

Two Novel Nanoporous Supramolecular Architectures Based on Copper(I) Coordination Polymers with Uniform (8, 3) and (8²10) Nets: In Situ Formation of Tetrazolate Ligands

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Received January 15, 2005

The hydro/solvothermal reactions of Cu(I)/Cu(II) salt, NaN₃, and acetonitrile in water or methanol yield two noninterpenetrated supramolecular networks containing 1D hexagonal and square nanochannels, {[Cu(Mtta)]·0.17H₂O}_n (**1**) and its pseudopolymorph [Cu(Mtta)]_n (**2**) (Mtta = 5-methyl tetrazolate), involving ligand in-situ formation by cycloaddition of nitriles and azides. The copper(I) centers in both complexes are all bridged by Mtta ligands, forming the different shapes of the cavity. **1** exhibits an unprecedented uniform (8, 3) topological metal network, whereas **2** is a 3-connected (8²10) metal net.

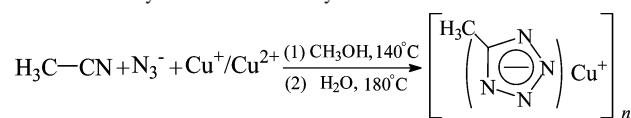
Network topologies promise great advances in the design and depiction of crystal structures, especially for the design of new potentially multifunctional materials with useful structural properties, such as porosity, gas storage, and ion exchange, or additional physical properties such as magnetism and nonlinear optical applications.¹ Much attention has been focused on the investigation of intriguing, often complicated, architectures and topologies in coordination chemistry.² Wells elucidated many topologies in his classic monographs on networks.³ He described a particularly fundamental class of networks called uniform nets, represented using the (*n*, *p*) notation. Although a variety of intriguing 3D 3-connected nets were predicted by Wells decades ago and a number of these special uniform networks were displayed by real crystal structures, including (6, 3), (12, 3), and various (10, 3),⁴ 3D 3-connected uniform (8, 3) nets were rarely documented.⁵

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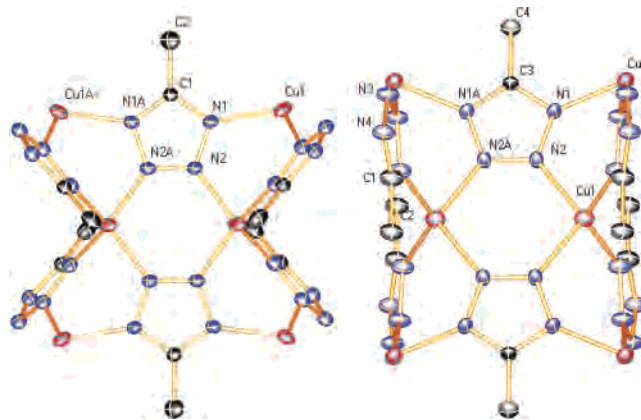
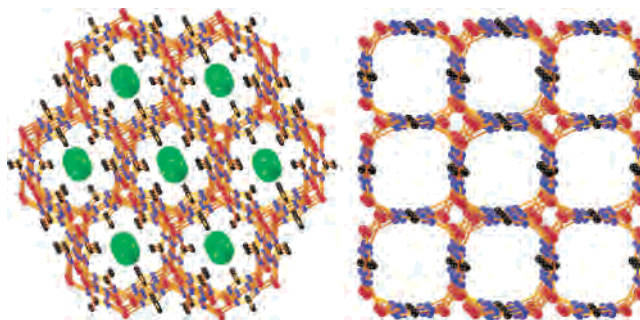
On the other hand, particular attention has recently been directed toward the use of polydentate aromatic nitrogen heterocycles ligands with five-membered rings (azoles). Among them, imidazoles and triazoles have been extensively used for their ability to construct open-framework networks with a wide diversity of topologies and nanoporous shapes.⁶ Tetrazoles exhibit a strong networking ability. However, they usually act as mono- or bidentate ligands in most of the reported adducts.⁷ Substituted tetrazole derivatives have also been studied for their potential properties as explosives or detonators.⁸ Recently, Sharpless et al. reported a safe and convenient method for the preparation of a variety of 5-substituted 1*H*-tetrazoles by the water-catalyzed addition of azide to nitriles in zinc salts as Lewis acid.⁹ Xiong et al. trapped the “Zn-intermediated” product by performing the synthesis under hydrothermal conditions.¹⁰ Herein, we report two supramolecular networks having different kinds of 1D nanochannels, {[Cu(Mtta)]·0.17H₂O}_n (**1**) and its pseudopolymorph [Cu(Mtta)]_n (**2**) (Mtta = 5-methyl tetrazolate) by Cu(I/II)-catalyzed Sharpless cycloaddition reactions of nitriles and azides (Scheme 1). Complex **1** is described as an unprecedented uniform (8, 3) topology metal network, whereas complex **2** is a 3D 3-connected (8²10) metal net.

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Scheme 1. Hydro/Solvothermal Synthesis of **1** and **2**

To construct unusual neural networks, in which tetrazoles act as a tetradentate ligand with a ligand-to-metal ratio of 1:1, a rational design is to use monovalent metals instead of divalent ones. In addition, it was previously reported that Cu(II) ions can be easily reduced into Cu(I) under basic hydrothermal conditions.¹¹ Based on this strategy, the reactions of equimolar NaN₃ and Cu(NO₃)₂ in acetonitrile/methanol (v/v 1:1) was carried out and afforded pale-green crystals, {[Cu(Mtta)]·0.17H₂O}_n (**1**) in a reasonable yield. However, the corresponding reaction in acetonitrile/water gave its pseudopolymorph [Cu(Mtta)]_n (**2**) in a very low yield. The polymers can also be attained by substituting CuSCN for Cu(NO₃)₂·3H₂O (Scheme 1). The relatively low yield of the two complexes partly results from N₂ formation due to the oxidation of azide by Cu(II), as indicated by the bubbles formed within the resulting mixture. The absence of a signal for the cyano group in the IR spectra of the polymers signifies a [2 + 3] cycloaddition between the cyano group and the azide anion. **1** and **2** are air-stable and insoluble in water and common organic solvents. However, they can be dissolved in concentrated aqueous HCl, indicating that the tetrazole ligands can be liberated by acidification.

X-ray single-crystal analyses of **1** and **2**¹² confirm the formation of 5-methyl tetrazolate and show that the new ligand acts as a μ₄-bridging ligand in each of the products. Rare examples with the μ₄-η¹:η¹:η¹:η¹ coordination mode

**Figure 1.** Fragment of the framework in **1** (left) and **2** (right).**Figure 2.** Perspective view of the network structure of **1** (left) and **2** (right) viewed along the direction of 1D channels.

have been observed in tetrazolate derivatives.¹³ The structures of both complexes consist of a 3D neutral networks based on tetraconnected copper centers that are joined through μ₄-tetrazolate anions. The copper atoms bound to the tetradentate Mtta ligands show significant out-of-plane displacements with respect to the “best plane” of the heterocycle (in the ranges of −0.17/+0.81 Å for **1** and +0.35/+0.80 Å for **2**). The two adjacent copper atoms are co-bridged only by a pair of tetrazolate ligands using neighboring N atoms (N1 and N2, N2 and N2A, N2A and N1A) (the dihedral angles of the two tetrazolate rings are 98.0° and 0° in **1** and 99.2° and 0° in **2**), forming a Cu₂CuN₂ six-membered ring (Figure 1).

Interestingly, the different dihedral angles and distorted direction of tetrazolate rings in the two complexes result in two different nanoporous structures. Complex **1** contains a large hexagonal 1D channel running along the *c* axis (Figure 2). The channels are mainly occupied by guest water molecules (marked in green). Approximately 13.0% of the crystal volume is occupied by free water molecules with a volume of ca. 273.1 Å³ in each unit cell.¹⁴ Methyl groups in the Mtta ligand point toward the center of the channels and partially fill the network cavities. In contrast, complex **2** contains a square 1D channel running along the *b* axis, with a void volume of ca. 101.3 Å³, 5.7% of each unit cell (Figure 2).

The 3D frameworks of complex **1** and **2** can be rationalized to be an unprecedented four-connected binodal (4³6²8)

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- (12) Crystal data for **1**: C₂H_{3.33}Cu₄N₄P_{0.17}, hexagonal, space group *R* $\bar{3}m$, *M*_r = 149.63, *a* = 16.0289(17) Å, *b* = 16.0289(17) Å, *c* = 9.4148(10) Å, α = 90.00°, γ = 120.00°, *V* = 2094.8(3) Å³, *Z* = 18, ρ_{calcd} = 2.135 g cm⁻³, μ = 4.545 mm⁻¹, *F*(000) = 1326, *T* = 298(2) K; *R*1 = 0.0363, *wR*2 = 0.0389, *GOF* = 1.193 for all data. Crystal data for **2**: C₂H₃CuN₄, orthorhombic, space group *Cccm*, *M*_r = 146.62, *a* = 11.3787(8) Å, *b* = 13.5544(9) Å, *c* = 11.5748(8) Å, α = 90.00°, β = 90.00°, γ = 90.00°, *V* = 1785.2(2) Å³, *Z* = 16, ρ_{calcd} = 2.182 g cm⁻³, μ = 4.735 mm⁻¹, *F*(000) = 1152, *T* = 296(2) K; *R*1 = 0.0361, *wR*2 = 0.0895, *GOF* = 1.114 for all data. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo *K*α, γ = 0.71073 Å). The structures were solved with direct methods and refined with full-matrix least-squares technique using SHELXTL (Sheldrick, G. M. *SHELXTL*, version 6.10; Bruker Analytical X-ray Systems: Madison, WI, 2001). Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically (C–H = 0.960 Å). The crystallographic calculations were conducted using the SHELXL-97 programs.

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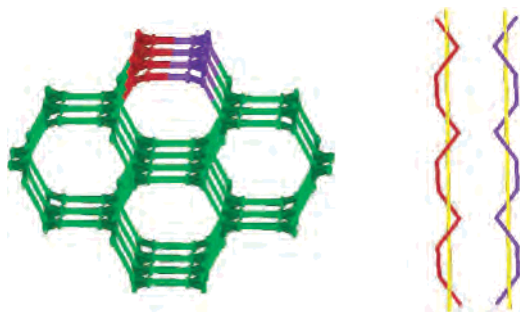


Figure 3. 3D 3-connected uniform (8, 3) topology network in **1** (left) viewed along the *c* axis containing 3_1 helices with opposite handedness (right).

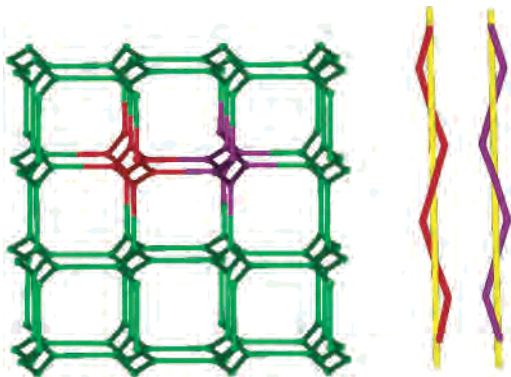


Figure 4. 3D 3-connected ($8^2 10$) topology network in **2** (left) viewed along the *b* axis containing 4_1 helices with opposite handedness (right).

($4^3 6^2 8$) topological net when the Mttal ligands are treated as a distorted square-planar node and Cu(I) as a tetrahedral node (see Figure S1 in the Supporting Information). To emphasize the Cu atom net bridged by Mttal ligands, each Cu atom can be regarded as a 3-connected node. The main reason is that each Cu(I) is bridged to the nearest neighbors by a pair of “double-bridge” ligands and each Cu(I) is surrounded by only three nearest-neighbor coppers [Cu...Cu separations of 3.484(2)–3.592(2) Å for **1** and 3.655(2)–3.883(2) Å for **2**; Cu...Cu...Cu angles of 112.1–135.8° for **1** and 104.3–151.4° for **2**; Figure 1]. By defining each four-coordinate Cu atom as a triconnected node, the 3D network in complex **1** can be rationalized to be an unprecedented, uniform 3-connected topological net. This net has short and long Schläfli vertical symbol of 8^3 and $8_2 8_1 8_1$ that contain 3-fold helices and pseudo-5-fold helices (Figure 3 and Figure S2). Each 3-fold helix has an opposite handedness relative to the adjacent three 3-fold helix. This is clearly different from other reported network topologies (8, 3)-*c*, such as Na[Ti₂(PS₄)₃],¹⁵ in which the “long” Schläfli symbol for this net is $8_2 8_2 8_2$ (Figure S3). Nevertheless, the 3D framework in complex **2** shows a different 3-connected topological structure ($8^2 10$), analogous to that of $\{[\text{Ph}_3\text{PCH}_2\text{Ph}][\text{Cd}(\text{tp})\cdot\text{Cl}]\cdot 2\text{H}_2\text{O}\}_n$ (tp = terephthalate),¹⁶ which contains 4-fold helices with opposite handedness (Figures 4 and S4).

An interesting phenomenon is that complex **2** without guest water molecules is produced from a hydrothermal reaction, whereas the complex **1** with guest water molecules comes from a solvothermal reaction. This might be due to the structural differences between the two complexes. The hexagonal channel in complex **1** is large enough to accommodate one water molecule, whereas the square 1D channel is too small to accept guest molecules, although a mass of water molecules exist in the reaction system.

To verify whether the framework of complex **1** is maintained after the removal of the guest water molecules, TGA and XRPD were used to investigate framework stability. The TGA results (Figure S5) reveal that there is no obvious weight loss in the range of 100–300 °C, which indicates that the guest water molecules in complex **1** are easily lost during the predrying procedure. The decomposition or sublimation of the complex starts at ~320 °C, and there is a weight loss of nearly 100% from 320 to 413 °C, implying that the complex entirely sublimates. The XRPD pattern (Figure S6c) of the desolvated solid prepared by being heated at 150 °C under vacuum for 20 h is almost identical to the simulated pattern (Figure S6a) and the pattern (Figure S6b) of the fresh sample after predrying. These indicate that the porous structure is robust even after the removal of the guest molecules. Unfortunately, for complex **2**, TGA and XRPD could not be conducted because of the very low yield and the difficulty of obtaining the pure form.

In summary, this work further supplements Sharpless’ cycloaddition reactions of nitriles and azides by using Cu(I/II) in place of Zn(II) as the catalyst to generate 5-substituted 1H-tetrazolate and obtained two structurally novel “Cu(I)-intermediated” products. Tetrazolates provide all of the available donor atoms to produce robust interesting polymeric networks, confirming the potentially rich coordination chemistry of these ligands. The (8, 3) topology of complex **1** is unprecedented, with an intriguing framework for the construction of other interesting coordination networks. Further systematic investigations will focus on the influence of hydro(solvo)thermal reaction condition on the diversity of M–Mttal networks and aim at increasing the porosity (for example, octahedral channel) of these frameworks by structural modifications of 5-substituting radical of the tetrazole.

Acknowledgment. The authors gratefully acknowledge the financial support by the National Natural Science Foundation of China (Nos. 29901004 and 20271031) and the Natural Science Foundation of Guangdong Province of China (No. 021240). Acknowledgment is also made to Professor Xiao-Ming Chen of Sun Yat-Sen University for the XRPD measurements.

Supporting Information Available: Syntheses, figures illustrating topological networks for **1** and **2**, and TGA and XRPD results for **1**. Crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC0500630

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