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A Large Protonated Water Cluster $H^+(H_2O)_{27}$ in a 3D Metal−Organic Framework

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Due to the fundamental importance of ubiquitous protonated water (the aqueous acids) in chemical and biological systems,[1−4] $H^+(H_2O)_n$, a microscopic model system of protonated water, is among the most thoroughly explored cluster ions for understanding the molecular structure of the hydrated protons, proton migration in liquid water, as well as the transfer of proton through a protein embedded in membranes[5,6] since it was found by mass spectrometry.[7] The advantage of water clusters is the possibility to obtain precise structural data of hydrogen-bonded simulations in diverse environments with various sizes.[8] This realization has led to the upsurge in vibrational spectroscopies for studying protonated water clusters $H^+(H_2O)_n$, with n from 6 to 27,[9,10] and in laser spectral evolution for directly monitoring the proton accommodation motif $H^+(H_2O)_n$, with n from 2 to 11.[11] Since the distinction of structural variation of larger protonated water clusters ($n > 20$) is beyond the scope of the vibrational spectroscopic precision,[8−10] we think that crystallographic structural studies of the large proton hydrate clusters stabilized in the lattices of crystal hosts, rather than the spectroscopic investigations, should provide much more detailed information characterizing these intriguing and important clusters.

Metal−organic frameworks (MOFs) have emerged as a promising new class of materials that often have crystalline, well-defined cavities (or channels) and can be used for including various guest species.[12−15] Until now, a number of neutral water oligomers, including discrete rings and clusters,[16−19] have been well-studied by X-ray diffraction methods. However, the design of the MOFs that can act as the hosts of the nanometer-sized cage structures of $H^+(H_2O)_n$ with a hydrated proton core embedded inside[9,10] is still a big challenge. Fortunately, we successfully used a globular Keggin structure $[PW_{12}O_{40}]^{3-}$ anion as a template[20] to obtain a new three-dimensional (3D) metal−organic porous framework (see Supporting Information Figure S1) in which a proton hydrate cluster $H^+(H_2O)_{27}$ was trapped.

Reaction of $CoHPW_{12}O_{40}\cdot nH_2O$ with 4,4′-bipyridine-*N*,*N*′-dioxide (dpdo) in acetonitrile/water solution gave compound **1**, $[Co_4(dpdo)_{12}][H(H_2O)_{27}(CH_3CN)_{12}][PW_{12}O_{40}]_3$ (see Supporting Information), which was a 3D non-interwoven framework (Figure 1) with cubic cavities occupied by the anions and water clusters.[21] Each cobalt ion occupies a special position and is bound by six identical dpdo ligands in an ideal octahedral geometry (see Supporting Information Figure S1). Despite the fact that the Co⋯Co separations (11.58 Å, half of an axial length) in the three directions are equal, the windows of the cubic cavities seem to be rectangular because the N(1)−O(9)−Co(1) angle is 120°. The diameter of a Keggin structure $[PW_{12}O_{40}]^{3-}$ anion (about 10.4 Å) fits the cubic cavity well, which avoids interpenetration and gives a porous structure for compound **1**. Because a template anion $[PW_{12}O_{40}]^{3-}$ is trivalent and a Co-based cubic cavity $Co(dpdo)_3$ is divalent, not all the cavities are filled by the anions. X-ray analysis clearly shows that three-quarters of the cavities are occupied by $[PW_{12}O_{40}]^{3-}$ anions, and the remaining one-fourth are inhabited by water clusters. In one unit cell, two water clusters occupy the vertexes and body-centers, and the six $[PW_{12}O_{40}]^{3-}$ anions are positioned at the centers of twelve edges and six faces. Because, in such a crystallization condition, the protonation of the surfaces of a Keggin structure $[PW_{12}O_{40}]^{3-}$ anion is impossible,[22,23] the water clusters thus are protonated to maintain the neutrality of the whole crystal. Twelve acetonitrile molecules dangle around the cluster via twelve N⋯H−O(water) hydrogen bonds (see Supporting Information Figure S4) and act as pillars between the framework and the water clusters. It is suggested that the acetonitrile molecules play an important role in stabilizing the water clusters by linking the water molecules with the heavy "building stones" $[PW_{12}O_{40}]^{3-}$ anions.

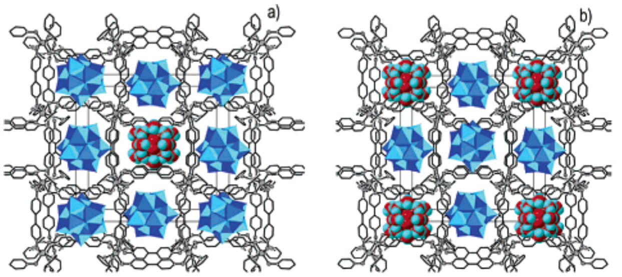

Figure 1. Packing diagram of compound **1** along the *c* axis showing the cubic molecular boxes as hosts containing polyanions (polyhedrons) and the protonated water clusters $H^+(H_2O)_{27}$ (space-filling) near A (002) and B (001) faces, respectively. Molecules in a crystal packed as ⋯ABABAB⋯ fashion. Acetonitrile molecules and hydrogen atoms were omitted for clarity.

It is especially interesting to note that the water cluster can be seen as two parts, a 26 water shell $(H_2O)_{26}$ and a monowater center, which act as a "host" and a "guest", respectively (Figure 2). In the $(H_2O)_{26}$ shell, eight O(2W) centers and twelve O(1W) centers are linked together featuring a hexahedral $(H_2O)_{20}$ cluster with each face being an octagonal water ring $(H_2O)_8$ (see Supporting Information Figure S3). Six O(3W) centers, which are disordered into twelve positions, occupy the six faces of the $(H_2O)_{20}$ hexahedron and bond to O(1W) via H-bonds. The chair-like hexagonal O(1W)−O(2W)−O(1W)−O(2W)−O(1W)−O(3W) ring is quite similar to those of cubic ice *I*c and has been reported as a building block in many forms of ice and relevant liquid.[24,25] It should be noted that such a special geometry comes from the pentagonal dodecahedra, one of the most stable water clusters,[26,27] of which each O⋯O hydrogen bond [O(1W)⋯O(1W)] of the pentagonal rings is broken by inserting a disordered water molecule O(3W) and the volume of the water shell is enlarged. As a result, the

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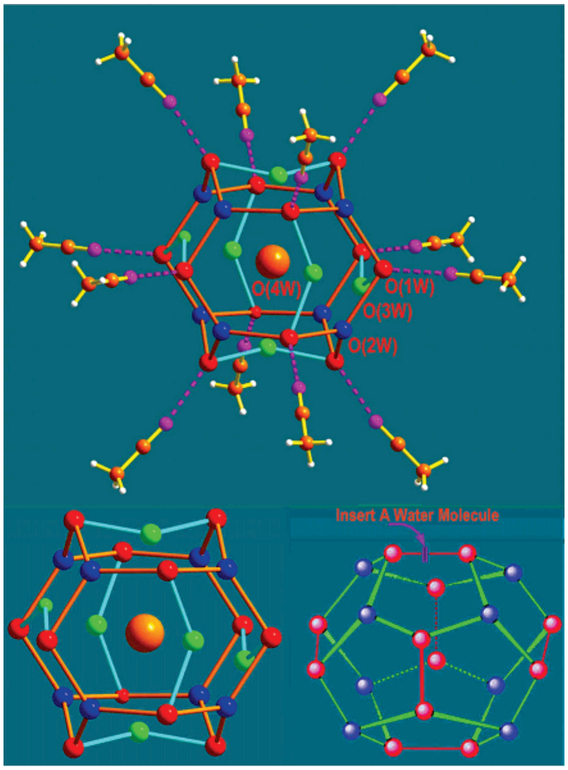

Figure 2. Perspective view of the [$H^+(H_2O)_{27}(CH_3CN)_{12}$] cluster (upper), showing the molecular ice shell $(H_2O)_{26}$ formed by O(1W) (red), O(2W) (blue), and O(3W) (green), and the monowater center O(4W) (orange). Selected O···O separations (Å): O(1W)···O(2W) 2.74, O(1W)···O(3W) 2.64, O(3W)···O(4W) 3.57, O(2W)···O(4W) 3.97, N2···O(1W) 2.81. The framework of oxygen atoms of the $H^+(H_2O)_{27}$ cluster and the sketch map showing the insertion of a water molecule within an O−O hydrogen bond of the ideal pentagonal dodecahedron shell (bottom).

hexagonal ring, the most common building block in ice[28] and bulk water,[29] substitutes the pentagonal ring. Thus, the $(H_2O)_{26}$ shell with O_h symmetry is of particular interest as it simulates the water−water interactions and the properties of both condensed phase (such as bulk water and ice) and gas phase (such as small isolated water clusters).

Though the basic structure of the water cluster can be determined easily according to the result of the X-ray structure analysis, the X-ray structure is not refined at a level that can isolate the position of the hydrogens, and therefore it cannot identify the position of the proton; that is, though charge neutrality requires the water clusters to be protonated, it is not clear whether the proton sits in the interior or on the surfaces of the water shell. Considering the most rational distribution of charges in the solid-state structure of **1** with the cubic symmetry, it is suggested that the excess proton might be positioned in the center and occurs in the context of the H_3O^+ (Eigen) form of a hydronium ion.[30] A conformation calculation based on the B3LYP/6-31g** method with the positions of oxygen atoms fixed suggests that the excess proton resides inside the clathrate structure (see Supporting Information).

In a summary, a three-dimensional porous metal−organic cationic framework was assembled, in which a protonated clathrate hydrate $H^+(H_2O)_{27}$ was captured and stabilized. The structural characterization of a large protonated water cluster is significant because it provides an opportunity to characterize these intriguing clusters in much greater detail in the future through fine techniques. The result of the X-ray diffraction study and the calculation both suggest that the excess proton is positioned in the center; in other words, the center core of the protonated water cluster is an Eigen $(H_3O)^+$ model of a hydronium ion.

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Supporting Information Available: Synthetic details, spectroscopy data (PDF), the Gaussian calculation, and X-ray structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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