Helical supramolecular host with aquapores anchoring alternate molecules of helical water chains†‡

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Unprecedented 1D helical chains of hydrogen bonded water molecules, showing both handedness and anchored onto a helical supramolecular host formed from the self assembly of a dicopper(II) complex (1) containing pentadentate Schiff base (L) and *p*-hydroxycinnamate in 1·2H₂O, propagate along the crystallographic 2₁-screw axis and the compound shows two endotherms due to loss of water molecules at 61.5 and 88.5 °C in the differential scanning calorimetry giving an overall change of enthalpy value of ~ 36 kJ mol⁻¹ per water molecule.

Among different types of structures water clusters can assume through hydrogen bonding network, a 1D chain arrangement of water molecules is of contemporary interest due its occurrence in several biological processes related to water and ion transport.[1–3] Structural studies have shown that the highly dynamic water molecules in the membrane channel protein aquaporin-1 assumes single file arrangement of water molecules in the constricted pore having cationic residues for their selective passage.[4] A better ordered chain of water molecules exist in gramicidin A membrane channels for rapid transport of proton.[5] While 1D chains are prevalent in biological systems where helical protein matrix acts as a stabilizing host, such chains are relatively rare in synthetic hosts.[6,7] Herein we report the crystal structure of a metal complex which shows the formation of a helical supramolecular structure by a self assembly process with pores in which the lattice water molecules form unprecedented helical 1D chains by weak hydrogen bonding interactions. A significant observation is the weak hydrogen bonding of the alternate water molecules in the chain to the host supramolecular structure.

Complex [Cu₂L(O₂CCH=CHC₆H₄-*p*-OH)] (**1**), where L is pentadentate trianionic Schiff base *N,N'*-1,3-diyl-bis(salicylaldimino)propan-2-ol, is prepared from a reaction of [Cu₂L(O₂CMe)][8] with the sodium salt of *p*-hydroxycinnamic acid in methanol (Scheme 1).§ Single crystals of **1**·2H₂O belong to the orthorhombic space group *P2₁nb* (*Z* = 4).¶ The complex consists of an asymmetrically dibridged dicopper(II) unit having an alkoxo bridge of the Schiff base and the *p*-hydroxycinnamate showing three-atom bridging mode (−2*J* = 116 cm⁻¹, the singlet–triplet separation energy). There are two lattice water molecules in the crystallographic asymmetric unit. They are not involved in any metal–ligand
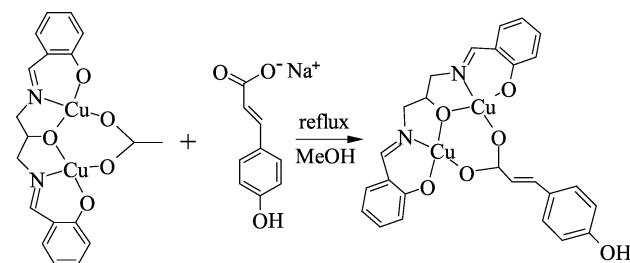
interaction. Each copper has square planar CuNO₃ coordination geometry giving a Cu···Cu distance of 3.475(2) Å. The basal planes at the copper(II) centers are nearly coplanar forming an angle of 9.7(3)°. The –CH=CHC₆H₄– moiety of the *p*-hydroxycinnamate is nearly planar giving an angle of 15.3(7)° between the –CH=CH– group and the aromatic C₆H₄ ring. The cinnamate ligand with a pendant –OH group forms an angle of ~ 30° with the plane of the {Cu₂L}⁺ moiety.

Complex **1** self assembles to form a helical supramolecular structure involving the O(6)#3 atom of the pendant –OH group of the *p*-hydroxycinnamate and the phenoxy oxygen atom O(1) of the Schiff base belonging to different asymmetric units (Fig. 1). The tilt angle between the planar {Cu₂L}⁺ and the carboxylate ligand could be responsible for the formation of the helical structure. The space filling model along *a*-axis displays the pores[9] of approximate size of 3.88 × 8.81 Å² in which the water chains are located. The lattice water molecules are found to propagate along the crystallographic 2₁-screw axis in a helical fashion showing weak hydrogen bonding interactions (Table 1, Fig. 1). Atoms O(7) and O(8) of the water molecules are hydrogen bonded giving a distance of ~ 2.9 Å. The O(7) atom is hydrogen bonded to O(8)#2 atom of another asymmetric unit giving a O···O distance of ~ 3.0 Å. The helical host acts as a template for the formation of the helical chain of water molecules. The angles O(8)···O(7)···O(8)#2 and O(7)···O(8)···O(7)#1 in the helix are 116.0(8) and 114.3(9)°, respectively. The unit cell packing diagram shows the presence of four helices located at the center of the *b*- and *c*-axes with half site occupancy. The helices exhibit both left and right handedness in a 1:1 ratio (Fig. 2(a)).
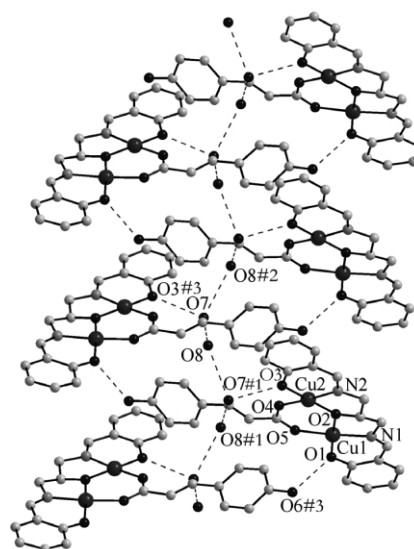

Scheme 1 Synthetic scheme of complex **1**.

Fig. 1 A perspective view of the helical supramolecular structure in **1**·2H₂O showing the hydrogen bonds and the atom labeling scheme for the metal and the heteroatoms. Selected bond lengths (Å) and angles (°) in the dicopper(II) complex are: Cu(1)···Cu(2) 3.475(2), Cu(1)–O(1) 1.905(7), Cu(1)–O(2) 1.911(7), Cu(1)–O(5) 1.914(6), Cu(1)–N(1) 1.935(7), Cu(2)–O(3) 1.901(7), Cu(2)–O(2) 1.926(7), Cu(2)–N(2) 1.932(8), Cu(2)–O(4) 1.939(7), Cu(1)–O(2)–Cu(2) 129.8(3).

Table 1 Selected bond lengths and angles associated with the helical water chain and the host structure (D, donor atom; A, acceptor atom)

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O(8)–H···O(7)	0.96[b]	2.01	2.92(3)	159.7
O(7)–H···O(8)#2	0.96[b]	2.23	2.98(3)	135.5
O(7)–H···O(3)#3	0.96[b]	1.86	2.78(2)	163.0
O(6)–H···O(1)#3	0.98(16)	1.84	2.67(1)	140.5

[a] Symmetry codes: #1: $x-\frac{1}{2},-y,-z+1$; #2: $x+\frac{1}{2},-y,-z+1$; #3: $x+\frac{1}{2},-y+1,-z+1$. [b] restrained.
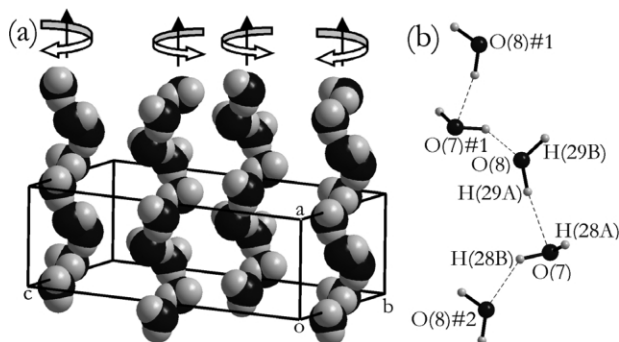
Fig. 2 Unit cell packing diagram of $\mathbf{1}\cdot 2H_2O$ showing left and right handedness (1:1 ratio) of the helical water chains (a) and the hydrogen bonding along the 1D water chain (b).

The hydrogen atoms of the water molecules are located from the difference Fourier map (Fig. 2(b)). In each water molecule, one hydrogen atom and one lone pair of electron are involved in the formation of 1D helix. The supramolecular structure acts as a host to stabilize the water chain. The propagation of the hydrogen bonding network in the host is perpendicular to the axis of the helical water chain. The alternate water molecules in the chain are hydrogen bonded to the host. As shown in Fig. 1, the O(7) atom is hydrogen bonded to the phenoxo oxygen atom O(3)#3 of the Schiff base giving a O(7)···O(3)#3 distance of ∼ 2.8 Å.

We have studied the thermal stability of the water molecules in $\mathbf{1}\cdot 2H_2O$ by thermogravimetric analysis (TGA) and differential scan calorimetry (DSC) (Fig. 3). The TGA experiments show weight loss of 4.6% in the temperature range 25–140 °C. The observed value is lower than the theoretical value of 5.8% for the loss of water molecules. The discrepancy is due to weight loss even at 25 °C indicating dynamic nature of the water molecules in the solid state. The lability of the water molecules is again evidenced from the DSC experiments where sample incubation has been done at −10 °C followed by heating at a rate of 5° min⁻¹ to 100 °C. The plot shows two endotherms at 61.5 and 88.5 °C. The calorimetric data are in agreement with the crystal structure of $\mathbf{1}\cdot 2H_2O$ showing water molecules in two different chemical environments, *viz.* "free" and "bound" form with respect to their interaction to the supramolecular host. While the water molecule O(7), anchored to the host, shows trifurcated hydrogen bonding due to its interaction with the phenoxo oxygen atom of the Schiff base, the water molecule O(8) in the chain is expected to be relatively labile in absence of any interaction with the host structure. The overall change of enthalpy per water molecule is ∼ 36 kJ mol⁻¹. The
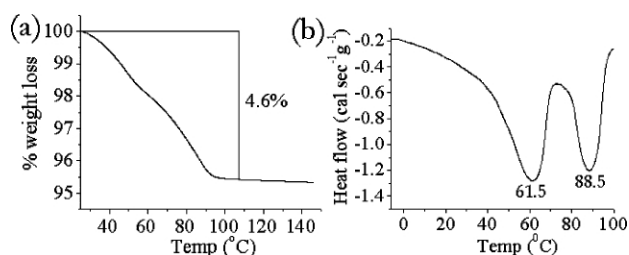

Fig. 3 Thermogravimetric plot showing the weight loss of the sample on increasing the temperature (a) and the DSC plot exhibiting two endotherms for the loss of water molecules (b).

powder XRD pattern of $\mathbf{1}\cdot 2H_2O$ resembles closely that of the rehydrated sample obtained after exposing the dehydrated species to moisture (Fig. S4‡).

The thermal data for $\mathbf{1}\cdot 2H_2O$ are similar to the values recently reported for a 1D chain of water molecules anchored on an organic host made of imidazole bases.[6] While the imidazole structures show all the water molecules bonded to the host in a "zig-zag" motif, complex $\mathbf{1}\cdot 2H_2O$ is novel in displaying binding of alternate water molecules in a helical chain and thus making our results comparable to the water chains in the membrane channels. Again, there is another recent report on self-assembled chain of water molecules in a crystal host made of 1,4,7,10-tetraazacyclodecane, showing linkages of tetrameric water clusters that do not model the water chains in biological processes.[7]

In summary, the supramolecular structure of the host, derived from the self assembly of a dicopper(II) complex, acts as a helical template in the formation of unprecedented type of helical 1D chain of water molecules and the crystal structure of $\mathbf{1}\cdot 2H_2O$ exemplifies a synthetic model for the water chains in helical membrane proteins with aquapores for transmembrane water or proton transport.

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