

Formation of infinite 2D water layers in a crystal host

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Abstract

A self-assembled, (H₂O)₃₈ cluster stabilized by a mono-nuclear copper(II) complex **1** namely {[Cu(phen)₂(CO₃)]·7H₂O} is characterized by X-ray diffraction studies. The adjacent (H₂O)₃₈ clusters connect together resulting in an infinite 2D water layer structure. The water morphology is stable at room temperature, but upon thermal decomposition, the water loss is irreversible. © 2009 Cai Hua Zhou. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

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Being water plays an indispensable role in life-sustaining processes, investigations on the structure, properties and functions of water have received more attention than any other substance [1–3]. Structural studies on “discrete” water clusters within the lattice of a crystal host have significantly advanced our knowledge toward the first step of understanding the behavior of bulk water [4–6]. Growth of larger water clusters, and how these clusters link themselves to form a larger network of water molecules is still a challenging scientific endeavor [7–9]. A surge of publications dealing with the structure of some interesting polymeric water molecule motifs in crystal hydrates of organic compounds and coordination complexes has appeared [10–14]. Very recently, two-dimensional (2D) water/ice layers containing large 10-, 12-, 18- and 45-membered water rings have been observed in the solid state [15–19]. These polymeric water morphologies, the size of which lies in between water clusters and bulk water, have physical properties very closely associated with those of bulk water. Therefore, the above studies have significantly advanced the understanding of water structures as well as provided novel structural aspects of water and new insights into water with implications for biological environments. Herein, we describe the formation of an unprecedented, infinite 2D water layer consisting of (H₂O)₃₈ clusters stabilized by a crystal host (complex **1**), where each cyclic (H₂O)₃₈ cluster consists of six five-membered rings and two four-membered rings. Hydrogen-bonding interactions between the 2D layers of water and complex **1** create a unique, infinite through-channel.

Single-crystal diffraction analysis [20] reveals that **1** contains two phenanthroline ligands, one Cu(II), one carbonate dianion, and seven free water molecules in the asymmetric unit. Four pyridine nitrogen atoms from two phenanthroline ligand units and two oxygen atoms from carbonate dianion coordinated Cu(II), leading to an octahedral geometry structure. There lies a bidentate binding mode of the carbonate ligand, the extension of these Cu–

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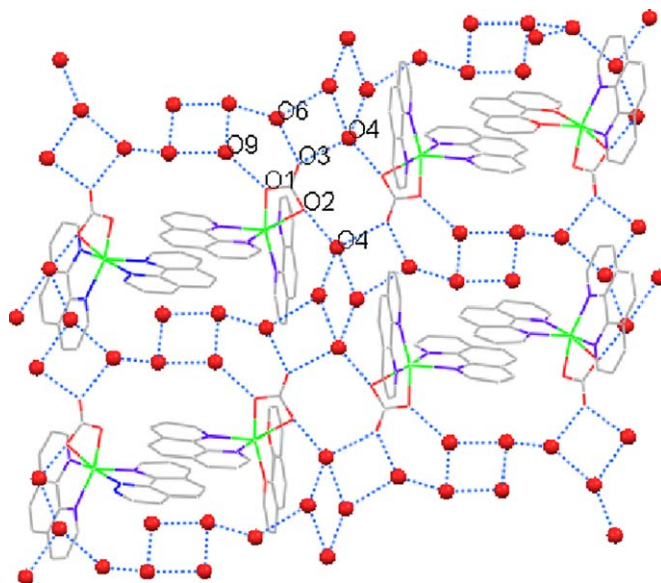


Fig. 1. 2D sheet structure in crystallographic *ab* plane (hydrogen atoms are omitted for clarity).

O bonds [Cu–O5 2.287(6) and Cu–O4 2.683 (6) Å] should ascribe to the Jahn–Teller effect. The complex **1** is associated with free water molecules through O1–H···O9w, O2–H···O4w, O3–H···O4w and O3–H···O6w hydrogen-bonding interactions form a 2D sheet structure in crystallographic [0 0 1] plane (Fig. 1). The 2D sheets are further extended along [0 0 1] plane by hydrogen bonds among water molecules generating a 3D supramolecular structure. (see supporting information, Fig. S2).

In order to investigate the function of organic–metal complexes stabilizing various water topologies in environments resembling those in living systems, we have examined the topology structure of the supramolecular assembly of the water molecules. Seven water molecules exist in coordination complex crystal host, which formed an infinite 2D water layer in the [1 0 0] plane by hydrogen bonds. The 2D water layer is composed of a unique $(\text{H}_2\text{O})_{38}$ cluster with symmetric center (Fig. 2), which is formed by a type of tetramer and a type of pentamer. Basically, the

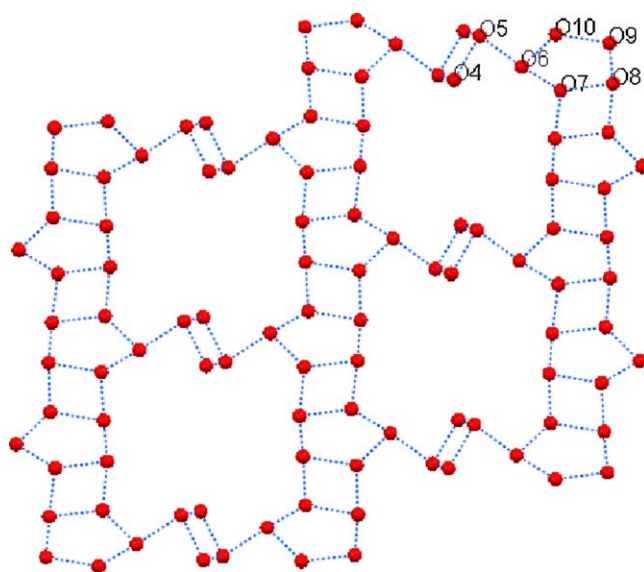


Fig. 2. The 2D layer of water is composed of a unique $(\text{H}_2\text{O})_{38}$ clusters (hydrogen atoms are omitted for clarity).

(H₂O)₃₈ cluster unit is an assembly of six (H₂O)₅ and two (H₂O)₄ subunits. Water molecules connected together by hydrogen bonds. According to the classification system of common aggregation states adopted by hydrogen-bonded water molecules [21], this cycle (H₂O)₃₈ belongs to a L38(10)5(2)4(2)4(1) pattern, and it possesses D_{2d}-symmetry. Although the data collection for the complex **1** is carried out under liquid-nitrogen temperature conditions (100 K) most of the water hydrogen atoms were never located, however, positions of the water molecules constituting the 2D supramolecular architecture were determined unequivocally. The subunit (H₂O)₅ comprised five different oxygen atoms (O6w, O7w, O8w, O9w, O10w) whose conformation is similar to cyclopentane with one water molecule raising up above the plane formed by the other four oxygen atoms. The water pentamer topology described here is in agreement with the puckered ring achieved from both experimental and theoretical studies by Liu et al. [22]. Adjacent pentamers connected each other by the way of centers of inversion, these pentamers produce a 1D T4(2)5(2) water tape along *c* axis via hydrogen bonds between O7w and O9w, O8w and O10w (see supporting information, Fig. S2). Another (H₂O)₄ subunit is formed by two symmetry-related O4w and O5w presenting a rigid parallelogram geometry, and the distances of the length and width, that is, the two distinct O4w···O5w distances are 2.843 and 2.939 Å, respectively. The hydrogen bonds (O5w···O6w) link this parallelogram geometry (H₂O)₄ with the neighboring (H₂O)₅ subunit along the *b* axis, and finally result in the formation of a big (H₂O)₃₈ cluster. However, we consider “bridged tetramers” are a more appropriate description for the (H₂O)₄ subunit, because the bond distance of O5w···O6w is 2.930 Å, which is longer than O–O average bond distance (2.8398 Å) in (H₂O)₃₈ cluster. Formation of the 2D water layered is generated by simple shift of the (H₂O)₃₈ cluster, when viewed down the *a* axis. Alternate arrangement of the complex **1** and the 2D-layered water produce infinite through-channels along *a* direction. The CPK diagram of the 3D supramolecules structure clearly shows that the phenyl rings of the coordination complex **1** are located inside these channels.

Interestingly, the hydrogen-bonding motif of the 2D water layer of (H₂O)₃₈ clusters in the self-assembled system presented herein, in which three water molecules (O6w, O4w, O9w) are involved in the formation of four hydrogen bonds, and others (O5w, O7w, O8w, O10w) are involved in the formation of three hydrogen bonds. Apart from the interactions with the surrounding cyclic water rings, the O4w water molecule of the tetramer has hydrogen-bonding interaction with two oxygen atoms (O2, O3) of carbonate dianion in the complex **1**. Whereas O6w and O9w water molecule of pentamer are also forming O···O short contacts with the O3 and O1 of carbonate dianion, respectively, the ranges of hydrogen bonds between waters and carbonate dianion are from 2.634 to 2.698 Å. The geometry of the 38-membered basic ring is imposed by the cooperative effect which include Ow···Ow interactions between fused four- and five-membered rings and O–H···Ow interactions among water molecules and complex **1**.

In summary, we have characterized a novel 2D water layer structure composed by a unique (H₂O)₃₈ cluster. This new (H₂O)₃₈ cluster has D_{2d} symmetry structure. The manner of self-assembled tetrameric water and pentameric clusters during the formation of (H₂O)₃₈ cluster is unprecedented. We believe that the water structure demonstrated herein brings to a novel mode of the cooperation for water molecules self-assemble. This discovery is helpful in improving the modeling of some of the unexplained properties of water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ccl.2009.03.030](https://doi.org/10.1016/j.ccl.2009.03.030).

Reference

- [1] P. Ball, H₂O: A Biography of Water, Weidenfeld & Nicolson, London, 1999.
- [2] R. Ludwig, Angew. Chem. Int. Ed. 40 (2001) 1808.
- [3] K. Nauta, R.E. Miller, Science 287 (2000) 293.
- [4] F.N. Keutsch, J.D. Cruzan, R.J. Saykally, Chem. Rev. 103 (2003) 2533.
- [5] L.J. Barbour, G.W. Orr, J.L. Atwood, Nature 393 (1998) 671.
- [6] J.L. Atwood, L.J. Barbour, T.J. Ness, P.L. Raston, J. Am. Chem. Soc. 123 (2001) 7192.

- [7] A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtman, B. Botar, M.O. Talismanova, *Angew. Chem. Int. Ed.* 42 (2003) 2085.
- [8] R.J. Doedens, E. Yohannes, M.I. Khan, *Chem. Commun.* (2002) 62.
- [9] S.K. Ghosh, P.K. Bharadwaj, *Angew. Chem. Int. Ed.* 43 (2004) 3577.
- [10] N.S. Oxtoby, A.J. Blake, N.R. Champness, C. Wilson, *Chem. Eur. J.* 11 (2005) 1.
- [11] K. Liu, J.D. Cruzan, R.J. Saykally, *Science* 271 (1996) 929.
- [12] T. Head-Gordon, G. Hura, *Chem. Rev.* 102 (2002) 2651.
- [13] R. Carballo, B. Covelo, C. Lodeiro, E.M. Vázquez-López, *Cryst. Eng. Commun.* 7 (2005) 294.
- [14] S. Neogi, P.K. Bharadwaj, *Inorg. Chem.* 44 (2005) 816.
- [15] U. Mukhopadhyay, I. Bernal, *Cryst. Growth. Des.* 6 (2006) 363.
- [16] (a) K. Raghuraman, K.K. Katti, L.J. Barbour, N. Pillarsetty, K.V. Katti, *J. Am. Chem. Soc.* 125 (2003) 6955, Examples;
(b) R. Custelcean, C. Afloroaei, M. Vlassa, M. Polverejan, *Angew. Chem. Int. Ed.* 39 (2000) 3094.
- [17] (a) S. Pal, N.B. Sankaran, A. Samanta, *Angew. Chem. Int. Ed.* 42 (2003) 1741, Examples;
(b) B.Q. Ma, H.L. Sun, S. Gao, *Chem. Commun.* 2220 (2004).
- [18] (a) B.Q. Ma, H.L. Sun, S. Gao, *Angew. Chem. Int. Ed.* 43 (2004) 1374, Examples;
(b) C. Janiak, T.G. Scharman, *J. Am. Chem. Soc.* 124 (2002) 1401;
(c) R. Carballo, B. Covelo, N. Fernández-Hermida, E. García-Martínez, E.M. Vázquez-López, *Cryst. Growth. Des.* 6 (2006) 629.
- [19] P.S. Lakshminarayanan, E. Suresh, P.J. Ghosh, *Am. Chem. Soc.* 127 (2005) 13132.
- [20] Synthesis was under hydrothermal conditions. A mixture of CuCO_3 (0.5 mmol, 62 mg), phenanthroline (1.0 mmol, 180 mg), and 10.0 mL of distilled water was stirred fully in air, and then sealed in a Teflon-lined stainless steel container, which was heated at 160 °C for 4 days. After the sample was cooled to room temperature, blue block-like crystals were produced in 69% yield. Anal. Calcd for $\text{C}_{25}\text{H}_{30}\text{CuN}_4\text{O}_{10}$: C, 49.18; H, 4.92; N, 9.18. Found: C, 49.21; H, 4.93; N, 9.20. § Crystal data: Compound 1, $\text{C}_{25}\text{H}_{30}\text{CuN}_4\text{O}_{10}$, $M = 610.07$, monoclinic, $P2_1/c$, $a = 9.9327(16)$, $b = 26.361(4)$, $c = 10.5516(17)$ Å, $\alpha = 90^\circ$, $\beta = 106.55(2)^\circ$, $\gamma = 90^\circ$, $V = 2653.7(7)$ Å³, $Z = 4$, $D_c = 1.527$ Mg m⁻³, $\mu = 0.888$ mm⁻¹, $F(000) = 1268$, GOF = 1.056, crystal size 0.22 mm × 0.26 mm × 0.11 mm. A total of 16726 reflections were collected and unique reflections are 5312 (Rint = 0.0191). R1 and wR2 are 0.0507 and 0.1355, respectively, the data were collected on a SMART CCD 1000 with Mo K α radiation ($\lambda = 0.71073$ Å) at 273 K. The structures were solved by direct methods and refined by a full matrix least squares technique based on F2 using SHELXL 97 program. All hydrogen atoms were located from the difference Fourier maps and refined anisotropically. All hydrogen atoms were located from the difference Fourier maps and refined anisotropically.
- [21] (a) M. Mascal, L. Infantes, J. Chisholm, *Angew. Chem. Int. Ed.* 45 (2006) 32, Examples;
(b) L. Infantes, J. Chisholm, S. Motherwell, *Cryst. Eng. Commun.* 5 (2003) 480.
- [22] K. Liu, M.G. Brown, J.D. Cruzan, R.J. Saykally, *Science* 271 (1996) 62.