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Molecular Ice with Hybrid Water–Bromide Network around a Cryptand with a Bromide Ion Included in the Cavity to Form a Host-within-a-Host-Like Structure

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A new mode of association of water molecules is described. Adamantanoid water clusters bonded to bromide ions as well as other water molecules form a cage within which bromide-encapsulated aza cryptands reside to form a host-within-a-host-like structure. The structure of this adamantanoid water decamer is remarkably similar to that of cubic ice (I_c). The average O···O distance is 2.78 Å, which is close to 2.75 Å present in I_c, and the average O···O···O angle of 109.40° is also close to the tetrahedral angle in ice I_c.

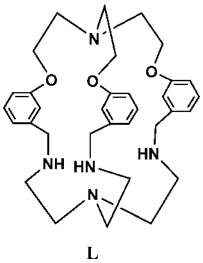
Introduction

Complexation of anions by different host molecules has become an area of intense research[1] because the function of anions is essential in biological systems and in diverse enzymatic reactions. Anions are also implicated[2] in several diseases such as cystic fibrosis, Alzheimer's disease, etc. In addition, different environmental problems are associated with anions. Herein, we report the supramolecular association of ten water molecules into "molecular ice", which further connects other such units and a cluster of water and bromide ions to form a 3D cage within which lies a cryptand that encapsulates a bromide ion in its cavity. There are other cryptands also present with empty cavities.

The importance of water and its well-discussed anomalies have resulted in a large number of theoretical as well as experimental studies[3–6] that cover a broad range of topics on the structure of water. For ice, there are several crystalline[7] and amorphous[8] phases known. Phases I_h and I_c are the two most common forms[7a] of ice and are strikingly similar in structure. They differ only in the stacking sequence of the puckered layers relative to one another such that the interconnecting rings are in the boat conformation in ice I_h whereas they assume a chair conformation in ice I_c. This form of ice is also called cubic ice and its formation is of utmost importance in cryobiology where formation of ice upon cooling the sample is the primary cause of cell damage. Biological samples are better preserved in I_c which form tiny crystals all around and do not lead to extensive solute segregation,[9] whereas I_h causes massive cell damage. Cubic ice is also likely to be present[10] in the outer spheres of some of the planets of our solar system, including earth.

Results and Discussion

Complex **1** was isolated as colorless crystals[11] from an aqueous methanolic solution of **L**[12] (Scheme 1) in the presence of HBr in 65% yield. The asymmetric unit of **1** consists of two bridges from two different cryptand units, seven water molecules, and three bromides, where one of the bromides (Br1) sits on a crystallographic threefold symmetry axis. The atom Br1, included in the cryptand cavity, pulls the two bridgehead N atoms towards itself thereby decreasing their interatomic distance to 8.452 Å from the observed value of 9.904 Å [12] in **L**. This bromide is H-bonded with the three protonated secondary amines in the three bridges (N6···Br1, 3.278 Å; N6–H2···Br1, 148.55°) and three aromatic CH protons (C20···Br1, 3.439 Å; C20–H20···Br1, 127.73°) to complete a distorted octahedral coordination (Figure 1) geometry. The second bromide (Br2), which occupies a position outside the cryptand cavity, forms one strong N–H···Br hydrogen bond (N6···Br2, 3.286 Å; N6–



L

Scheme 1. Illustration of aza cryptand **L**.

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H1···Br2, 119.59°) with the bromide-encapsulated cryptand and two strong N–H···Br hydrogen bonds (N3···Br2, 3.262 Å; N3–H2···Br2, 127.55°, and N3···Br2, 3.262 Å; N3–H1···Br2, 141.85°) with the bromide-free cryptand, thereby acting as a linker among the cryptand units. Thus, each of the protonated secondary amines of the "tren" end of the bromide-encapsulated cryptand makes two contacts: one N–H···Br1 and one N–H···Br2. Each of the protonated secondary amines of the bromide-free cryptand also makes two different N–H···Br2 intermolecular contacts (Figure 2).

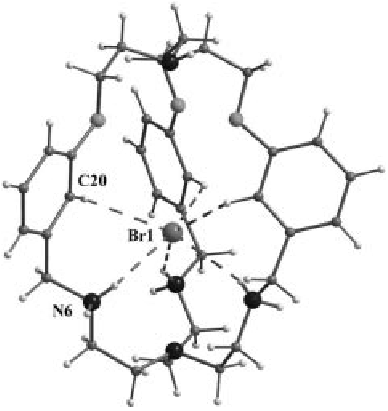

Figure 1. A perspective view showing a bromide ion (Br1) encapsulated inside the cryptand cavity.

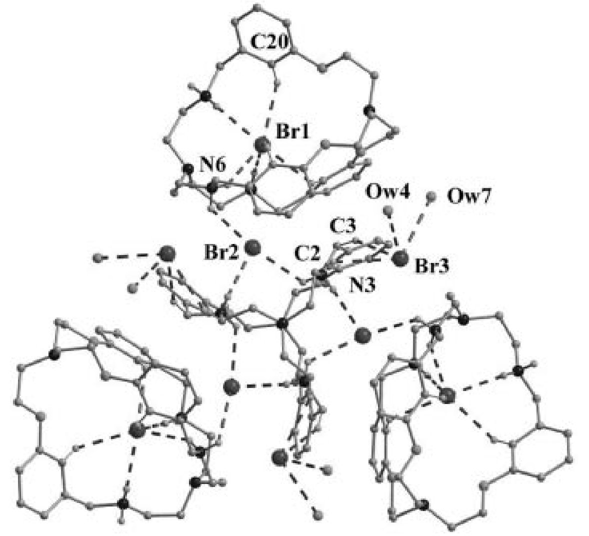

Figure 2. A view showing different hydrogen bonding interactions of the three bromide ions. Only those H atoms that are involved in H-bonding are shown.

Out of the seven water molecules present in the asymmetric unit, four are involved with other symmetry related H_2O molecules to form an adamatanoid $(H_2O)_{10}$ cluster whereas the rest join these $(H_2O)_{10}$ clusters to form a layer of supramolecularly assembled water molecules. Br3 ions are H-bonded to the layer of water molecules that reinforce the structure. Overall, there are three different types of H-bonding networks associated with the adamantanoid water cluster (three Ow2···Ow7···Br3, three Ow3···Ow5···Ow6, and three Ow4···Br3···Ow7 networks). Six adamantanoid units form a 3D cage-like supramolecular network through connections with the remaining H_2O molecules and Br3 ions. The bromide-encapsulated cryptand lies within this cage and assumes a host-within-a-host-like structure (Figure 3), which resembles the Russian nesting doll.[13]

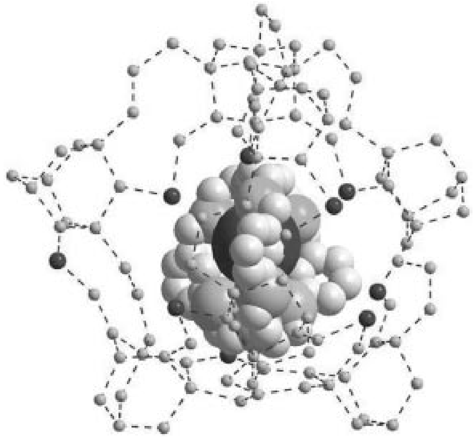

Figure 3. A view of the host within a host structure. Bromide encapsulated cryptand moiety is shown in space-filling model. Hydrogen atoms are omitted for clarity. Color code: C light grey, N medium grey, O dark grey, Br black.

Figure 4 represents the coordination environment of the adamantanoid water cluster, which consists of four different types of water molecules with respect to their noncovalent interactions. The $(H_2O)_{10}$ cluster is termed "molecular ice" because this is the smallest unit of naturally occurring cubic ice. The structure of this adamantanoid water decamer in **1** is remarkably similar to that of ice I_c.[14] The average O···O distance in **1** is 2.78 Å, which is close to 2.75 Å, present in I_c.[14] The average O···O···O angle of 109.40° in the structure is also close to the tetrahedral angle in ice I_c.[14] The distance across the water decamer from Ow2 to Ow4 is slightly lower [6.282(2) Å] than the value (6.35 Å) observed in I_c.[15] Adamantanoid $(H_2O)_{10}$ clusters detected in the voids of a

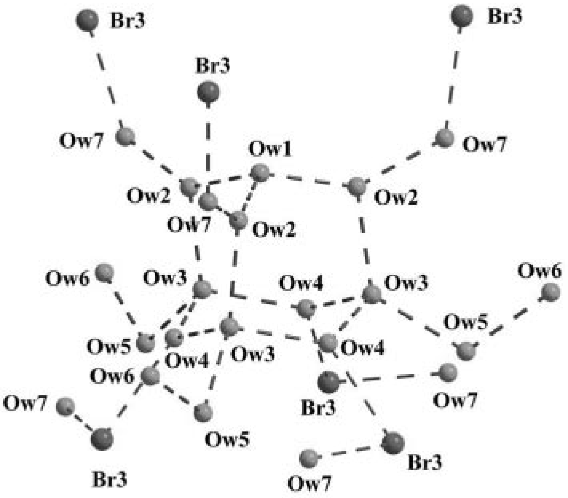

Figure 4. A close view of the adamantanoid water cluster and its environment.

cupric complex[16] or within a hydrophobic self-assembled cage[17] have comparable noncovalent parameters. Notably, the Ow6 makes three H-bonded contacts with three Ow5 and creates three fused nonameric units;[18] each nonamer contains two water molecules of one adamantanoid unit (Ow2, Ow3), two water molecules of another adamantanoid unit (Ow3, Ow4), two Ow5, and one Br3 ion. Figure 5 shows the packing diagram of the different constituent units present in **1**.

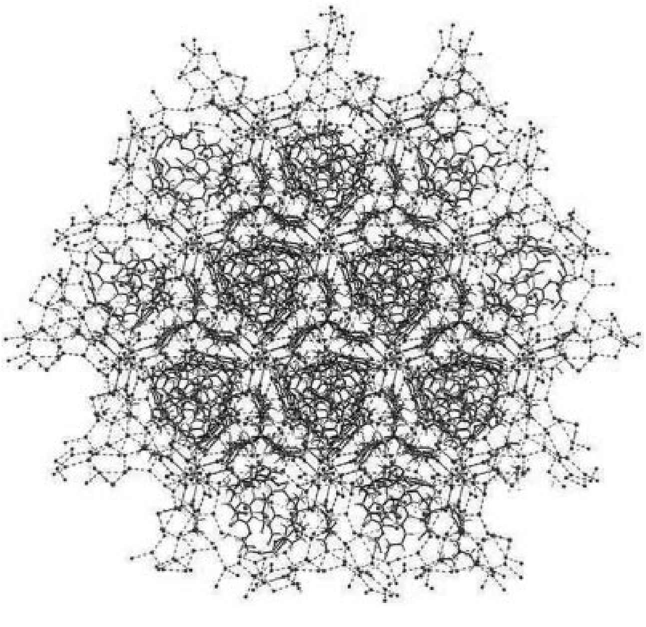

Figure 5. Packing diagram of **1** viewed along the two bridgehead N atoms of the bromide encapsulated cryptand.

Compound **1** exhibits a strong broad peak at about 3404 cm^{-1} in the IR spectrum, and this peak is attributed[18] to O–H stretching pertaining to the water cluster. The O–H stretching vibration for I_c appears[14] as a broad band centered around 3200 cm^{-1}. The difference in the stretching vibrations of **1** in comparison to I_c is due to its different environment. Thermal gravimetric analysis[18] reveals that **1** loses 9.55% of weight at 120 °C, which corresponds to ca. 10 molecules of water. The rest of the water molecules are lost along with decomposition of the compound after only 250 °C, which signifies that the remaining water molecules are tightly held in the crystal lattice. After heating[18] the compound at 120 °C to remove ten molecules of water, the IR spectrum shows the broad peak characteristic of the remaining association of water molecules. Powder X-ray data taken[18] before and after heating the sample in vacuo at 120 °C for 2 h show that once the bulk of the water molecules are removed, the lattice breaks down.

Conclusions

In conclusion, we have shown that a bromide-encapsulated cryptand is surrounded by a cage formed by connecting molecular ice-like water clusters with other water molecules and bromide ions. Thus, the structure looks like a Russian nesting doll. The understanding of three-dimensional structures of this and similar systems have profound effects in several areas, from molecular self-assembly,[19] gas clathrate hydrates,[20] to cryobiology.[9] We are presently working along these lines.

Experimental Section

Cryptand **L** was synthesized as reported[12] previously from our lab. Complex **1** was synthesized by allowing a solution of the cryptand (84 mg, 0.15 mmol) in aqueous methanol (6 mL, 1:1, v/v) in the presence of HBr to concentrate. After a few days, crystals of $\{[H_3\mathbf{L}][H_4\mathbf{L}]\cdot(Br)_7\cdot 15H_2O\}_n$ (**1**) appeared as colorless rectangular plates in 65% yield. $C_{66}H_{127}Br_7N_{10}O_{21}$ (1956.10): calcd. C 40.52, H 6.54, N 7.16; found C 40.46, H 6.59, N 7.08.

Supporting Information (see footnote on the first page of this article): FTIR spectrum, TGA curve, and PXRD analysis of **1**. Additional figures that show the structure of the cryptand cage-like structure.

Acknowledgments

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[11] Crystal data for **1**: Colorless, hexagonal, crystal dimensions $0.16 \times 0.12 \times 0.11$ mm, cubic, $P\,2_13$, $Z = 12$, $a = 20.880(5)$, $b = 20.880(5)$, $c = 20.880(5)$ Å, $V = 9103(4)$ Å^3, $\rho_{\text{calcd.}} = 1.454$ g cm^{-3}, $T = 100(1)$ K, $\mu = 3.154$ mm^{-1}, $\theta_{\max} = 28.23°$, 7554 reflections collected of which 5483 were unique. $R_1 = 0.0767$, $wR_2 = 0.1975$ with a GOF of 1.062 for $I > 2\sigma(I)$; residual electron density: 2.465 and –1.349 e Å^{-3}. The X-ray data were collected with a Bruker SMART APEX CCD diffractometer by using graphite monochromated Mo-K_α radiation (0.71069 Å). The following programs were used during data collection and refinement: SMART (version 5.628 to acquire frame data), SAINT (version 6.45 to determine final unit parameters and integrate frame data). The structure was solved by the direct methods and refined on F^2 using SHELX-97 (G. M. Sheldrick, *SHELX-97: Program for the Solution and Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**). The hydrogen atoms of the water molecules could not be located in the difference Fourier maps with certainty although other H atoms could be located. The non-hydrogen atoms were refined anisotropically. CCDC-616374 contains the supplementary crystallographic data for this paper. This data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[18] See Supporting Information.

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