"Compressed" Icelike Structures between Molecular Films Comparable with Ice Phase III

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An icelike supramolecular structure is found in a self-assembled quasi 3-D crystalline hydrate in-between the layers of Cu^{II} tris(pyridylthio)methyl hydroxide complexes, which is comparable with compressed pure ice III.

Water changes its structure depending on the confining circumstance as in the limited space, biological channels, and on the surface of substances.[1–3] Such polymorphs are essential to the assembly of water molecules which controls the nature of its existence in the particular environment. To understand such behavior of water, many have attempted to elucidate the properties and structures in constrained phases separated by interfaces.[1,2,4,5] The structural investigation of discrete water molecules in organic/inorganic crystalline hydrates provides a direct aspect into the networks of water molecules with the surroundings. They have been found in a discrete water hexamer,[6] infinite 2-D layered water clusters of $(H_2O)_{45}$,[7] $(H_2O)_{12}$ rings in a 2-D supramolecular icelike layer,[8] a 2-D water cluster[9] (and many clathrates),[10] and an ice layer.[11]

Recently, we found 2-D clathrate hydrates and 2-D water sheets sandwiched by the layers of copper complexes of [CuF(tptm)] (tptm = tris(pyridylthio)methyl) in a supramolecular structure.[12,13] The structure is constructed with a strong hydrogen-bonding interaction, concerted with a π–π stacking between the complexes and weak van der Waals interactions of the sulfur atoms between the layers of the complexes.

Here, we report the crystalline hydrate of $2[Cu(OH)(tptm)]\cdot 13H_2O$ forming a massive icelike structure, which resembles the ice III phase, sandwiched by layers of copper complexes (Figure 1).[14]

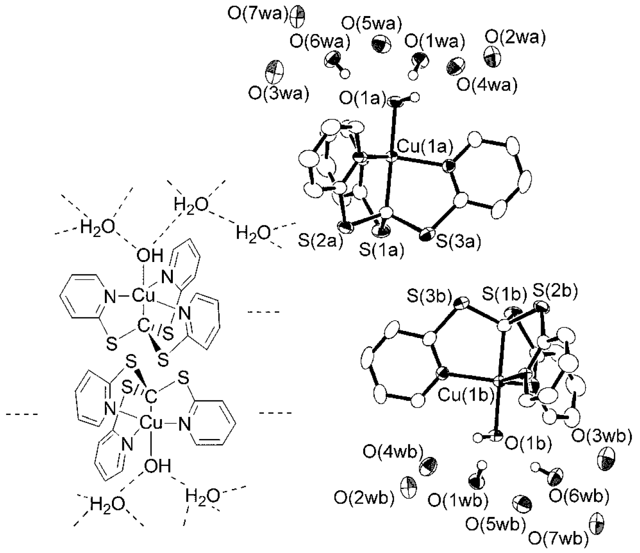

Figure 1. Schematic representation and ORTEP drawing of $2[Cu(OH)(tptm)]\cdot 13H_2O$. Two independent copper complex molecules and thirteen water molecules exist in the asymmetric unit. The hydrogen atoms of the complexes are omitted for clarity. The hydrogen atoms of the water molecules could not be located because of the positional disorder due to the crystallographic symmetries.

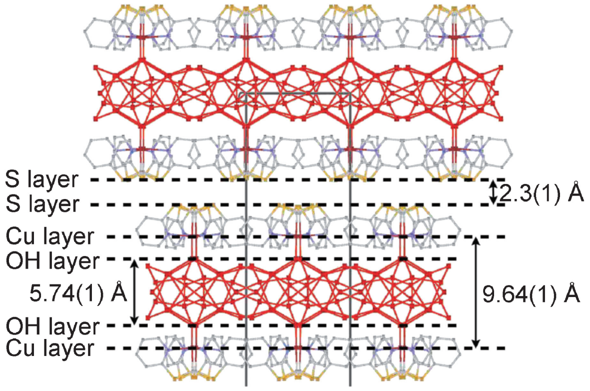

Figure 2. Crystal structure of $2[Cu(OH)(tptm)]\cdot 13H_2O$ viewed along the *a* axis. Atoms are represented by colors: oxygen (red), copper (brown), sulfur (yellow), carbon (white), and nitrogen (blue).

Water molecules and the hydroxide ligands of the copper complexes are hydrogen-bonded resulting in the formation of sheet structure sandwiched by 2-D arrays of copper complex molecules (Figures 2 and 3). Both sheets of the copper complexes and water molecules are extended parallel to the (001) plane, and they are stacked perpendicular to the (001) plane to form an infinite layered structure. Although each sheet of the copper complexes contains only one of the two crystallographically independent complexes, the sheets are almost identical. Three pyridine rings in each copper complex are stacked with pyridine rings of the neighboring complexes in the same sheet in face-to-face and/or edge-to-face fashions.[15]

Water molecules are sitting in-between the planes formed by the OH ligands coordinating to the copper atoms.

All water molecules are connected by hydrogen bonding to form the quasi 3-D network while [CuF(tptm)] constructed the 2-D network with water molecules, in which each axial F ligand was connected to O atoms via two H atoms. The array of the water molecules resembles icelike structure with five- and six-membered rings in the network, which is different from that of ice I_h but resembles ice III[16] (Figure 3, left). Consequently, the hydrogen-bonded O···O distances of the water molecules ranged

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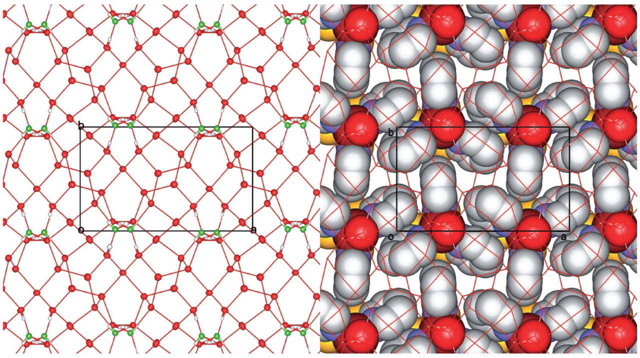

Figure 3. Hydrogen-bonding network: the oxygen atoms of the water molecules and the hydroxide ligands are represented by red and green, respectively (left), and the 2-D array of copper complex molecules (right).

between 2.636(3) and 2.841(4) Å (2.77(5) Å average), and the O···O···O angles are in the range of 85.46(13) to 147.2(16)°, which are comparable to those in ice phases under high pressure (Table S1).[17] The density of water molecules in-between the complex sheets is estimated to be ca. 1.1 g·cm^{-3}, indicating that the water molecules are thickly packed similar ice III (Figure S1).[17]

The aggregated water molecules are held by the OH ligands which are located in the (001) plane at regular intervals of 7.757(4) and 9.031(4) Å along the *a* and *b* axes, respectively. In the interfacial region away from the OH ligands in the layer, the C–H groups of the pyridine rings in the tptm ligands, which stand nearly perpendicular to the plane of the 2-D sheet, have hydrophobic interaction with the water molecules (Figure 3, right). The closest distance of the carbon atom in the pyridine ring to the water oxygen atom $C_{Py}H \cdots O_{water}$ is 3.280(6) Å for C(5a)···O(3wa). In-between these interfacial regions, the water molecules aggregated together forming a [5^4,6^2] minimum water cluster, which are also supported by the OH ligand in the sheets of the complexes.

The structural features of the water layer are quite similar to a molecular dynamic simulation performed by Debenedetti and co-workers.[4] They predicted a crystalline phase between hydrophobic walls with a 6 Å separation and 0.5 GPa or more. In our case, the distance between the walls defined by the O atoms of the hydroxide ligands on the complexes is 5.74(1) Å and the walls have large hydrophobic area formed by the pyridine rings of the tptm ligands. From this similarity to the ice phase III, the pressure to the water phase in the crystal of the hydrated copper complex can be estimated to be 0.5 GPa, and the formation of the icelike water clathrate is attributed to this "Hydrophobic Wall" pressure. Such phenomena were observed and reported also in aquaporin[3] and on a precious metal surface such as Ru.[5]

The positions of the hydrogen atom of the OH ligand and one of two hydrogen atoms of each of the two water molecules just around the OH ligand were determined by X-ray crystallography from the differential Fourier maps (Figure 1). The hydrated copper complex with three adjacent water molecules can be reproduced by DFT calculation, which represents the orientation of water molecules around the OH ligand.[17] However, in the crystallographic analysis, the positions of the other hydrogen atoms of the water molecules are disordered, and no peaks were found because of the crystallographical symmetries and, therefore, can not be determined. Based on the determined hydrogen atoms, some sets of orientations of the other hydrogen atoms of the water molecules are logically determined. This feature of the aggregated water molecules is similar to the nature of ice III,[16] i.e., the orientation of the hydrogen atoms cannot be identified.

In summary, an icelike supramolecular structure was found in a self-assembled quasi 3-D crystalline hydrate, which is comparable with the compressed pure ice phase III. Possibly, a pressure-like effect is produced by the stacking of the water layer between the hydrophobic interfaces constituted of the pyridine groups of the tptm ligands. By the hydrogen bonding, the copper complexes and water molecules are aggregated, self-assembled, and layered with the help of the hydrophilic/hydrophobic interactions, the van der Waals interaction, and the π–π interaction between the copper complexes. These results provide useful information to interpret the interactions of water molecules on the surface at interfacial regions in biochemical systems.

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Published on the web (Advance View) March 21, 2009; doi:10.1246/cl.2009.366