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Hydrogen-bonded supramolecular structures constructed from trinuclear copper units

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Abstract Four copper complexes with similar trinuclear copper units, $[Cu_6(Bmshp)_2(SO_4)_2(H_2O)_7]\cdot 2H_2O$ (**1**), $[Cu_3(Bmshp)(ClO_4)_2(H_2O)_4]\cdot 5H_2O$ (**2**), $[Cu_3(Bmshp)(DMF)_4(H_2O)_2]\cdot H_2O\cdot 2DMF\cdot 2ClO_4$ (**3**) and $[Cu_3(H_2Bcshp)(ClO_4)_2(H_2O)_4]\cdot 3H_2O$ (**4**) (H_4Bmshp = 2,6-bis[(3-methoxysalicylidene)hydrazinocarbonyl]pyridine, H_6Bcshp = 2,6-bis[(3-carboxylsalicylidene)hydrazinocarbonyl]pyridine), were synthesized and characterized by elemental analysis, IR and single crystal X-ray diffraction analysis. Due to the different anions, solvents and ligands used in the syntheses, complexes **1**–**4** exhibit diverse supramolecular structures constructed from the corresponding trinuclear copper units via H-bonds.

Introduction

Crystal engineering is a subject devoted to achieving the assembly of molecules into desirable supramolecular architectures [1] and studying their potential applications in the fields of microelectronics, nonlinear optics, porous materials and other technologies [2–8]. As an important part of crystal engineering, the construction of supramolecular structures via self-assembly using individual discrete polynuclear metal complexes as molecular building blocks has particularly attracted a lot of attention in recent decades. The process of this self-assembly is based on the extension among individual molecules by weak covalent or noncovalent interactions, including Van der Waals, electrostatic and hydrophobic interactions, hydrogen bonds, as well as π–π and ion-π stacking [9–16]. Among them, hydrogen bonding interactions provide an important tool in the formation of ordered supramolecular chains, layers and three-dimensional frameworks [17]. Examples of the construction of multi-dimensional supramolecular structures from zero-dimensional discrete polynuclear metal blocks via hydrogen bonding interactions have been widely reported [1, 11, 17–21]. From these reported works, we can see that the building blocks are usually metal carboxylate clusters and amide-containing complexes due to their inclination to form H-bonds of COOH···N, COOH···O and N–H···O, etc. 2,6-Pyridine-diacylhydrazone ligands possess high flexibility and alterable coordinating sites on the end groups around the N–N single bonds, which may be favorable for the construction of discrete polynuclear units [22–27]. It is reasonable to expect that interesting polydimensional hydrogen-bonded supramolecular architectures constructed from these polynuclear units (as building blocks) could be obtained by modifying the end groups around the N–N bonds with functional groups suitable for the formation of hydrogen bonds.

Herein, we present the syntheses and structures of four copper complexes based on two 2,6-pyridine-diacylhydrazone ligands, $[Cu_6(Bmshp)_2(SO_4)_2(H_2O)_7]\cdot 2H_2O$ (**1**), $[Cu_3(Bmshp)(ClO_4)_2(H_2O)_4]\cdot 5H_2O$ (**2**), $[Cu_3(Bmshp)(DMF)_4(H_2O)_2]\cdot H_2O\cdot 2DMF\cdot 2ClO_4$ (**3**) and $[Cu_3(H_2Bcshp)$-

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$(ClO_4)_2(H_2O)_4]\cdot 3H_2O$ (**4**) (H_4Bmshp = 2,6-bis[(3-methoxysalicylidene)hydrazinocarbonyl]pyridine, H_6Bcshp = 2,6-bis[(3-carboxylsalicylidene)hydrazinocarbonyl]pyridine). The four complexes exhibit similar trinuclear structural units. However, different hydrogen-bonded supramolecular structures constructed from the trinuclear copper units are obtained due to the differences of anions, solvent molecules and functional groups on the ligands in the complexes.

Experimental

All reagents and solvents were purchased commercially as reagent grade and used without further purification. 2,6-Pyridine-dicarboxylic hydrazide was synthesized by literature methods [28]. IR spectra were recorded in the range 4,000–400 cm^{-1} on a Perkin-Elmer PE Spectrum One FT/IR spectrometer using KBr pellets. Elemental analyses were performed on a Perkin-Elmer PE 2400 II CHN elemental analyzer.

Preparation of 2,6-bis[(3-methoxysalicylidene)hydrazinocarbonyl]pyridine (**H_4Bmshp**) [29]

H_4Bmshp was prepared by the reaction of 2,6-pyridine-dicarboxylic hydrazide (1.95 g, 0.01 mol) with 2-hydroxy-3-methoxybenzaldehyde (3.04 g, 0.02 mol) under reflux in ethanol for 4 h. A yellow precipitate was isolated by filtration and washed with ethanol and ether (yield 92%). Anal. Calc. for $C_{23}H_{21}N_5O_6$ (463.45): C, 59.6; H, 4.6; N, 15.0. Found: C, 59.9; H, 4.8; N, 14.7. IR (cm^{-1}): 3453(s), 3243(s), 1673(s), 1608(m), 1540(s), 1252(s), 1080(s), 732(s).

Preparation of 2,6-bis[(3-carboxylsalicylidene)hydrazinocarbonyl]pyridine (**H_6Bcshp**)

H_6Bcshp was prepared by the reaction of 2,6-pyridine-dicarboxylic hydrazide (1.95 g, 0.01 mol) with 2-hydroxy-3-carboxybenzaldehyde (3.32 g, 0.02 mol) under reflux in ethanol for 4 h. A yellow precipitate was isolated by filtration and washed with ethanol and ether (yield 93%). Anal. Calc. for $C_{23}H_{17}N_5O_8$ (491.42): C, 56.2; H, 3.7; N, 9.4. Found: C, 56.4; H, 3.9; N, 9.5. IR (cm^{-1}): 3436(s), 3274(m), 1670(s), 1606(m), 1542(m), 1237(m).

Preparation of $[Cu_6(Bmshp)_2(SO_4)_2(H_2O)_7]\cdot 2H_2O$ (**1**)

A DMF (10 mL) solution of H_4Bmshp (0.0926 g, 0.2 mmol) was layered on an aqueous solution (10 mL) of $CuSO_4\cdot 5H_2O$ (0.1520 g, 0.6 mmol) in a glass tube. Dark green block crystals were collected after 7 days' diffusion in a yield of 60%. IR (cm^{-1}): 3409(s), 1649(m), 1603(s), 1542(s), 1216(s), 1126(m), 1081(w).

Preparation of $[Cu_3(Bmshp)(ClO_4)_2(H_2O)_4]\cdot 5H_2O$ (**2**)

A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.1105 g, 0.3 mmol) in methanol (8 mL) was slowly added to a solution of H_4Bmshp (0.0463 g, 0.1 mmol) in methanol (5 mL). The resulting solution was stirred for 3 h and then filtered. The filtrate was allowed to evaporate at room temperature, giving dark green crystals of **2** suitable for single crystal X-ray diffraction after 2 weeks in a yield of 38%. Anal. Calc. for $C_{23}H_{35}Cl_2Cu_3N_5O_{23}$ (1011.08): C, 27.3; H, 3.5; N, 6.9. Found: C, 27.5; H, 3.6; N, 6.8. IR (cm^{-1}): 3429(s), 1620(m), 1603(m), 1546(s), 1219(s), 1116(s), 1102(s), 1085(s).

Preparation of $[Cu_3(Bmshp)(DMF)_4(H_2O)_2]\cdot H_2O\cdot 2DMF\cdot 2ClO_4$ (**3**)

A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (0.1105 g, 0.3 mmol) in ethanol (8 mL) was slowly added to a solution of H_4Bmshp (0.0463 g, 0.1 mmol) in DMF (5 mL). The resulting solution was stirred for 4 h and then filtered. The filtrate was allowed to evaporate at room temperature, giving dark green crystals of **3** suitable for single crystal X-ray diffraction after 4 weeks in a yield of 40%. Anal. Calc. for $C_{41}H_{65}Cl_2Cu_3N_{11}O_{23}$ (1341.56): C, 36.7; H, 4.9; N, 11.3. Found: C, 37.0; H, 5.0; N, 11.2. IR (cm^{-1}): 3429(s), 1651(s), 1602(m), 1543(s), 1217(s), 1142(s), 1110(s), 1087(s).

Preparation of $[Cu_3(H_2Bcshp)(ClO_4)_2(H_2O)_4]\cdot 3H_2O$ (**4**)

A methanol solution (8 mL) of $Cu(ClO_4)_2\cdot 6H_2O$ (0.1105 g, 0.3 mmol) was added to a methanol (5 mL) solution of H_6Bcshp (0.0491 g, 0.1 mmol) with two drops of Et_3N (ca. 0.1 mL). The resulting solution was stirred for 3 h and then filtered. The filtrate was allowed to evaporate at room temperature, giving dark green crystals suitable for single crystal X-ray diffraction after 2 weeks in a yield of 41%. IR (cm^{-1}): 3433(s), 1677(s), 1624(m), 1590(m), 1551(s), 1426(m), 1226(m), 1145(s), 1110(s), 1087(s).

X-ray crystallography study

Suitable single crystals of **1**–**4** were selected and mounted in air onto thin glass fibers. X-ray diffraction studies on **1**, **3**, **4** were performed at 298(2) K except **2** at 291(2) K, using a Bruker CCDArea Detector with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using the *SHELXS-97* program package and refined against F^2 by full-matrix least-squares methods with *SHELXL-97* [30]. All nonhydrogen atoms were anisotropic and hydrogen atoms on C atoms were included on calculated positions, riding on their carriers. Complex **1** reveals highly disordered solvents, SO_4^{2-} anions and coordinated water molecules within the lattice interstices. The diffraction data of **1** were treated by the "*SQUEEZE*" method as implemented in *PLATON* [31]. For the solution of the structure of complex **4**, there are still some solvent accessible voids indicated by *PLATON* program. However, we could not find any suitable Q peaks for any solvent molecules in the difference Fourier map by the program. Thus, this unsolvable solvent was squeezed using *PLATON* program. Although the structure refinement is a little poor, the structure was properly modeled with reasonable refinement parameters for all resolved atoms. This indicates that the trinuclear skeleton and the resolved guest water molecules of **4** were determined without any doubt. The present data of **4** reveal a supramolecular structure different from those of **1**–**3**, which provides enough information for us to clarify the diversity of H-bonded supramolecular structures constructed from similar trinuclear copper units. A summary of crystallographic and structural refinement data for **1**–**4** is given in Table 1. Selected bond lengths and bond angles for **1**–**4** are listed in Table S1. Hydrogen bonds for **1**–**4** are listed in Table 2. CCDC 792038–792041 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

Structure description of complex 1

The single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the triclinic space group $P\bar{1}$. It presents a centrosymmetric hexanuclear structure formed by the connection of two trinuclear units $[Cu_3(Bmshp)(H_2O)_{3.5}]$ via two SO_4^{2-} anions. The SO_4^{2-} ligand in **1** is disordered over two positions. One part of the disordered SO_4^{2-} ligand coordinates to Cu1 in a monodentate mode, while the other part, which is further disordered with a water molecule over the same position of Cu2, behaves as a μ_2-bridge linking Cu2 and $Cu1^a$. As shown in Fig. 1, the H_4Bmshp ligand in each trinuclear unit loses its four protons to coordinate to three Cu(II) atoms (Cu1, Cu2 and Cu3) as a nonadentate ligand with its two $–OCH_3$ groups free from coordination. Cu1 is four-coordinated in a distorted square planar geometry by a $N_{pyridyl}$ atom (N1) and two $N_{pyridyl\text{-}acylamide}$ atoms (N2 and N4) from one $Bmshp^{4-}$ ligand and one oxygen atom (O7 or $O14^a$) from the disordered SO_4^{2-} anion. Cu2 and Cu3 are five-coordinated in distorted square pyramidal geometries. Three of the coordinating sites of Cu2 and Cu3 are occupied by an $O_{pyridyl\text{-}acylamide}$ atom (O1 for Cu2 and O2 for Cu3), an $O_{phenolic}$ atom (O3 for Cu2 and O5 for Cu3) and a $N_{pyridyl\text{-}hydrazine}$ atom (N3 for Cu2 and N5 for Cu3) from $Bmshp^{4-}$. The remaining two coordinating sites are occupied by one oxygen atom (O15) from one water molecule and another oxygen atom (O11/O20) from the disordered SO_4^{2-}/H_2O ligands for Cu2, and two oxygen atoms (O16 and O17) from two water molecules for Cu3, respectively. The bond distances of C1–O1 and C1–N2, C7–O2 and C7–N4 in pyridyl-acylamide groups of $Bmshp^{4-}$ are 1.306(13) Å and 1.333(14) Å, 1.320(13) Å and 1.263(13) Å, respectively, suggesting the coordination of acylamide groups to Cu(II) in the enolic form [32].

Complex **1** presents various hydrogen bonds (Table 2; Fig. 2). The coordinated water ligands on Cu2 form hydrogen bonds $O15–H15A\cdots O5^b$ and $O15–H15A\cdots O6^b$ with the $O_{phenolic}$ and $O_{methoxy}$ atoms on $Cu3^b$ from the adjacent hexanuclear unit. While the coordinated water ligands on Cu3 interact with the $O_{methoxy}$, O_{water}, $O_{phenolic}$ and $O_{sulfate}$ atoms on $Cu2^c$ from another adjacent hexanuclear unit, forming hydrogen bonds $O16–H16B\cdots O4^c$, $O17–H17B\cdots O15^c$, $O16–H16A\cdots O20^c$, $O16–H16A\cdots O3^c$, $O16–H16A\cdots O11^c$ and $O16–H16A\cdots O13^c$. The hexanuclear units of **1** are extended into a 1D chain via these intermolecular hydrogen bonds. Furthermore, adjacent 1D chains are connected via interchain hydrogen bonds $O17–H17A\cdots O8^d$ (between one coordinated water ligand on Cu3 and one oxygen atom of SO_4^{2-} anion) and $O19–H19A\cdots O1^e$ (between one guest water molecule and the $O_{pyridyl\text{-}acylamide}$ atom on Cu2), as well as intramolecular hydrogen bond $O15–H15B\cdots O19$ between one coordinated water ligand on Cu2 and the guest water molecule, to form a 2D supramolecular network of **1**.

Structure description of complex 2

Complex **2** crystallizes in the triclinic space group $P\bar{1}$ and presents a trinuclear structure $[Cu_3(Bmshp)(ClO_4)_2(H_2O)_4]$, which is similar to the trinuclear secondary building unit $[Cu_3(Bmshp)(H_2O)_{3.5}]$ of **1**. As shown in Fig. 3, Cu1 is five-coordinated in a distorted trigonal bipyramidal geometry by a $N_{pyridyl}$ atom (N3), two $N_{pyridyl\text{-}acylamide}$ atoms (N2 and N4) from $Bmshp^{4-}$ and two oxygen atoms (O2 and O3) from two water ligands. Cu2 and Cu3 show the same coordination environment of distorted square pyramidal geometries. The coordination atoms are an $O_{pyridyl\text{-}acylamide}$ atom (O13 for Cu2 and O14 for Cu3), an $O_{phenolic}$ atom (O11 for Cu2 and O15 for Cu3), a $N_{pyridyl\text{-}hydrazine}$ atom (N1 for Cu2 and N5 for Cu3) from $Bmshp^{4-}$, an oxygen atom (O1 for Cu2 and O4 for Cu3) from water and a disordered oxygen atom (O18/O18′ for Cu2 and O24/O24′ for Cu3) of ClO_4^- anion. The bond distances of C–O and C–N in pyridyl-acylamide groups of $Bmshp^{4-}$ are about 1.27 and 1.33 Å, respectively,

Table 1 Crystallographic data and refinement summary for **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{46}H_{52}Cu_6N_{10}O_{29}S_2$	$C_{23}H_{35}Cl_2Cu_3N_5O_{23}$	$C_{41}H_{65}Cl_2Cu_3N_{11}O_{23}$	$C_{23}H_{27}Cl_2Cu_3N_5O_{23}$
Formula weight	1654.34	1011.08	1341.56	1003.02
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	10.1795(8)	10.5593(13)	14.6377(13)	9.8385(10)
b (Å)	13.9093(14)	11.1133(14)	14.7695(14)	11.4596(13)
c (Å)	14.5460(17)	17.129(2)	16.1666(18)	18.790(2)
α (°)	64.008(2)	74.789(2)	69.7630(10)	76.614(2)
β (°)	75.989(3)	87.596(2)	66.6160(10)	78.212(2)
γ (°)	74.774(3)	76.209(2)	74.066(2)	66.0380(10)
V(Å^3)	1767.0(3)	1883.2(4)	2971.5(5)	1868.8(4)
Z	1	2	2	2
D_{Calc} (g cm^{-3})	1.555	1.783	1.499	1.783
μ (Mo-Kα) (mm^{-1})	1.915	1.915	1.236	1.929
F(000)	836	1026	1386	1010
θ (°)	1.57–25.01	2.31–25.01	1.49–25.01	2.10–25.01
Reflections collected/unique (R_{int})	8531/5867 (0.0522)	13025/6478 (0.0291)	15591/10331 (0.0348)	8794/6289 (0.0852)
Goodness-of-fit on F^2	1.086	1.013	1.021	0.941
R indices [$I > 2\sigma\ (I)$]	$R_1 = 0.0939$, $wR_2 = 0.2423$	$R_1 = 0.0431$, $wR_2 = 0.1063$	$R_1 = 0.0514$, $wR_2 = 0.1126$	$R_1 = 0.1354$, $wR_2 = 0.2973$
R indices (all data)	$R_1 = 0.1603$, $wR_2 = 0.2684$	$R_1 = 0.0658$, $wR_2 = 0.1193$	$R_1 = 0.1098$, $wR_2 = 0.1490$	$R_1 = 0.2255$, $wR_2 = 0.3482$
Largest diff. peak and hole (e A^{-3})	1.012, −0.884	0.678, −0.618	0.699, −0.499	0.896, −0.948

suggesting that the acylamide groups are coordinated to Cu(II) in the enolic form [32].

The Bmshp^{4-} ligand in **2** behaves a nonadentate ligand to coordinate to three Cu(II) centers. Its two –OCH_3 groups are free from coordination. All nonhydrogen atoms of Bmshp^{4-} ligand and three Cu(II) atoms in **2** are nearly coplanar, with the ClO_4^- anions on Cu2 and Cu3 lying on different sides of this plane. Such planarity and similar coordination were also observed in those reported trinuclear copper complexes $[Cu_3(L1)(DMSO)_5(H_2O)][ClO_4]_2{\cdot}H_2O$ (L1 = 2,6-bis[(salicylidene)hydrazinocarbonyl]pyridine) [32], $[Cu_3(L2\text{-}4H)(H_2O)_3(CH_3OH)](NO_3)_2$ (L2 = 2,6-bis[(3-hydroxylsalicylidene)hydrazinocarbonyl]pyridine) [33] and $[Cu_3(2poap\text{-}2H)(H_2O)(DMF)_3(CH_3OH)_2](BF_4)_4$ [34].

There are two coordinated water ligands on the central Cu(II) (Cu1) in **2**. One is hydrogen bonded to the O_{phenolic} atom on Cu3 from one adjacent trinuclear unit (O3–H5W···O15^h H-bond at O···O = 2.752(5) Å). While the other water is hydrogen bonded to the O_{methoxy} and O_{phenolic} atoms on Cu2 from another adjacent trinuclear unit (O2–H4W···O11^f and O2–H4W···O12^f H-bonds at O···O = 2.846(5) and 3.073(5) Å). These O–H···O hydrogen bonds help to build 1D supramolecular chains of **2** (Table 2; Fig. 4).

Besides four coordinated water ligands, there exist five guest water molecules in **2**. Four of them (O6, O9, O10 and O5) are hydrogen bonded with each other to form a four-membered water aggregate, exhibiting O6–H11W···O9^m, O9^m–H17W^m···O10^m and O10^m–H19W^m···O5 H-bonds with angles in the range of 126°–179°. At the same time, two terminal water molecules of this four-membered aggregate form hydrogen bonds with the coordinated waters on central Cu1 and terminal Cu3 in two trinuclear units from two adjacent 1D chains (O2–H3W···O6 and O5–H9W···O4^l H-bonds), respectively. These interactions extend the four-membered water aggregate into a six-membered one. Two adjacent six-membered aggregates are further connected by the O10^m–H20W^m···O10^s and O4^l–H7W^l···O9^s H-bonds to form an interesting centrosymmetric twelve-membered water aggregate (Fig. 4). Each 1D chain is linked to adjacent ones via the twelve-membered water aggregates, forming a 2D network of **2** as shown in Fig. 4. Furthermore, adjacent 2D sheets of **2** are extended into a 3D framework via the further intermolecular hydrogen bonds between the fifth guest water molecules, ClO_4^- anions and coordinated water ligands (Fig. S1).

Table 2 Hydrogen bonds (Å and °) for **1**–**4**

D–H···A	*d* (H···A)	*d* (D···A)	<DHA
1			
O15–H15A···O6^{b}	2.23	3.053(13)	162.3
O15–H15A···O5^{b}	2.24	2.811(12)	125
O15–H15B···O19	1.89	2.717(15)	165.6
O16–H16A···O20^{c}	1.98	2.83(2)	178.9
O16–H16A···O11^{c}	2.2	3.01(2)	161.3
O16–H16A···O3^{c}	2.58	3.006(11)	112.5
O16–H16A···O13^{c}	2.65	3.22(3)	125.3
O16–H16B···O4^{c}	2.37	3.021(13)	134
O17–H17A···O8^{d}	1.95	2.71(2)	148.4
O17–H17B···O15^{c}	1.88	2.629(12)	146.7
O19–H19A···O1^{e}	2.25	3.055(14)	157.7
O20–H20A···O7^{a}	2.6	3.39(3)	154.9
2			
O1–H1W···O6^{f}	2.47	3.235(8)	151
O1–H1W···O2^{f}	2.63	3.357(5)	144.6
O1–H2W···O18′^{g}	1.92	2.763(14)	176.4
O1–H2W···O18^{g}	2.01	2.829(15)	162.1
O2–H3W···O6	1.82	2.663(6)	172.8
O2–H4W···O11^{f}	2	2.846(5)	177.7
O2–H4W···O12^{f}	2.64	3.073(5)	113.4
O3–H5W···O15^{h}	1.9	2.752(5)	174
O3–H6W···O7^{i}	1.92	2.756(5)	168.5
O4–H7W···O9^{j}	2.06	2.860(9)	156.9
O4–H8W···O5^{k}	2.34	3.190(7)	177.5
O5–H9W···O4^{l}	1.86	2.699(6)	169.2
O5–H10W···O21^{k}	2.41	3.142(8)	145.3
O5–H10W···O15^{k}	2.65	3.150(6)	118.7
O6–H11W···O9^{m}	2	2.595(10)	126.1
O6–H12W···O17^{n}	2.2	2.929(14)	145
O6–H12W···O17′^{n}	2.28	2.940(13)	134.8
O7–H13W···O20^{n}	2.01	2.834(8)	163.1
O7–H14W···O24^{l}	2.24	3.063(18)	164.4
O7–H14W···O24′^{l}	2.3	3.114(18)	160.7
O8–H15W···O12^{n}	2.31	3.002(6)	139
O8–H15W···O11^{n}	2.19	2.968(5)	151.7
O8–H16W···O23^{o}	2.23	3.023(7)	155.7
O9–H17W···O10	1.83	2.632(18)	156.2
O9–H18W···O22^{o}	2.11	2.956(10)	174.3
O9–H18W···O21^{o}	2.52	3.078(10)	123.8
O10–H19W···O5^{m}	2.18	3.037(16)	178.4
O10–H20W···O10^{p}	1.7	2.53(4)	163.5
3			
O7–H7A···O22^{q}	1.78	2.606(7)	162.1
O7–H7B···O3^{r}	1.99	2.825(5)	168.5
O7–H7B···O4^{r}	2.49	2.975(5)	116.8
O8–H8A···O23^{s}	1.88	2.732(5)	175.3
O8–H8B···O5^{h}	2.07	2.911(5)	172.2
O8–H8B···O6^{h}	2.5	2.972(5)	116
O23–H23D···O10^{t}	2.11	2.961(6)	174.1
O23–H23E···O21^{m}	1.87	2.716(7)	173.9
4			
O4–H4···O3	1.78	2.521(14)	149.1
O7–H7···O6	1.8	2.529(14)	147.5
O9–H9A···O13^{i}	1.96	2.74(3)	152.8
O9–H9B···O21^{i}	1.83	2.56(3)	142.5
O10–H10A···O22^{m}	1.96	2.75(2)	153.1
O10–H10B···O5^{u}	2	2.796(15)	154.9
O15–H15A···O21	2.13	2.92(2)	153.7
O15–H15B···O8^{v}	1.82	2.610(15)	153.2
O20–H20A···O15^{u}	2.45	3.26(2)	160.1
O20–H20B···O23^{u}	2.19	2.69(3)	117.2
O21–H21A···O18^{m}	2.28	3.12(4)	168.4
O21–H21B···O19^{n}	1.95	2.79(3)	167.7
O22–H22A···O5^{w}	1.94	2.788(19)	177
O22–H22B···O14^{t}	2.06	2.91(4)	177.9
O23–H23B···O17^{m}	1.94	2.79(3)	179.9
O23–H23A···O15	2.58	3.43(3)	179.9

Symmetry codes: $^{b}x, y+1, z$; $^{c}x, y-1, z$; $^{d}-x+2, -y+1, -z+1$; $^{e}-x+2, -y+2, -z+1$; $^{f}-x+2, -y, -z+1$; $^{g}-x+3, -y, -z+1$; $^{h}-x+2, -y, -z$; $^{i}x+1, y, z$; $^{j}x+1, y-1, z-1$; $^{k}-x+1, -y, -z$; $^{l}x-1, y+1, z$; $^{m}-x+1, -y+1, -z+1$; $^{n}x-1, y, z$; $^{o}-x+1, -y, -z+1$; $^{p}-x+1, -y+1, -z+2$; $^{q}x+1, y, z-1$; $^{r}-x+1, -y+1, -z$; $^{s}x, y, z-1$; $^{t}x, y, z+1$; $^{u}x+1, y-1, z$; $^{v}x-2, y+1, z$; $^{w}x, y-1, z+1$

Structure description of complex **3**

Similar to **2**, complex **3** crystallizes in the triclinic space group $P\bar{1}$ and presents the similar trinuclear copper unit $[Cu_3(Bmshp)(DMF)_4(H_2O)_2]^{2+}$. The structural difference of **3** from **2** is that the apical site and one of the basal positions of Cu2 and Cu3 are occupied by two DMF molecules in **3**, but by ClO_4^- anion and one H_2O molecule in **2** (Fig. 5). This might be due to the strong coordinating ability of DMF solvent used in the synthesis of **3**. The C–O and C–N bond distances in pyridyl-acylamide groups of $Bmshp^{4-}$ are about 1.26 and 1.32 Å, respectively, which suggests that the acylamide groups coordinate to Cu(II) the enolic form [32]. The two $-OCH_3$ groups of the $Bmshp^{4-}$ ligand in **3** are still free from coordination, which is similar to the cases in **1** and **2**. All nonhydrogen atoms of the $Bmshp^{4-}$ ligand and three Cu(II) centers are nearly coplanar, with the two coordinated DMF ligands on the apical positions of Cu2 and Cu3 lying on different sides of this plane.

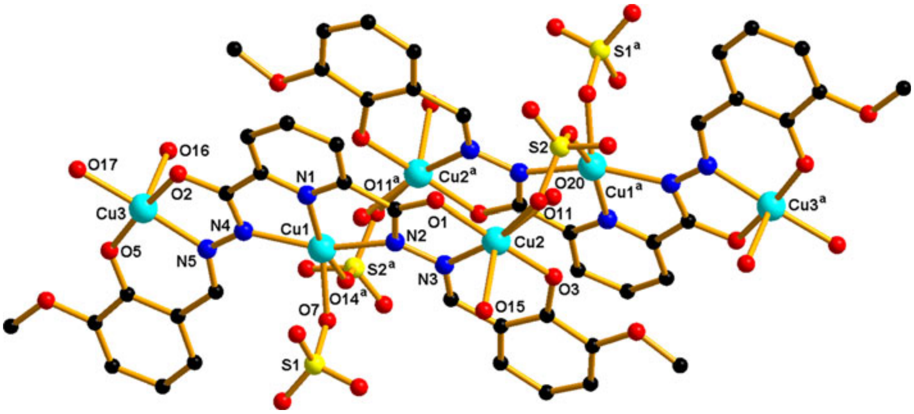

Fig. 1 The perspective view of the structure of **1**, showing the connection of two trinuclear units by SO_4^{2-} anions. H atoms and guest water molecules are omitted for clarity. Symmetry code: $^a-x+1, -y+2, -z+1$

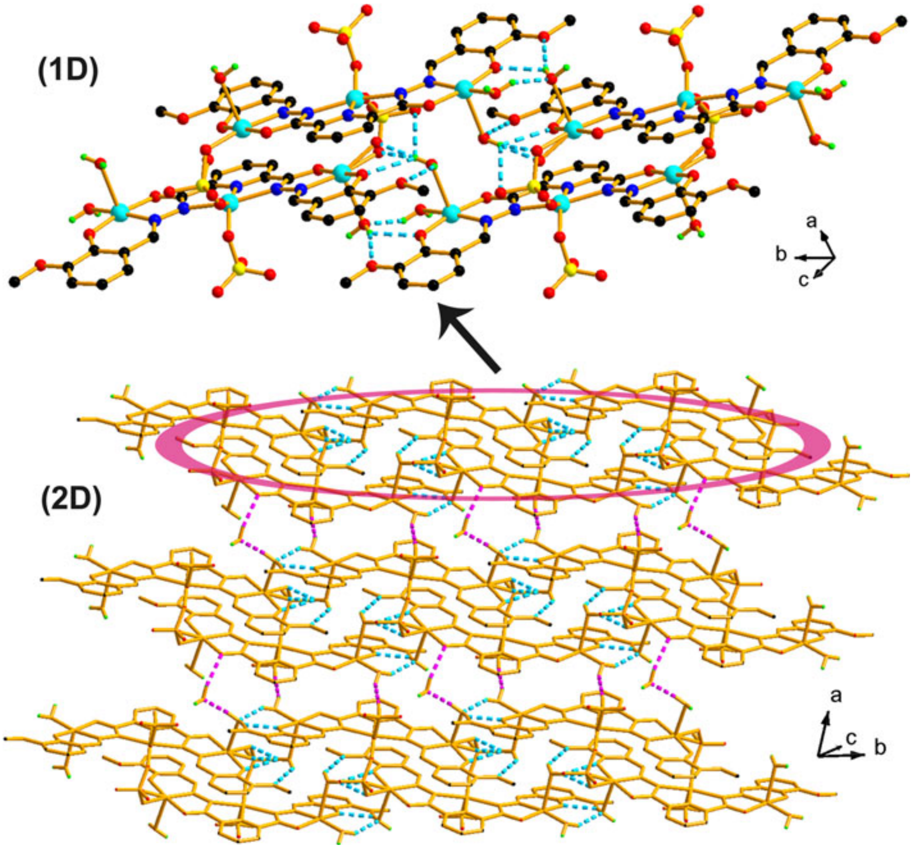

Fig. 2 1D H-bonded chain and 2D H-bonded network of **1**

In complex **3**, two coordinated water ligands on Cu1 form hydrogen bonds O7–H7B···O3^r, O7–H7B···O4^r, O8–H8B···O5^h and O8–H8B···O6^h with the $O_{methoxy}$ and $O_{phenolic}$ atoms on terminal Cu2 and Cu3 from two adjacent trinuclear units. With the aid of these hydrogen bonding interactions, complex **3** is extended into a 1D chain similar to that of complex **2** (Table 2; Fig. 6). Each 1D chain is further extended into a 2D network and 3D framework via electrostatic interactions between $[Cu_3(Bmshp)(DMF)_4(H_2O)_2]^{2+}$ cations and ClO_4^- anions (Fig. S2).

Structure description of complex 4

Similar to **2** and **3**, complex **4** also crystallizes in the triclinic space group $P\bar{1}$ and presents a similar trinuclear copper unit $[Cu_3(H_2Bcshp)(ClO_4)_2(H_2O)_4]$ as shown in Fig. 7. However, the main ligand in **4** is H_6Bcshp, instead of H_4Bmshp for **1**–**3**. The difference of H_6Bcshp from H_4Bmshp is that the $–OCH_3$ group of H_4Bmshp is substituted by the –COOH group in H_6Bcshp. The H_2Bcshp^{4-} ligand in **4** coordinates to three Cu(II) centers as a

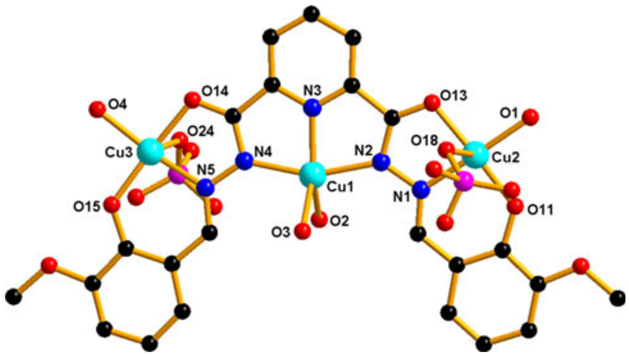

Fig. 3 The perspective view of the trinuclear structure of **2**. H atoms and guest water molecules are omitted for clarity

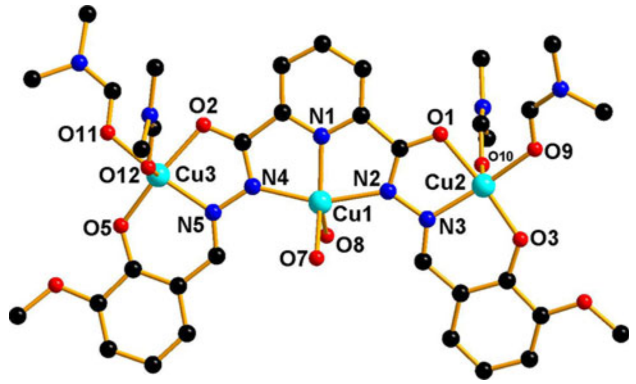

Fig. 5 The perspective view of the trinuclear structure of **3**. H atoms, guest ClO_4^- anions and solvent molecules are omitted for clarity

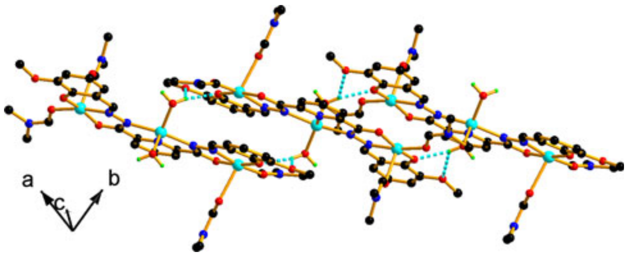

Fig. 6 1D chain of **3** formed by intermolecular H-bonds

nonadentate ligand with its two –COOH groups free from coordination. The C–O and C–N bond distances in pyridylacylamide groups of H_2Bcshp^{4-} are ca. 1.28 and 1.34 Å, respectively, which suggests that the acylamide groups coordinate to Cu(II) in the enolic form [32]. As for **1**–**3**, all nonhydrogen atoms of the main ligand (H_2Bcshp^{4-}) and three Cu(II) atoms in **4** are nearly coplanar, with the two coordinated ClO_4^- anions on Cu2 and Cu3 lying on different sides of this plane.

The adjacent trinuclear units of **4** form hydrogen bonds O15–H15B···O8$^{\mathrm{v}}$ (O···O = 2.610(15) Å) between the coordinated water ligand on Cu2 from one trinuclear unit and the $O_{\mathrm{carboxylate}}$ atom from the adjacent trinuclear unit, which extend **4** into a 1D chain (Fig. S3). Each chain is further connected to form a 2D network via another two types of H-bonds, type A and type B, as shown in Fig. 8. One guest water molecule in **4** forms hydrogen bonds

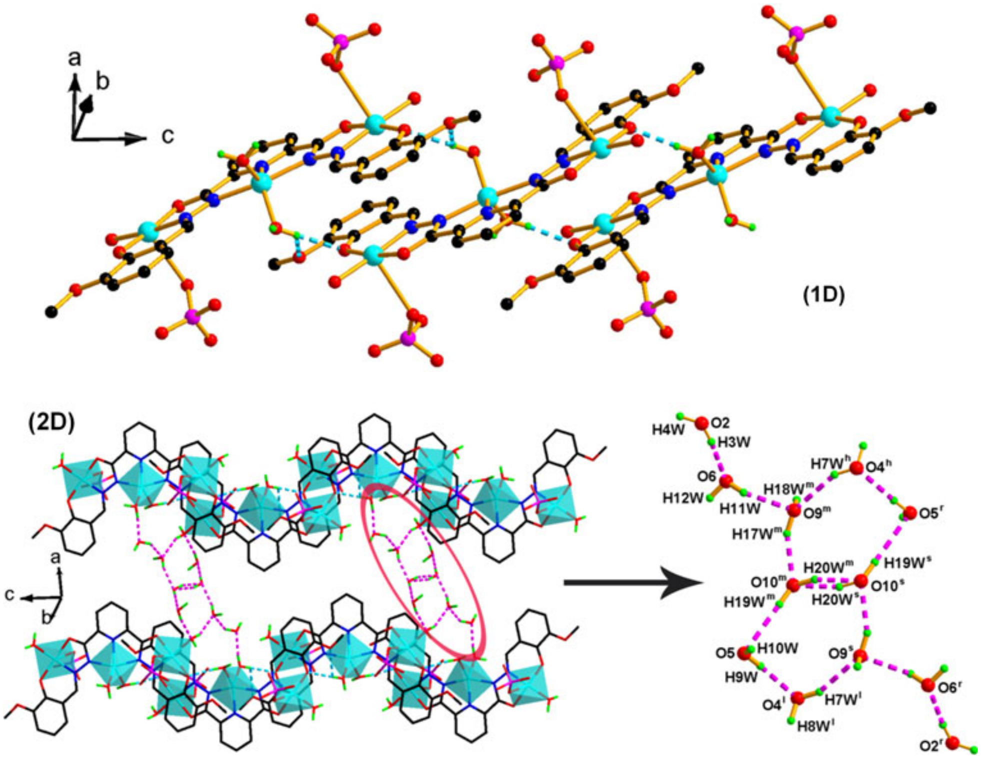

Fig. 4 1D H-bonded chain and 2D network formed by the twelve-membered H-bonded water aggregates of **2**. Symmetry code: $^{\mathrm{l}}-x+1, -y+1, -z+1$; $^{\mathrm{n}}x-1, y+1, z$; $^{\mathrm{s}}x, y, z-1$

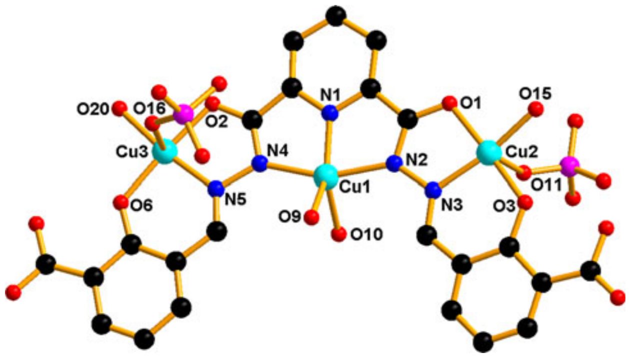

Fig. 7 The perspective view of the trinuclear structure of **4**. H atoms and guest water molecules are omitted for clarity

(O20–H20B···O23^{u} and O23–H23A···O17^{m}) with the coordinated water on Cu3 from a trinuclear unit I and the $O_{ClO_4^-}$ atom on Cu3 from the adjacent trinuclear unit II, composing type A hydrogen bonds with the O···O distances and O–H···O angles in the ranges of 2.69–2.79 Å and 117°–180°, respectively. Another guest water molecule in **4** forms hydrogen bonds (O10–H10A···O22^{m} and O22–H22A···O5^{w}) with one of the coordinated water ligand on Cu1 from trinuclear unit I and the $O_{carboxylate}$ atom from the other adjacent trinuclear unit III, composing type B hydrogen bonds (Table 2). The neighboring H-bonded 1D chains are linked alternatively by type A and type B hydrogen bonds to form a 2D network of **4** exhibiting two kinds of grid networks, with grid dimensions of 18.3126 × 11.2546 Å and 18.3125 × 15.0119 Å, respectively, as shown in Fig. 9. Adjacent 2D sheets of **4** are further extended into a 3D framework via the intermolecular hydrogen bonds between the third guest water molecules, –COOH groups, coordinated water ligands and ClO_4^- anions (Fig. S4).

Structural discussion

The 2,6-pyridine-diacylhydrazone ligands of Bmshp^{4-} and H_2Bcshp^{4-} adopt the same nonadentate binding mode coordinating to three copper atoms with their two $-OCH_3$ and –COOH groups free from coordination, which result in the formation of similar trinuclear units with one diacylhydrazone ligand and three metal atoms in **1**–**4**. However, hydrogen bonds in the four complexes are extremely different due to the differences of anions, solvent molecules and functional groups on the ligands in the complexes, which lead to the formation of a variety of supramolecular structures constructed by trinuclear copper units via H-bonds.

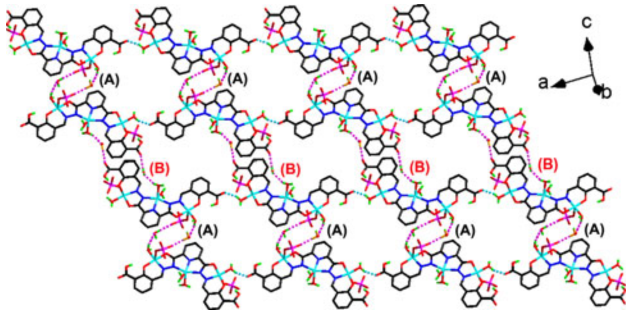

Fig. 9 2D network of **4** formed by the interlacing type A and type B hydrogen bonds

In complex **1**, the SO_4^{2-} anions are involved both in the coordination and in the hydrogen bonding interactions. The μ_2-bridging coordination of SO_4^{2-} anions links two trinuclear copper units into a hexanuclear complex unit. The hexanuclear units, which act as basic building blocks of the supramolecular structure of **1**, are linked into 2D supramolecular networks by hydrogen bonds between coordinated waters and the $O_{methoxy}$, $O_{phenolic}$ atoms of Bmshp^{4-} ligand, hydrogen bonds between coordinated water and coordinated water, hydrogen bonds between guest water molecules and the oxygen atom of SO_4^{2-} or the $O_{pyridyl\text{-}acylamide}$ atom of the ligand, as well as those between coordinated water and guest water molecules. In complex **2**, the use of hydrated copper perchlorate as a starting material and methanol as solvent in the synthesis leads to the formation of a trinuclear complex with one ClO_4^- anion and one water molecule for every terminal Cu(II), and two water ligands on the central Cu(II). The trinuclear complex units are the basic building blocks of the supramolecular structure of **2**. The hydrogen bonds between coordinated water ligands on the central Cu(II) and

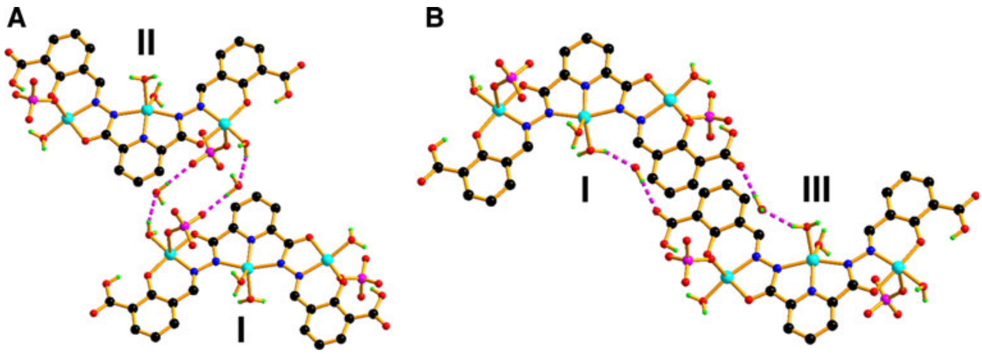

Fig. 8 Type A and type B hydrogen bonds in **4** (I, II and III are symbols of trinuclear units)

$O_{methoxy}$ or $O_{phenolic}$ atoms of $Bmshp^{4-}$ ligands link the trinuclear units into a 1D supramolecular chain and those between coordinated water ligands and guest water molecules, which feature a twelve-membered water aggregate, connect the supramolecular chains into 2D supramolecular networks. Based on the 2D networks, the 3D supramolecular framework of **2** is built. The use of DMF in the synthesis of **3** results in the isolation of the trinuclear complex with two DMF ligands coordinating to terminal Cu(II) atoms and two water ligands binding to the central Cu(II). The ClO_4^- anions are not involved in coordination. The presence of the coordinating DMF ligands on the terminal Cu(II) atoms, rather than the water ligand and ClO_4^- anion as in the case of **2**, blocks the propagation of hydrogen bonds from the sites of the terminal Cu(II) atoms. As a result, hydrogen bonds in complex **3** are formed mainly between the coordinated water ligands of the central Cu(II) and the $O_{methoxy}$, $O_{phenolic}$ atoms of the $Bmshp^{4-}$ ligands, which gives only a 1D chain as the supramolecular structure of complex **3**. In the case of complex **4**, the trinuclear complex unit is similar to that of **2** in terms of the compositions and their binding fashions. However, the use of H_6Bcshp ligand which bears a –COOH substituent group leads to a connection fashion of the trinuclear complex units via hydrogen bonds different from that of **2**. It can be seen that the trinuclear complex units are linked into 1D chains via the hydrogen bonds between the coordinated water ligands on Cu2 and the $O_{carboxylate}$ atom of the H_2Bcshp^{4-} ligand, and the 1D chains are connected into a 2D grid network by two types of hydrogen bonds involving guest water molecules, coordinated water ligands, –COOH groups of the ligand and ClO_4^- anions. The 2D networks are further then constructed into 3D supramolecular frameworks.

Conclusion

In this work, copper complexes **1**–**4** were synthesized and structurally characterized. All four complexes exhibit similar trinuclear copper units with one organic ligand and different numbers of inorganic anions and solvent molecules. The diverse supramolecular structures constructed via hydrogen bonds are obtained due to the differences of anions, solvents and ligands used in the syntheses of the four complexes. Complex **1** presents a 2D supramolecular network with hexanuclear complex units as basic building blocks which are formed from two trinuclear copper units by the linkage of the bridging coordination of SO_4^{2-} anions. Complex **2** shows a 3D supramolecular framework with trinuclear complex units as basic building blocks, in which characteristic twelve-membered hydrogen-bonded water aggregates are observed. Complex **3** exhibits only a 1D supramolecular chain due to the presence of coordinated DMF solvent ligands. Complex **4** displays a 3D supramolecular framework, in which the hydrogen bonds are different from those in **2** because of the existence of –COOH groups in the H_2Bcshp^{4-} ligand.

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