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# Unique example of a T3(2)4(2)3(2)6(2) water tape containing acetate–water hybrid hexamer in a heterometallic schiff base complex host

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ABSTRACT

The novel T3(2)4(2)3(2)6(2) tape, constructed by acetate–water hybrid hexamer $[(H_2O)_4(CH_3COO)_2]^{2-}$, water trimers and tetramer, has been observed for the first time in a heterometallic Schiff base complex host, $[Cu(vanpn)Na(CH_3COO)(H_2O)]$. $2H_2O$, {$H_2$*vanpn = N,N′-propylene-bis(3-methoxysalicylideneimine)*}. The present findings provide insight and serve as a prototype for stabilizing other pure and hybrid water clusters.

Because water is so essential to life on Earth, water clusters have been the subject of extensive experimental and theoretical research [1,2]. A number of discrete water clusters including tetramers [3], pentamers [4], hexamers [5,6], octamers [7], decamers [8,9], and higher order clusters [10] have been identified. Despite of many theoretical and experimental efforts, understanding the behavior of solid and liquid water at the molecular level still remains a challenge [11]. At the molecular level, water clusters are thought to facilitate the transfer of a proton along the hydrogen bonded chain [12], which is not only a fundamental biological process [13], but also a key mechanism for the generation of electrical power in hydrogen fuel cells [14]. Interestingly, this area continues to intrigue the scientific community both in terms of basic research and technological applications [15]. In particular, the structural characterization of water clusters is crucial in correlating and predicting the properties of bulk water at a molecular level. It is known that, in the solid state, most of the organic hosts forming water clusters are directly linked to water molecules via hydrogen bonding interactions [4].

It is possible to classify a number of common aggregation states adopted by hydrogen-bonded water molecules as: D (discrete chains), R (discrete rings), C (infinite chains in one dimension involving no rings), T (infinite tapes in one dimension involving rings), L (infinite layers in two dimensions), and U (unclassified structures) [16]. Many infinite water tapes in one dimension involving rings are reported in the literature. For example, six-membered and four-membered rings may be fused to form T4(2)6(2) tape [17], four-membered rings may be connected by sharing a water to form a T4(1) tape [18] etc. There are also some interesting examples, where a four-membered ring is fused with a ten-membered ring or with a eight-membered ring to form a T10(2)4(2) tape [19] or a T8(1)4(1) tape [20] respectively. In order to retrieve a sample of hydrated structures, we used the CSD search program ConQuest (version 5.32, November 2010; last updates Feb 2011). We included only those structures that have at least one acetate/water contact with an O···O distance less than the sum of their van der Waals radii and R-factor < 10% (266 hits on May 18, 2011).

In the present paper, we report for the first time, the synthesis and characterization of a new type of hybrid hexamer $[(H_2O)_4(CH_3COO)_2]^{2-}$ fused with water trimers and tetramer to form a one-dimensional T3(2)4(2)3(2)6(2) tape (Chart 1). Although the finding was totally serendipitous and not designed, the unique tape is expected to draw attention for the presence of fused tetracyclic moiety containing water trimer, tetramer and acetate–water hybrid hexamer in the same tape. This unique tape is stabilized in a heterometallic Schiff base complex host, $[Cu(vanpn)Na(CH_3COO)(H_2O)].2H_2O$, {Where $H_2$vanpn is N,N′-propylene-bis(3-methoxysalicylideneimine)}. The hybrid hexamer bears a similar structural topology as the cyclic hexamer, $(H_2O)_6$ [21] or cyclohexane. The participation of two oxygen atoms from two carboxylate groups with four water molecules in forming a six-membered ring has not been found in the aforementioned search [22] to form a T3(2)4(2)3(2)6(2) tape.

The reaction of copper(II) acetate monohydrate with $H_2$*vanpn* and sodium acetate at ambient temperature produces green precipitate of the complex [23]. Diffraction quality single crystals [24] are grown from the acetonitrile solution. The ligand ($H_2$*vanpn*) is prepared by

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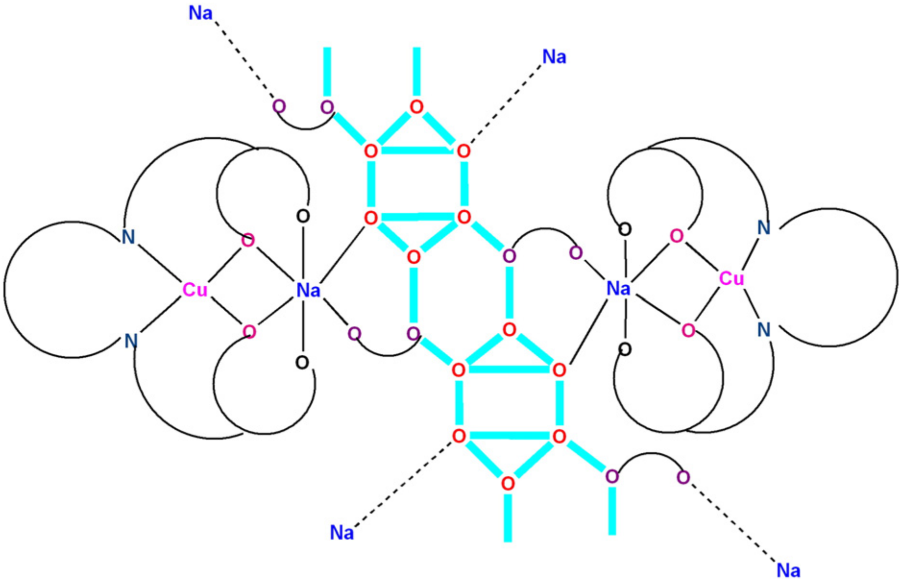


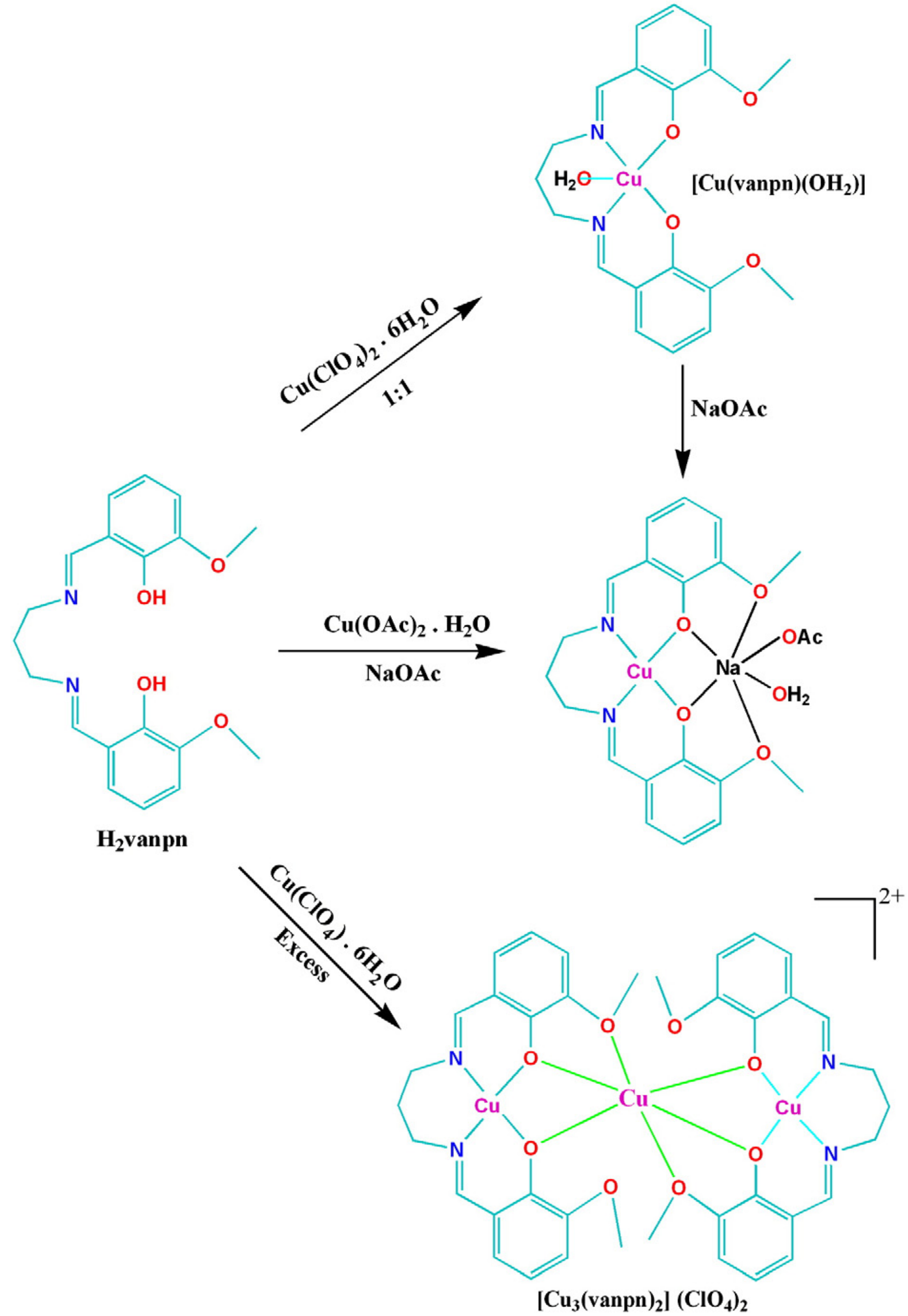
**Chart 1.** Coexistence of water trimer, tetramer and acetate–water hybrid hexamer in [Cu(vanpn)Na($CH_3COO$)($H_2O$)]. $2H_2O$ forming a T3(2)4(2)3(2)6(2) tape.

the 1:2 condensation of the 1,3-propanediamine with 3-methoxysalicyldehyde in methanol following the literature method [25]. *$H_2$vanpn* is then made to react with copper(II) acetate monohydrate and stirring with sodium acetate to prepare the complex. When copper(II) acetate is refluxed with *$H_2$vanpn* only, a different complex [Cu(vanpn)($OH_2$)] is produced, where copper(II) assumes a square-pyramidal geometry. The X-ray structure of this complex is reported elsewhere [26]. The coordinated water in the complex [Cu(vanpn)($OH_2$)] is involved in H-bonding with the methoxy oxygen of a second, thereby forming a H-bonded dimer. When sodium ion is incorporated in the system, the geometry of copper(II) ion is changed from square pyramidal to square planer. The H-bonding framework changes drastically on the incorporation of sodium in the $O_4$ compartment of the tetradentate Schiff Base. The mononuclear complex [Cu(vanpn)($OH_2$)] can also be prepared by refluxing $Cu(ClO_4)_2 \cdot 6H_2O$ with *$H_2$vanpn* in 1:1 ratio, but, in this synthetic procedure, $Cu(ClO_4)_2 \cdot 6H_2O$ and *$H_2$vanpn* ratio must be maintained to 3:2; otherwise a trinuclear complex [Cu(vanpn)Cu(vanpn)Cu]$(ClO_4)_2$ is produced. The structure of this is reported by a different group [27]. The formation of the complexes is shown in Scheme 1.

Elemental analysis (carbon, hydrogen and nitrogen) was performed using a Perkin–Elmer 240C elemental analyzer. IR spectra in KBr (4500–500 $cm^{-1}$) were recorded using a Perkin–Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile (1200–350 nm) were recorded in a Hitachi U-3501 spectrophotometer. The magnetic susceptibility measurements were done with an EG & PAR vibrating sample magnetometer, model 155 at room temperature and diamagnetic corrections were made using Pascal's constants. The thermal behavior of the complex was studied in a dynamic nitrogen atmosphere (150 mL $min^{-1}$) at a heating rate of 10 °C $min^{-1}$ using thermogravimetric (TG) and derivative thermogravimetric (DTG) techniques in a Perkin Elmer (SINGAPORE) Pyris Diamond TG/DTA instrument. Electrochemical measurements were performed in acetonitrile solution under a dry nitrogen atmosphere in conventional three-electrode configurations using a Pt diskworking electrode, Pt auxiliary electrode and Ag/AgCl reference electrode, with tetrabutylammonium hexafluorophosphate as supporting electrolyte in the potential range from −2 to 2 V, and were uncorrected for junction contribution. The value for the Fc–Fc+ couple under our conditions is 0.5 V. The magnetic susceptibility measurements were done with an EG & PAR vibrating sample magnetometer, model 155 at room temperature and diamagnetic corrections were made using Pascal's constants.

The structure determination reveals that the complex crystallizes in the monoclinic space group $P2_1/c$ with the asymmetric unit consisting of hetero-metallic complex [Cu(vanpn)Na($CH_3COO$)($H_2O$)] and two lattice water molecules. A representative ORTEP diagram is shown in Fig. 1. The central copper atom is coordinated by the two nitrogen atoms, N(8) and N(12), and two phenoxo oxygen atoms, O(2) and O(3), forming the distorted square planner geometry. There is a slight distortion to the square plane and the deviations of the coordinating atoms N(8),N(12),O(2) and O(3) from the least-square mean plane through them are 0.162(2), −0.161(2), −0.193(2) and 0.192(1) Å respectively and that of copper atom from the same plane is 0.046 Å. The conformation of the saturated six-membered ring {Cu(1)–N(8)–C(9)–C(10)–C(11)–N(12)} is closer to screw boat with the puckering parameters [28] Q = 0.610(2) Å, θ = 116.99(19)°, φ = 332.2(2)°. The N(8)–Cu(1)–N(12) angle is 96.45(7)° as expected for a typical six-membered chelate [29]. On the other hand, the sodium ion is surrounded by two phenoxo oxygen atoms, {O(2), O(3)} and two methoxy oxygen atoms {O(1), O(4)} of the Schiff base, one oxygen atom, O(100), of water molecule and one oxygen atom, O(11), from acetate group, to form a distorted octahedral geometry. The distance of Na-O(methoxy) is larger than that of Na-O(phenolate). The Cu(1)···Na(1) intra-molecular distance is 3.476 Å. The bridging angles Cu(1)–O(2)–Na(1) and Cu(1)–O(3)–Na(1) are 107.88(7)° and 108.01(6)°, respectively. The Cu(1)–O(2)–O(3)–Na(1) core is almost planar, the dihedral angles between the O(2) Cu(1)O(3) and O(2) Na(1)O(3) planes being 5.23°.

The enclathrated and coordinated water molecules as well as acetate groups are self-assembled through hydrogen bonds along the *b* axis to form a complex 1D network. The hydrogen bonding geometry and the water network are shown in Fig. 2 and hydrogen bond distances are given in Table S2. The most striking feature of the present system is that it contains cyclic water trimers, tetramers and hexamers fused with one another. Cyclic water tetramers (Fig. 3a) are formed by two types of water molecules, the lattice water molecules W1 and its symmetry related counterpart $W1^i$, the coordinated water molecule W2 and symmetry related $W2^i$, the corresponding oxygen atoms of which are represented by O(100), O($100^i$), O(102) and O($102^i$) respectively. The average hydrogen bond distance within the water tetramer is 2.8321 Å, which is closer to the respective distance of bulk liquid water (2.85 Å) [30] than to that of ice (2.76 Å for ice Ih at 90 K) [31]. O(102) and O($102^i$) act as two hydrogen bond acceptors and O(100) and O($100^i$) as hydrogen bond donors



**Scheme 1.** Synthesis of the complex.

to form the cyclic water tetramer. The four oxygen atoms within the cyclic tetramer lie in a plane. Interestingly, the individual water tetramer is hydrogen bonded to two neighboring free water molecules (W3and W3$^{i}$) [32] yielding an extended hexamer (Fig. 3b). Instead of describing this water cluster as hexamer, however, one can also think of the formation of two trimeric water clusters (Fig. 3c) (by W1, W2, W3; and W1$^{i}$, W2$^{i}$, W3$^{i}$) fused with the water tetramer. The bond angle between the planes of trimer and tetramer is found to be 65.98°. All the oxygen atoms act as both hydrogen bond acceptors and hydrogen bond donors alternatively. The water trimer clusters lie in the plane. This fused system of trimers with tetramer is linked among themselves again through a fused hexa nuclear ring formed by two lattice water, (W2 and W3) and an oxygen atom (O12) of the acetate group and obviously their symmetry-related counterparts (W2$^{j}$, W3$^{j}$ and O12$^{j}$) (Fig. 3d). In that hexamer, O(12) and O(12$^{j}$) act as hydrogen bond acceptors with O(102) and O(102$^{j}$) as hydrogen bond donors where as O(101) and O(101$^{j}$) involve in both hydrogen bond acceptor and donor. The average hydrogen bond distance within the acetate–water hybrid hexamer is 2.736 Å, which is closer to the respective distance of ice (2.76 Å for ice Ih at 90 K) [21] than to that of bulk liquid water (2.85 Å) [22]. Hydrogen bonded acetate–water hybrid hexamer is in a chair conformation.

Although the role of water has been extensively analyzed in the assembly of crystalline materials, no concrete rule has yet been established. However, it is generally assumed that water normally plays two types of role: firstly, it fills the void space in porous materials and secondly, it acts as balancing agent for the number of donors and acceptors when there is a mismatch between a set of hydrogen-bonding partners [33]. In recent years, there have been a number of reports of crystalline materials encapsulating water clusters of various nuclearities [34] and morphologies [4], either remaining in the void

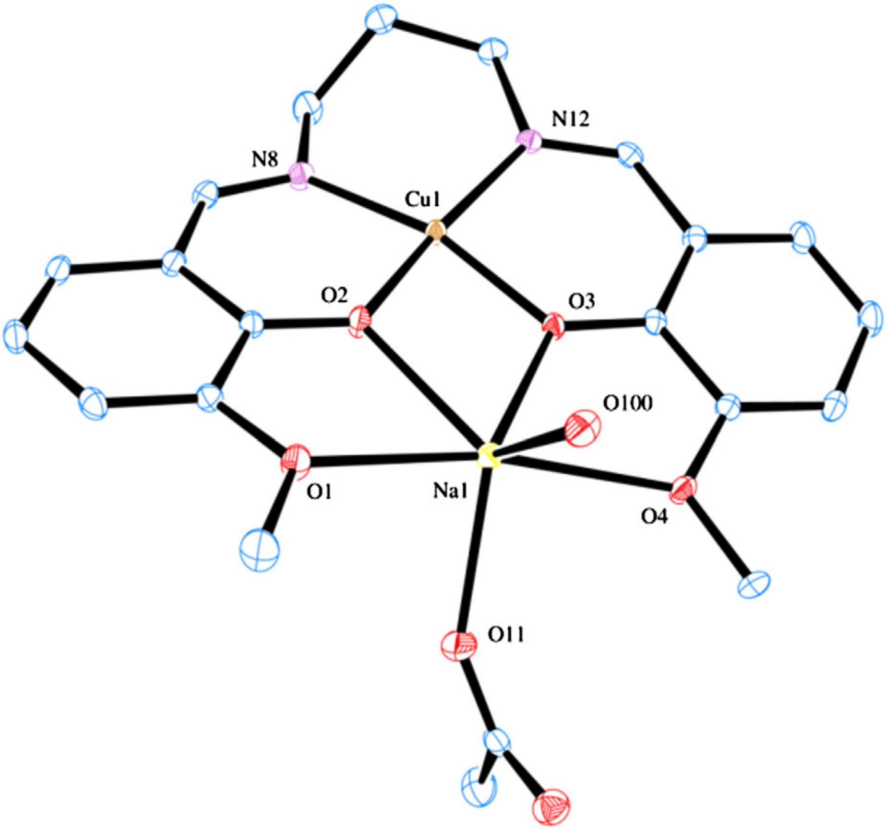


**Fig. 1.** ORTEP3 diagram of the complex with 25% ellipsoid probability. Hydrogen atoms and lattice water molecules are not shown for clarity. Selected bond distances (Å): Cu(1)–O(2) 1.9288(15), Cu(1)–O(3) 1.9238(14), Cu(1)–N(8) 1.9705(19), Cu(1)–N(12) 1.9778(17), Na(1)–O(1) 2.4831(18), Na(1)–O(2) 2.3601(17), Na(1)–O(3) 2.3613(16), Na(1)–O(4) 2.4953(16), Na(1)–O(11) 2.2690(2), Na(1)–O(100) 2.3350(2). Bond angles are given in supplementary Table S1.

space or as a constituent of the supramolecular network itself. The water tetramers are one of the important water motifs that have been observed in crystalline materials in more instances than the other water motifs [2]. This suggests that water molecules have an inherent tendency to self-organize themselves especially in the form of the water tetramer even in the presence of other molecular building blocks. The isolation and crystal structure of the complex unambiguously show not only the presence of fused trimers and tetramer but also the presence of an acetate–water hybrid hexamer to form a T3(2)4(2)3(2)6(2) tape.

The bidentate ligand, acetate, has extensively been used to link the transition metal ion and Na by coordination driven self-assembly to form discrete 2-D and 3-D species with well defined shape and sizes [35,36]. But, surprisingly, in all the complexes containing both copper

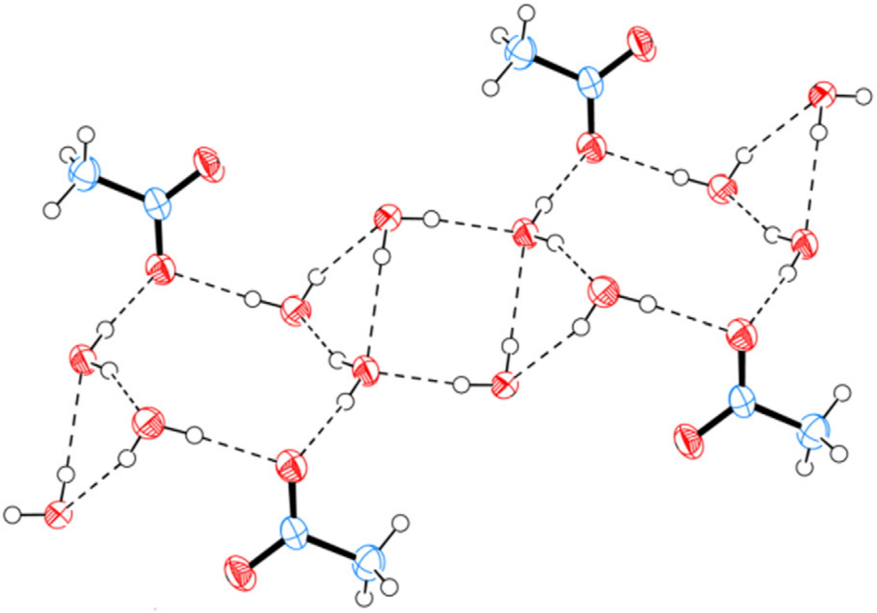


**Fig. 2.** T3(2)4(2)3(2)6(2) tape containing water trimers, tetramers and acetate–water hybrid hexamer.

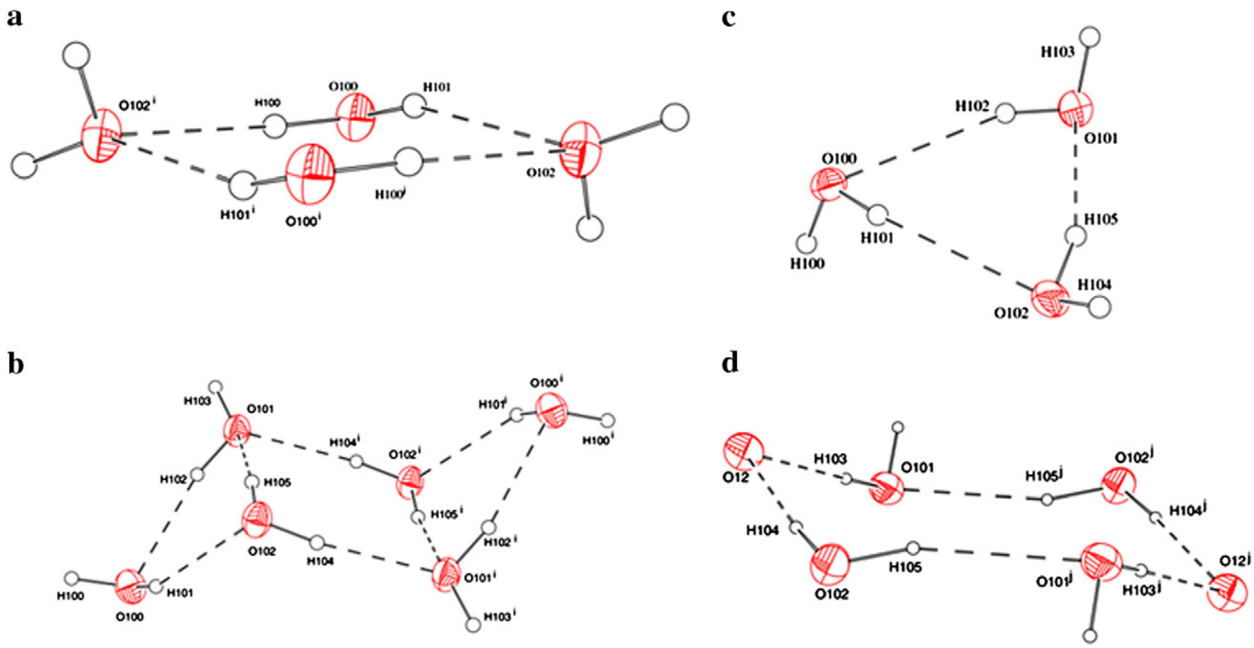


**Fig. 3.** ORTEP3 diagrams showing (a) cyclic water tetramer (b) extended hexamer (c) cyclic water trimer (d) acetate water hybrid hexamer.

and sodium, acetate is acting as bridging ligand [37] and among them, only one complex contains a Schiff base [36a]. Most interestingly, best to our knowledge, there is no report of crystal structure of a complex containing copper, sodium and acetate where acetate is used as a terminal ligand and attached with sodium only [37].

The Hirshfeld surfaces [38] of the complex are illustrated in Fig. 4a, showing surfaces that have been mapped over a $d_{norm}$ (range of −0.5 to 1.5 Å), shape index and curvedness. The surface is shown as transparent to allow visualization of the molecular moiety, in a similar orientation for all structures, around which they are calculated.

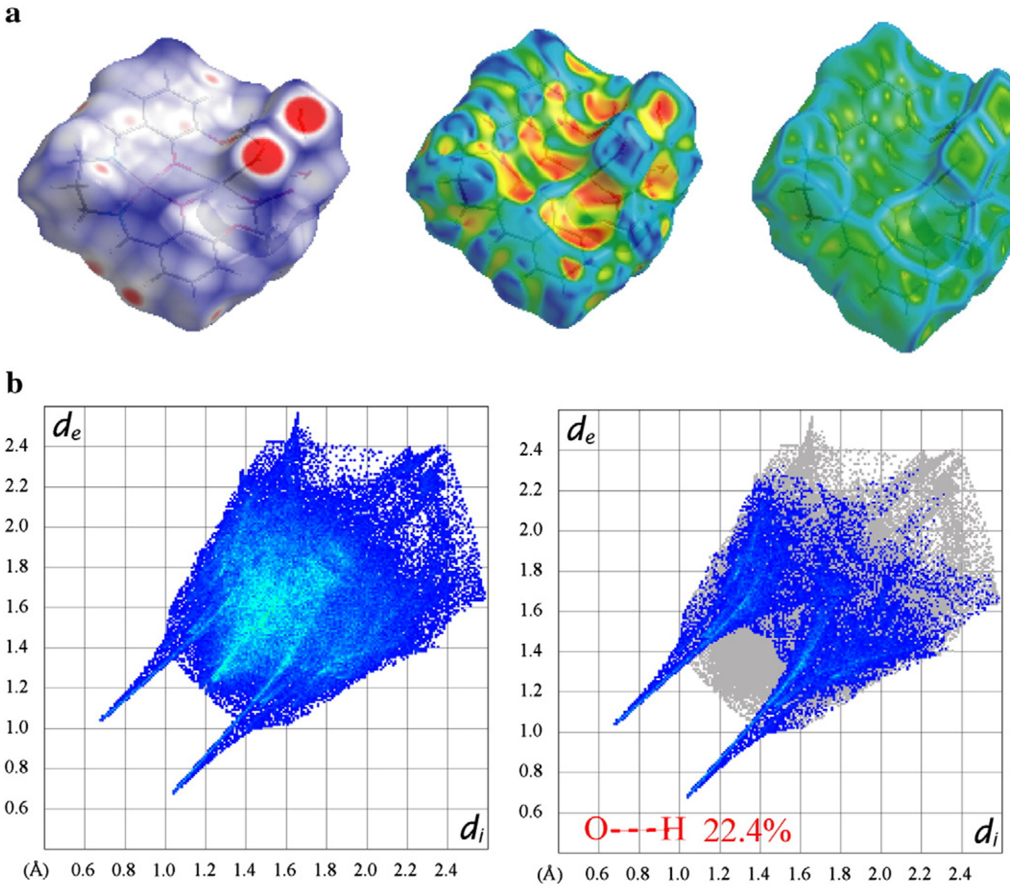


**Fig. 4.** (a) Hirshfeld surface mapped with $d_{norm}$ (left), shape index (middle), and curvedness (right). (b) Fingerprint plot: Full (left) and resolved into O···H/H···O (right) contact showing the percentage of contact contributed to the total Hirshfeld Surface area of molecule.

The dominant interaction between O···H atoms can be seen in the Hirshfeld surface as the red areas in Fig. 4a. Other visible spots in the Hirshfeld surfaces correspond to H···H contacts. The small extent of area and light color on the surface indicates weaker and longer contact other than hydrogen bonds. The O···H/H···O intermolecular interactions appear as distinct spikes in the 2D fingerprint plot (Fig. 4b). Complementary regions are visible in the fingerprint plots where one molecule act as donor ($d_e > d_i$) and the other as an acceptor ($d_e < d_i$). The fingerprint plots can be decomposed to highlight particular atoms pair close contacts. This decomposition enables separation of contributions from different interaction types, which overlap in the full fingerprint. The proportion of O···H/H···O interaction are comprising of 22.4% of the Hirshfeld surfaces for each molecule of the complex. The O···H interaction is represented by a spike ($d_i = 0.676$, $d_e = 1.026$ Å) in the bottom left (donor) area of the fingerprint plot (Fig. 4b), indicating H-atoms of $H_2O$ molecule are interacting with O-atom of the acetate group. The H···O interaction is also represented by another spike ($d_e = 0.676$, $d_i = 1.026$ Å) in the bottom right (acceptor) region of fingerprint plot, where acetate oxygen also acts as acceptor to the H atoms of the $H_2O$ molecule and these oxygen-based interactions represent the closest contacts in the structures and can be viewed as a pair of large red spots on the $d_{norm}$ surface (Fig. 4a). The relative contribution of the different interactions to the Hirshfeld surface is calculated for this complex as well as some similar complexes (Fig. S1) available in the CSD.

In the IR spectrum of the complex, distinct bands due to the azomethine (C–N) group within 1649–1573 $cm^{-1}$ are customarily noticed [39]. The spectrum exhibits a broad band centered at 3401 $cm^{-1}$ attributable to the O-H stretching frequency of the water cluster, which is similar to that of liquid water (3490 $cm^{-1}$) [40]. Thermogravimetric analysis shows a weight loss of ~10% in the temperature range 80–110°C which corresponds to the loss of 3 water molecules (calc. 10%). In the DTA curve, there is an endotherm peak, corresponding to the release of water molecule (Fig. S2). The dehydrated species does not absorb any water molecules on exposure to open atmosphere. In the IR spectrum of the dehydrated species, the broad band at ca. 3490 $cm^{-1}$ is missing, confirming the elimination of the water molecule on heating.

The redox property of the complex exhibits a quasi-reversible copper(II)/copper(I) reduction. The criteria of reversibility are checked by observing constancy of peak–peak separation ($\Delta E_p = E_{pa} - E_{pc}$) and the ratio of peak heights ($i_{pa}/i_{pc} \sim 1$) with variation of scan rates [41]. Only very few copper(II)/copper(I) couples exhibit truly reversible electrochemical behavior because copper(II) has a tendency toward six-coordinate tetragonal geometries while copper(I) appears to prefer four-coordinate tetrahedral geometries. The subsequent rearrangement of the copper coordination sphere upon the reduction of the copper(II) species typically leads to a relatively slow chemical reaction following the electron transfer process. Reversible behavior can only be seen in cases where the geometry of the copper complex is essentially the same before and after the reduction. The only coordination number that is common to both oxidation states is four, and even in these systems copper(I) may have regular tetrahedral coordination sphere but copper(II) always involves a compressed tetrahedral or square planer geometry. In the present study, complex exhibit quasi-reversible signals. It has been observed that no well defined oxidative or reductive responses could be observed on running further in the positive or negative potential. The $E_{1/2}$ and $\Delta E_p$ values for these redox couples are given in Table 1. All the redox signals remain virtually invariant under different scan rates (0.01–1.0 V $s^{-1}$) in the temperature range 300–280 K. Solvent dependent shift and change in electrochemical reversibility of redox couples are not significant.

**Table 1**
Electrochemical data.

| $Cu^{II}/Cu^{I}$ | | | |
|---|---|---|---|
| $E_{pa}$(V) | $E_{pc}$(V) | $E_{1/2}$(V) | $\Delta E_p$ (mV) |
| −1.51 | −1.59 | −1.55 | 80 |

Although there is an abundance of discrete water clusters reported in the literature, the formation of the acetate–water hybrid hexamer described in this work has not been observed before in a metal organic framework host. The coexistence of water trimers and tetramers with this hybrid-hexamer forming a T3(2)4(2)3(2)6(2) tape makes the system unique. Given the novel role of water clusters in chemical and biological systems, the present findings provide insight and serve as a prototype for stabilizing other pure and hybrid water clusters.

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## Appendix A. Supplementary data

Crystallgraphic data for the analysis have been deposited with the Cambridge Crystallographic data Centre, CCDC No 814315. Copies of this information may be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data to this article can be found online at doi:10.1016/j.inoche.2012.01.008.

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[22] CSD search file 1.pdf (Supporting Information).

[23] The Schiff base ligand, *H₂vanpn*, was synthesized by refluxing 1,3-diaminopropane (10 mmol, 0.84 mL) with 3-methoxysalicyldehyde (20 mmol, 3.04 g) in methanol (20 ml) for ca. 1 h. To prepare the complex, a methanol solution of copper(II) acetate monohydrate (1 mmol, 0.2 g) was added to the methanol solution of *H₂vanpn* (1 mmol, 0.342 g) and refluxed for 1 hr. A solution of sodium acetate (1 mmol, 0.085 g) in methanol was then added to it and stirred for 15 mins. A green colored complex was precipitated out and was recrystallized from acetonitrile solution to obtain prismatic dark green single crystals suitable for X-ray diffraction. Yield: 0.34 g (61%). Anal. Calc. for $C_{22}H_{32}CuN_2NaO_9$ (540): C, 40.40; H, 5.04; N, 4.32; Found: C, 40.3; H, 4.9; N, 4.4; UV–Vis, $\lambda_{max}$(nm) ($\varepsilon_{max}$ (dm$^3$mol$^{-1}$ cm$^{-1}$)) (acetonitrile), 565 (130), 366 (4355), Magnetic moment = 1.74 BM.

[24] A crystal of dimensions 0.34 × 0.32 × 0.14 mm$^3$ was mounted in inert oil and transferred to the cold gas stream of the cooling device. Data have been collected at 193 K on a STOE IPDS diffractometer using graphite monochromated Mo-Kαradiation and corrected for absorption using indexed faces. Programs used: SIR92 — A program for crystal structure solution. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 1993, 26, 343–350. SHELXL-97 — A program for crystal structure refinement. G. M. Sheldrick, Acta Cryst., 2008, A64, 112–122. Crystal data: Fw-539.99; monoclinic, $P2_1/c$, a = 11.4435(8), b = 8.7183(6), c = 23.3113(17) Å, β = 92.062(8)°,$d_{calc}$ (g cm$^{-3}$) = 1.543, *F*(000) = 1124, Z = 4. 334 parameters were fit to 4052 unique reflections to give R1, wR2 [I > 2 σ (I)] = 0.0295, 0.0606.

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[38] Hirshfeld surfaces [42–44] and the associated 2D-fingerprint [45–47] plots were calculated using Crystal Explorer [48], which accepts a structure input file in CIF format. Bond lengths to hydrogen atoms were set to standard values. For each point on the Hirshfeld isosurface, two distances $d_e$, the distance from the point to the nearest nucleus external to the surface and $d_i$, the distance to the nearest nucleus internal to the surface, are defined. The normalized contact distance ($d_{norm}$) based on de and $d_i$ is given by $d_{norm} = \frac{(d_i - r_i^{vdw})}{r_i^{vdw}} + \frac{(d_e - r_e^{vdw})}{r_e^{vdw}}$ where $r_i^{vdw}$ and $r_e^{vdw}$ are the van der Waals radii of the atoms. The value of $d_{norm}$ is negative or positive depending on intermolecular contacts being shorter or longer than the van der Waals separations. The parameter $d_{norm}$ displays a surface with a red-white-blue color scheme, where bright red spots highlight shorter contacts white areas represent contacts around the van der Waals separation, and blue regions are devoid of close contacts. For a given crystal structure and set of spherical atomic electron densities, the Hirshfeld surface is unique [49], and it is the property that suggests the possibility of gaining additional insight into the intermolecular interaction of molecular crystals.

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