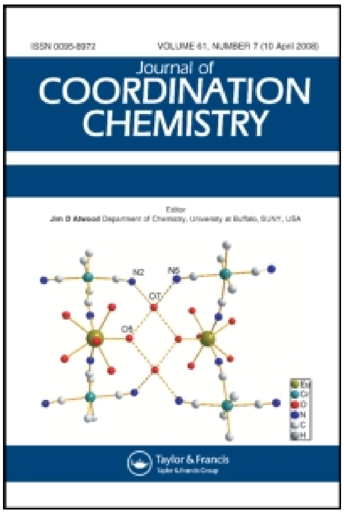

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Dinuclear copper(II) complex and 1-D copper(II) complex with taurine Schiff base: synthesis, crystal structure, and properties

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Dinuclear copper(II) complex and 1-D copper(II) complex with taurine Schiff base: synthesis, crystal structure, and properties

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A dinuclear copper(II) compound, $[Cu(btssb)(H_2O)]_2 \cdot 4(H_2O)$ (**1**), and a 1-D chain copper(II) compound, $[Cu(ctssb)(H_2O)]_n$ (**2**) [where H_2btssb is 2-[(5-bromo-2-hydroxy-benzylidene)-amino]-ethanesulfonic acid and H_2ctssb is 2-[(3,5-dichloro-2-hydroxy-benzylidene)-amino]-ethanesulfonic acid], were prepared and characterized. Compound **1** crystallizes in the monoclinic space group $P2_1/c$, with $a = 10.109(2)$ Å, $b = 20.473(4)$ Å, $c = 6.803(1)$ Å, $\beta = 100.32(3)^\circ$, $V = 1385.1(5)$ Å^3, and $Z = 2$; R_1 for 1796 observed reflections $[I > 2\sigma(I)]$ was 0.0357. The geometry around each copper(II) can be described as slightly distorted square pyramidal. The $Cu^{II} \cdots Cu^{II}$ distance is 5.471(1) Å. Compound **1** formed a 1-D network through O–H $\cdots$ O hydrogen bonds and 1-D water chains exist. The 1-D chain complex **2** crystallizes in the triclinic space group $P\bar{1}$, with $a = 5.030(2)$ Å, $b = 7.725(2)$ Å, $c = 17.011(5)$ Å, $\alpha = 92.706(4)^\circ$, $\beta = 97.131(4)^\circ$, $\gamma = 102.452(3)^\circ$, $V = 638.6(3)$ Å^3, and $Z = 2$; R_1 for 1897 observed reflections $[I > 2\sigma(I)]$ was 0.0171. In **2**, Cu(II) was also a slightly distorted square pyramid formed by two oxygens and one nitrogen from ctssb, one oxygen from another ctssb, and one water molecule. The complex formed a 1-D chain through O–S–O bridge of ctssb ligand. The 1-D chain further constructed a double chain through O$-$H $\cdots$ O hydrogen bonds.

Keywords: Crystal structure; Water chain; Coordination polymer

1. Introduction

Compounds containing dimer water [1, 2], water rings [1–6], water chains [7–9], metal–water chain [10], water network [11], water ring chains [12], and water–methanol intermix clusters [13] have considerable interest because many water forms are poorly understood. Water chains appear to facilitate the selective permeation [14] of water across membranes and also to be important [15] in control of proton fluxes in a variety of biomolecules.

Coordination geometry around metal ions and bonding mode of ligands are the primary considerations in metal-mediated self-assembly reactions. Relatively small

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modification in the bridging ligand may give large changes in the overall structure of the assembly [16]. Numerous other factors, such as solvent, concentration, counterion, and temperature also play a role in the formation of products [17, 18]. Herein, using two different ligands which are only different in halogen, we synthesize two different complexes: $[Cu(btssb)(H_2O)]_2 \cdot 4(H_2O)$ (**1**) and $[Cu(ctssb)(H_2O)]_n$ (**2**).

2. Experimental

All reagents were commercial grade materials and used without purification. Elemental analyses (C, H, N, S) were performed by a PE 1700 CHN auto elemental analyzer. IR spectra were recorded on a Spectrum One Perkin-Elmer FT-IR spectrophotometer (KBr disc) from 4000 to 400 cm^{-1}. The crystal structure was determined by single-crystal diffraction and SHELXL crystallographic software. The thermal gravimetric (TG) analysis was performed on a TG209. Raman spectra were recorded on a Renishaw plc., Wotton-under-Edge, UK (single-crystal sample) from 3500 to 50 cm^{-1}.

2.1. *Preparation of btssbH$_2$ and ctssbH$_2$*

The H_2btssb (2-[(5-bromo-2-hydroxy-benzylidene)-amino]-ethanesulfonic acid) and H_2ctssb (2-[(3,5-dichloro-2-hydroxy-benzylidene)-amino]-ethanesulfonic acid) ligands were prepared according to a literature procedure [19].

2.2. *Preparation of $[Cu(btssb)(H_2O)]_2 \cdot 4(H_2O)$ (1)*

A solution of H_2btssb (1 mmol, 0.308 g) in ethanol (20 mL) was added slowly to a solution of $CuCl_2 \cdot 2H_2O$ (1 mmol, 0.170 g) in water (15 mL). The mixture was stirred for 1 h at room temperature, filtered, and the filtrate was allowed to stand at room temperature. Blue block single crystals for X-ray diffraction were obtained in a yield of 0.280 g (66%, based on Cu). Anal. Calcd (%) for $C_{18}H_{28}Br_2Cu_2N_2O_{14}S_2$: C, 25.51; H, 3.33; N, 3.31; S, 7.57. Found: C, 25.46; H, 3.48; N, 3.37; S, 7.52.

2.3. *Preparation of $[Cu(ctssb)(H_2O)]_n$ (2)*

Compound **2** was synthesized in a similar way to that described for **1** except that H_2btssb was replaced by H_2ctssb. Yield: 0.147 g (38.9%, based on Cu). Anal. Calcd (%) for $C_9H_9Cl_2CuNO_5S$: C, 28.62; H, 2.40; N, 3.71; S, 8.47. Found: C, 28.58; H, 2.47; N, 3.72; S, 8.44.

2.4. *Crystal structure determination*

Single-crystal X-ray diffraction analyses of **1** and **2** were carried out on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω–θ scan technique at 293 K. Raw frame data were integrated with SAINT [20]. The structures were solved by direct methods with SHELXS-97 and

Table 1. Crystallographic data for **1** and **2**.

Molecular formula	$C_{18}H_{28}Br_2Cu_2N_2O_{14}S_2$	$C_9H_9Cl_2CuNO_5S$
Formula weight	847.44	377.69
Temperature (K)	298(2)	298(2)
Crystal color and form	Blue, block	Blue, block
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	10.109(2)	5.030(2)
b	20.473(4)	7.725(2)
c	6.803(1)	17.011(5)
α		92.706(4)
β	100.32(3)	97.131(4)
γ		102.452(3)
Volume (Å^3), Z	1385.1(5), 2	638.6(3), 2
Calculated density (g cm^{-3})	2.032	1.964
Absorption coefficient (mm^{-1})	4.461	2.305
$F(000)$	844	378
θ range for data collection (°)	1.99–28.34	2.42–25.10
Reflections collected/unique	2459/1796	2217/1897
Completeness to $\theta = 25.02$ (%)	99.9	98.2
Parameters	181	173
Goodness-of-fit on F^2	1.067	1.033
R_1 $[I \geq 2\sigma(I)]^{a,b}$	0.0357	0.0419
wR_2 (all data)^{a,b}	0.0913	0.1130
Largest difference peak and hole (e Å^{-3})	0.671 and −0.521	1.173 and −0.689

$^a R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $^b wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

refined by full-matrix least-squares on F^2 using SHELXL-97 [20]. The empirical absorption correction was applied with SADABS [20]. All non-hydrogen atoms were refined anisotropically while all hydrogens were set in calculated positions and refined by a riding mode. The crystallographic details for **1** and **2** are provided in table 1 while selected bond distances and angles are listed in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Structure of [Cu(btssb)(H$_2$O)]$_2$·4(H$_2$O) (1)*

Single-crystal X-ray diffraction analysis reveals that **1** (blue block) crystallizes in the monoclinic space group $P2_1/c$ (figure 1). The copper(II) is five-coordinate by two O and one N (O1, O2, N1) from btssb ligand, one O (O4a, symmetry code: (a) $x+1$, $-y+1$, $-z+2$) from another btssb, and one O (O5) from a terminal water, forming a slightly distorted square pyramid. Cu is chelated by a tridentate btssb and bridged by another btssb (Cu1–N1, 1.955(3) Å, Cu1–O1, 1.886(3) Å, Cu1–O2, 1.963(3) Å, Cu1–O5, 1.980(3) Å, and Cu1–O4$^{(i)}$, 2.429(3) Å, symmetry code:$^{(i)}$ $1-x$, $1-y$, $1-z$). Each pair of Cu(II) ions is bridged by a pair of *syn–syn* sulfonates of btssb into a dinuclear complex with an intramolecular Cu $\cdots$ Cu distance of 5.471(2) Å, which is longer than the copper $\cdots$ copper distances in dimeric copper(II) carboxylates (2.59–2.747 Å) [21].

Table 2. Selected geometric parameters (Å, °) for **1**.

Cu1–O1	1.886(3)	Cu1–O5	1.980(3)
Cu1–N1	1.955(3)	Cu1–O4$^{(i)}$	2.429(3)
Cu1–O2	1.963(3)	Cu1 ··· Cu1a	5.471(2)
O1–Cu1–N1	94.6(1)	O2–Cu1–O5	83.6(1)
O1–Cu1–O2	168.4(1)	O1–Cu1–O4$^{(i)}$	96.0(1)
N1–Cu1–O2	94.1(1)	N1–Cu1–O4$^{(i)}$	98.2(1)
O1–Cu1–O5	86.6(1)	O2–Cu1–O4$^{(i)}$	90.4(1)
N1–Cu1–O5	171.0(1)	O5–Cu1–O4$^{(i)}$	90.5(1)

Symmetry code: $^{(i)}$ $-x+1$, $-y+1$, $-z+1$.

Table 3. Selected geometric parameters (Å, °) for **2**.

Cu1–O1	1.878(3)	Cu1–O2	1.951(3)
Cu1–O5	1.956(3)	Cu1–N1	1.958(4)
Cu1–O4$^{(i)}$	2.384(3)	Cu1 ··· Cu1$^{(i)}$	5.030(2)
O1–Cu1–O2	166.6(2)	O1–Cu1–O5	84.9(1)
O2–Cu1–O5	85.1(1)	O1–Cu1–N1	94.3(2)
O2–Cu1–N1	94.7(2)	O5–Cu1–N1	174.3(2)
O1–Cu1–O4$^{(ii)}$	99.4(1)	O2–Cu1–O4$^{(ii)}$	89.8(1)
O5–Cu1–O4$^{(ii)}$	91.7(1)	N1–Cu1–O4$^{(ii)}$	94.0(2)

Symmetry codes: $^{(i)}$ $-x+1$, y, z; $^{(ii)}$ $x+1$, y, z.

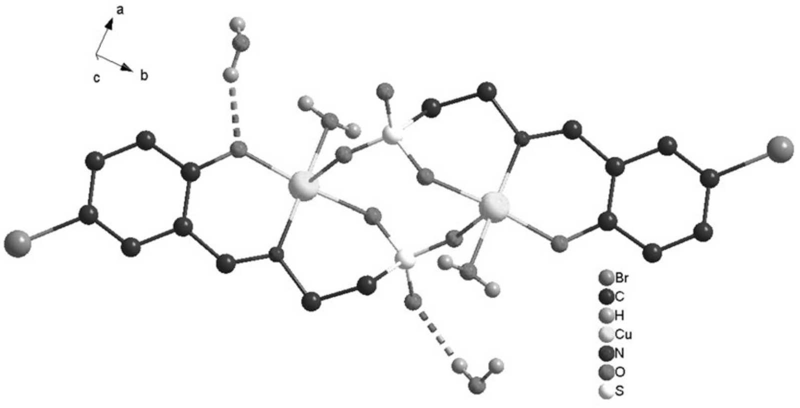
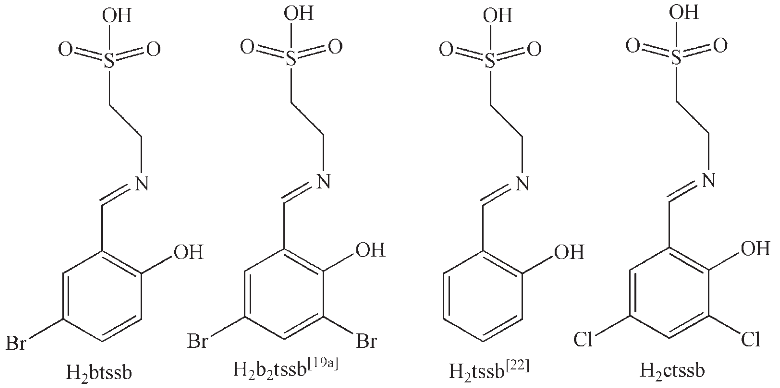


Figure 1. The structure of **1** showing coordination of Cu(II). Dashed lines indicate hydrogen bonds.

Three dinuclear copper complexes were constructed using taurine Schiff base (2-[(3, 5-dibromo-2-hydroxy-benzylidene)-amino]-ethanesulfonic acid (H_2b_2tssb), 2-[(2-hydroxy-benzylidene)-amino]-ethanesulfonic acid (H_2tssb), or 2-[(3-formyl-5-methyl-2-hydroxy-benzylidene)-amino]ethanesulfonic acid (H_2L)) [19a, 22]. Herein, a 1-D water chain and tetranuclear water cluster were observed in **1** and $[Cu_2L_2(H_2O)_4] \cdot 5H_2O$ [22b], respectively, while $[Cu_2(b_2tssb)_2(CH_3OH)_2]$ and $[Cu(tssb)(H_2O)]_2 \cdot 2H_2O$ did not have water ring or water chain. The structure of the four ligands is similar with only



Scheme 1. The ligand structures of taurine Schiff bases.

substituting groups different (scheme 1), suggesting that relatively small modification in the bridging ligand may give large changes in the overall structure of the assembly [16]. O1W in the chain forms four hydrogen bonds, two as a donor and two as an acceptor, while O2W is a double donor and single acceptor because of the sideways hydrogen bonding (figure 2). The free hydrogen available with each water molecule acts as a donor to the available phenolate oxygen and sulfonate oxygen (table 4), further stabilizing the chain structure. Thus, in **1**, O1W exhibits four-coordination which is the same as each oxygen in an assembly of water molecules. Hydrogen-bond-deficient water molecules are found at the surface of ice [23], and recent X-ray absorption spectroscopy and Raman scattering studies of liquid water also suggest that significant numbers of oxygens show less than tetracoordination in liquid water [24]. The oxygens of water in the chain are not coplanar but form an unprecedented wave pattern extending along the crystallographic *c*-axis (figure 2). Water exhibits short-range O ··· O order in the X-ray diffraction radial distribution curve at 2.7 Å, whereas in the gas phase, this value is ~0.2 Å longer [25]. In **1**, wide variation in the hydrogen bonding interaction is observed (range of O ··· O distances, 2.673–2.865 Å; range of O–H ··· O angles, 154.5–173.4°), attributable to the fact that water in the chain is sufficiently flexible to respond to changes in the chain's environment. Here, both water–host and water–water interactions are important for the stability of the overall structure (figure 3).

3.2. *Structure of [Cu(ctssb)(H_2O)]$_n$ (2)*

The molecule of **2** which crystallizes in the triclinic space group $P\bar{1}$ is shown in figure 4. Copper(II) has a slightly distorted square pyramid formed by two O and one N from ctssb, one O from another ctssb ligand, and one water molecule (Cu1–N1, 1.958(4) Å; Cu1–O1, 1.878(3) Å, Cu1–O2, 1.951(3) Å, Cu1–O5, 1.956(3) Å, and Cu1–O4$^{(i)}$, 2.384(3) Å, symmetry code: $^{(i)}$ $-x+1$, y, z). Compound **2** further formed a 1-D chain by sulfonate bridges. In intrachain, the Cu ··· Cu distance is 5.030(2) Å, which is shorter than the Cu ··· Cu distance of **1**. The 1-D chain further constructed a double chain through O–H ··· O hydrogen bonds (O5–H5A ··· O4$^{(ii)}$, 2.906(5) Å; O5–H5B ··· O3$^{(iii)}$,

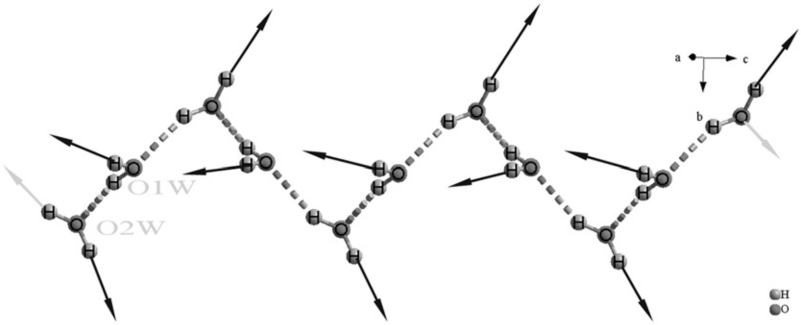


Figure 2. 1-D water chain of **1**.

Table 4. Hydrogen bond geometry (Å, °) for **1**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O5–H5B···O1W$^{(i)}$	0.85	1.92	2.761 (4)	173
O5–H5A···O3$^{(ii)}$	0.85	2.01	2.822 (4)	159
O1W–H1WA···O1$^{(iii)}$	0.85	1.97	2.768 (4)	156
O1W–H1WB···O2W$^{(iv)}$	0.85	1.94	2.779 (6)	171
O2W–H2WA···O1W$^{(v)}$	0.85	1.88	2.673 (6)	155
O2W–H2WB···O3	0.85	2.06	2.865 (5)	157

Symmetry codes: $^{(i)}$ $x, y, z+1$; $^{(ii)}$ $-x+1, -y+1, -z+2$; $^{(iii)}$ $x, -y+1/2, z-1/2$; $^{(iv)}$ $-x+1, -y+1, -z+1$; $^{(v)}$ $-x+1, y+1/2, -z+1/2$.

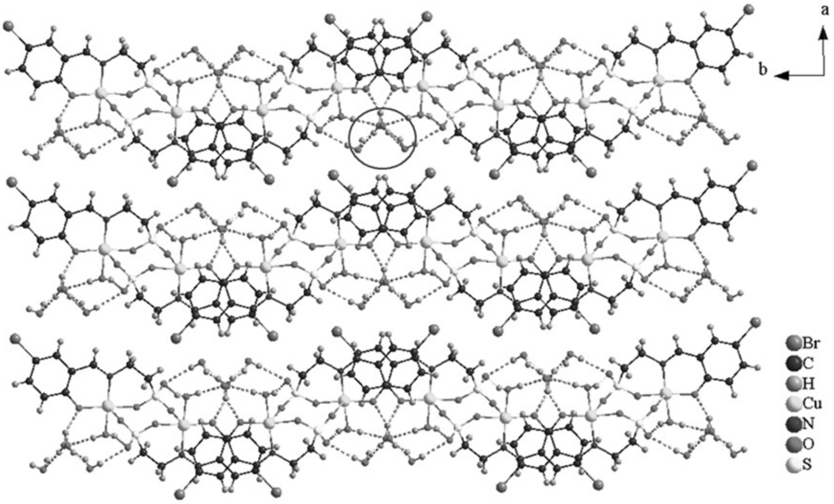


Figure 3. Packing drawing of **1**. Dashed lines indicate hydrogen bonds.

2.744(5) Å, symmetry codes: $^{(ii)}$ $-x, -y+1, -z+1$; $^{(iii)}$ $-x+1, -y+1, -z+1$, table 5) (figure 5). The ligands btssb and ctssb are similar (scheme 1), but the structures of **1** and **2** are completely different, suggesting that relatively small modification in the bridging ligand gives large changes in the overall structure of the assembly [16].

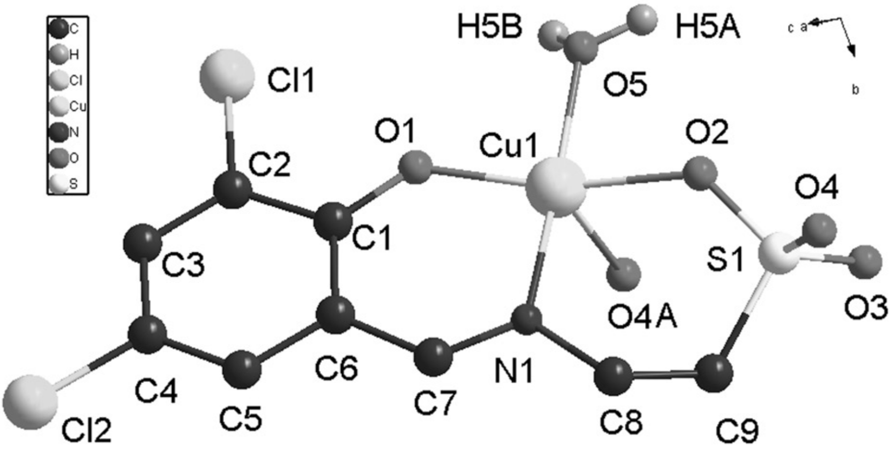


Figure 4. The structure of **2** showing coordination of Cu(II). Part of the hydrogens were omitted.

Table 5. Hydrogen bond geometry (Å, °) for **2**.

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O5–H5A···O4$^{(ii)}$	0.85	2.06	2.906(5)	171.4
O5–H5B···O3$^{(iii)}$	0.85	1.96	2.744(5)	153.3

Symmetry codes: $^{(ii)}$ $-x, -y+1, -z+1$; $^{(iii)}$ $-x+1, -y+1, -z+1$.

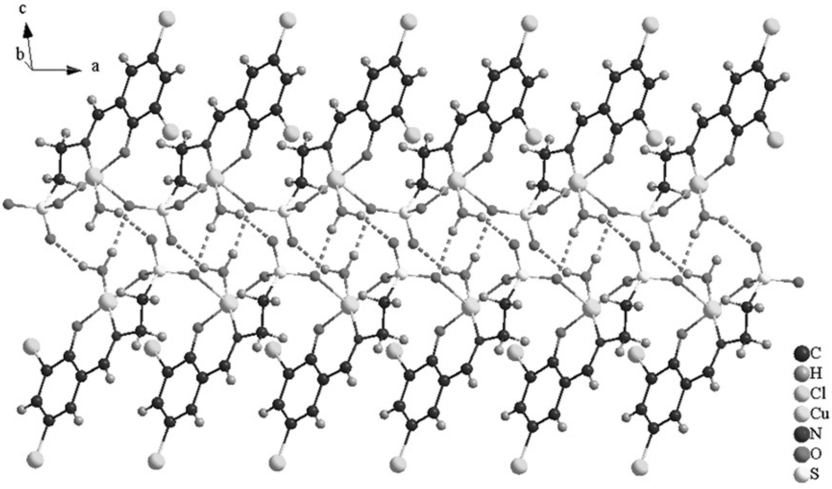


Figure 5. The double chain of **2**. Dashed lines indicate hydrogen bonds.

3.3. *Thermal and spectroscopic properties*

The interaction between the host and the water chains is moderately strong, as the TG analysis with a 5.4 mg sample in nitrogen shows that weight loss occurs in stages beginning at 85°C (8.3% corresponding to all the water chains (calculated 8.5%))

to above 146°C. Complete decomposition is achieved at ~305°C (Supplementary material). The FT-IR spectra of **1** show a broad band centered around 3400 cm^{-1}, attributable to O–H stretching frequency of the water chain [3]. This broad band vanishes on heating **1** under vacuum at 115°C for 2 h, suggesting escape of water chains from the lattice. Deliberate exposure to water vapor for 2 days does not lead to reabsorption of water into the lattice as monitored by FT-IR spectroscopy. The IR spectrum of ice shows the O–H stretching at 3220 cm^{-1} [26], whereas the stretching vibrations in liquid water appear at 3490 and 3280 cm^{-1} [26] (Supplementary material). Hence, the water chain in **1** shows O–H stretching similar to that of liquid water.

Bands at 2861, 2919, 2946, and 2992 cm^{-1} in the Raman spectrum (Supplementary material) is to fill 1-D water chain with all the waters involved in hydrogen bonding similar to liquid water [26].

In summary, we have synthesized and obtained crystal structures of two new taurine Schiff base copper complexes. A 1-D water chain is observed in **1**, while **2** is a 1-D chain coordination polymer which further forms a double chain through hydrogen bonds. The study demonstrates that the nature of the ligand plays an important role in directing the topologies of the complexes.

Supplementary material

Crystallographic data for the title complex in the CIF format have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 661989 and 774742. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-366033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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