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Assembly of a 3D nanoporous framework $[Cu_6(OH)_4(tib)_8]_n^{8+}$ from Cu(II) and the flexible tripodal ligand tib†

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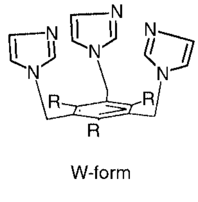
Received (in Cambridge, UK) 8th January 2001, Accepted 19th April 2001
First published as an Advance Article on the web 15th May 2001

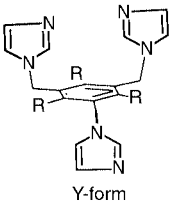
The structural characterization of a 3D nanoporous complex $\{[Cu_6(tib)_8(OH)_4](OH)_8\cdot 22H_2O\cdot 4MeOH\}_n$ 1 [tib = 1,3,5-tris-(imidazol-1-ylmethyl)benzene] assembled from the tripodal ligand tib and $Cu(MeCO_2)_2$ shows that π–π interactions resulting from the novel T-shaped conformation of the ligand are the key trigger for the construction of the backbone of a framework with channels of size 12.00 × 18.91 and 10.30 × 13.66 Å.

Employing multidentate organic ligands and metal ions to construct organic–inorganic hybrid materials[1] *via* coordinative metal–ligand bonds has become a major strategy.[1,2] Frameworks with specific topologies such as honeycomb grids and interpenetrating nets have been obtained by assembly of suitable metal ions with rationally designed rigid tripodal ligands such as 1,3,5-trisbenzonitrile (tcb),[3] 1,3,5-tris(4-ethynylbenzonitrile)benzene (teb)[4] and 2,4,6-tris(4-pyridyl)-1,3,5-triazine (tpt).[5–7] For example, tcb gives an extended honeycomb framework[3] by assembly with AgO_3SCF_3, while in the case of tpt, a (12,6) interpenetrating net[6] was obtained by reaction of the ligand with $Ni(NO_3)_2$. Recently, Robson and coworkers[7] reported another honeycomb-like framework[7] obtained by assembly of $Cu(MeCO_2)_2$ with the rigid tripodal ligand tpt.

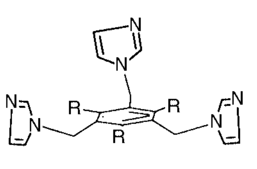
In order to investigate the relationship between the topology of the assembly and the conformation of the ligand, two flexible tripodal ligands, 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene (titmb)[8,9] and 1,3,5-tris(imidazol-1-ylmethyl)benzene (tib)[10] were employed. Our previous work showed that titmb has two conformations, namely, *cis,cis,cis*-conformation (W-form) and *cis,trans,trans*-conformation (Y-form). An extended honeycomb framework with large cavities[8] was formed with titmb in W-form, whilst a 2D sheet-like framework[9] containing the ligand in both W- and Y-form was obtained from $Cu(dien)^{2+}$ ions and titmb. Most recently, a study also showed that a discrete M_3L_2 cage-like complex was assembled from tib in W-form with zinc(II) acetate.[10]



W-form



Y-form



T-form

We report herein, to our knowledge, the first example of a 3D nanoporous complex $\{[Cu_6(tib)_8(OH)_4](OH)_8\cdot 22H_2O\cdot 4MeOH\}_n$ assembled from the tripodal ligand tib, in which π–π interactions play important roles in the construction of the backbone of the framework. In addition all the tib ligands are in a novel, unprecedented T-form conformation.

Standing of a blue MeOH–H_2O solution of tib and $Cu(MeCO_2)_2\cdot 2H_2O$ (L : M = 3 : 2) overnight resulted in the formation of blue sheet-like crystals with the formulation $\{[Cu_6(tib)_8(OH)_4](OH)_8\cdot 22H_2O\cdot 4MeOH\}_n$ **1**‡ and the structure was characterized by crystallographic analysis.§ Complex **1** shows no feature for carboxyl antisymmetric (ν_{asym} 1560 cm^{-1}) or symmetric (ν_{sym}, 1416 cm^{-1}) vibrations in the IR spectrum, indicating the absence of acetate anion, in agreement with the elemental analyses and crystallographic results.

There are two types of coordination environments for the copper ions (Fig. 1). Cu1 is coordinated by four N atoms from four tib ligands and one O atom from one OH anion giving a distorted N_4O square-pyramidal geometry, in which the four N atoms form the equatorial plane. By contrast Cu2 is coordinated only by four N atoms from four tib, leading to a distorted N_4 square-planar geometry.

It is interesting that in this complex, all tib ligands are in the T-form, as (Fig. 1). One imidazolyl ring lies outside the phenyl plane, but the centers of the other two imidazolyl rings are in the plane of the phenyl group and situated in a linear manner, to form a capital ‘T’. Each tib is ligated to three copper atoms *via* the nitrogen atoms of the three imidazolyl groups. Two adjacent tib ligands adopt a top-to-bottom orientation and are joined together by atoms Cu1 and Cu1a to generate a rhombic Cu_2L_2

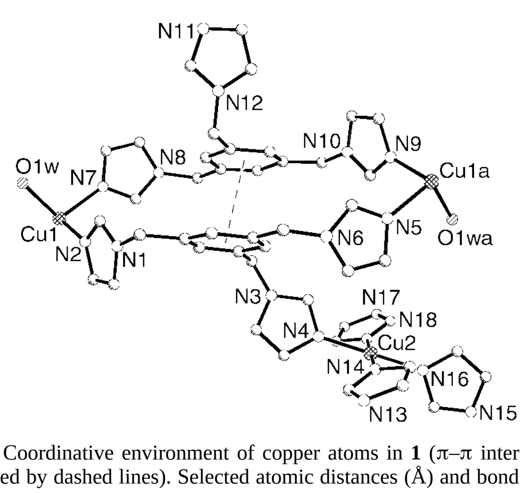


Fig. 1 Coordinative environment of copper atoms in **1** (π–π interactions indicated by dashed lines). Selected atomic distances (Å) and bond angles (°): Cu1–N 1.981(6)–2.006(6), Cu1–O 2.357(8); N–Cu1–N 88.3(2)–91.8(2)/161.1(3)–179.6(3), N–Cu1–O 89.1(3)–101.3(3); Cu2–N 1.991(6), N–Cu2–N 88.2(2)–91.8(2)/180. Cu1–Cu1a 13.76. All hydrogen atoms and solvate molecules are omitted for clarity.

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† Electronic supplementary information (ESI) available: part of packing diagram selected to show Cu··O interactions and O··O hydrogen interactions (Fig. 1S). See http://www.rsc.org/suppdata/cc/b1/b100325i/

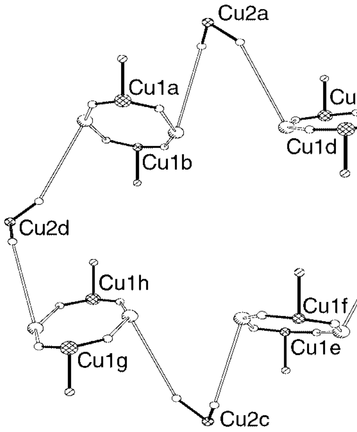

Fig. 2 Schematic drawing of a $Cu_{12}L_8$ macrocyclic ring in the *xz* plane. The large cross-hatched ellipsoids and small hatched ellipsoids represent Cu and O atoms respectively, while the large and small ellipsoids represent phenyl rings and coordinated N atoms, respectively. Heavy lines represent the Cu–N bonds while open lines connect the phenyl rings with coordinated N atoms. All hydrogen atoms and solvate molecules are omitted for clarity.

unit (as shown in Fig. 1), in which strong π–π interactions formed between the two tib ligands, with the two parallel phenyl rings separated by 3.55 Å, and a Cu1$\cdots$Cu1a distance of 13.76 Å.

Four independent Cu_2L_2 units are joined together by four other Cu atoms, forming an $Cu_{12}L_8$ macrocyclic repeating unit which is composed of $Cu_{12}C_{144}N_{48}$ (as shown in Fig. 2); the total volume of the unit, 23.19 × 18.91 × 13.66 Å, is the same as the cell unit. Repeating the $Cu_{12}L_8$ units in space, a 3D nanoporous framework is then formed (Figs. 3 and 4), in which there are two types of channels with different sizes. Along the *y* axis, a channel with hole dimensions of 12.00 × 18.91 Å, which are defined by the Cu–Cu seperation, is shown in Figs. 2 and 3. However, when viewed along the *z* axis, four Cu_2L_2 units with each two sharing a Cu atom are connected by two other Cu atoms, forming a rectangular Cu_8L_8 unit ($Cu_8C_{144}N_{48}$) opening with dimensions of 10.30 × 13.66 Å (Fig. 4). There are $22H_2O$ and 4MeOH molecules in a complete $Cu_{12}L_8$ repeating unit, all within the channels. Indeed, all the modeled water molecules in this structure are in close contact to either Cu^{2+} ions (*e.g.* Cu1–Ow4 3.097(12) Å, Cu2–Ow2 2.642(10) Å) or the hydrogen atoms of methanol and water molecules (Fig. 1S, see ESI†). The free pore volume of a unit is estimated, using the PLATON program[11] (squeeze), to be 847 Å^3 (15.0% of the total).

The result described here shows that $\pi\cdots\pi$ interactions, resulting from the novel T-shaped conformation of the ligand, are the key trigger for the construction of the backbone of the framework. This is the first example determined by X-ray structure analysis showing a 3D nanoporous structure constructed by Cu(II) ions and a flexible tripodal ligand. This work also shows that the topology of assembly is obviously affected by the ligand conformation. The novel T-form of tib is favourable in the formation of $\pi\cdots\pi$ interactions between two nearest adjacent ligands. This nanoporous complex may have the ability to selectively enclathrate moderately sized guests. Encapsulation reactions of guest molecules are now under study.

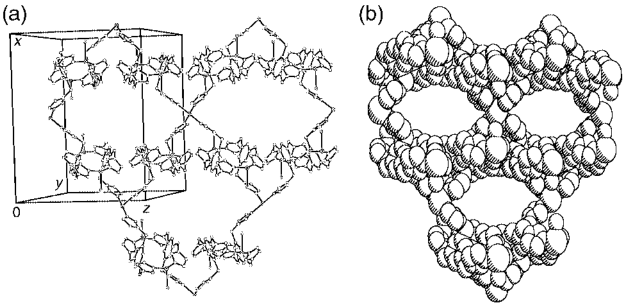

Fig. 3 Structure views of **1** in the *xz* plane, showing the macrocyclic channels. (a) Structure of three channels with cell axes. (b) A space-filling model. All hydrogen atoms and solvate molecules are omitted for clarity.

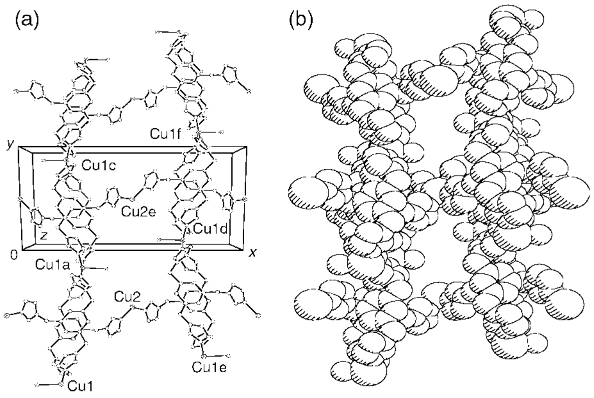

Fig. 4 Structure views of **1** in the *xy* plane, showing the rectangular channels. (a) Structure of two channels with cell axes. (b) A space-filling model. All hydrogen atoms and solvate molecules are omitted for clarity.

We are grateful for funding from the NNSF of China and the postdoctoral fund of Guangdong province and a special fund from the Ministry of Education of China for the vitalization education plan of the 21st century for H.-K. L.

Notes and references

‡ *Experimental:* a solution of tib (48 mg, 0.15 mmol) in methanol (5 ml) was added to an aqueous solution (10 ml) of $Cu(MeCO_2)_2\cdot 2H_2O$ (22 mg, 0.1 mmol) at room temperature. The mixture was filtered after stirring for *ca.* 1 h to give a blue solution. Standing of this filtrate overnight resulted in the formation of blue sheet-like crystals. Yield 10% (Found: C, 49.52; H, 5.47; N, 18.61%. Calc. for $C_{148}H_{208}N_{48}Cu_6O_{34}$ ($[Cu_6(tib)_8(OH)_4](OH)_8\cdot 18H_2O\cdot 4CH_3OH$): C, 49.58; H, 5.84; N, 18.75%. IR(KBr) cm^{-1}, 3411br, 3115s, 3033m, 1638w, 1611w, 1572w, 1522s, 1440m, 1401w, 1345w, 1287w, 1237m, 1100vs, 1030m, 948w, 839w, 742m, 659m, 632w.

§ *Crystal data* for **1**: $C_{148}H_{216}N_{48}Cu_6O_{38}$, M = 3656.92, blue sheet, crystal dimensions 0.15 × 0.11 × 0.04 mm, monoclinic, $P2_1/c$, a = 13.662(2), b = 23.197(4), c = 18.914(4) Å, β = 110.074(3)°, U = 5630.1(17) Å^3, Z = 1, T = 294(2) K, R (wR) = 0.0920 (0.2710) for 9552 reflections with $[I > 2\sigma(I)]$. CCDC 156828. See http://www.rsc.org.suppdata/cc/b1/b100325i/ for crystallographic data in .cif or other electronic format.

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