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A Water Pipe Held Up by a Polyoxometalate Supported Transition Metal Complex: Synthesis and Characterization of $[Cu_2(phen)_2(CH_3COO)(CH_3COOH)(H_2O)_2][Al(OH)_6Mo_6O_{18}]\cdot 28H_2O$

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A water pipe, formed exclusively from lattice water molecules, is stabilized in an organic–inorganic hybrid material $Cu_2(phen)_2(CH_3COO)(CH_3COOH)(H_2O)_2][Al(OH)_6Mo_6O_{18}]\cdot 28H_2O$ (**1**). Compound **1** consists of an Anderson-type heteropolyanion, a copper acetate dimer, and 28 lattice water molecules. Once the relevant crystal is removed from the mother liquor it loses water molecules, which results in the demolition of the water pipe.

Water is a major constituent of our planet earth and it plays an important role in many natural systems, but it is not a fully understood liquid. There has been extensive investigation of water structures in recent years in which helical protein matrixes act as a stabilizing host[1] because water aggregations are prevalent in many biological systems. Studies on small water clusters and their noncovalent interactions are significant because these stabilize the supramolecular systems both in solution and in the solid state and there is a clear need to understand how such aggregates influences the overall structures of their surroundings.[2] It has been demonstrated that a giant icosahedral metaloxide-based spherical polyoxometalate (POM) cluster can encapsulate an icosahedral $(H_2O)_{100}$ cluster.[3] Other POM clusters are also found to stabilize small water clusters.[4] There are reports on several types of water polymers that have been crystallographically identified; these include chains,[5] tapes/layers,[6] and helices[7] etc. Infantes and Motherwell have described the patterns of water clusters within the Cambridge Structural Database (CSD), and they have classified them as discrete rings and chains, infinite chains and tapes, and layer structures.[8] According to their CSD search, a water pipe/tube was not known until 2002. There are two reports of water tubes in recent time: both are stabilized with inorganic coordination compounds.[9] Very recently, Mascal et al. have written a popular article on water oligomers in crystalline hydrates by choosing 17 random recent publications that describe unprecedented assemblies of water molecules and compared these structures against those already in the CSD.[10] However, the context of a water pipe/tube is not discussed in this essay. We describe here the crystallographic observation of a new type of water pipe that was identified in supramolecular channels and formed in a polyoxometalate-based inorganic–organic hybrid compound, $[Cu_2(phen)_2(CH_3COO)(CH_3COOH)(H_2O)_2]$ $[Al(OH)_6Mo_6O_{18}]\cdot 28H_2O$ (**1**).

Compound **1** was synthesized in an organo–aqueous medium containing copper nitrate, sodium molybdate, aluminum chloride, acetic acid, acetonitrile, and sodium acetate. The blue crystals of **1** with block morphology were separated on standing at room temperature in 28% yield (based on Mo). These crystals are unstable when they are removed from the mother liquor, loss of crystallinity was registered. Thus, the data collection was performed on a single-crystal of **1** suspended in a capillary that contained frozen mother liquor (at liquid nitrogen temperature).

Compound **1** consists of an Anderson anion, $[Al(OH)_6Mo_6O_{18}]^{3-}$, a dimeric copper complex cation $[Cu_2(phen)_2(CH_3COO)(CH_3COOH)(H_2O)_2]^{3+}$ and 28 lattice water molecules. Thus, the asymmetric unit in the crystal of compound **1** is composed of half of a dimeric complex cation, half of the Anderson heteropolyanion, and 14 solvent water molecules as shown in Figure 1. An Anderson anion $[Al(OH)_6Mo_6O_{18}]^{3-}$ consists of seven edge-shared octahedra, six of which are molybdenum octahedra arranged hexagonally surrounding the aluminum octahedra (see Figure S4 in Supporting information). In compound **1**, copper dimer $[Cu_2(phen)_2(CH_3COO)(CH_3COOH)(H_2O)]^{3+}$ acts as a cation that compensates for the anionic charge of the Anderson anion resulting in the formation of the title compound. The copper ion adopts a square pyramidal geome-

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try, whereby the basal sites are occupied by two phenanthroline nitrogen atoms and two acetate oxygen atoms (Cu–N = 2.01 Å; Cu–O = 1.956 Å), and the axial position is occupied by water oxygen atoms. The axial Cu–O distance is 2.154 Å, which is relatively longer than those in the basal plane. Intradimer Cu···Cu separation of 2.988 Å has been observed, which is comparable to the Cu···Cu separation of 3.05 Å in the similar dimer reported in the literature.[11] The phenanthroline ligands of the copper dimer are almost parallel to each other and they are also ring-to-ring stacked, which reveals intramolecular π-π interactions [C_t–C_t = 3.632 (2) Å; MPS = 3.355 Å].

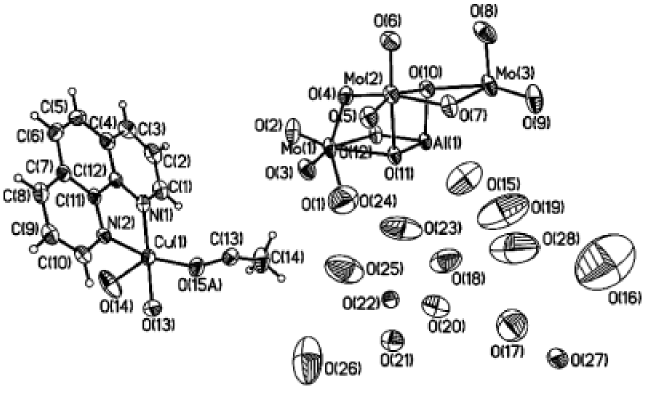

Figure 1. Thermal ellipsoidal plot (at 50% probability) of the asymmetric unit in compound **1**, which consists of half of the dimeric copper complex cation, half of the Anderson heteropolyanion and 14 solvent water molecules.

The most fascinating aspect of this work is the formation of a water pipe that is formed exclusively from lattice water molecules present in the crystal of **1**. There are 14 lattice water molecules in the asymmetric unit in the crystal structure of **1** (see Figure 1). These are O(15) through O(28). Out of these 14 lattice water molecules, 13 are involved in the formation of a $(H_2O)_{13}$ cluster [the O(24) water is not involved in hydrogen bonding interactions] as shown in Figure 2. The growing and repetitive arrangement of the $(H_2O)_{13}$ cluster leads to the construction of a new type of water pipe as shown in Figure 3. The relevant O···O hydrogen bond lengths are given in Table 1. Water hydrogen atoms could not be located in the crystal structure. Among the 13 lattice water molecules that are involved in the construction of the water pipe, two water molecules [O(22) and O(26)] are disordered. Each of these is disordered over two positions [O(22), O(22A) and O(26), O(26A), respectively].

The dimensions of the inner diameter of the water tube are found to be 8.527 × 8.061 Å^2. The packing of the water pipes in the unit cell is shown in Figure 4. The existence of such an unstable pipe (vide supra) has been made possible by the interactions with its surroundings that include an Anderson heteropolyanion and a dimeric copper complex cation. There are extensive hydrogen bonding interactions between surface oxygens of the Anderson anion (terminal, bridging, and μ_3-O oxygens), crystal waters (water tube), and copper coordinated waters as shown in Figure 5a (see also Figures S10–S12 in Supporting information for detailed interactions between the water pipe and its surrounding). The packing of the Anderson heteropolyanions and the dimeric copper complex cations in the crystal forms a grid-type supramolecular framework having channels (when viewed looking down the crystallographic *c* axis). These channels accommodate the water pipes that run along the crystallographic *c* axis too (see Figure 5b).

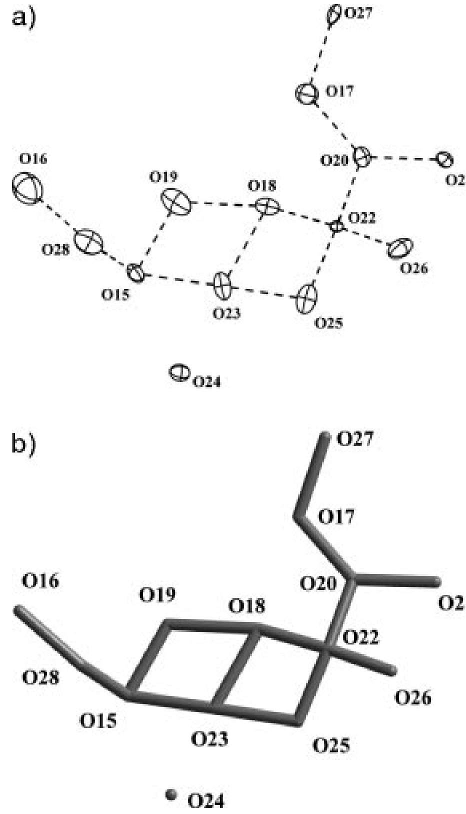

Figure 2. Hydrogen bonding interactions among lattice water molecules O(15) through O(28), which results in the formation of a $(H_2O)_{13}$ cluster. O(24) water remains non-hydrogen bonded in the crystal. (a) thermal ellipsoidal and (b) wire-frame representations. The disordered part of O(22) and O(26) are not shown.

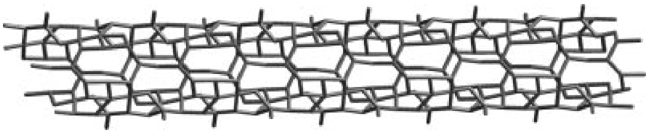

Figure 3. The generation of a water pipe formed by the repetition of $(H_2O)_{13}$ cluster (as shown in Figure 2).

Table 1. O···O hydrogen bond lengths [Å] in water tube (see Figure 2).

O15···O19	2.736(11)	O15···O23	3.051(9)
O15···O28	3.137(12)	O16···O28	2.750(15)
O17···O27	2.801(10)	O17···O20	2.834(10)
O18···O22	2.579(10)	O18···O23	3.050(10)
O18···O19	3.152(14)	O20···O22	2.549(9)
O20···O21	2.819(7)	O22···O25	2.613(13)
O22···O26	2.379(19)	O23···O25	2.922(10)

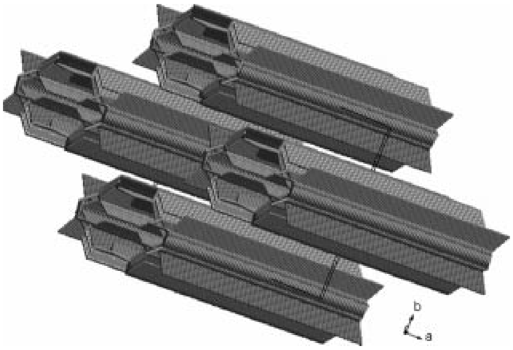

Figure 4. The packing of the water tubes in the unit cell excluding the Anderson anions and dimeric copper complex cations.

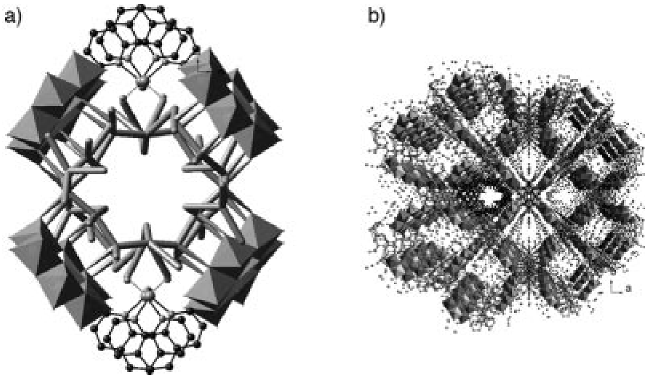

Figure 5. (a) Front view of the water pipe, supported by its surroundings that include dimeric copper complex cations and Anderson heteropolyanions through noncovalent interactions. Anderson anion is shown in polyhedral representation and water tube in sticks representation. Acetate carbons and hydrogens are not shown for clarity. (b) The perspective view of the water tubes in the square-grid channels (3 × 3 cell). Only one water tube is shown for clarity. The view is along the crystallographic *c* axis.

In the present study, we could not determine the precise number of water molecules forming the water pipe by thermogravimetric (TG) studies because once the relevant crystals are removed from the mother liquor (synthesis), they lose their single crystallinity and form a powdery material. TG studies were performed on the powdery compound. The TG curve shows the first weight loss starts at around 100 °C with the loss of 13.50%. This corresponds to the loss of ca.16 crystal water molecules. The molecules lost at this stage were identified as water molecules from the corresponding mass spectrum (TGA-Mass). This clearly tells us that the relevant crystal already looses 12 water molecules at room temperature before its TG measurements start. This is consistent with the X-ray powder diffraction studies and the visual observation (single-crystals convert to powder) during the process of removing the crystals from the mother liquor.

In conclusion, we have described here the crystallographic observation of a supramolecular water pipe that is exclusively constructed from solvent/lattice water molecules. We believe that the heteropolyanion and the copper dimeric complex play an important role in the stabilization of such an unusual and unstable water tube. Conversely, the water pipe acts as a support to hold the host chemical entities (grid-framework) as evidenced by the loss of crystallinity that occurs when lattice water molecules are lost during the drying process of the relevant crystal at room temperature. To the best of our knowledge, this is the first crystallographically characterized water tube in a POM-based hybrid material.

Experimental Section

General: Infrared spectra were recorded with a JASCO-5300 FTIR spectrophotometer. Powder X-ray diffraction data were collected with a Phillips PW 3710 diffractometer. EDAX analyses were performed with Philips XL 30 SEM equipment.

Synthesis of $[Cu_2(phen)_2(CH_3COO)(CH_3COOH)(H_2O)_2][Al(OH)_6Mo_6O_{18}]\cdot 28H_2O$ (1): To a stirred aqueous (50 mL) solution of aluminum chloride (1.5 g, 6.21 mmol), a solution of sodium molybdate (3.5 g, 14.46 mmol) in water (100 mL) was mixed followed by the addition of an aqueous methanolic solution (100 mL; water/MeOH, 1:1) of 1,10-phenanthroline (0.2 g, 1 mmol) and copper acetate (1 g, 5 mmol). To this reaction mixture, sodium acetate (3 g, 22.04 mmol) was added. Finally, the whole reaction mixture was acidified with glacial acetic acid until the pH reached 3.4. The mixture was then stirred for 10 min and filtered in a 250 mL conical flask. Blue crystals of **1** were obtained after one week from the filtrate. Yield: 1.5 g (28% based on molybdenum).

Note: Crystals of **1** lose single crystallinity when they are removed from the mother liquor. The single-crystals lose a considerable amount of solvent/lattice water molecules (as is evidenced by TGA studies, vide infra) immediately after they are separated from the mother liquid and convert to a powdery form.

X-ray Crystallographic Study: One single crystal of dimensions $0.45 \times 0.22 \times 0.10$ mm^3 was placed in a capillary tube with its mother liquor and cooled to liquid nitrogen temperature with immediate effect (for details see Supporting Information). CCDC-613002 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Synthesis, X-ray powder diffraction studies, TGA studies, structure refinement data, structural description and interactions of compound **1**

Acknowledgments

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