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A Well-Resolved uudd Cyclic Water Tetramer in the Crystal Host of [Cu(adipate)(4,4-bipyridine)]·$(H_2O)_2$

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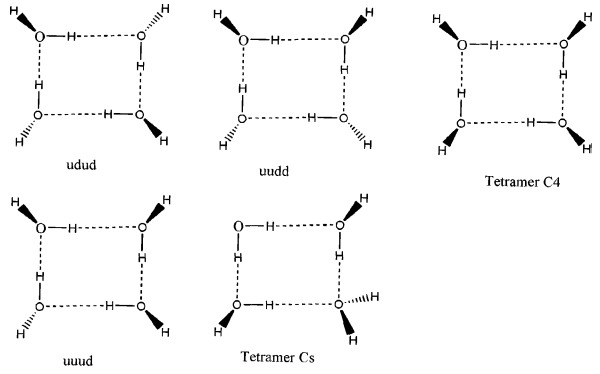
A well-resolved uudd cyclic water tetramer was reported in the crystal host of [Cu(adipate)(4,4-bipyridine)]·$(H_2O)_2$, showing the contribution of the water cluster to the stability of the crystal host and the role of cooperative association of the water cluster and the crystal host in the formation of the water cluster.

Water is of fundamental importance in life.[1] Exploration of the possible structures and stabilities of water clusters in diverse environments is a key to obtain insight into the nature of water−water interactions in bulk water or ice, as well as in biological and chemical processes.[2,3] In the past decades, considerable attention has been paid to the theoretical[4,5] and experimental studies[2,6−8] of small water clusters. The cyclic water tetramer, as a simple two-structure model for liquid water,[9] is of particular interest. Although theoretical studies on the basis of ab initio electronic structure calculations have predicted several configurations of cyclic water tetramers (Chart 1),[1c,10] and even some of them have been characterized by far-infrared vibration−rotation tunneling spectroscopy[11] or found in different crystal hosts,[12] crystallographic observation and analysis of an uudd cyclic water tetramer has not been possible so far. Here we report a well-resolved uudd water tetramer in the solid-state structure of a metal−organic coordination polymer of [Cu(adipate)(4,4-bipyridine)]·$(H_2O)_2$ (**1**).

Chart 1. The Calculated Configuration of Cyclic Water Tetramer



Complex **1** was prepared by hydrothermal reaction of $Cu(NO_3)_2·3H_2O$ (0.24 g, 1 mmol), adipic acid (0.15 g, 1 mmol), and 4,4′-bipridine (0.16 g, 1 mmol) in a 1:1 aqua−ethanol solution (20 mL) at 180 °C for above 4 h.[13] The crystal structure[14] at −100 °C reveals that **1** consists of one copper(II) cation, one 4,4′-bipridine and adipate ligand, and two water molecules. Each 4,4′-bipridine ligand with its

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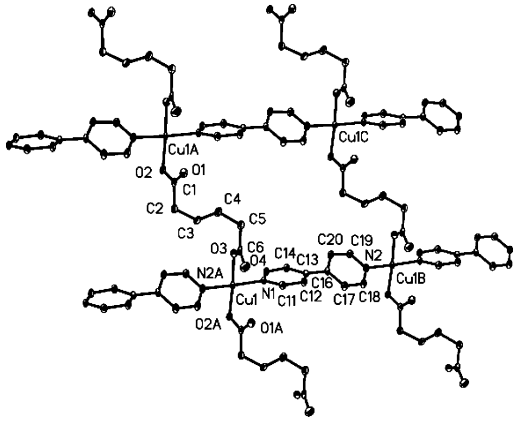

Figure 1. ORTEP plot showing 4-connected 2D structure in **1**.

terminal nitrogen atom coordinated to a copper(II) ion and every carboxylate of adipate ligand monodentately linked to a copper(II) ion generates a 4-connected two-dimensional (2D) structure as shown in Figure 1. This 2D structure is further extended into a 2D box through the symmetry-related O2 atoms in one layer occupying an apical position of the symmetry-related copper(II) atoms in another layer (Cu−O = 2.495(3) Å) as shown in Figure 2a. The copper(II)··· copper(II) distance between the two layers is 3.560(2) Å.

Interestingly, a cyclic water tetramer is perpendicularly located in each cavity of the 2D box and hydrogen-bonded to the symmetry-related O3 atoms with symmetry-related O1W (O1W···O3 = 2.822(4) Å). The most remarkable feature in **1** is that the 2D box is connected into a 3D structure (Figure 2b) only by the water tetramer through hydrogen bonding between symmetry-related O2W and symmetry-related O4 atoms of carboxylates from the left and right 2D box (O2W···O4 = 2.853(5) Å), respectively, indicating that the water tetramer plays a crucial role in contributing to the stability of the host of **1**.

The coordination environment of the water tetramer is shown in Figure 3. Each water monomer in the cluster is

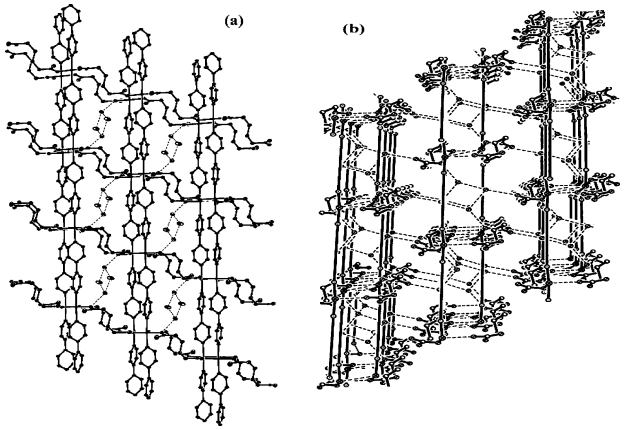

Figure 2. ORTEP plot showing (a) 2D box viewed along the *c* axis; (b) 2D box connected into 3D structure by the water tetramer through hydrogen bonding of symmetry-related O2W and symmetry-related O4 atoms of carboxylate from left and right 2D box viewed along the *b* axis, in which the line represents 4,4′-bipridine ligand.

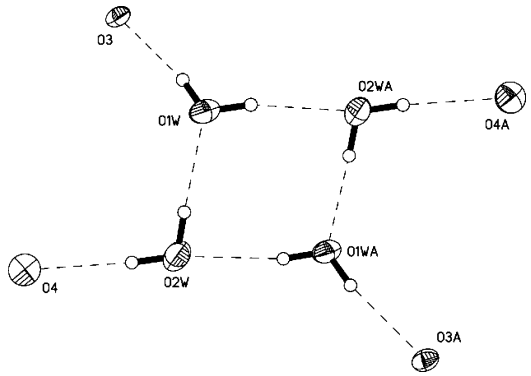

Figure 3. ORTEP plot showing the cyclic water tetramer and its immediate environment as found in **1**.

involved in the formation of three hydrogen bonds, with two from water−water interaction and one from water−host interaction. Within the cluster, the four water molecules are fully coplanar and each water monomer acts as both single hydrogen bond donor and acceptor. Interestingly, the remaining hydrogen atoms of O1W and O2W are 0.50 and 0.18 Å above the ring, respectively, while the remaining hydrogen atoms of O1WA and O2WA are 0.50 and 0.18 Å below the ring, respectively. Such an arrangement results in the formation of an irregular uudd water tetramer that, to the best of our knowledge, has not been experimentally observed so far.

The hydrogen bond distances and angles within the water tetramer are as follows: O2W···O1W = 2.775(5) Å, O1W···O2WA = 2.896(6) Å, ∠O2W−H2WA···O1W = 178(5)°, ∠O1W−H1WA···O2W = 167(5)°). The average hydrogen bond distance within the water tetramer is 2.834 Å, significantly longer than 2.78 Å estimated in the udud water tetramer of $(D_2O)_4$[11] in the gas phase,[11] and 2.743 Å calculated in the discrete udud water tetramer.[4]

Theoretical predictions show that the udud water tetramer is the global minimum and its dissociation energy is 247 cm^{-1} (ASP-P) and 375 cm^{-1} (ASP-NB) higher than that of uudd water tetramer.[15] The formation of a less stable uudd water tetramer in **1** indicates that the cooperative association

(13) The detailed preparation for **1** is as follows: To a 20 mL 1:1 aqua−ethanol solution of $Cu(NO_3)_2 \cdot H_2O$ (0.24 g, 1 mmol), adipic acid (0.15 g, 1 mmol), and 4,4′-bipridine (0.16 g, 1 mmol) was added 1:1 $NH_3 \cdot H_2O$. When the pH value of the mixture was adjusted to ca. 7, the solution was put into a Teflon-lined Parr, heated to 180 °C for 4 h, and then cooled to room temperature at the rate of 5 °C/h. After the solution was transferred into a 25 mL beaker, the solution was slowly evaporated (2 months), giving crystals of **1** in 43% yield.

(14) Crystal structure analysis: The data were collected on a Bruker Apex-2000 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) with $\omega/2\theta$ scan mode at 173 K. Lorentz−polarization and absorption corrections were applied. Structural solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program package, respectively. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were generated geometrically (C−H = 0.96 Å), and those of the aqua ligands were located from the difference maps; all the hydrogen atoms were assigned the same isotropic temperature factors and included in the structure-factor calculations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystal data for **1**: crystal dimensions 0.25 × 0.22 × 0.16 mm, triclinic, space group $P\bar{1}$, $a = 9.611(6)$ Å, $b = 9.674(6)$ Å, $c = 10.878(7)$ Å, $\alpha = 107.109(10)°$, $\beta = 114.993(9)°$, $\gamma = 95.996(10)°$, $V = 845.1(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.571$ g cm^{-3}, $M = 399.88$, μ(Mo Kα) = 1.328 mm^{-1}. Of the 3519 symmetry independent reflections ($2.23° < \theta < 27.00°$), 2890 reflections are observed ($I > 2\sigma(I)$). On the basis of all these data and 242 refined parameters, $R1 = 0.0507$, $wR2 = 0.1383$, and GOF on F^2 of 1.097 were obtained.

of the water cluster and crystal host plays an important role in stabilization of the water cluster.

In summary, we have, for the first time, experimentally presented a well-resolved uudd cyclic water tetramer, showing the contribution of the water cluster to the stability of the host, and the role of the cooperative association of the water cluster and crystal host in the formation of the water cluster. Because it is impossible for water clusters in solution and in the solid state to be discrete, the precise structural data and the cooperative association of the water cluster and crystal host in **1** may be helpful in improving our understanding of the contribution of water clusters to the stability and function of the biological assemblies, as well as anomalous properties of water.

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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