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Discrete cubic water cluster: An unusual building block of 3D supramolecular network

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ABSTRACT

A unique discrete octameric cluster of lattice water molecules in the lattice voids produces a 3D supramolecular architecture through hydrogen bonding interactions. These cubic water clusters have not been structurally documented so far and illustrate new modes of supramolecular association of water molecules.

Water is the most significant chemical ingredient of the planet's surface, and has been extremely essential for the genesis of life on the earth [1]. The structural elucidation of water clusters in diverse environments is the key to gain insight into the nature of water–water interactions. Water clusters $(H_2O)_n$ are omnipresent in nature and play a significant role in the stabilization of supramolecular systems both in the solution and in the solid state for a better understanding of the interactions of water aggregates and their surroundings [2]. Small water clusters have been extensively studied both theoretically and experimentally since they can lead to an understanding of the structure of bulk water along with its anomalous behavior [3]. The water cluster is included as an indispensable part of the structure in some cases, such as crystalline water, and coordination water [4]. A variety of water clusters with odd numbers [5], even though trimers [6], and pentamers [7], are familiar in crystal hydrates and even numbered clusters like tetramers [8], hexamers [9], octamers [10], decamers [11], dodecamers [12], tetradecamers [13], hexadecamers [14], octadecamers [15] and icosadecamer [16] are well-known. According to a simple two-structure model for liquid water, cubic-shaped water octamers can dissociate into cyclic water tetramers, which appear to be the principal species present in liquid water. The features of water aggregates still have been inadequately understood for researchers due to its delicate nature. Most water clusters are obtained occasionally, and the construction of water clusters is still a challenging scientific venture, since it is complicated to envisage the shapes and structures of the water clusters in various surroundings [17].

Intermolecular interactions between water molecules within the cluster and surrounding ions play a pivotal role in building the stabilized packing motifs. Recently, Vittal and co-workers show that the water cluster can be sustained by weak interactions with BF_4^- and ClO_4^- [18]. The interactions between the anions with water aggregates are very rare though a few anion–water clusters are reported in the literature [18,19]. This communication reports a unique cubic water cluster which plays a crucial role in building a three-dimensional supramolecular architecture.

Slow evaporation of aqueous solution of $CuCl_2$ and 4-(dimethylamino)pyridine [DAP] in a 2:1 molar ratio afforded blue crystals with the composition $[Cu(DAP)_4]Cl_2\cdot 2.5H_2O$, (**1**) as indicated by X-ray diffraction and elemental analysis. X-ray crystallography (Crystal data and structure refinement parameters are given in Table S1) reveals that the Cu1 adopts octahedral coordination geometry in which two Cl atoms stand at the apical positions and four pyridine ring nitrogen atoms comprise the equatorial plane. In the molecular moiety, the pyridine ring nitrogen atom (N1) lies on an inversion center $(x - y, -y, -z + 1/2)$ to complete the octahedral $Cu\{N_4Cl_2\}$ geometry with 2.5 solvent water molecule in the asymmetric unit (Fig. S1). The crystal packing of the title complex is stabilize through O–H···Cl, O–H···O, C–H···Cl and C–H···O hydrogen bonding interactions (Table S2). The most surprising feature in the title complex is the formation of hydrogen-bonded discrete water cluster (Fig. 1). The structure was found as the discrete cubic cluster, in which the two water molecules (O1 and O1*) occupy opposite vertices of the cube. The striking feature of this cluster is that each water molecule situated at the vertices connects with three water molecules and every water molecule is linked by one of the two vertices of water molecule along with another two H_2O via hydrogen bonds (Fig. 1). Each hydrogen atom of the two vertices of water oxygen atoms (O1 and O1*) is along the edge of the cube, so that they can entrap the rest of the six water molecules to complete the discrete cluster. Surprisingly, each

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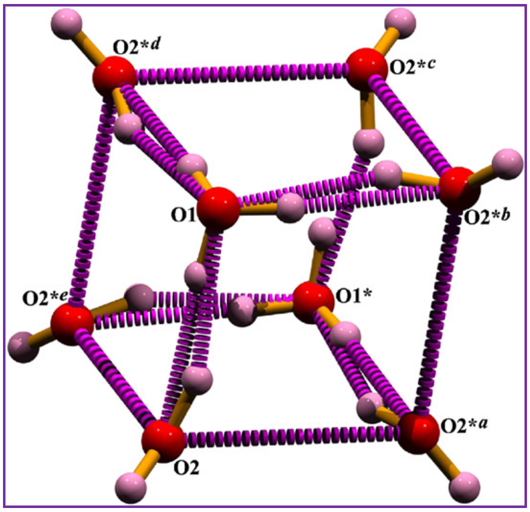

Fig. 1. View of the octameric cubic water cluster in **1**.

water molecule recognizes themselves by dual self-complementary hydrogen bonding interactions along the edges of the cube. The O···O separation distance within the octamer ranges from 2.744(2)Å to 3.011(3)Å with an average value of 2.875(2)Å, which is longer than the value in ice I_c (2.75 Å) and ice I_h (2.759 Å) [20], but can be compared with the corresponding values observed in liquid water (2.854 Å) [21]. The O···O···O bond angles in the octamer lie in the range from 79.29(12)° to 106.38(15)°, with an average value of 88.34°, which is different from the preferred ideal tetrahedral angle found in ice I_h and I_c [22].

In the solid-state, the solvent water oxygen atom O2 in the molecule at (x, y, z) acts as a donor to the partner water oxygen O1, again this O1 atom acts as a donor to O2 in the molecule at (−x + y, 1 − x, z), so generating a $R_2^2(4)$ dimeric ring (Fig. 1) which can be represented by the graph set notation $D_1^1(2)D_1^1(2)R_2^2(4)$ [23]. These ring motifs are generated in between (O1 – O2), (O1 – O2^{*b}), (O1 – O2^{*d}) (O1* – O2^{*a}), (O1* – O2^{*c}) and (O1* – O2^{*e}) (Fig. 1). The solvent water oxygen atom O1 placed at the vertices of the discrete cube in the molecule at (x, y, z) acts as a triple donor to three water oxygen atoms (O2, O2^{*b}, O2^{*d}) of the vertices in the molecule at (−x + y, 1 − x, z), so forming a discrete cubic water cluster. Similarly another oxygen atom O1* connects the O2^{*a}, O2^{*c} and O2^{*e} to complete the novel cubic framework (Fig. 1). This discrete cluster reflects the anomalous nature of water due to the flexible hydrogen bonds. Within the aggregation, each water molecule (O1 and O1*) is involved in six hydrogen bonds, giving a total of 12 hydrogen bonds. The overall supramolecular build-up of the water cluster is the result of the self-assembly through multidirectional self-recognition between the water molecules (Fig. 1). Within this self-assembled cubic water framework, six solvent water oxygen atoms O2 in the molecule at (x, y, z) act as a donor to the metal coordinated Cl atoms of the molecular moiety at (2/3 − x + y, 1/3 + y, −1/6 + z). On either side of the metal center, another Cl atom is acting as an acceptor to the lattice water atom O2 of the cubic water cluster, so forming a three-dimensional network in the title complex (Fig. 2). The molecular architecture viewed down through *c*-axis has been depicted in Fig. 2 where the cubic water cluster (inset of Fig. 2) has been sustained by a weak interaction with Cl^- ion. This multi-way self-recognition has been facilitated by an active participation of O – H···O and O – H···Cl halogen bonds which leads the complex into three dimensional supramolecular network structure (Fig. 2). The schematic presentation of this unique supramolecular framework has been depicted in Fig. 3, where it has been clearly visible how the water molecules aggregate themselves through self-complementary interaction within the hexagonal metal centers by binding the Cl atoms. It is also clear from Fig. 3 that the water clusters are well-trapped in isolated cavities surrounded by the six metal coordinated anions which are again surrounded by the six cations. Fig. 3 shows the orthogonal projection of the coxeter plane of cubic water cluster instead of tilted vertex views. The orthogonal projection of the cubic cluster sustained by weak interactions with Cl^- ions is depicted in the inset of Fig. 3.

Again, this water cluster plays a very crucial role in building another 3D assembly of the title structure. The vertex water oxygen atom O1 now acts as an acceptor in the molecule at (x, y, z) to the methyl carbon atom C6 in the molecule at (x, −1 + y, z), so the O1 atom is juxtaposing by three partner molecules through C6 – H6B···O1 hydrogen bonds. Another O1 atom situated along the diagonal also acts as a triple acceptor through the weak C6 – H6B···O1 hydrogen bonds, so generating another

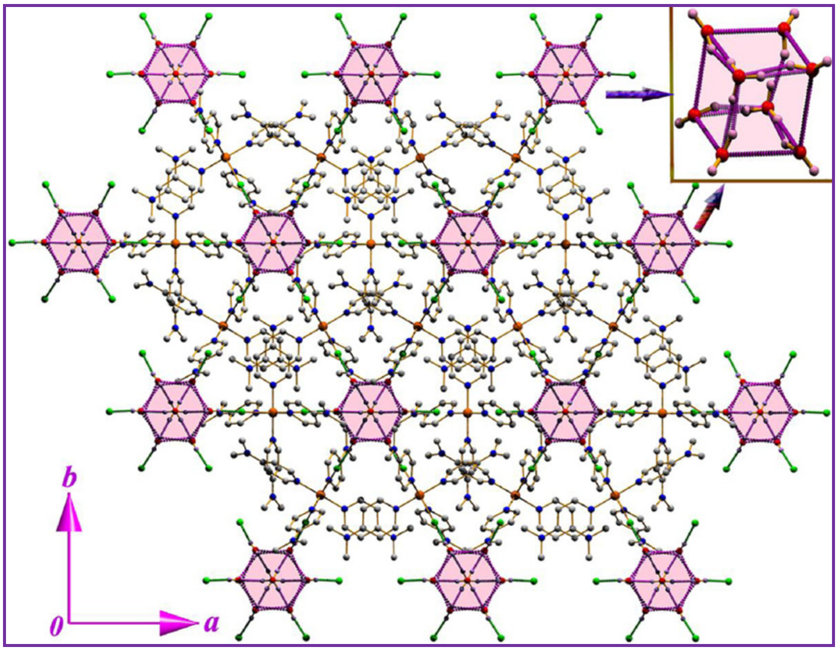

Fig. 2. Perspective view of the 3D supramolecular framework generated through the unique water cluster. Inset: Tilted view of the cubic water cluster.