Chemie

Self-Assembly

A Dodecameric Water Cluster Built around a Cyclic Quasiplanar Hexameric Core in an Organic Supramolecular Complex of a Cryptand**

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The fundamental importance of water in many biological, chemical, and physical processes has prompted intensive research efforts, but it is still not a fully understood liquid. Hydrogen-bonding interactions and their fluctuations are known[1] to determine the properties of water, some of which are regarded as "anomalous". However, the complexities involved in describing these interactions correctly have been a major stumbling block. Therefore, structural data of hydrogen-bonded water clusters in organic molecular crystals within inorganic–organic hybrid frameworks are very important for correctly describing the association of water molecules in different surroundings. This realization has led to theoretical[2–9] and experimental[10–22] studies of a number of small water clusters. The structural possibilities associated with the hexamer is quite extensive and theoretical calculations[23] have shown several local minima on the potential energy surface that correspond to a number of cyclic structural isomers. Out of these, the five low-energy ones, namely, "cage", "prism", "book", "boat", and "cycle" are almost isoenergetic (that is, within ca. 0.7 kcal mol^{-1}). The "cage" structure is the most stable conformation at very low temperature. The lattice of a crystalline host, on the other hand, may offer an environment for stabilizing a higher-energy hexamer. To date, chair,[15,19,24] boat,[17,19] and planar[18] forms have been characterized in crystalline hosts. The planar ring is the basic structural motif found in the ice II structure[25] under high pressure. This is also a prominent structural unit[26] in liquid water as determined by computer simulations. Recently, Nauta and Miller detected[13] the "quasiplanar" hexamer within a helium droplet.

Organic compounds with functional groups similar to those present in biological molecules can stabilize water clusters of different sizes and shapes in environments resembling living systems.[27] Herein, we report the X-ray structure of a hitherto unknown dodecameric water cluster built around a quasiplanar $(H_2O)_6$ unit in an organic supramolecular complex of a laterally nonsymmetric cryptand. A ring of twelve hydrogen-bonded water molecules was reported[28]

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earlier in an inorganic framework. Theoretical calculations on the dodecamer have revealed[29] the existence of several low-energy structures with fused cubic geometry. Other structures with slightly higher energy include cagelike structures containing four- or five-membered rings and two high-symmetry ones with two six-membered rings and six four-membered rings.

Previously, we found that the cryptand **L** (Scheme 1) crystallizes[30] from organic solvents such as acetone or acetonitrile without any association among the cryptand
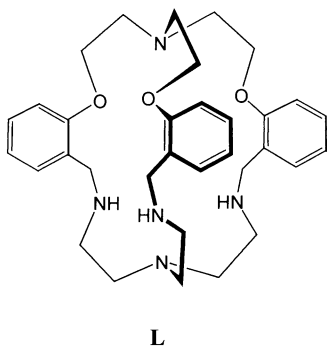
Scheme 1. The laterally nonsymmetric azacryptand **L**.

molecules. However, it is clear that the secondary amines present in the three cryptand strands can potentially act as hydrogen-bond acceptors or donors. Compound **1** was isolated as colorless hexagonal crystals[31] from an aqueous solution of **L** in acetonitrile in the presence of pyridine vapor. Each cryptand molecule binds one H_2O molecule inside the cavity and three H_2O molecules outside (Figure 1) through hydrogen-bonding interactions. The water molecule (Ow3) inside the cavity is within hydrogen-bonding distance from the ethereal O atoms as well as the secondary amino N atoms in the three cryptand strands. The H atoms attached to Ow3 could not be located in the difference map probably because they were disordered. The H_2O molecule bonded outside
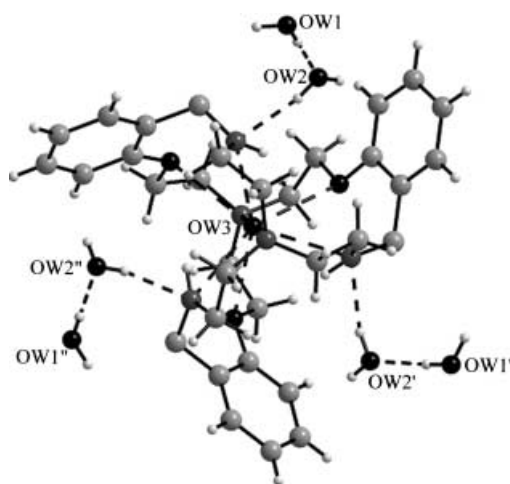

Figure 1. The mode of binding of water molecules with **L** viewed along the pseudo threefold axis of the cryptand.

(Ow2) acts as a hydrogen-bond donor to one of the secondary amino nitrogen atoms of the cryptand with a N···O distance of 2.79 Å. The Ow2 molecule also acts as a hydrogen-bond donor to Ow1, with a nonbonding distance of 2.82 Å. Six such units combine to make a quasiplanar cyclic hexameric core attached to six other water molecules at the periphery to form an overall dodecameric cluster (Figure 2). The O atoms at the
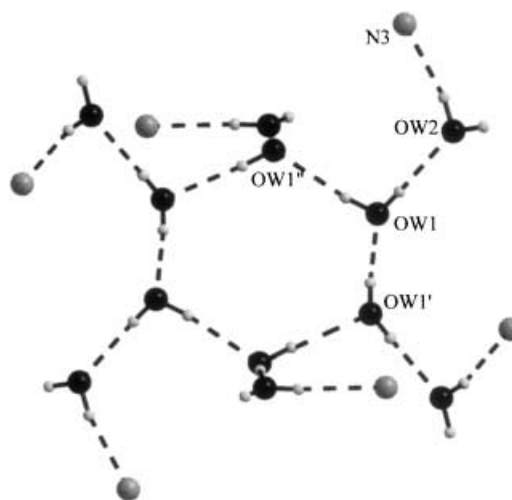

Figure 2. A simplified view of the dodecameric water cluster. Distances [Å]: OW1···OW2 2.827(6), OW1···OW1′ 2.801(6); angles [°]: OW2···H-OW1 172.26(2), OW1···H-OW′ 173.65(2), OW1′···OW1···OW1″ 119.58(1), OW2···OW1···OW1′ 109.36(2), OW2···OW1···OW1″ 104.38(2).

periphery are not coplanar with the core unit, but are situated alternately above and below the plane described by the hexamer so as to accommodate the six bulky cryptand units. These noncovalent interactions lead to a giant supramolecular unit consisting of six cryptand molecules surrounding the $(H_2O)_{12}$ cluster. Each of these units acts as a secondary building unit (SBU) and is further hydrogen bonded with H_2O molecules through the remaining secondary amines of the cryptand (Figure 3), thus resulting in propagation of the supramolecular assembly.[32] Each O atom of the dodecameric cluster is tricoordinate. Such hydrogen-bond-deficient water molecules are present[33] at the surface of liquid water and hexagonal ice. The hexameric core in the current assembly adopts a quasiplanar benzene-like cyclic structure. Although this is a higher-energy isomer, it is stabilized by the environment. The crystallographically imposed symmetry makes all the O···O distances in the hexameric core the same at 2.801 Å. This value compares[34] well with the range 2.77–2.84 Å observed in the ice II phase. Bulk water also shows[34] a short-range order in the O···O X-ray diffraction radial distribution curve of 2.85 Å. The O···O distance between the water molecule at the core and the one connected to it at the periphery is 2.827 Å.

Thermal analysis of the compound shows that onset of water loss starts at about 50°C and complete loss of water takes place within 100°C. The compound melts at 138°C, which is slightly lower than that of the cryptand (145°C).
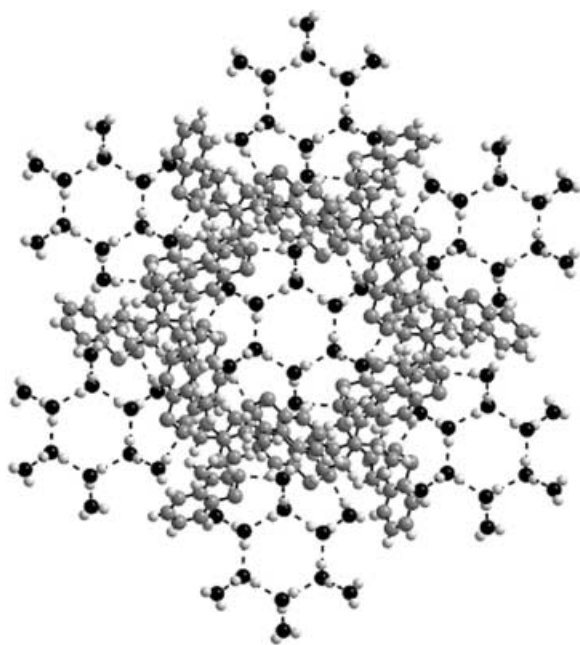
Figure 3. Building of the water clusters in **1** viewed down the crystallographic *c* axis.

The vibrational stretching frequencies of the O–H bonds pertaining to the water cluster have been characterized by FTIR spectroscopic analysis of **1**.[32] A sharp peak appears at 3635 cm^{-1} in the spectrum followed by a broad absorption centered around 3410 cm^{-1}. The IR spectrum of **1** after removal of the water is virtually superimposable on that of a standard sample of the cryptand **L**. Thus, the peak at 3635 cm^{-1} can be assigned to the $(H_2O)_{12}$ core structure. The O–H stretching vibration for the quasiplanar water hexamer appears[18] as a broad band centered around 3400 cm^{-1}; the O–H stretching vibration for the same cluster in a helium droplet appears at 3325 cm^{-1}.[13] In comparison, this vibration of the planar hexamers in ice I and II phases occur[35] at 3220 cm^{-1}. In the case of **1**, the structured band centered around 3410 cm^{-1} is attributable to the planar $(H_2O)_6$ core structure and the difference in the stretching vibration arises from its different environment.

Powder X-ray diffraction studies of the compound before and after water expulsion showed major changes[32] in the diffraction patterns which were attributable to the complete breakdown of the host lattice on exclusion of water.

In summary, we have characterized a novel dodecameric water cluster in an organic supramolecular structure. The present mode of association of twelve water molecules has not been predicted theoretically or previously found experimentally. The supramolecular self-assembly observed here is the result of hydrogen-bonding interactions between water molecules as well as between water molecules and cryptand molecules. The understanding of three-dimensional structures of water clusters has profound effects in several areas: from molecular self-assembly[36] to protein structures.[37] Attempts should thus be made to simulate water crystallization in restricted environments such as organic and inorganic host lattices. We are currently probing whether cryptands with

biologically relevant functional moieties can stabilize various water clusters.

Experimental Section

Cryptand **L** was synthesized as reported previously.[30] Compound **1** was synthesized by allowing a solution of the cryptand in aqueous pyridine or aqueous acetonitrile to evaporate at room temperature. After a few days, crystals of **L**·7H$_2$O (**1**) appeared as colorless hexagonal plates in ca. 55% yield. Elemental analysis: calcd for **L**·7H$_2$O C$_{33}$H$_{59}$N$_5$O$_{10}$ (%): C 57.79, H 8.67, N 10.21; found: C 57.83, H 8.49, N 10.36.

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[31] Crystal data for **1**: Colorless, hexagonal, crystal dimensions $0.18 \times 0.16 \times 0.13$ mm, trigonal, space group $R\bar{3}$, $Z = 3$, $a = 14.023(5)$, $b = 14.023$ (5), $c = 33.249(5)$ Å, $V = 5662.3(2)$ Å^3, $\rho_{calcd} = 0.199$ g cm^{-3}, $T = 100$ K, $\mu = 0.015$ mm^{-1}, $\theta_{max} = 28.32°$, 3139 reflections collected of which 2834 were unique. $R_1 = 0.0684$, wR2 = 0.2004 with a GOF of 1.050 for $I > 2\sigma(I)$; residual electron density: 1.347 and -0.854 e Å^{-3}. The X-ray data were collected on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo$_{K\alpha}$ 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 intregate frame data). The structure was solved by direct methods and refined on F^2 using SHELX-97 (G. M. Sheldrick, Program for the solution and refinement of crystal structures, University of Göttingen, Germany, **1997**) package. The hydrogen atoms connected to the OW3 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. H atoms were not refined. CCDC-230380 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[32] See Supporting Information.

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