An unprecedented twofold interpenetrating (3,4)-connected 3-D metal–organic framework†

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An unprecedented twofold interpenetrating (3,4)-connected topology of the Cu_3L_4-type metal–organic framework was prepared using *N,N′,N″*-tris(4-pyridinyl)-1,3,5-benzenetricarboxamide (L) as a trigonal three-connection node and the copper(II) ion as a square planar four-connection node, where the framework contains remarkably large 1-D solvent channels.

In recent years, there has been considerable interest in porous metal–organic frameworks (MOFs) with regular and accessible cavities. Although this field aims at the discovery and synthesis of new materials for practical applications that use their functional aspects, including catalysis, storage, separation, sensors, and electronics,[1] it would be difficult to achieve a major advance without understanding the structural aspects of such materials. Recent reviews on the framework topologies and other geometrical characteristics of network solids reflect this importance.[1,2] The classification of structures by Wells lays the foundation for the general understanding of inorganic solids, as well as MOFs.[3] Many 3-D structures with mineral topologies, such as $CdSO_4$, NbO, Pt_3O_4, pyrite, quartz, rutile, halite, and sodalite have been reported recently as the result of attempts to obtain geometric characteristics with designable functionalities.[4]

The key steps in building coordination frameworks are to rationally design the appropriate ligands and to choose metal ions with suitable coordination geometries.[2,5] In the synthetic design of metal–organic open frameworks, a low coordination number (<6) with more directional covalent bonds is desirable for creating an open architecture.[6] There has been increasing interest in the use of three-connected centers as basic structural units for the construction of open-framework materials.[7] Three-connected centers, when used alone, tend to form low-dimensional structures, and when used in combination with four-connected centers lead to a variety of 3-D open-framework architectures.[8] However, most of the studies have focused on the (3,4)-connected nets with tetrahedral four-connected centers.[9] If all square planar four-connected nodes are linked exclusively to trigonal three-connected nodes and *vice versa*, two distinct (3,4)-connected nets are obtained: Pt_3O_4 and a twisted boracite net.[2b,10] Until now, only five examples of (3,4)-connected MOFs with square planar four-connected motifs were known.[7a,11] All of them are either augmented Pt_3O_4 or augmented twisted boracite nets, where the paddle wheel Cu(II) center serves as an augmented square planar tetratopic node. To our surprise, there have been no reports of (3,4)-connected MOFs with a simple square planar node.

Here we describe the synthesis, and structure, of a (3,4)-connected MOF with a Cu^{2+} ion as a simple square planar four-connection node and a ligand, *N,N′,N″*-tris(4-pyridinyl)-1,3,5-benzenetricarboxamide (L), as a trigonal three-connection node. This work is part of our research program aimed at the systematic study of (3,4)-connected open-framework architectures.[12]

The reaction of L with copper(II) nitrate trihydrate (4 : 3) in DMSO produced, after standing undisturbed for three days, blue needle-like crystals of **1** in 31.6% yield.§ The asymmetric unit of the crystal structure of **1** is shown in Fig. 1.¶ Two crystallographically independent four-connected Cu^{2+} centers, one in the general position and the other in the crystallographic twofold axis site, and two crystallographically independent but topologically equivalent three-connected ligands lead to a novel twofold interpenetrating (3,4)-connected Cu_3L_4 network structure. The coordination geometry of the Cu1 atom is Jahn–Teller distorted octahedral with four N atoms of the pyridine groups from four different L ligands occupying the corners of a square.[13] The bond lengths of Cu1–N range from 1.971(6) to 2.028(6) Å (Table S2†). The two apical positions of the Cu1 atom are occupied by two oxygens from a water molecule[14] and a nitrate anion, with Cu1–O4A and Cu1–O1N bond lengths of 2.447(8) and 2.711(9) Å, respectively. The coordination environment of the other Jahn–Teller distorted octahedral Cu2 atom, which is in the crystallographic twofold axis site,[13] is similar to that of the Cu1 center except for the two water molecules[14] ligated at the apical positions instead of a water molecule and a nitrate anion. The bond lengths of Cu2–N of the pyridine groups are 1.876(7) and 1.967(6) Å and the bond length of Cu2–O4N of the water molecule is 2.545(4) Å.
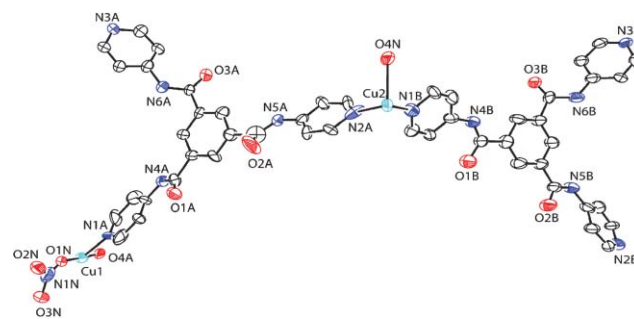
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† Electronic supplementary information (ESI) available: Synthesis of ligand and MOF, simplified view of network, crystal information, hydrogen-bonding table, and XRD pattern. See DOI: 10.1039/b702216f
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Fig. 1 ORTEP view of the asymmetric unit of **1** with thermal ellipsoids at 20% probability displacement; the hydrogen atoms and the unligated solvent molecules are omitted for clarity.

Despite the simplicity of the building blocks, the overall structure of 3-D network **1** is quite complicated (Fig. 2A). In a simplified view, it is composed of alternating planar four-connection Cu^{2+} and trigonal three-connection L nodes. The two types of nodes are linked to each other to form an extended framework (Fig. S1†). According to Wells,[3] such networks with three- and four-connection nodes belong to the (3,4)-connected net family.

The individual (3,4)-connected net in **1** can be specified by the Schläfli symbol[2b,10] $(4.8^2)(8^6)(4^2.8^2.10^2)$ (Fig. 2B), which is different from the other (3,4)-connected nets with square planar tetratopic nodes: Pt_3O_4 net $(8^3)(8^6)$ and twisted boracite net $(6^3)(6^2.8^2.12^2)$.[15] To the best of our knowledge, this is the first example of a (3,4)-connected net that has two topologically different square planar four-connected vertices.

The trigonal units (representing the central benzene ring of L) of the two discrete nets in the network structure are displaced from each other by 6.65 Å. The rings of one net are penetrated by links of the other so that they are truly catenated. As shown in Fig. 2A and 3, the two interpenetrating nets hold each other through hydrogen bonding between the N–H of the amide group of the ligand and the oxygen atom of the adjacent nitrate (Table S3†), which is coordinated with a four-connected node (Cu^{2+}) of the other net. The van der Waals interactions between the nets provides further stabilization of the interwoven nets. This interweaving allows mutual reinforcement of the exceptionally large L moieties. The two different coordination environments of Cu^{2+} and the non-covalent interactions between the two nets

Fig. 3 View of the 3-D network illustrating the intermolecular hydrogen bonding, shown as yellow dashed lines: d(H4B⋯O2N [$-x$, $-y + 1$, $-z + 1$]) = 2.22 Å and $\angle$ N4B–H4B⋯O2N [$-x$, $-y + 1$, $-z + 1$] = 162.0°.

mentioned above work together to influence the formation of two topologically different four-connected nodes.

The large channels with a diameter of ∼18 Å (Fig. 2A) are filled with water and disordered DMSO, whose presence was supported by FT-IR spectroscopy. The solvent volume is 71% of the crystal volume, a value seldom observed for interpenetrating networks, which generally incorporate either very little (up to 20% of the crystal volume) or no free volume.[16]

Interpenetration has been considered a major obstacle in the achievement of porous crystalline structures with large free volume. In other words, the smaller the degree of interpenetration (n = 3 or 2 in the MOF), the greater the optimum amount of available free volume that can be achieved. As shown in Fig. 4, the diameter of the ring of one net (red), which another net (blue) has interpenetrated, is 14.3 Å and the length of the three-connected ligand (from the center of the benzenes to the nitrogen atom of pyridine) is 7.93 Å. On the other hand, the diameter of the four-connected node [Cu(pyr)$_4$] is 9.6 Å, which is too large to let a third net fit in the space remaining after two interpenetrating frameworks form. This results in wide channels and large void volume. However, the net is not robust enough to sustain its porosity. The XRD data of the air-dried network **1** showed an amorphous pattern with an extremely broad but high intensity band around 22° in 2θ, which suggests the presence of a large number of interatomic distances around 4 Å (Fig. S2†).
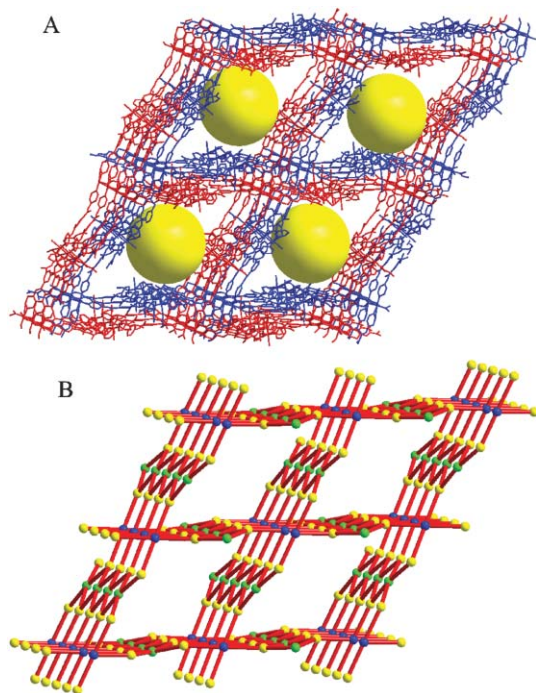

Fig. 2 (A) 3-D porous network of **1**, with solvent molecules omitted for clarity. Rhombic channels are observed along the *b*-axis. Two individual nets are indicated by different colors (blue and red). The diameter of the yellow balls inside the channels is 18 Å. (B) The $(4.8^2)(8^6)(4^2.8^2.10^2)$ net of **1**, three types of nodes are differentiated by color: yellow refers to three-connected nodes; blue and green refer to two topologically different four-connected nodes.
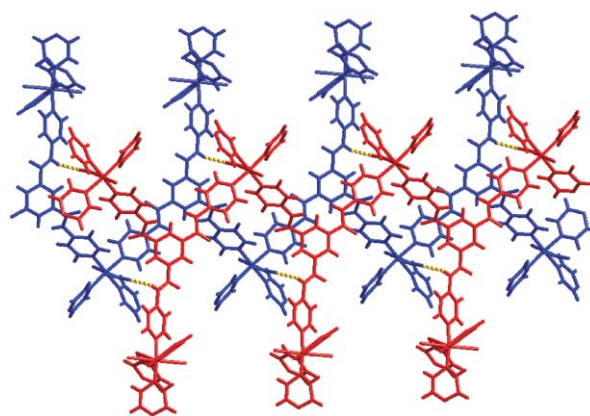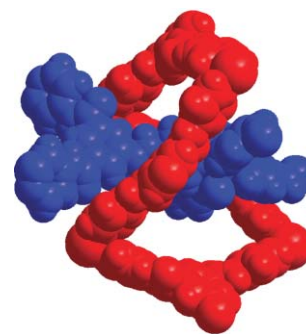

Fig. 4 A space-filling version of the part that highlights the interwoven nature of the 3-D network. Hydrogen atoms have been omitted. Atoms of different nets are shown in different colors (blue and red).

In summary, when a trigonal ligand, with hydrogen-bonding capable amide groups, as a three-connected node was combined with Cu(II) metal ions as pseudo-square planar four-connected nodes, an unprecedented (3,4)-connected network, which is different from the well-known Pt_3O_4 and twisted boracite nets, was obtained. We think the nitrate-mediated hydrogen-bonding interaction between the two nets, where the nitrate is weakly ligated at the apical position of the Cu^{2+} center (the green colored node in Fig. 2B), influences the formation of two topologically different square planar four-connected nodes. This MOF shows an extremely large solvent volume, which is due to the long trigonal linking ligand and the limited interpenetration (twofold). This might offer a new way to explore the synthesis of MOFs with large free volumes. If it can be made robust, this may offer new gas storage or catalytic potential.

Notes and references

§ A total of 0.1403 g (0.3200 mmol) of ligand, 0.0465 g (0.248 mmol) of $Cu(NO_3)_2\cdot 3H_2O$, and 15 mL of dimethyl sulfoxide (DMSO) were mixed and stirred for *ca.* 10 min, then filtered. Blue needle-like crystals were obtained after standing undisturbed at room temperature for three days. Yield 0.0673 g, 31.6%. Elemental analysis: $[Cu_3L_4(NO_3)_2(H_2O)_3]$ $(NO_3)_4\cdot 3(DMSO)\cdot 3(H_2O)$ $(C_{102}H_{102}N_{30}O_{39}S_3Cu_3$, fw = 2658.93): calcd C, 46.08; H, 3.87; N, 15.80%. Found: C, 46.18; H, 3.39; N, 15.47%. IR (KBr): ν(C=O), 1695 cm^{-1}; ν(N–H), 3170 cm^{-1}.

¶ *Crystal data* for $[Cu_3L_4(NO_3)_2(H_2O)_3](NO_3)_4$:[17] $C_{96}H_{72}Cu_3N_{30}O_{30}$, M = 2316.46, orthorhombic, T = 100(2) K, space group *Pnna*, a = 56.792(11), b = 14.331(3), c = 32.170(6) Å, V = 26 183(9) Å^3, Z = 4, μ = 0.279 mm^{-1}, synchrotron radiation (λ = 0.70000 Å), 49 789 reflections measured, 13 803 unique [R_{int} = 0.2134] which were used in all calculations. Structure refinement following modification of the data for the non-framework region as disordered electron densities with the SQUEEZE routine in PLATON:[18] final $R1$ = 0.0787 (I > $2\sigma(I)$), w$R2$ = 0.1739, GOF = 0.687, max./min. residual electron densities 0.212/−0.506 e Å^{-3}. CCDC 631720. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702216f

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13 The Jahn–Teller distorted octahedral Cu center (Cu1) is directly bonded to O1N, O4A and N1A atoms in the asymmetric unit. The remaining coordination at Cu1 is completed by N3A which is related by lattice translation (x, 1 + y, z), N2B, related by a combination of an *a*-glide operation and a lattice translation (1/2 + x, y, 1 − z), and N3B related by another combination of the same *a*-glide operation and another lattice translation (1/2 + x, 1 + y, 1 − z). The other octahedral Cu center (Cu2) is bonded to three atoms (N2A, N1B, and O4N) from the asymmetric unit and the remaining three atoms are related by a twofold axis operation (x, 1/2 − y, 3/2 − z).
14 We have tentatively assigned these electron densities as those of the oxygen atoms of the coordinated water molecules because no further residual densities corresponding to DMSO molecules or nitrate anions were found in the vicinity of these electron densities.
15 Long vertex symbols for net **1**: $(4.8.8)_4(8_2.8_2.8_2.8_2.8_2.8_2)_2$-$(4.4.8_3.8_3.16_{30}.16_{30})$; Pt_3O_4 net: $(8_5.8_5.8_5)_4(8_2.8_2.8_4.8_4.8_4.8_4)_3$; twisted boracite net: $(6.6.6)_4(6_2.6_2.8_2.8_2.12_2.12_2)_3$.
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