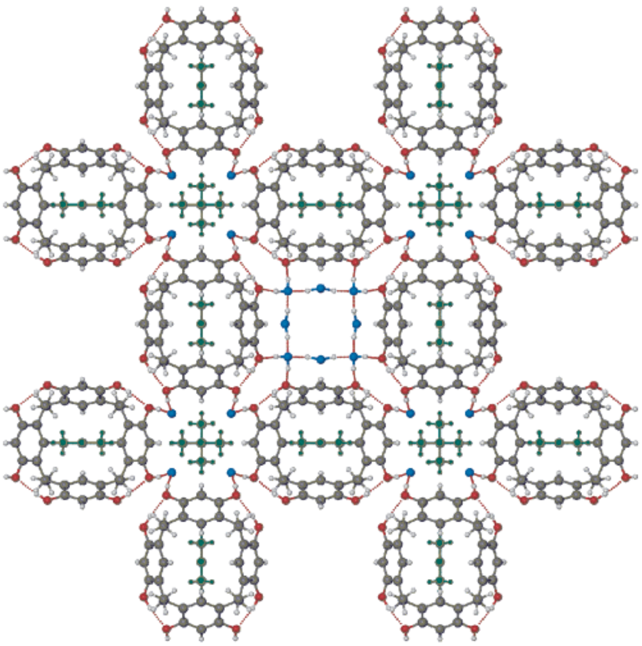


Figure 1. View down the crystallographic *c* axis and perpendicular to the calix[4]resorcinarene bilayers. The water $(H_2O)_8$ cluster is shown in the center and hydrogen bonds are represented as dotted lines. (Colors: carbon, gray; oxygen, red, hydrogen, white; acetone, green; water oxygen atoms, blue.)

Within each bilayer, the calix[4]resorcinarene molecules are oriented in an alternating up−down fashion and adjacent macrocycles are held together by an intricate array of bridging hydrogen bonds to water molecules. Facing bowls are translated laterally relative to one another such that they do not form dimeric supramolecular capsules as observed in a calix[4]resorcinarene structure previously reported by us.[5] The van der Waals surface of the bilayer is severely undulated and adjacent layers are rotated by 90° relative to one another with their macrocycles eclipsed. The cavities of the eclipsed molecules are oriented in the same direction and linear columns of calix[4]resorcinarene molecules that span the layers are thus apparent. Each cavity is occupied by a molecule of acetone with its carbonyl group directed outward. Although the layers interpenetrate to form a snug van der Waals fit, two deep crystallographically unique indentations are formed between the calix[4]resorcinarenes within each bilayer. These voids are occupied by intriguing arrangements of both acetone and water molecules.

One of the voids contains two acetone molecules with their C═O axes aligned and their $CH_3{-}C{-}CH_3$ moieties mutually perpendicular. Interestingly, the closest contact between these two molecules is that of 2.804(7) Å between the oxygen atoms.

---

* Corresponding author. E-mail: atwoodj@missouri.edu.
† University of Missouri-Columbia.
‡ Monash University.

(1) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Nature* **1998**, *393*, 671.
(2) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Chem. Commun.* **2000**, 859.
(3) (a) Ugalde, J. M.; Alkorta, I.; Elguero, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 717. (b) Chaplin, M. F. *Biophys. Chem.* **2000,** *83*, 211. (c) Blanton, W. B.; Gordon-Wylie, S. W.; Clark, G. R.; Jordan, K. D.; Wood, J. T.; Geiser, U.; Collins, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3551. (d) Custelcean, R.; Afloroaei, C.; Vlassa, M.; Polverejan, M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3094.
(4) Crystal data for **2**: $C_{38}H_{60}O_{16}$; M = 772.86, colorless prismatic crystal, 0.40 × 0.35 × 0.20 mm^3, tetragonal, $P4_2/nmc$ (No. 137), $a = b = 16.2553(7)$ Å, $c = 15.034(1)$ Å, $V = 3972.4(4)$ Å^3, $Z = 4$, $D_{calcd} = 1.292$ g cm^{-3}, $F(000) = 1664$, λ(Mo Kα) = 0.71073 Å, $T = 173$ K, reflections collected/unique, 23815/2363 (R(int) = 0.0800). Final GooF = 0.948, $R1 = 0.0441$, $wR2 = 0.1096$, R indices based on 1489 reflections with $I > 2\sigma(I)$ (refinement on F^2), 160 parameters, 8 restraints, Lp and absorption corrections applied, $\mu = 0.100$ mm^{-1}.
(5) Rose, K. N.; Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Chem. Commun.* **1998**, 407.

10.1021/ja015757k CCC: $20.00

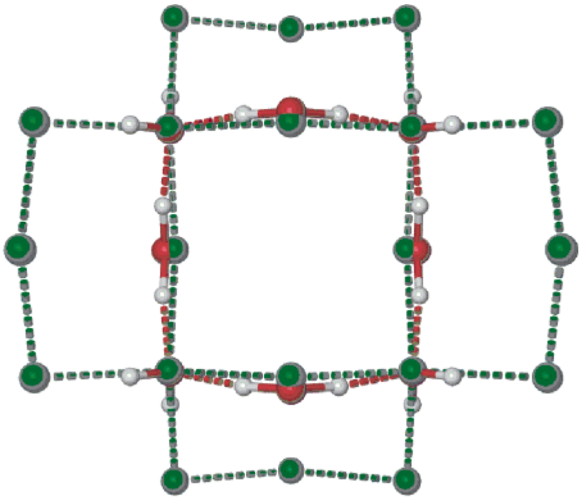


Figure 2. The water octamer oxygen atoms (red) overlaid on a subset of the lattice of Ice I*c* (green). Hydrogen atoms (white) are shown for the water octamer, but not for the ice lattice where they are disordered. Hydrogen bonds are indicated as fragmented cylinders.

Although it was initially thought that this arrangement was the result of symmetry-imposed disorder, solution and refinement of the structure in the space group *P*1 showed that this was not the case. A Cambridge Structural Database search yielded several previously reported structures with intermolecular carbonyl O···O contacts in the range 2.5−2.9 Å, but none exhibit a linear C═O···O═C arrangement as observed in the present structure. Nevertheless, the main focus of this contribution is concentrated on the fascinating arrangement of eight water molecules in the second void to form a hydrogen-bonded cluster.

The crystallographically unique part of the $(H_2O)_8$ cluster consists of two-half-occupancy water molecules, one on a mirror plane and one on a 2-fold rotation axis. The entire cluster is generated from these units by $-4m2$ symmetry and the overall conformation is cyclic. Figure 2 shows that the puckered arrangement of the water cluster can be superimposed remarkably well on a subset of the continuous lattice of ice I*c* (this particular motif is not present in any of the other ice polymorphs). The cluster is held together by eight symmetry-equivalent internal hydrogen bonds (O···O, 2.745(6) Å; ∠O−H···O, 170.0(2)°, ∠O···O···O, 109.5(2)° and 116.4(2)°). Within the ring, four water molecules serve as double hydrogen bond donors and the remaining four as double acceptors. The donor and acceptor water molecules are arranged in an alternating fashion. The *intra*cluster hydrogen bond accepting water molecules donate hydrogen bonds to phenolic oxygen atoms belonging to four surrounding calix-[4]resorcinarene molecules (2.703 Å, 159.0°) and every water hydrogen atom is thus involved in a hydrogen-bonded interaction. The van der Waals volume available to the water octamer is ca. 228 Å^3, yielding an effective density of 1.05 g/cm^3 for the cluster. This value is significantly higher than that of 0.934 g/cm^3 obtained for ice I*c* at −130 °C and implies that the water octamer is highly stabilized by its environment in the supramolecular lattice. Furthermore, we believe that the water molecules in the structure impart a high degree of rigidity to the lattice by forming a strong hydrogen-bonded network and that this accounts for the unusually close proximity of the two acetone oxygen atoms to one another.

Theoretical predictions of low-energy structures of water octamers suggest that cage-like conformations are the most stable. Most likely, this is because cage structures maximize the formation of hydrogen bonds within the cluster while interactions with the surrounding environment are ignored. Clearly gas-phase predictions of water cluster geometry have little bearing on the solid or liquid state where there is a subtle interplay between the formation of a stable configuration and its interaction with its surroundings. Indeed, water clusters in solution as well as in the solid state cannot be considered to be discrete and this is undoubtedly true for clusters that reside in the clefts of biological macromolecules which can be regarded as existing in a hybrid solid−liquid state. Possibly the most important constraints on the geometry of the cluster are (1) that the oxygen atoms should be separated by distances of about 2.7 Å, (2) that they should be distributed approximately tetrahedrally with respect to one another, and (3) that the cluster should occupy the space available to it optimally while forming favorable interactions with surrounding functionalities.

Acknowledgment. This work was supported by the National Science Foundation and the Australian Research Council.

Supporting Information Available: Crystallographic information file (CIF) and thermal ellipsoid plots (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA015757K