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Crowned Tetrameric Spirocyclic Water Chain: An Unusual Building Block of a Supramolecular Metal−Organic Host

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ABSTRACT: A 3D supramolecular metal−organic host could be realized in solid in which the water assembly as a whole acted as a building block of the 3D framework with rectangular channels where guest molecules reside, adding a new dimension to water cluster research where the role of water has been shifted from its usual behavior of guest to that of a host. The crystal structure of the compound, $\{[Cu(mal)_2](picH)_2{\cdot}5H_2O\}_n$, **1** [mal = malonate dianion, picH = protonated 2-amino-4-picoline], synthesized from purely aqueous media, shows that the Cu(II)−malonate 2D coordination polymeric sheets are locked together by the water assembly that lines up perpendicular to the Cu(II)−malonate sheets constituting a 3D infinite supramolecular host where within the channels protonated 2-amino-4-picoline auxiliary ligands are accommodated. A spirocyclic tetrameric water chain having a dimeric crown on it describes the composition of the water assembly that runs down the *c*-axis.

Water, an elixir of life on our planet, is ubiquitous and covers two-thirds of the globe. However, a complete understanding of water's behavior is still lacking, and the quest to understand water's anomalous behavior continues.[1] The realization that condensed-phase behavior must be explained in terms of water clusters[2] led to the recent upsurge in water cluster research. Information on small water clusters in the gas phase was obtained through laser spectroscopic experiments,[3] supported by *ab initio* calculations.[4] Water's ability to form flexible hydrogen bonds with its neighboring molecules has led to the detection of various ordered water assemblies[5−10] in various deformed geometries.[11] The key to understanding the behavior of water is the precise structural data of various hydrogen-bonded networks. One can now even think of engineering the water assembly inside organic and metal−organic frameworks (MOFs) in a systematic way by gradually tuning its environment and studying its effect on the hydrogen-bonded networks.[8b,12] An understanding of this mutual interaction, especially when the components of the framework resemble molecular building blocks in biology, can possibly unravel the role of ordered water in bio-environments.

The water tetramer, one of the main cluster components incorporated in models to simulate anomalous behavior[1] of water, has been predicted to be cyclic and planar[2b] and has been structurally characterized within MOFs by a number of groups.[13] A polymeric chain structure having cyclic tetramers as its basic units has recently been discovered in organic crystalline hosts.[14,15] Herein we report a corner-sharing highly ordered tetrameric water chain with additional water forming a dimeric crown (Figure 1). The chains act as sidewalls, supporting 2D metal−carboxylate sheets, to generate a 3D supramolecular host having rectangular channels (Figure 2). This unique host accommodates guest 2-amino-4-picoline ligands in their protonated forms within the channels.[16] The presence of a cyclic dimeric crown of the tetrameric water chain is unprecedented, neither predicted theoretically nor observed experimentally, and has rendered the present water assembly a unique topology. This is also the first report of an infinite 1D tetrameric water chain in a metal−organic environment.

The complex **1**, $\{[Cu(mal)_2](picH)_2{\cdot}5H_2O\}_n$ [mal = $C_3H_2O_4$ = malonate dianion; picH = $C_6H_8N_2H$ = protonated 2-amino-4-picoline], was synthesized from purely aqueous media simply by mixing the reactants in stoichiometric ratio.[16] Elemental (C, H, N) analyses, thermogravimetric analyses (TGA), IR spectra, and X-ray powder diffraction (XRPD) studies characterized **1**, and its structure was established by single-crystal structure determination. *Ab initio*

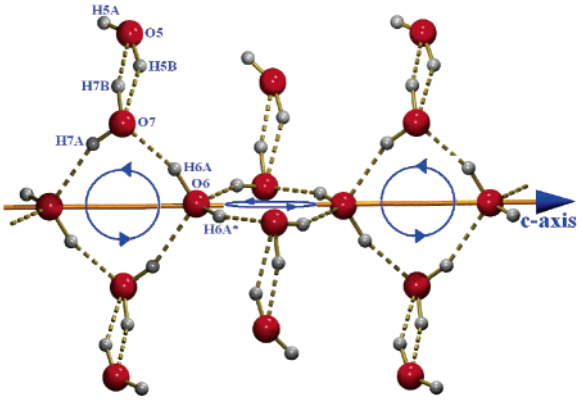

Figure 1. Corner-shared crowned infinite water chain, displaying the spirocyclic topology of tetramers around the chain axis (shown as arrow). The homodromic donor−acceptor arrangement has been indicated as blue circle.

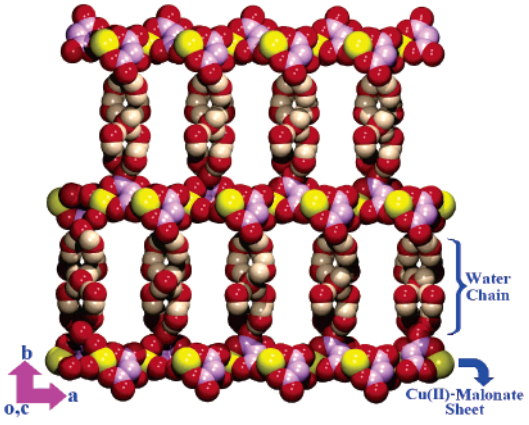

Figure 2. Cu(II)−malonate planes supported by water chains forming rectangular channels with brick-wall topology. Color code: Cu, yellow; O, red; N, blue; C, light-purple; H, tan.

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calculations were performed to estimate the stability of the water chain, and variable temperature magnetic moment (VTM) susceptibility data were collected to examine the magnetic coupling between the metal centers.

X-ray structure analysis of **1** reveals that the Cu(II)−malonate 2D coordination polymeric sheets are locked together by the hydrogen-bonded water assembly constructing a 3D infinite supramolecular host with brick-wall topology. Malonate by its rarely observed[17] *syn*−*anti* bridging mode has successively stitched octahedral Cu(II) centers into a two-dimensional rectangular grid structure.[16] Each Cu(II) atom in the grid is located on the center of symmetry forming a distorted octahedron with a CuO_6 chromophore. Two oxygen atoms (O1 and O3) of malonate and their centrosymmetric counterparts (O1*and O3*) form the equatorial plane, and the oxygen atoms O4 and O4* occupy the *trans* axial positions.

Three water molecules (O5, O6, and O7) by cooperative hydrogen bonding interaction form a one-dimensional spirocyclic water chain, while the O6 and O7 water molecules form a cyclic planar tetrameric water cluster (Figure 1). The tetramer is nearly planar with maximum deviation from the mean plane for the O7 atom being 0.08 Å and forms a rhombus with its two arms 2.805 and 2.784 Å in length and angles 82.45° and 97.55°. The planarity of the water tetramer and the distance between successive oxygen atoms of a cyclic tetramer was predicted to be 2.79 Å from laser spectroscopic (vibration−rotation−tunneling, VRT) experiment[18] and matches well with our results. Successive tetramers join each other sharing a common corner (O6) together with the rotation of the tetrameric planes by 86.44° with respect to each other building the spirocyclic topology of the chain. The O6 atoms lie along the axis of the chain with an O6···O6 distance of 3.683 Å, and O7 atoms occupy off-axis corners with 4.204 Å separation. The O5 water molecules constitute the crown of the chain through the formation of a cyclic water dimer with O7 atom. The basic tetrameric core of the chain reported here tends closer to VRT data when compared with Pal et al.[14] or Raghavaiah et al.[15] Pal et al.[14] preferred to describe their tetrameric chain as a bridged tetramer because they viewed the chain as successive tetramers (O···O distance 2.897 Å) joined by two water bridges with long O···O separation (3.004 Å), while Raghavaiah et al.[15] call their chain corner-shared, where all four O···O distances are quite different (2.755−2.824 Å). A closer look at the tetrameric chains that we present here reveals that all donor−acceptor arrangements in the plane are in the same counterclockwise direction, and this homodromic arrangement might have added extra stability to the chains.

An uncoordinated O2 atom from malonate protrudes out of the mean plane of the 2D Cu(II)−malonate sheet and acts as a hydrogen-bonding acceptor for the crown water, O5. Thus, the water chains line up perpendicular to the Cu−malonate sheet and tie up the sheets from above and below through O5−H5A···O2 interactions resulting in a 3D supramolecular host with brick-wall topology having rectangular channels (Figure 2). These channels run along the crystallographic *c*-axis and accommodate guest 2-amino-4-picoline ligands in their protonated forms. Association of these auxiliary ligands with the channel wall is through N−H···O hydrogen bonding. Methyl terminals of these picoline ligands direct toward the middle of the channel, making this region hydrophobic.[16] A weak $\pi-\pi$ interaction between picoline aromatic rings helps their stacking in the channel.

Thermogravimetric analyses[16] of complex **1** show that dehydration starts at ∼60 °C and all lattice water is lost at 130 °C (calculated for five lattice water molecules 15.15%, found 14.85%). The range of temperature for dehydration led one to believe that the hydrogen-bonding association of the water molecules in the self-assembled template is strong enough. Complete decomposition of the dehydrated structure was achieved at ∼480 °C. The IR spectrum[16] of complex **1** exhibits a band centered at 3438 cm^{-1} that may be assigned to O−H stretching of the water cluster. On deliberate exposure to ambient atmosphere for a few days (34−36 °C, relative humidity 85−88%), the heated sample (2 h at 130 °C under 0.1 mmHg) did not reabsorb water as evidenced from no characteristic O−H stretching, and the X-ray powder diffraction patterns of the complex[16] show major changes both in the peak positions and their intensities before and after water expulsion, suggesting a complete breakdown of the 3D host lattice due to the removal of crystal water. This irreversible water loss is also supported by the TG curve[16] of such heated samples where the water loss steps completely disappeared.

In keeping with the structure of **1**, in which each Cu(II) is linked with four different Cu(II) ions through carboxylate bridges in *syn*−*anti* fashion, analysis of the magnetic data reveal a weak ferromagnetic coupling between the Cu(II) ions.[16]

For a quantitative understanding about the stability of the water chain obtained in our crystal, at first we have retrieved the tetrameric unit, $(H_2O)_4$, from the crystal structure and performed *ab initio* geometry optimization of the H-atom positions with 6-31G basis set by freezing the positions of the heavy oxygen atoms. In the next set of calculations, we have considered two adjacent corner-shared tetrameric units, $(H_2O)_7$, which is the basic repeating unit of the whole chain, and performed the *ab initio* geometry optimization of the H-atom positions keeping oxygen atoms fixed. We consider the stabilization energy of the cluster association having *n* number of water molecules ($\Delta E_{n-\mathrm{mer}}$) to be equal to $E_{n-\mathrm{mer}} - (nE_{\mathrm{monomer}})$. Monomer energy was calculated by optimizing a single H_2O molecule at the same level of theory.[16] In the calculation of stabilization energy, the basis set superposition error (BSSE) was taken into account following the Morokuma decomposition scheme. Zero-point vibrational energy (ZPVE) was taken care of for the optimized geometry. The corrected stabilization energy of the tetramer, $(H_2O)_4$, and that for the two adjacent corner-shared tetramers, $(H_2O)_7$, were thus found to be −27.77 and −51.12 kcal mol^{-1}, respectively. All calculations have been performed with PC GAMESS package.[19]

In summary, we have characterized a water cluster with a hitherto unknown topology, and for the first time, we have designed a 3D supramolecular metal−organic host in which water-assembly as a whole acted as a building block of a 3D framework where organic molecules reside as guests within the channels. This is a step forward toward a new paradigm where the role of water/water cluster has shifted from the usual behavior of guest to that of a host. These studies also reveal that the "corner-sharing spirocylic" chain motif for tetramer is robust enough to be stabilized even in a metal−organic environment and is also flexible enough to accommodate additional water, keeping its basic tenet intact, and that might be attractive for theoretical modeling and understanding water's anomalous behavior. Knowledge obtained from this study may also aid to model various biological processes such as proton transfer, water structure inside channels and in energy-transduction proteins, and the role of ordered water in biological systems that often bear carboxylate and amino groups.

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Supporting Information Available: CIF for **1**, experimental details, hydrogen-bonding parameters in **1**, along with those mentioned in text as ref 16. This material is available free of charge via the Internet at http://pubs.acs.org.

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