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Assembly of supermolecular complexes with tripodal ligand titmb and tib: a 2D rhombic grid network assembled from 2-connected tib

Hong-Ke Liu,[*a,b] **Wei-Yin Sun,**[a] **Wen-Xia Tang,**[a] **Hai-Yan Tan,**[b] **Hua-Xin Zhang,**[b]
Ye-Xiang Tong,[b] **Xiao-Lan Yu**[b] **and Bei-Sheng Kang**[b]

[a] *State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China. E-mail: hongke_liu@ hotmail.com*
[b] *School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou 510275, China*

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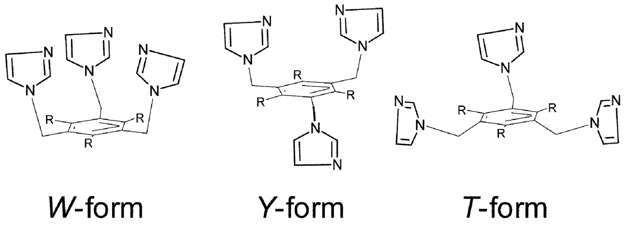
A 2D rhombic grid network complex $[Cu_4(tib)_8](CH_3COO)_8 \cdot 32H_2O$ (**6**) has been prepared by reaction of the tripodal ligand 1,3,5-tris(imidazol-1-ylmethyl)benzene (tib) with $Cu(CH_3COO)_2$ in aqueous solution and characterized by single crystal X-ray diffraction. In the solid state, the tripodal ligand tib acts as a 2-connected ditopic bridging ligand. Studies about the influences that control the supramolecular assembly and crystal packing process of complexes (**1**–**6**), which are assembled from tripodal ligands titmb and tib with metal atoms, not only illustrate that hydrogen bonds play a very important role in the construction of supramolecular complexes, but also that the reaction conditions together with the metal atoms co-affect inorganic supramolecular formation. Results show that the formation of N ··· H–OH hydrogen bonds between the hydrogen atoms of the solvent water molecules and the imidazole coordinative nitrogen atoms of the third arm of tib makes the tripodal ligand tib act as a 2-connected bridging ligand when it coordinates with copper(II) atoms. It is found that the conformations of the tripodal ligands tib and titmb (titmb = 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene) are obviously controlled by the reaction conditions. When reacted in organic solvents, both of the titmb and tib are in the same W-form; when water is present in the solvent, the conformations of the two tripodal ligands will change from the W-form to the Y-form; when reacted in water, tripodal ligand tib is in a novel Y-form. Results also show that the coordination geometry of the metal atoms also plays an important role in the construction of supramolecular complexes. In 2D/3D complexes **1**, **2**, **5** and **6**, the involved transitional metal atom is the same – all are copper(II) atoms – and the coordination geometry of copper is square-planar N_4 or square-based pyramid N_5 or N_4O_1, while in the discrete cage complexes **3** and **4**, the involved transitional metal atoms are the zinc(II) and silver(I) atoms, and the coordination geometries of zinc and silver are tetrahedral N_2O_2 or linear N_2, respectively. These studies show that the hydrogen bonds play a very important role in the crystal packing process of this infinite 2D rhombic grid network complex **6**. There are no large channels formed in the 2D complexes **1** and **2**, but large channels are formed by the columnar packing of the 2D (4,4) rhombic grid layers of complex **6** along the *a* axis, and in which the cubic O_8 chains are accommodated.

Introduction

Metal-directed assembly has been proved to be a useful methodology in the construction of inorganic supramolecular arrays and significant progress has been achieved.[1–3] Frameworks with specific topologies such as honeycomb grids and cages have been obtained by the assembly of suitable metal ions with rationally designed tripodal ligands[4–8] such as 1,3,5-tricyanobenzene (tcb),[4] 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt).[5] For example, tcb[4] gives an extended honeycomb framework by assembly with AgO_3SCF_3, while in the case of tpt[5] an M_6L_4 type of cage was obtained by reaction of the ligand with $Pd(en)(NO_3)_2$, and honeycomb frameworks have also been obtained by the assembly of $Cu(CH_3COO)_2$ with tpt.[8] In our previous works, two flexible tripodal ligands – 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb)[9–11] and 1,3,5-tris(imidazol-1-ylmethyl)benzene (tib)[12] – were employed; it was shown that titmb has two conformations, namely the *cis*,*cis*,*cis*-conformation (W-form) and the *cis*,*trans*,*trans*-conformation (Y-form) (Scheme 1), and tib only shows one – the *cis*,*cis*,*cis*-conformation (W-form) (Scheme 1). An extended honeycomb framework $[Cu_3(titmb)_2(OCOCH_3)_6] \cdot H_2O$ (**1**)[9] with large cavities was formed from titmb in W-form with $Cu(OCOCH_3)_2$, whilst a 2D sheet-like framework $\{[Cu(dien)]_3(titmb)_2\}(ClO_4)_6 \cdot H_2O$ (**2**)[10] containing the ligand in both W- and Y-forms was obtained by reaction of $Cu(dien)^{2+}$ ions with titmb, and study also showed that a discrete M_3L_2 cage-like complex $[Zn_3(tib)_2(CH_3COO)_6] \cdot 4H_2O$ (**3**)[12] has been assembled from tib in the W-form with zinc(II) acetate. Two Ag_3L_2 cage complexes $[Ag_3(titmb)_2](ClO_4)_3$ (**4**)[11] have been obtained by assembly of titmb in W-form with silver(I) perchlorate. The results imply that the assembly of the framework strongly depends on the nature of the metal ions as well as the ligands.



Scheme 1

Recently, a 3D nano-porous complex $[Cu_6(tib)_8(OH)_4](OH)_8 \cdot 22H_2O \cdot 4CH_3OH$ (**5**)[13] assembled from tib and $Cu(CH_3CO_2)_2$

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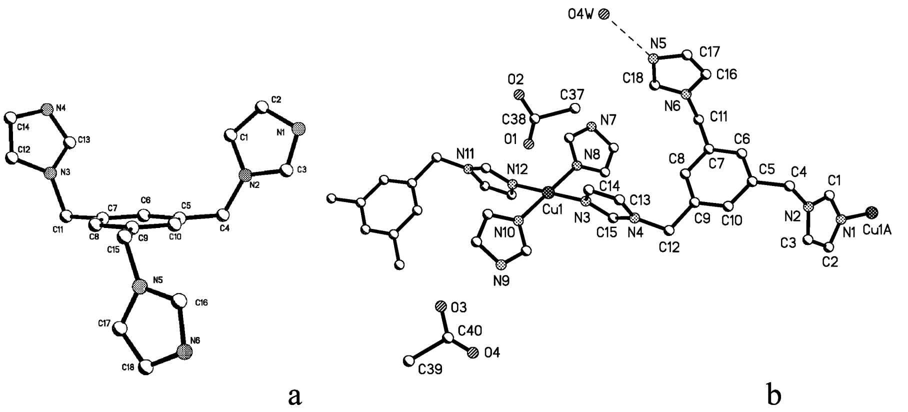

Fig. 1 (a) Single-crystal structure of ligand tib. (b) Molecular structure of $[Cu_4(tib)_8](CH_3COO)_8{\cdot}32H_2O$ (**6**) and the N $\cdots$ H–OH hydrogen bond is indicated by the dashed line. All hydrogen atoms are omitted for clarity.

was structurally characterized and the result shows that π–π interactions are the key trigger for the construction of the backbone of the framework. In this complex, tib shows an unexpected T-form conformation (shown in Scheme 1). An understanding of how these considerations affect metal coordination, ligand conformations, and crystal packing are central to controlling the coordination of supramolecular arrays using these ligands.

There is growing interesting in finding alternative approaches for the building of new, inexpensive and easy-to-prepare supramolecular systems. In order to study the influences which control the supramolecular assembly and crystal packing processes, the tripodal ligand tib and $Cu(CH_3CO_2)_2$ were reacted under conditions different from the previous work,[13] and resulted in a 2D rhombic grid network complex $[Cu_4(tib)_8](CH_3COO)_8{\cdot}32H_2O$ (**6**) in which tib acts as a 2-connected ditopic ligand and is present in a novel Y-form conformation. It is found that the formation of N $\cdots$ H–OH hydrogen bonds between the hydrogen atoms of the solvent water molecules and the imidazole pendant nitrogen donor of the third arm of tib makes the tripodal ligand tib act as a 2-connected bridging ligand when coordinates with copper(II) atoms. Comparing the reaction conditions of complexes **1**–**6**, it is found that the conformations of the tripodal ligands tib and titmb are obviously controlled by the reaction conditions. Comparing of the metal atoms involved in complexes **1**–**6**, the results also show that the coordination geometry of the metal atoms also plays an important role in the construction of supramolecular complexes. Comparing the packing arrangements of the three two-dimensional networks **1**, **2** and **6** shows that hydrogen bonds play a very important role in the crystal packing process of this infinite, 2D, rhombic grid network complex **6**.

Results

Crystal structure of tib and complex 6

The single crystals of tib suitable for X-ray analysis were obtained from its aqueous solution, and crystallographic analysis established the structure of tib (Fig. 1a), which showed that tib in the free solid state is in the *cis*,*trans*,*trans*-conformation (Y-form) (Scheme 1), with two imidazolyl planes, 1 (composed by N1, N2, C1, C2 and C3) and 2 (composed by N3, N4, C12, C13 C14) on the same side of the phenyl plane, with a third (composed by N5, N6, C16, C17 and C18) on the other side forming a capital 'Y'. In this structure, the three imidazolyl rings (1, 2 and 3) of each tib are inclined to the phenyl ring at angles of 84.0, 69.5 and 82.5°, respectively; the dihedral angles between planes 1 and 2, planes 1 and 3, planes 2 and 3 are 59, 11.1 and 68.9°, respectively. The distances between N1 and N4, N4 and N6, and N6 and N1 are 8.269, 8.267 and 10.539 Å, respectively.

Table 1 Selected bond distances (Å) and angles (°) for complex **6**

Cu1–N6	2.007(4)	Cu1–N6#3	2.007(4)
Cu1–N4#4	2.047(4)	Cu1–N4#2	2.047(4)
N6–Cu1–N6#3	180.0(3)	N6–Cu1–N4#4	88.24(15)
N6#3–Cu1–N4#2	91.76(15)	N6–Cu1–N4#2	91.76(15)
N6#3–Cu1–N4#2	88.24(15)	N4#4–Cu1–N4#2	180.00(8)

Symmetry transformations used to generate equivalent atoms: #1: *x*, *y*, *z*; #2: $-x, y + 1/2, -z + 1/2$; #3: $-x, -y, -z$; #4: $x, -y - 1/2, z - 1/2$.

Allowing a blue, aqueous solution of tib and $Cu(CH_3COO)_2{\cdot}2H_2O$ (L:M = 2:1) to stand for a period of three months resulted in the formation of pale blue cubic crystals of **6** with the formulation $[Cu_4(tib)_8](CH_3COO)_8{\cdot}32H_2O$ from a blue oil. The crystal structure of complex **6** is shown in Fig. 2. Here, the tib ligand is again in the novel *cis*,*trans*,*trans*-conformation (Scheme 1) as in the free solid state, the three imidazolyl rings of each tib are inclined to the phenyl ring at angles of 73.2, 86.7 and 114.3°, respectively, and the distances between N1, N3 and N5 are 10.180, 6.360 and 10.427 Å, respectively (Fig. 1b). It is interesting to note that the tripodal ligand tib acts as a 2-connected bridging ligand in **6**. This unexpected coordination performance is very different from that in the previous work.[9–13] Each tib is attached to two copper atoms with two nitrogen atoms (N1 and N3) from the two *trans*-oriented imidazolyl arms, the third (N5) remains uncoordinated to the copper atom but forms an N $\cdots$ H–OH hydrogen bond with an N $\cdots$ O distance of 2.80 Å. (Fig. 1b). The copper ion is coordinated by four N atoms from four independent tib ligands, giving a distorted N_4 square-planar geometry (Fig. 1b), while the acetate anions are un-coordinated to their Cu ion, but there are interactions between these acetate anions and nearby Cu atoms with a Cu–O distance of 2.47 Å, and each copper atoms forms two Cu–O interactions (Fig. 1b and Fig. 2). The Cu–N distances [2.006(4) and 2.047(4) Å] of complex **6** are similar to the 1.998(3) Å of complex **1**[9] and *ca.* 1.981(6)–2.006(6) Å of complex **5**, and the bond angles N–Cu–N are in the range of 88.2(2)–91.8(2)/180°, respectively (Table 1). Four tib ligands are joined together by four adjacent Cu atoms, forming a 48-membered Cu_4L_4 rhombic unit composed of $Cu_4C_{28}N_{16}$ on the *bc* plane (Fig. 2a) and looking down the *b* axis (Fig. 2b), the Cu_4L_4 rhombic unit is like the Arabic number '8', two copper atoms Cu1I and Cu1B are in an absolute superposition and Cu1G is at the top and the Cu1M is at the bottom of the Arabic number '8'. In this unit, the benzene planes of the two tib ligands in the opposite position are parallel with each other and the dihedral angle between the benzene planes of the adjacent tib is 72.6°, and the dihedral angle between the two imidazolyl planes which coordinate to the same copper atom is 75.4°. Each tib uses two of the three imidazolyl arms to form the 48-membered Cu_4L_4 unit, and the uncoordinated third imidazolyl

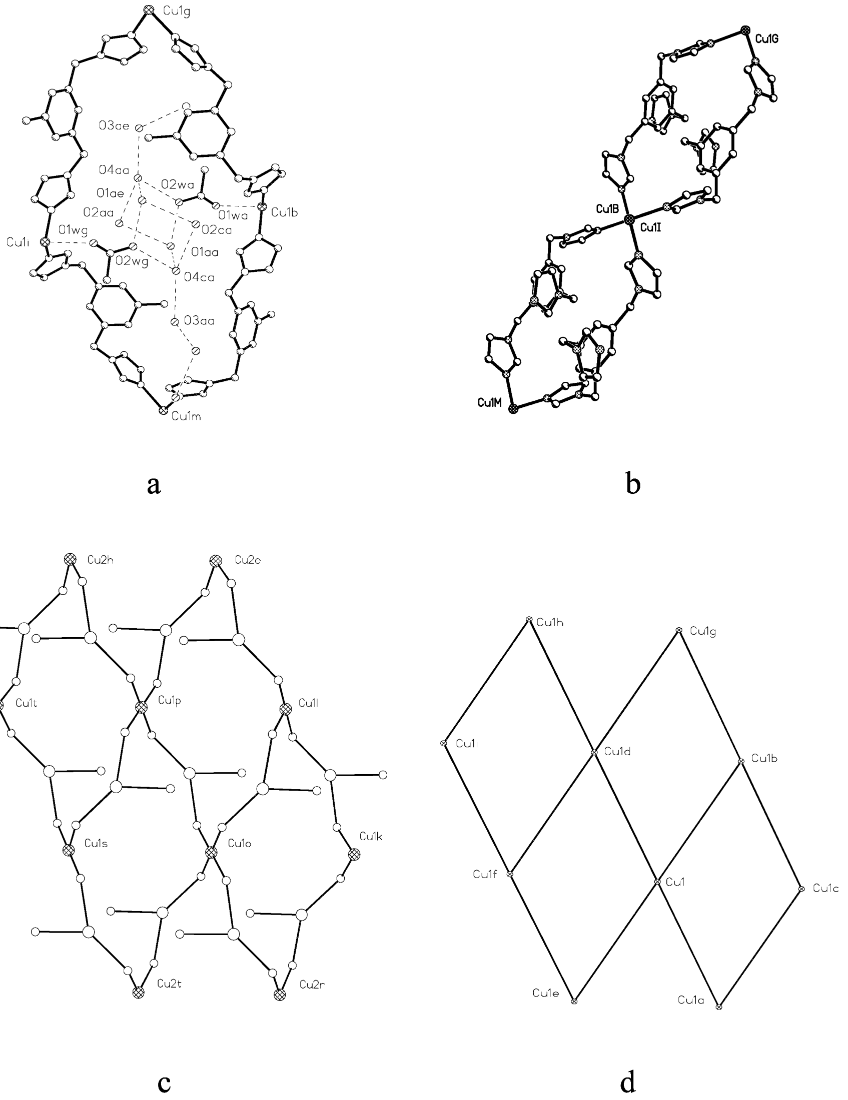

Fig. 2 View of **6** showing the two-dimensional rhombic Cu_4L_4 grid network. (a) Structure of a Cu_4L_4 rhombus in which a cubic O_8 cluster is formed. The perspective view is in the *bc* plane. (b) Structure of the Cu_4L_4 rhombus (down the *b* axis). (c) Schematic drawing of the two-dimensional grid network. The hatched circles represent Cu atoms, and the big and small circles represent phenyl rings and imidazolyl rings, respectively. (d) The two-dimensional sheet consisting of the four-membered rings where only copper(II) atoms are presented. All the hydrogen atoms are omitted for clarity.

arms of tib are arranged well-regulated in the space: the third arms from the tib which coordinate with Cu2h point to the left, while other third arms from the tib which coordinate with Cu1s point to the opposite direction, and the four copper atoms form a planar rhombus with each side of Cu–Cu exactly 13.51 Å while the smallest and largest Cu–Cu separations within the rhombic cavity are 12.13 and 24.14 Å, respectively (Fig. 2a). Repeating this Cu_4L_4 unit along the *ac* plane, an infinite 2D network is generated (Fig. 2c) and Fig. 2d shows the two-dimensional sheet where only the copper atoms are presented. This is a (4,4) grid-like network consisting of the Cu_4 rhombic unit where the distance between two adjacent copper atoms in the 2D network is 13.51 Å, and the angle formed by the three adjacent copper atoms, *e.g.* Cu1i–Cu1f–Cu1d, is 53.3°, and Cu1f–Cu1i–Cu1h, is 126.7° within the Cu_4 rhomboid. This means each Cu_4 motif is nearly a perfect rhombus. All of the acetate anions and some of water molecules are accommodated in these cavities. There are interactions between acetate anions and nearby Cu atoms with the Cu–O distance of 2.47 Å (as shown in Fig. 2a).

A further important aspect in the crystal structure of **6** is the hydrate structure.[14] There are two kinds of configurations formed by the water and acetate anions *via* hydrogen bonds (Fig. 2a and Fig. 3). Fig. 2a illustrates the incorporation of the six water molecules of crystallization and two oxygen atoms from two acetate anions forming a cubic O_8 cluster with heterodromic hydrogen bonds in the rhombic cavity. The O–O distances of the heterodromic hydrogen bonds are in the range 2.56–3.03 Å, and the O–O–O angles are in the range of 75.0–117.8° (Table 2). The dimensions of this cube are 2.85 × 2.68 × 2.87 Å. Fig. 3 illustrates the incorporation of the two other water molecules of crystallization and two oxygen atoms from two adjacent O_8 cubes forming a quadrangle O_4 cluster with homodromic hydrogen bonds. Two oxygen atoms (O3aa and O3af) of the quadrangle cluster are hydrogen-bonded further to the nearby imidazolyl N atoms (N5ac and N5ae) of the 2-connected tib ligands which are not utilized for the metal coordination. The O–O distances of homodromic hydrogen bonds are in the range 2.58–2.83 Å, and the O–O–O angles are in the range of 55.6–136.7° (Table 3). Thus, each cubic O_8

Table 2 Heterodromic hydrogen-bonding scheme in complex **6** (distances in Å, angles in °)

O4aa–O2wa	2.68	O4aa–O3ae	2.83
O1ae–O2ca	3.03	O4aa–O2aa	2.80
O1aa–O2aa	3.03	O1ae–O2wg	2.56
O4aa–O1ae	2.87	O1aa–O2wa	2.56
O2wg–O4ca	2.68	O4ca–O2ca	2.80
O–O–O	*ca.* 75.0–118.7		

Table 3 Homodromic hydrogen-bonding scheme in complex **6** (distances in Å, angles in °)

O3aa–O4ab	2.58	O3af–O4ca	2.83
O3aa–N5ae	2.80	O3af–O4ab	2.83
O3aa–O3af	2.69	O3af–N5ac	2.80
O3aa–O4ca	2.58		
O–O–O	*ca.* 55.6–136.7		

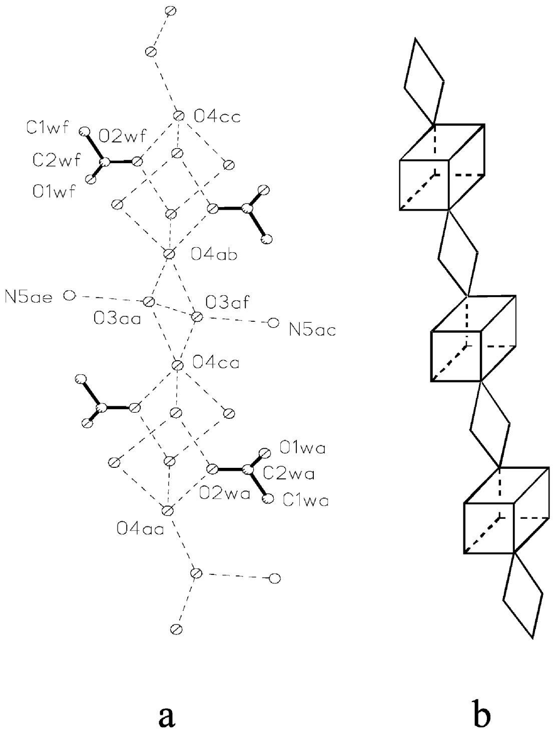

Fig. 3 (a) Hydrate structure of the one-dimensional cubic O_8 cluster chain along the *a* axis. (b) Schematic drawing of the one-dimensional cubic O_8 cluster chain along the *a* axis. All the hydrogen atoms are omitted for clarity.

cluster and quadrangle O_4 cluster share two corners and form a one-dimensional cubic O_8 chain along the *a* axis (as shown in Fig. 3).

The packing arrangement of two-dimensional network layers of complex **6** is illustrated in Fig. 4. 2D (4,4) rhombic grid layers pack along the *a* axis forming large channels to accommodate the cubic O_8 chains and the layers are bonded together by hydrogen bonds to construct a 3D infinite nanoporous network. The nearest Cu–Cu distance of the adjacent sheets is 10.56 Å.

Discussion

It is common to find reports on the construction of infinite 2D rhombic grid networks with ditopic organic ligands, such as 4,4′-bipyridine[15] and pyrazine.[16] Aryl tripodal ligands[2–13] are usually employed for the design and construction of extended frameworks and cage-like complexes since they act as 3-connected bridging ligands when coordinated with metal atoms, such as in complexes **1**–**5** where both tripodal ligands titmb and tib act as 3-connected bridging ligands when coordinated with metal atoms. However, in complex **6** the tripodal ligand tib acts as a ditopic bridging ligand: the third (N5) remains uncoordinated to the copper atom, but forms an N ··· H–OH hydrogen bond with an N ··· O distance of 2.80 Å. This result clearly shows that the formation of the N ··· H–OH hydrogen bond makes the tripodal ligand tib act as a 2-connected bridging ligand when it coordinates with copper(II) atoms.

Complex $[Cu_3(titmb)_2(OCOCH_3)_6]\cdot H_2O$ (**1**)[9] was synthesized by reaction of titmb with $Cu(CH_3COO)_2\cdot 2H_2O$ (L:M = 2:1) in methanol–diethyl ether conditions in which titmb is in the W-form; complex $\{[Cu(dien)]_3(titmb)_2\}(ClO_4)_6\cdot H_2O$ (**2**)[10] was obtained by diffusion of diethyl ether into aqueous acetonitrile containing $Cu(dien)^{2+}$ ions and titmb with both the W- and Y-forms; $[Zn_3(tib)_2(CH_3COO)_6]\cdot 4H_2O$ (**3**)[12] was assembled from tib and zinc(II) acetate in ethanol in which tib is in the W-form. Complex $[Ag_3(titmb)_2](ClO_4)_3$ (**4**)[11] has been obtained by slow diffusion between two layers of an aqueous solution of $AgClO_4\cdot H_2O$ and a solution of titmb in ethanol, and in this complex all of the titmbs are in the same W-form. Allowing a blue MeOH–H_2O solution involving tib and $Cu(CH_3COO)_2\cdot 2H_2O$ (L:M = 3:2) to stand overnight resulted in the formation of **5** with the formulation $\{[Cu_6(tib)_8(OH)_4](OH)_8\cdot 22H_2O\cdot 4CH_3OH\}_n$[13] where tib shows an unexpected T-form conformation. However, allowing a blue aqueous solution involving tib and $Cu(CH_3COO)_2\cdot 2H_2O$ (L:M = 2:1) to stand over a period of three months resulted in the formation of pale blue cubic crystals of **6** with the formulation $[Cu_4(tib)_8](CH_3COO)_8\cdot 32H_2O$ from a blue oil in which the tib is in a novel Y-form. Comparing the reaction conditions of the complexes **1**–**6**, we can find that the conformations of the tripodal ligands tib and titmb are obviously controlled by the reaction conditions: when reacted in a organic solvent, both the titmb and tib are in the same W-form, such as is seen in complexes **1** and **3**; when water is present in the solvent system, the conformations of the two tripodal ligands will change from the W-form to the Y-form [for example, both the W-form and the Y-form are present in complex **2** and there is an intermediate conformation of the Y-form (*i.e.* the T-form) in complex **5**]; when reacted in water, the tripodal ligand tib is in a novel Y-form in complex **6**. These results show that the reaction conditions play an important role in controlling the conformations of the tripodal ligands and the construction of supramolecular complexes.

In comparing complexes **1**–**6**, it is interesting that **1**, **2**, **5** and **6**, are infinite 2D/3D extended structures but that **3** and **4** are finite M_3L_2 cage structures. In complexes **1**, **2**, **5** and **6**, the transitional metal atom involved is the same copper(II) atom, the coordination geometry of copper is square-planar[9,10] N_4 or a square-based pyramid[13] N_5 or N_4O_1, respectively, while in complexes **3** and **4**, the transitional metal atoms involved are zinc(II) and silver(I) atoms, where the coordination geometries of zinc and silver are tetrahedral[12] N_2O_2 or linear[11] N_2, respectively. This result shows that the coordination geometry of the metal atoms also plays an important role in the construction of supramolecular complexes.

Complexes **1**, **2** and **6** are all 2D extended structures, but the packing arrangements of these three two-dimensional network layers are different. There are no large channels formed in complexes **1**[9] and **2**;[10] instead, the efficient space filling has been achieved by the formation of π–π interactions between titmb of sheets *N* and *N* + 2 inside the hole of sheet *N* + 1 in complex **1** and a center-symmetric mode between every two adjacent sheets for complex **2**. However, the 2D (4,4) rhombic grid is packed in columns along the *a* axis and large channels are formed to accommodate the cubic O_8 chains and the layers are bonded together by hydrogen bonds to construct a 3D infinite nano-porous network. These results also show that the hydrogen bondings play a very important role in the crystal packing process of this infinite 2D rhombic grid network complex $[Cu_4(tib)_8](CH_3COO)_8\cdot 32H_2O$ (**6**).

The hydrogen substructures of the crystal phase by solvent molecules have been observed in metal structures of the poly(azolyl)borates[17] as dimers and teramers; hexamers have also been reported[18] and a 2D hydrogen-bonded network has also been found in the metal structures of aryl hexapodal ligands.[19] The hydrate substructure of the one-dimensional cubic O_8 chain in complex **6** is novel and unique.

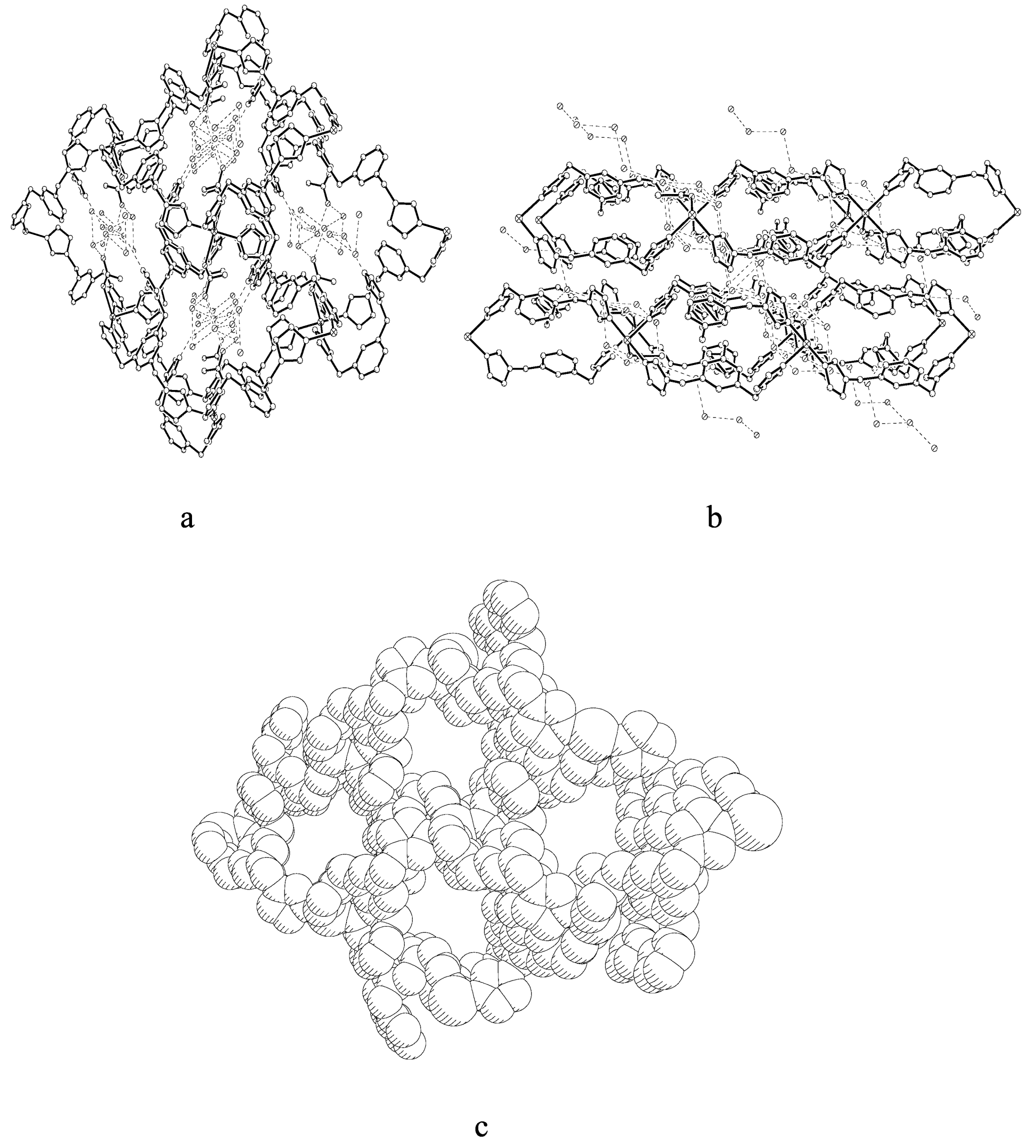

Fig. 4 Crystal packing diagram of **6**. (a) Packing of the 2D rhombic grid layers along the *a* axis forming large channels to accommodate the cubic O_8 chains (indicated with the dashed lines). (b) Packing diagram of the 2D rhombic grid layers along the *b* axis showing the cubic O_8 chains (indicated with the dashed lines). (c) Space-filling diagram of the 3D infinite nano-porous network.

Properties

The structure of supramolecular networks of the titled complex suggests a porous structure which contains guest water molecules. It is important that such a porous structure should be stable even after removal of guest molecules in view of the development of molecular-based materials. TGA and DTA of the crystalline sample of **6** showed the loss of all guest water molecules under 186 °C. However, the X-ray powder pattern of the crystals after removing the water molecules showed that they did not remain identical to those of the original crystals and the backbone of complex **6** collapsed. Complex **6** shows carboxyl antisymmetric (ν_{asym}) and symmetric (ν_{sym}) vibrations at 1576 and 1395 cm^{-1}, respectively, in the infrared (IR) spectrum. The separation between the ν_{asym} and ν_{sym} frequencies (181 cm^{-1}) is smaller than that in our previous work (204 cm^{-1}),[9] indicating the weaker coordinative bonding between the acetate anions and the Cu(II) ions and the coordination of the acetate anion to the copper atom is monodentate,[20,21] which is in agreement with the crystallographic results. The electronic spectra of complex **6** in aqueous solution at room temperature show a bond maximum at 610 nm (16390 cm^{-1}) due to the Cu(II) d–d transition. [Cu^{II}-$(OCOH_3)_2$(2-MeIm)$_2$] (2-MeIm = 2-methylimidazole) exhibits a d–d transition at 675 nm in methanol solution.[20] Complex **6** is soluble in hot water, dimethylformamide and dimethyl sulfoxide, but insoluble in methanol, ethanol, acetone and less polar solvents such as diethyl ether, chloroform and benzene.

Conclusion

A 2D rhombic grid network complex $[Cu_4(tib)_8](CH_3COO)_8 \cdot 32H_2O$ (**6**) has been prepared by reaction of the tripodal ligand tib with $Cu(CH_3COO)_2$ and the structure has been characterized by single crystal X-ray diffraction. In the solid state, tib acts as a ditopic bridging ligand and all the tib ligands are in a novel W-form conformation. It is found that the formation of the N ··· H–OH hydrogen bonds between the hydrogen atoms of the solvent water molecules and the imidazole coordinative nitrogen atoms of the third arm of tib makes the tripodal ligand tib act as a 2-connected bridging ligand when it coordinates with copper(II) atoms. Comparing the reaction conditions of the complexes **1**–**6**, it is found that the conformations of the tripodal ligands tib and titmb are clearly controlled by the reaction conditions. When reacted in an organic solvent, both of the titmb and tib are in the same W-form; when water is present in the solvent system, the conformations of the two tripodal ligands will change from the W-form to the Y-form; and when reacted in water, the tripodal ligand tib is in a novel Y-form. Comparing the metal atoms involved in the complexes **1**–**6**, the results show that the coordination geometry of the metal atoms also plays an important role in the construction of supramolecular complexes. In complexes **1**, **2**, **5** and **6**, the transitional metal atom involved is the same, all are copper(II) atoms, the coordination geometries of copper being square-planar N_4 or square-based pyramidal N_5 or N_4O_1, respectively, whereas in complexes **3** and **4**, the transitional metal atoms involved are zinc(II) and silver(I), their coordination geometries being tetrahedral N_2O_2 or linear N_2, respectively. Comparing the packing arrangements of the three two-dimensional network layers **1**, **2** and **6**, it shows clearly that the hydrogen bonds play a very important role in the crystal packing process of this infinite 2D rhombic grid network complex **6**. There are no large channels formed in complexes **1** and **2**, but large channels are formed by the columnar packing of the 2D (4,4) rhombic grid layers of complex **6** along the *a* axis, and in which the cubic O_8 chains are accommodated. Therefore, the results of these studies not only illustrate that hydrogen bonds play a very important role in the construction of supramolecular complexes, but also the reaction conditions together with the metal atoms co-affect inorganic supramolecular formation. Further studies of the reaction of titmb and tib ligands with other transition metal ions are in progress.

Experimental

Synthesis of 6

A solution of tib (32 mg, 0.10 mmol) in water (15 ml) was added to an aqueous solution (5 ml) of $Cu(CH_3COO)_2\cdot 2H_2O$ (11 mg, 0.05 mmol) at room temperature. The mixture was filtered after stirring for *ca.* 1 hour to give a blue solution. Allowing this filtrate to stand for a period of three months resulted in the formation of pale-blue cubic crystals. Yield 10%. Found: C, 49.84; H, 5.95; N, 17.40%. Calc. for $C_{160}H_{232}N_{48}Cu_4O_{48}$ ($[Cu_4(tib)_8](CH_3COO)_8\cdot 32H_2O$): C, 49.91; H, 6.08; N, 17.46%.

Crystallography

A pale-blue crystal of size 0.2 × 0.15 × 0.10 mm was mounted on a Bruker CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and the intensity data of **6** were collected at room temperature. All absorption corrections were performed using the SADABS program. The structure was solved by the direct methods (SHELXS) and refined by the full-matrix least-squares method against F_o^2 (SHELXL-97). All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically. Details of the crystal parameters, data collection and refinement for complex **6** and tib ligand are listed in Table 4. Selected bond distances and angles, the O–O distances and the O–O–O angles of heterodromic hydrogen bonds and homodromic hydrogen bonds are listed in Tables 1, 2 and 3, respectively.

CCDC reference numbers 157077 and 162985.

See http://www.rsc.org/suppdata/dt/b2/b201446g/ for crystallographic data in CIF or other electronic format.

Physical measurements

Elemental analyses were carried out on a Perkin-Elmer 240C elemental analyzer, at the Center of Materials Analysis, Zhongshan University. Infrared (IR) spectra were recorded on a Nicolet FT-IR 170SX spectrophotometer using KBr disks. Electronic spectra for the complex in aqueous solution were obtained on a Shimazu 240 spectrophotometer.

Table 4 Summary of crystal data and refinement results for complex **6** and tib

	6	Tib
Empirical formula	$C_{80}H_{116}N_{24}Cu_2O_{24}$	$C_{18}H_{22}N_6O_2$
Formula weight	1925.04	354.42
T/°C	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	10.565(2)	18.590(4)
b/Å	12.130(3)	16.384(3)
c/Å	17.726(4)	11.721(2)
β/°	103.72(3)	102.20(3)
U/Å^3	2206.8(7)	3489.3(12)
Z	4	8
μ/mm^{-1}	0.571	0.092
Measured/independent reflections	12735/5465	12786/7487
R_{int}	0.0483	0.0216
R [$I > 2\sigma(I)$]	0.0810	0.0446
$wR2$ [$I > 2\sigma(I)$]	0.2218	0.1161

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