Regulated Formation of 2D Water Layers with Alternating Six-membered Quasi-planar and Chair Cluster Units by 1D Supramolecular Chain

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Crystals of 4-methylamino-6-oxopyrimidine (**1**) grown from aqueous alcohol were found to contain 2D water layers consisting of hexameric water clusters with alternating quasi-planar and chair conformations, which are apparently regulated by interactions with the supramolecular aggregate of $\mathbf{1}_n$ through hydrogen bonds.

Research to better understand water behavior has focused particular attention on water clusters in a variety of phases of ices, liquid water, and biomolecular hydrates and on connecting the structure of the various cluster types with their observed properties.[1] The advantage of this approach is that quantitative information about the local interactions between the water molecules can be obtained.[2] Connections among water clusters produce low-dimensional water clusters, in particular, the 2D water layers,[3–6] which consist of the edge-shared water hexamer,[7,8] are useful in that their structures can be related to ices or to theoretical models.[9] Now these 2D water layers can be formed as all-chair,[3] all-boat,[4] chair–boat,[5] or intermediate conformations[6] by varying the host environments in which they occur. However, little is known with regard to how low-dimensional water clusters link together to form 3D network structures by hydrogen bonding. Since such 2D water arrays have usually been observed in the crystal of the suitable host, it is important to investigate the interactions between the 2D water layer and the host molecules. Here, we report the characterization of a regulated 2D water layer, having the six-membered quasi-planar and chair cluster units, and we show the interaction of these structures spread across a self-assembled host molecule.

We chose 4-methylamino-6-oxopyrimidine (**1**)[10] as a basic unit for a supramolecular aggregate, because the molecule **1** has two hydrogen-bonding donor (D) sites and three acceptor (A) sites and was assumed to be self-assembled by cooperative intermolecular hydrogen bonds (Figure 1a).

Upon recrystallization from aqueous ethanol, the compound **1** gave colorless plates which contained two molecules of water, as revealed by X-ray crystallography (Figure 1b).[11] As we hoped, the molecule **1** was paired with itself by the N2–H1···O1 (2.751 Å) hydrogen bonding to form a centrosymmetric dimer. The dimer was further connected with the other dimer pairs by the N1–H2···N3 (2.944 Å) hydrogen bonding, resulting in an infinite 1D chain (Table 1S).[12]

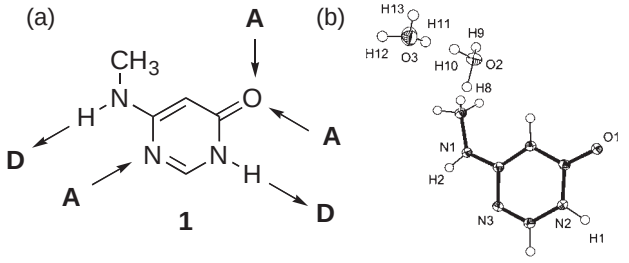

Figure 1. (a) Schematic representation of the hydrogen-bonding sites of **1**. (b) The ORTEP representation of $\mathbf{1}\cdot 2H_2O$ with the selected numbering scheme.

On the other hand, the two water molecules in the asymmetric units were attached by the disordered protons H9, H10, H11, and H13, each with an occupancy of 0.5, and were connected to each other by hydrogen bonding (Table 1S).[12] However, these two water molecules in the crystal actually formed a distorted honeycomb 2D structure via the hydrogen-bonding network.[13] We found that the 2D water layer consisted of the two six-membered water clusters, quasi-planar ring A and chair B, which were aligned alternately parallel to the crystallographic *b* axis (Figure 2a). The quasi-planar ring A is comprised of two O2 atoms and four O3 atoms, and the reverse is true for the chair ring B. The averaged O2–O3 distance (2.87 Å) in the six-membered water clusters was found to be close to that in liquid water (2.85 Å) rather than that found in the hexagonal ice I_h (2.76 Å).[1] In the quasi-planar ring A, the average of the O–O–O angle (118.4°) was somewhat larger than the value of 109.5° for the tetrahedral angle found in ice I_h,[1] and the two O2 atoms were out of the mean plane of the four O3 atoms by 0.55 Å (Figure 2b). In the chair ring B, one of the O–O–O angles was significantly narrower (97.8°) than the other O–O–O angles (119.3–122.2°) (Figure 2c).

Since the edge-sharing oxygen atoms in 2D water are subjected to three-centered hydrogen bonding with neighboring waters, the question arises as to the nature of the hydrogen-bonding connectivity motif. Therefore, we analyzed the location of

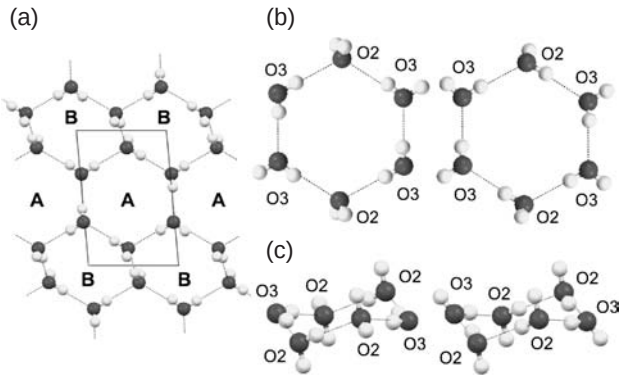

Figure 2. (a) Viewed along the crystallographic *c* axis and showing the two independent rings, A and B, which are alternatively aligned in the 2D water layer. Dashed lines represent the hydrogen bonding. (b) The water cyclic hexamer of the quasi-planar A and (c) chair B, adopting the two different hydrogen-bonding motifs.

the disordered protons in detail. Because of a half occupancy of protons, the two different hydrogen-bonding motifs are present in ring A and ring B, respectively. In one motif, the hydrogen atoms of the two O3 water molecules act as double hydrogen-bond donors, and the lone pairs of O2 atoms as acceptors (left side of Figures 2b and 2c). In another motif, the six-membered rings are connected in a clockwise or a counterclockwise manner through single donor and acceptor water molecules (right side of Figures 2b and 2c).

To the best of our knowledge, the O–H stretching frequencies in honeycomb-like 2D water layers have not been reported. In the present case, we were fortunate enough to locate the bands by the comparison of the IR spectrum between $\mathbf{1}\cdot 2H_2O$ and anhydrous **1**. The crystals of $\mathbf{1}\cdot 2H_2O$ showed a broad band centered at 3386 cm^{-1} with a shoulder band around 3474 cm^{-1} which was absent in anhydrous **1** (Figure 1S).[12] The former band is close to the O–H stretching band for cyclic water hexamers in the He droplets[7] and in the solid parahydrogen matrix,[8] appearing at 3335 and 3319 cm^{-1}, respectively. On the other hand, the latter shoulder is near the O–H stretching band for liquid water at 3490 cm^{-1}.[1]

The self-assembled 1D chain structure of $\mathbf{1}_n$ is stacked with neighboring chains that are separated by 3.26 Å. The supramolecular aggregate of $\mathbf{1}_n$, therefore, appears to regulate 2D water layers by exposing the polar carbonyl groups and the hydrophobic methyl groups to the water molecules. Specifically, the hydration sites of the molecular aggregate $\mathbf{1}_n$ act as a template with a 2D regularity, and the two 2D water layers are separated from each other by a distance of 10.4 Å created by the supramolecular aggregates $\mathbf{1}_n$ (Figure 3). Notably, the two contrary interactions, hydrophilic and hydrophobic, were observed by forming O2–H8···O1 (2.72 Å) and three C–H···O (2.67–2.71 Å) hydrogen bonds. Further support for the interactions between the intercalated $\mathbf{1}_n$ and the water layers are provided by FT-IR spectroscopy (Figure 1S).[12] Upon dehydration, the carbonyl stretching band for **1** shifted from 1624 to 1639 cm^{-1}. The hydrogen-bonded N2–H1 stretching frequency was reflected by its shift to a lower frequency, from 2684 to 2672 cm^{-1}. Significantly strong interactions of the regulated hydration also came from the stability of the crystals. The water molecules in $\mathbf{1}\cdot 2H_2O$ did not show any sign of loss at room temperature as judged by TG and DSC analyses (Figures 2S and 3S).[12] As the temperature was raised, the water was gradually released from 93 to 125 °C, with the total weight loss of 22.4% corresponding to 2 molecules of water.

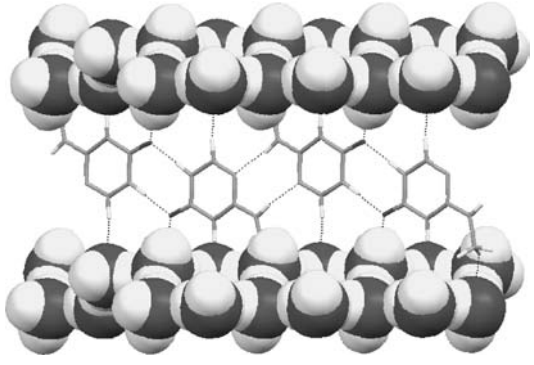

Figure 3. Viewed along the crystallographic *b* axis and showing the intercalation of the supramolecular chain of $\mathbf{1}_n$ between two 2D water layers. Dashed lines represent the hydrogen bonding.

In summary, we have shown the supramolecular association of 2D water layers with the self-assembled $\mathbf{1}_n$. The structures and OH vibrations of the observed 2D water layers more closely resemble liquid water than ice when their properties are related to those of hexameric water clusters. The regulated hydration at both hydrophilic and hydrophobic interfaces in $\mathbf{1}_n$ may serve as a model for other phenomena, such as water surfaces and macromolecule hydration.

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11 $\mathbf{1}\cdot 2H_2O$: Anal. Calcd for $C_5H_{11}N_3O_3$: C, 37.26; H, 6.88; N, 26.07%. Found: C, 37.31; H, 6.82; N, 26.14%. Crystal data: $C_5H_{11}N_3O_3$, $M_r = 161.16$, triclinic, $P\bar{1}$ (no. 2), $a = 4.9585(3)$, $b = 7.5475(4)$, $c = 10.443(1)$ Å, $\alpha = 83.622(4)$, $\beta = 87.979(3)$, $\gamma = 84.641(2)°$, $U = 386.58(5)$ $Å^3$, $Z = 2$, $T = 113$ K, $D_{calcd} = 1.384$ g cm^{-3}, μ (Mo Kα) = 1.14 cm^{-1}, $2\theta_{max} = 55.0°$, 3422 reflections collected of which 1707 were unique, 152 parameters, GOF = 1.83, $R_1 = 0.039$ ($I > 2(\sigma)I$), $wR_2 = 0.121$ ($I > 2(\sigma)I$). CCDC 615777.
12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
13 According to classification of water aggregates,[14] the observed motif is classified as L6(6)6(6). Professor M. Mascal searched for this class of water aggregates in the CSD and found eleven matches. CSD refcodes are as follows; BIKVIA10, BUSJII, ECOVAT, EKETET, FUMVIS, HOSHIG, IMIPID, SUGBAX01, WINGBIG, ZUXBUP, and ZUXBUP01. However, the observed conformations of the water hexamer are different from all eleven structures.
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