Metal–Organic Frameworks

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Crystal Engineering: Toward Intersecting Channels from a Neutral Network with a bcu-Type Topology**

*Tzuoo-Tsair Luo, Hui-Lien Tsai, Shang-Li Yang, Yen-Hsiang Liu, R. Dayal Yadav, Chan-Cheng Su, Chuen-Her Ueng, Lee-Gin Lin, and Kuang-Lieh Lu**

A great deal of interest has developed in the synthesis of metal–organic coordination polymers as they offer opportunities for preparing materials with controllable functionalities.[1] Although remarkable progress has been made in this new field of chemistry and materials science, largely due to efficient design strategies,[2,3] it is still difficult to prepare metal–organic frameworks with predictable topologies, even structures composed of simple inorganic salts.[4] The mimicking of topologies of natural minerals has rapidly become one of the most challenging issues in the design of metal–organic frameworks.[3c] Many 3D structures with mineral topologies such as NbO, quartz, pyrite, rutile, sodalite, $CdSO_4$, and halite[5] have been reported recently from attempts to obtain geometric characteristics with designable functionalities. From the reported characterization of the net topologies,[6] all of these networks are based on the use of three-, four-, or six-connected building blocks.[5] Connectivities of five, seven, or eight are extremely rare as a result of limitations in the symmetry or steric hindrance associated with connected nodes.[7,8] Although the body-centered cubic (bcu) net[8a–c] and the fluorite (flu) net[8d] are commonly seen in textbooks, such topologies with eight connecting nodes in a cubic geometry have only appeared in a few examples. To fulfill their geometric limitations, an eight-coordinated metal center or an eight-connecting polynuclear metal cluster block would be required; neither is easily achieved.[8] The former has been obtained with eight-coordinated lanthanide ions or $[M(CN)_8]^{4-}$ to form the bcu-type net,[8a,b] and the latter by using an eight-connecting cluster containing a tetracadmium carboxylate moiety and a four-connecting ligand to form the flu-type net. However, the bcu-type topology with only an eight-connecting polynuclear metal cluster unit has not yet been realized.

As part of our ongoing efforts in the design and synthesis of functional crystalline materials,[3e] we report herein the rare, porous bcu-type framework of $\{[Cu_3Cl_2(4\text{-ptz})_4(H_2O)_2]\cdot 3\,DMF\cdot 5\,H_2O\}_n$ (**1**), assembled from 5-(4-pyridyl)-tetrazolate (4-ptz) as a bridging ligand and an eight-connecting tricopper cluster ($Cu_3Cl_2^{4+} = Cu_3$ cluster) as a building block. To the best of our knowledge, this is the first bcu-type structure with an eight-connecting polynuclear metal cluster unit, and represents one of the highest connected topologies known for coordination polymers. The appropriate choice of an organic ligand with specific functional groups and geometry is also a major factor in achieving this target. The reasons for using the 4-ptz ligand are twofold: first, the tetrazole group is a widely known alternative to a carboxylate moiety, and second, the five-membered heterocyclic tetrazole group, which contains four N donors and a pyridine group, could serve both as a potential active coordination site and a hydrogen-bond acceptor, thus permitting the polymeric framework to be expanded through hydrogen-bonding interactions. Interestingly, until now, such coordination polymers based on tetrazole derivatives[9,10] have not been extensively studied, in contrast to metal carboxylates.[1e] Inspired by the work of Sharpless and co-workers,[11] the preparation of 5-substituted 1*H*-tetrazoles is now a safe and convenient route. Nevertheless, the generation of tetrazole-based coordination polymers would be a new and potentially useful research theme, which is currently in its infancy.

Compound **1** was synthesized by the reaction of copper(II) chloride and 5-(4-pyridyl)tetrazole (4-H-ptz) in DMF at ambient temperature in high yield by a single-step self-organization process (Scheme 1). The asymmetric unit consists of two Cu^{II} centers, one bridging chloride ion, one 4-ptz ligand, one coordinated water molecule, and other disordered guest molecules (Figure 1a). An analysis of the local symmetry of the two nonequivalent Cu centers reveals that the Cu1 center resides on a special symmetry site (SOF = 0.25) containing three mutually perpendicular twofold axes of rotation, and the Cu2 center resides on the other special symmetry site (SOF = 0.5) containing a twofold axis of rotation. Cu1 is bound to four tetrazole nitrogen atoms and two bridging chlorine atoms, and Cu2 is bound to two

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[*] Prof. Dr. Y.-H. Liu, Dr. R. D. Yadav, Prof. Dr. K.-L. Lu
Institute of Chemistry, Academia Sinica, Taipei 115 (Taiwan)
Fax: (+886) 2-27831237
E-mail: lu@chem.sinica.edu.tw

T.-T. Luo, Prof. Dr. C.-C. Su, Prof. Dr. C.-H. Ueng
Department of Chemistry, National Taiwan Normal University
Taipei 116 (Taiwan)

Prof. Dr. H.-L. Tsai
Department of Chemistry, National Cheng Kung University
Tainan 701 (Taiwan)

S.-L. Yang, Prof. Dr. L.-G. Lin
Department of Chemistry, Chinese Culture University
Taipei 111 (Taiwan)

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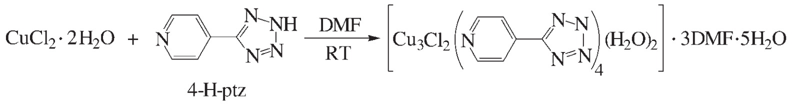

Scheme 1. Synthesis of **1** by a one-step organization; DMF = *N*,*N*-dimethylformamide.

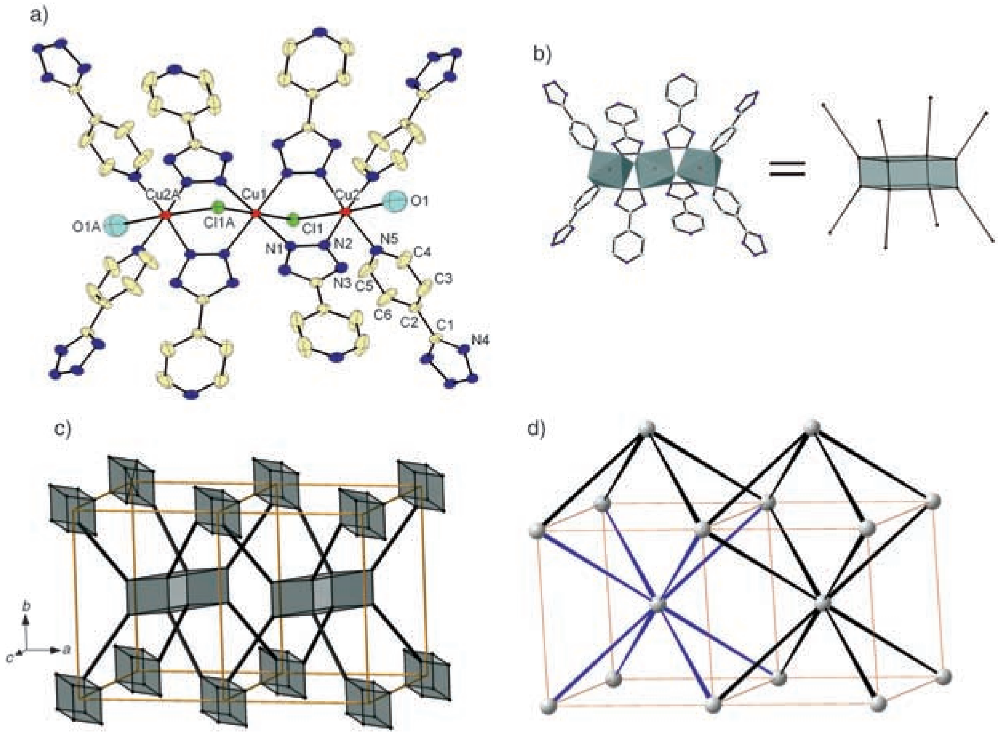

Figure 1. a) Local coordination environment of Cu^{II} in **1** (atoms are represented as 30% thermal ellipsoids); hydrogen atoms and disordered molecules have been omitted for clarity. b) Simplified view of an eight-connected Cu_3-cluster subunit. c) Perspective view of the network of **1** simplified according from part (b). d) The body-centered cubic lattice net (bcu net).

tetrazole nitrogen atoms, two pyridyl nitrogen atoms, one bridging chlorine atom, and one coordinated water molecule. The two nonequivalent Cu atoms adopt a distorted octahedral $(Cu1)Cl_2N_4$ and $(Cu2)ClN_4O$ coordination geometry, respectively. The tetrazole ligands adopt a bridging mode with a coordinating pyridyl group and a μ_2,η^2-tetrazolato bridge. The copper–copper separation, bridged by the chloride and tetrazole moiety of the 4-ptz ligands, is 3.545(1) Å. Each 4-ptz ligand coordinates through the 1,2-nitrogen atoms of the tetrazole group and the pyridyl nitrogen atom. Each Cu2 atom is weakly coordinated by a water molecule (Cu–O = 2.890(3) Å) resulting from a strong Jahn–Teller effect. Except for the coordinated water molecules, all donor atoms form reasonably strong bonds with the copper atoms. All of the Cu–N distances are in the range between 2.015(3) and 2.024(3) Å.

From further analysis of the structure of **1**, five unique features are apparent: 1) a three-dimensional neutral network with a bcu-type topology; 2) eight-connected Cu_3-cluster-building subunits; 3) large octahedron-shaped chambers; 4) potential functionalization sites on the copper atoms; 5) nanoscale open windows and a 3D intersecting channel system with an extra-framework volume of 57%.

The bcu-type topology of **1** is as follows: the motif of the Cu_3 cluster connected to eight 4-ptz linkers is represented by a box connected with eight bars (Figure 1b). The positions of the eight connecting nodes correspond to the four pyridyl nitrogen atoms and the centers of the 2,3-nitrogen atoms of the tetrazole group, which results in an eight-connected net with the Schlafli symbol $\{4^{24}6^4\}$ that resembles the topology of a bcu net (Figure 1c, d). To fulfill a bcu-type topology, our design strategies were focused on the selection of clusters with eight connectivities as secondary building units (SBUs)[12] as they provide a suitable geometry that permits the target structures to be constructed. The assembly of the eight-connected Cu_3 clusters and the tetrazolate ligand successfully forms the first example of a neutral body-centered-type metal–organic framework. Owing to limitations in geometry, the angle of the unit cell diagonals is distorted from 90° to 75.8° and the symmetry of the crystal system is lowered from cubic to orthorhombic (see Supporting Information).

As a result of the geometry of the bcu-type net, the combination of channels running parallel and perpendicular to each other gives rise to large pockets of extra-framework space. Considering the octahedron-shaped chamber (Figure 2a) in the framework, the diagonal distances of the chamber are 15.507(0) Å (Cu1–Cu1) and 19.917(3) Å (Cu1–Cu1). Such a chamber, with an inner void space, can accommodate at least two van der Waals spheres with maximum diameters of up to 7.14 Å without coming into contact with the framework. The calculated density (in the absence of guests) of compound **1** is 0.99 $g\,cm^{-3}$. Analysis with the PLATON[13] software tool

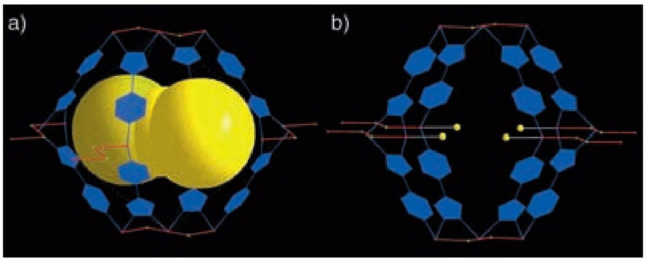

Figure 2. Views of the octahedron-shaped chamber: a) A few large van der Waals spheres with diameters of about 5.78–7.14 Å inside. b) Weakly coordinated water molecules on Cu_3 clusters act as removable shutters.

indicates that the extra-framework volume per unit cell is approximately 57%. The use of the "CAVITY" routine in PLATON indicates that the six largest voids are located at (0.3, 0, 0.625) and other symmetric sites with diameters of 7.14 Å, four other middle voids at (0, 0.5, 0) with diameters of 5.84 Å, and so on, with fourteen other cavities with diameters in the range of 5.78–5.04 Å (van der Waals surfaces considered). Furthermore, the overall shape of the void does not allow the packing of spheres larger than 7.14 Å, although several spheres with different diameters can be accommodated by the same large elongated void. The void is actually a large ellipsoid with a total volume of 1775 Å^3. These large free spaces within the framework cause the structure to be highly porous. In addition, four weakly coordinated water molecules serve to gate the chamber (Figure 2b). The O1–O1 distance is 4.63(1) Å, and the naked Cu2–Cu2 distance is 10.338(1) Å. Therefore, the chamber is a potential candidate for a microreactor with metal-containing active sites. These sites in crystalline porous materials have functionalities that could permit molecular recognition, catalysis, or gas storage.[3f]

An inspection of Figure 3 reveals that the overall array contains a 3D intersecting channel system and nanoscale open windows, with an approximate diameter of up to 10 Å. Notably, the 3D intersecting channels, which frequently occur in zeolites, are constructed by the interconnection of 1D channels from different directions. Coordination polymers with 3D intersecting channels are often unstable upon loss of solvent as a result of framework instability associated with high porosity.[1d]

Compound **1** is non-interpenetrating, despite the large pores and channels within its framework, mainly because the bcu-type net is not self-dual.[5a] The unique eight-connected Cu$_3$-cluster SBUs cause compound **1** to contain nbo-type intersecting channels, which is the dual net of body centered cubic (Figure 4). Thus, compound **1** is a perfect candidate for a highly porous network.

A thermogravimetric analysis of **1** shows that guest molecules are eliminated from the network (calcd. 71%; found 74%) when the temperature is increased from room temperature to about 220°C, after which decomposition of the framework occurs. Powder X-ray diffraction spectra recorded after heating samples of **1** at 220°C show some indication of stability upon the removal of guest molecules. However, the broadening and decrease of intensity of the peaks implies that the material appears to lose crystallinity gradually, thus producing an amorphous phase upon heating.

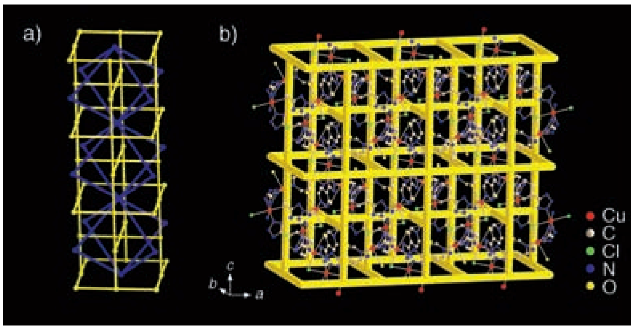

Figure 4. a) Dual relationship of the bcu net (blue) and the nbo net (yellow). b) The nbo-type intersecting channels (yellow) in the bcu-type framework of **1**.

The magnetic exchange coupling between the copper centers for compound **1** was analyzed based on the Curie–Weiss expression and a trinuclear magnetic model. The negative values of the Weiss constant and the magnetic exchange coupling constant indicate the antiferromagnetic characteristics of the copper centers. At temperatures below 20 K, the Cu^{II} ions are weakly antiferromagnetically coupled, with $J = -2.84\,\text{cm}^{-1}$ (based on the Hamiltonian $\mathcal{H} = -2J\,[(S_{Cu1}S_{Cu2}) + (S_{Cu1}S_{Cu2A})]$ and using the expression for the molar magnetic susceptibility $S = 1/2$ of a linear trinuclear system). The observed antiferromagnetic interaction is resolved into contributions arising from each Cu–ligand–Cu linkage. The propagation of the antiferromagnetic exchange interaction in the linear Cu$_3$ unit is expected to depend predominantly on 4-ptz bridges. It may be processed through the $d_{x^2-y^2}$ orbitals on the Cu^{II} ions that interact with the σ orbitals of the nitrogen atoms of the tetrazolate ligands, which are all situated in the equatorial plane and contain Cu–N–N–Cu torsion angles of −3.41°. Crystal engineering of the substituent on the 4-pyridyl moiety could increase the Cu–N–N–Cu torsion angles in the tricopper center and thereby change the exchange coupling from antiferromagnetic to ferromagnetic.[14]

In conclusion, compound **1** is the first porous, neutral, bcu-type structure that contains an eight-connected polynuclear cluster unit and a tetrazole-based ligand. The synthesis of bcu-type frameworks with expanded analogous ligands offers the

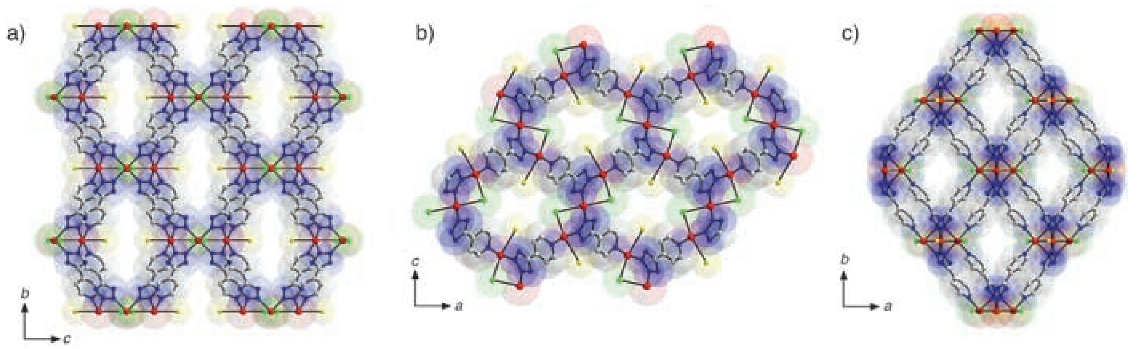

Figure 3. Superimposed space-filling representation of **1** showing channel openings along the *a*, *b*, and *c* axes. Hydrogen atoms have been omitted for clarity (red = Cu, blue = N, green = Cl, yellow = O).

potential for pore-size expansion in their nbo-type intersecting channel systems. The preparation of a rare framework from 4-ptz and Cu_3 clusters confirms the potential for synthesizing new structures of functional materials using tetrazole derivatives as ligands. Further research is currently in progress.

Experimental Section

1: A solution of $CuCl_2 \cdot 2H_2O$ (0.10 mmol) and 4-H-ptz (0.13 mmol) in DMF (8 mL) was stirred for 15 min. It was then allowed to stand at room temperature for several days, whereupon deep-blue, rhombus-like crystals were formed in 61% yield (based on 4-H-ptz). The solid product was washed with deionized water and ethanol, and dried in air. Elemental analysis (%) calcd for $C_{33}H_{51}Cl_2Cu_3N_{23}O_{10}$: C 33.27, H 4.31, N 27.04; found: C 33.59, H 4.51, N 25.66. The formula $[Cu_3Cl_2(4\text{-ptz})_4(H_2O)_2]\cdot 3DMF\cdot 5H_2O$ was assigned by elemental microanalysis, thermogravimetric analysis, and single-crystal X-ray diffraction studies.[15]

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[15] A suitable single crystal of **1** with dimensions $0.12\times0.10\times0.08\ \mathrm{mm}^3$ was mounted on the tip of a glass fiber and placed onto the goniometer head for indexing and intensity data collection using a Bruker Smart CCD diffractometer ($\mathrm{Mo}_{K\alpha}=0.71073$ Å). The raw frame data for **1** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects with the Denzo program. An empirical absorption correction was applied by using the Multiscan method. The structure of **1** was solved by direct methods and refined against F^2 by the full-matrix least-squares technique, using the WINGX, PLATON, and SHELX software packages. Except for the guest molecules, non-hydrogen atoms were refined with anisotropic displacement parameters, and the hydrogen atoms of aromatic rings were calculated and refined as riding modes. The water and DMF guest molecules that show positional disorder could not be fixed in the structure model. During the final stages of refinement, several Q peaks were found, which probably correspond to highly disordered solvent molecules and were fixed as oxygen atoms and refined with isotropic displacement parameters. The hydrogen atoms associated with the coordinated water molecules and disordered guest molecules could not be located from difference Fourier maps, and no attempt was made to place them. However, they are included in the empirical formula. Further details of experimental and magnetic studies are given in the Supporting Information. Crystal data for **1**: $C_{33}H_{51}Cl_2Cu_3N_{23}O_{10}$ $\{[Cu_3Cl_2(4\text{-}ptz)_4(H_2O)_2]\cdot(3\,DMF\cdot5\,H_2O)\}$, $M_r=1191.45$, orthorhombic, *Pnmn*, $a=12.3305(2)$, $b=15.5069(3)$, $c=15.6412(3)$ Å, $V=2990.72(9)$ Å^3, $Z=2$, $\rho_{\mathrm{calcd}}=1.366\ \mathrm{g\,cm^{-3}}$, $\mu=1.180\ \mathrm{mm^{-1}}$, $\lambda(\mathrm{Mo}_{K\alpha})=0.71073$ Å, $F(000)=1780$, $T=293(2)$ K, A total of 19921 reflections were collected in the range $\theta=4.12$–$27.49°$, of which 3538 were unique ($R_{\mathrm{int}}=0.0512$). Final R indices: $R_1=0.0399$, $wR_2=0.1716$ for 2818 reflections [$I>2\sigma(I)$]; $R_1=0.0725$, $wR_2=0.1830$ for 3538 independent reflections (all data) and 147 parameters, GOF = 1.060. CCDC-256347 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.