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A Hybrid Water–Chloride Structure with Discrete Undecameric Water Moieties Self-Assembled in a Heptaprotonated Octaamino Cryptand**

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Small water clusters are the subject of considerable theoretical and experimental interest as they can lead to an understanding of the structure of bulk water.[1–3] In the past several years, studies on the structural morphologies of water clusters in crystal hydrates have shown that the stabilization of discrete, even-membered water rings such as tetramers,[4] hexamers,[5] octamers,[6] decamers,[7] dodecamers,[8] tetradecamers,[9a] and hexadecamers,[9b] is common within the lattice of a crystal host. Studies on water clusters in different environment have significantly advanced the understanding of the structure of bulk water.[4–10] However, surprisingly little is known of the structural constraints required for stabilizing discrete odd-membered water cluster morphologies of higher nuclearity, even though trimers and pentamers are familiar in crystal hydrates,[11,12] and Férey et al. have isolated an $(H_2O)_{17}$ cluster inside a super-sodalite cage.[13] Here we describe the crystal structure of a discrete, propeller-shaped tricyclic $(H_2O)_{11}$ moiety stabilized by the heptahydrochloride **1** (Figure 1) of the octaamino cryptand $N(CH_2CH_2NHCH_2\text{-}p\text{-}C_6H_4\text{-}CH_2NHCH_2CH_2)_3N$ (L).[14] This study also shows the formation of a hybrid water–chloride structure where chloride encapsulated inside the cryptand cavity is hydrogen-bonded to the undecameric water cluster.

Recently, Mascal et al. have shown that a proper analysis should be done when reporting any new water morphology in a crystal lattice.[15] With this in mind, we performed a Cambridge Structural Database (CSD) search for a propeller-shaped motif having eleven water molecules with the help of the Cambridge Crystallographic Data Centre. Our search algorithm found thirteen matches for the "propeller-shaped" pattern in the CSD.[16] However, in all 13 structures the

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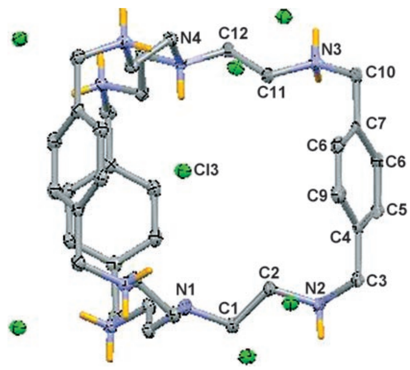

Figure 1. ORTEP diagram of **1**, the heptahydrochloride salt of **L**, with atom numbering scheme (hydrogen atoms attached to the carbon atoms have been omitted for clarity). C gray, Cl green, H yellow, N blue.

propeller-shaped pattern was not discrete but was embedded in an extended water network and our motif cannot be generated with a subset of water molecules included in these crystal structures. To the best of our knowledge, therefore, there is no structural information available for a discrete $(H_2O)_{11}$ cluster or its participation in the stabilization of a supramolecular assembly.[1–13,15,16]

A single crystal of the complex $\mathbf{1}\cdot(H_2O)_{11}$ ($L\cdot 7HCl\cdot 11H_2O$) was isolated from a methanol/water solution of the white solid that had been obtained upon addition of HCl to an acetonitrile solution of L. In our previous study, protonation of L with HCl in methanol gave the hexaprotonated salt containing disordered water molecules.[17] Complex **1** is expected to facilitate the formation of various water aggregates by forming a hydrogen-bonding network similar to biological systems since it displays different types of amino nitrogen atoms as well as encapsulated and surrounding chloride anions.

X-ray crystallographic analysis revealed that $\mathbf{1}\cdot(H_2O)_{11}$ crystallizes in the hexagonal space group $P6_3$ with two molecules in the unit cell. The chloride anion Cl3 and water molecules O1 and O5 occupy specific positions with C_3 symmetry. The heptaprotonated cryptand also has threefold symmetry, with the C_3 axis bisecting the apical nitrogens N1 and N4 and the hydrogen H4 attached to the bridgehead nitrogen N4. It is interesting to note that Cl3, which is encapsulated within the cryptand cavity, is positioned exactly in the plane of N1, N4, and H4. However, the distances between Cl3 and the bridgehead nitrogen atoms vary considerably (Cl3···N1 3.847 and Cl3···N4 3.059 Å), with a closer approach towards the protonated nitrogen making for a strong intramolecular N−H···Cl⁻ interaction. A further two chloride anions outside the cryptand cavity are involved in strong inter- and intramolecular H-bonding interactions. Except for the bridgehead nitrogen N1, all other amino nitrogen atoms are protonated and the N−C distances clearly account for the heptaprotoned cryptand moiety (N1−C1 1.4711(17), N2−C2 1.496(2), N2−C3 1.503(2), N3−C11 1.491(2), N3−C10 1.516(2), and N4−C12 1.5060(17) Å).

Eleven water molecules per molecule of **1** in this supramolecular complex form a "propeller-shaped" undecameric water cluster from symmetry-induced tricyclic fused pentameric $(H_2O)_5$ units (O1–O5) around the protonated cryptand host in the solid state (Figure 2a). An ORTEP drawing of one water cluster is shown in Figure 2b. The two water molecules on the threefold axis (O1 and O5) create a fused pentameric unit, which translates into a discrete "propeller-type" arrangement of water molecules around the C_3 axis passing through O1 and O5.The symmetry-related fused pentamers in the $(H_2O)_{11}$ units are strongly held together by O−H···O interactions, with the O···O distance ranging from 2.745 to 2.777 Å (average: 2.761 Å) and the O···O···O angle from 102.03° to 111.20° (average: 106.6°). Ab initio investigations by Sathyamurthy et al. have shown that the most stable geometry for an 11-mer water cluster is a fused pentamer with the eleventh water molecule hydrogen-bonded to one of the corners. These authors also proposed a

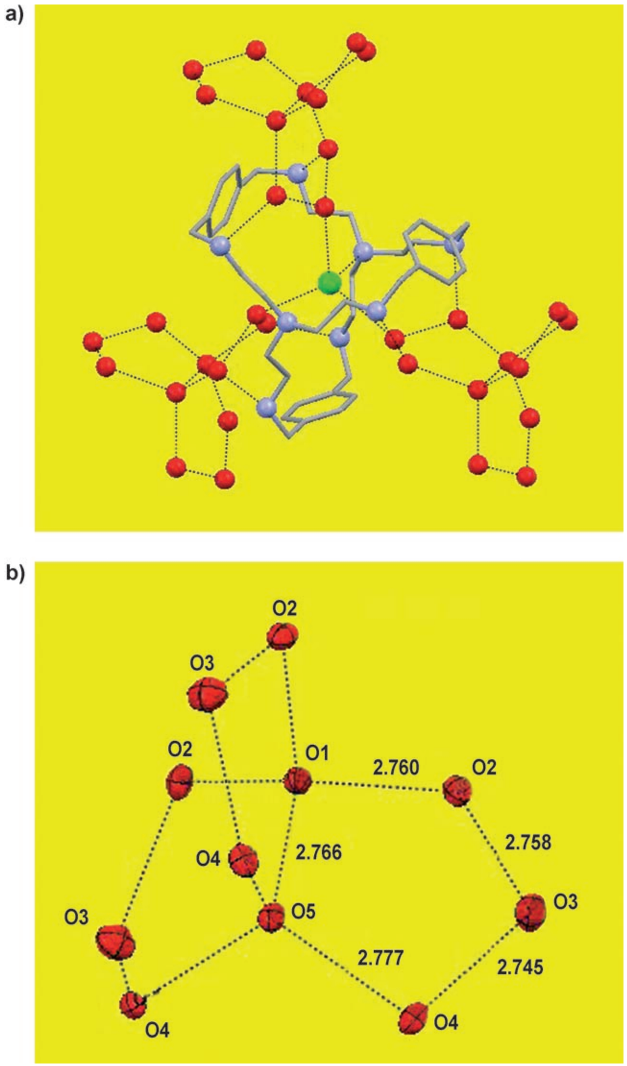

Figure 2. a) Anchoring of the encapsulated chloride (Cl3, green) inside the cryptand cavity by one N−H···Cl⁻ interaction and three O−H···Cl⁻ interactions; hydrogen-bonds are represented by dotted lines. C gray, N blue, O red. b) ORTEP diagram of the discrete $(H_2O)_{11}$ cluster. Hydrogen atoms are not depicted.

cuboid structure with a missing corner, which has a slightly higher energy than the fused pentameric structure.[18] However, our structural finding is of a discrete C_3 symmetric undecameric water cluster composed of three fused pentameric rings sharing a common edge. The difference between the theoretical prediction and our experimental finding may be due to the various hydrogen-bonding interactions of the water cluster with the cationic host moiety as well as with the surrounding anions, similar to the bound water in biological systems. We also believe that the symmetry of the host cryptand contributes to this unusual morphology of a discrete undecameric water cluster in the lattice.

The encapsulated chloride anion (Cl3) present inside the cryptand cavity forms strong N−H⋯Cl$^-$ and O−H⋯Cl$^-$ intramolecular interactions with the protonated apical amino hydrogen H4 and the water hydrogen H3C of the $(H_2O)_{11}$ cluster. Thus, the chloride anion within the cavity makes four contacts—one N−H⋯Cl$^-$ (N4⋯Cl3 3.059(3) Å; N4−H4⋯Cl3 180°) and three O−H⋯Cl$^-$ (O3⋯Cl3 3.253(2) Å; O3−H3C⋯Cl3 170°) intramolecular contacts—with the threefold symmetry-related $(H_2O)_{11}$ units, thereby extending the hydrogen-bonded supramolecular network (Figure 2a).

The hydrogen-bonding interactions of the undecameric water cluster with the surrounding organic moiety and chloride anion are depicted in Figure 3. The centrosymmetric water molecules O1 and O5 are only involved in O−H⋯O hydrogen bonding within the $(H_2O)_{11}$ cluster. In addition to the water cluster formation, O3 is also involved in hydrogen bonding to Cl3, as described earlier, whereas O2 and O4 are involved in one intramolecular O−H⋯Cl$^-$ interaction with Cl1 and Cl2, respectively, which lie outside the cryptand cavity, and one intermolecular N−H⋯O interaction with H31 and H22, respectively, of the amino nitrogens N3 and N2 of the surrounding cryptand moiety. Cl1 and Cl2, which occupy a position outside the cryptand cavity, form two strong C−H⋯Cl$^-$ and one N−H⋯Cl$^-$ intermolecular hydrogen bond with the heptaprotonated cryptand ligand. Details of these hydrogen-bonding interactions, along with their symmetry codes, are given in the Supporting Information. Thus, Cl1 and Cl2 also make four contacts (one intramolecular hydrogen bond with water hydrogens, two C−H⋯Cl$^-$ intermolecular contacts with methylene hydrogens, and one N−H⋯Cl$^-$ contact with the tertiary amino hydrogens of the cryptand).

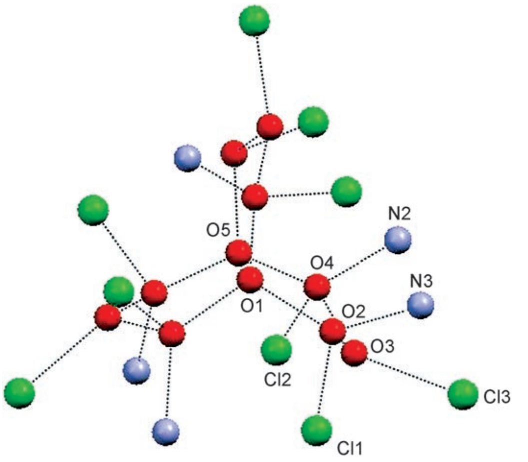

Figure 3. Interaction of $(H_2O)_{11}$ with the cryptand moiety and chloride ions.

Figure 4 shows the three-dimensional hydrogen-bonded supramolecular array involving the protonated cryptand moiety, the chloride anion, and the undecameric water cluster, along with several of their molecular interactions.

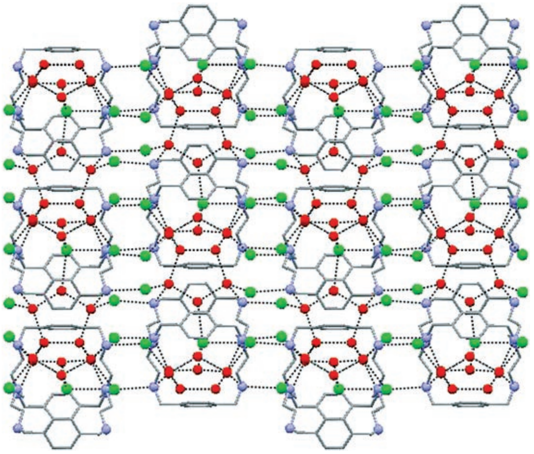

Figure 4. Packing diagram of **1**·$(H_2O)_{11}$ viewed down the *b* axis showing various inter- and intramolecular hydrogen-bonding interactions between the discrete $(H_2O)_{11}$ moiety, the chloride ions, and the amino nitrogens of the cryptand.

Thermal analysis of **1**·$(H_2O)_{11}$ shows that the first weight loss takes place in at 40–140 °C (13.62 %), corresponding to the loss of 7.94 molecules of water. The second weight loss starts at 150 °C and is completed at 260 °C (5.18 %), corresponding to a further 3.02 water molecules.[19] The total loss of 11 water molecules in these two steps can be attributed to the loss of the $(H_2O)_{11}$ cluster. Moreover, the removal of water molecules from the cluster at elevated temperature confirms that most of the water molecules have a strong interaction with heptaprotonated L and the chloride anions, as observed in the single-crystal X-ray studies.

The broad band centered around 3400 cm^{-1} in the FT-IR spectrum of **1**·$(H_2O)_{11}$ can be attributed to the O−H stretching frequency of the water cluster as it is similar to the stretching vibration of liquid water.[20] The IR spectrum of the same crystals after heating for six hours at about 140 °C under vacuum (0.1 mm) shows that the broad band has disappeared, thus suggesting the escape of the water cluster from the lattice. Powder X-ray diffraction studies on **1**·$(H_2O)_{11}$ before and after expulsion display changes in the diffraction patterns and intensities, which can be attributed to the complete breakdown of the host lattice upon exclusion of water.[19] This sample does not regain its original structure upon exposure to moisture, as determined by IR and TGA studies.

In summary, we have shown that the bound water in the lattice of a supramolecular host having cationic and neutral amine functionalities along with encapsulated and surrounding chloride anions has a discrete tricyclic $(H_2O)_{11}$ cluster morphology. This unique, discrete, propeller-shaped undecameric water cluster forms hydrogen bonds with both the host cryptand and surrounding chloride, and also forms strong hydrogen-bonding interactions with the chloride guest inside the host cavity. The present mode of stabilization of an undecameric water cluster morphology and its hydrogen-bonding interactions with the encapsulated chloride has not been predicted theoretically or reported experimentally.

Experimental Section

Compound L was prepared following a procedure reported previously and confirmed by ^{1}H NMR spectroscopy.[14] The complex **1**$\cdot(H_2O)_{11}$ was isolated from a methanol/water (4:1) solution of the white solid obtained upon addition of HCl to an acetonitrile solution of L. Colorless crystals suitable for X-ray analysis were grown by slow evaporation of this mixture at room temperature.

^{1}H NMR (200 MHz, D_2O): $\delta = 2.85$ (t, J(H,H) = 5 Hz, 12 H, NCH_2), 3.33 (t, J(H,H) = 5 Hz, 12 H, NCH_2CH_2), 4.30 (s, 12 H, $ArCH_2$), 7.49 ppm (s, 12 H, ArH). ^{13}C NMR (50 MHz, D_2O): $\delta = 45.2$ (NCH_2), 50.0 (NCH_2CH_2), 51.6 ($ArCH_2$), 130.4 (C_{Ar}), 132.4 ppm (CH_{Ar}). C,H,N analysis (%) calcd for $C_{36}H_{83}Cl_7N_8O_{11}$: C 41.09, H 7.95, N 10.65; found: C 41.25, H 7.68, N 10.57.

Crystal data for **1**$\cdot(H_2O)_{11}$ were collected at 100 K with a SMART APEX diffractometer equipped with a CCD area detector and a $Mo_{K\alpha}$ radiation source ($\lambda = 0.7107$ Å). A crystal was selected from the mother liquor, immersed in Paratone oil, and then mounted. Data collection, data reduction, and structure solution/refinement were carried out using the software package SMART APEX.[21] Graphics were generated with MERCURY 1.1.1.3.[22] Empirical absorption corrections were performed using equivalent reflections with the program SADABS. The structure was solved by direct methods and refined in a routine manner. Non-hydrogen atoms were treated anisotropically in all cases. Hydrogen atoms attached to the amino nitrogens and some of the water hydrogens were located from the difference Fourier map and refined isotropically. In other cases, the hydrogen atoms were geometrically fixed. We were unable to locate the hydrogen atoms of water molecules O1 and O5, which sit on the threefold axis, from the difference Fourier map. Crystal dimension: $0.32 \times 0.23 \times 0.17$ mm^3; $T = 100(2)$ K; hexagonal, space group $P6_3$; $a = b = 12.4720(4)$, $c = 21.2022(15)$ Å, $V = 2856.2(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.219$ g cm^{-3}, $\mu = 0.401$ mm^{-1}, $F(000) = 1116$, 16937 reflections collected of which 4480 were unique, 187 parameters were refined; $R_1 = 0.0318$, $wR_2 = 0.0880$; max./min. residual electron density 0.500/-0.217 e Å^{-3}. CCDC-295431 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.

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