

Copper Triazolate Networks

Two Unprecedented 3-Connected Three-Dimensional Networks of Copper(I) Triazolates: In Situ Formation of Ligands by Cycloaddition of Nitriles and Ammonia**

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*Dedicated to Professor Hai-fu Fan
on the occasion of his 70th birthday*

Networked coordination polymers are of great current interest for potential applications as materials and because of their intriguing variety of architectures and new topologies.^[1–3] It was suggested that, among numerous topological nets, the most important and plausible targets for designed synthesis are those with “simple, high-symmetry” structures.^[4] However, only a very limited number of types of simple three-dimensional (3D) 3-connected^[2] and 4-connected nets based solely on square-planar nodes, such as the cubic NbO ($6^4 8^2$),^[3a,b] tetragonal CdSO₄ ($6^5 8$),^[3c] “dense net” ($7^5 9$),^[3d] and 4.4.8₄.8₄.8₈.8₈^[3e] nets have been reported so far, in contrast to the widely established 2D 3-connected honeycomb or brickwall (6^3) and 4-connected square grids (4^4).^[1] Meanwhile, some 3-connected nets can be described as augmented 4-connected nets by substituting four adjacent 3-connected nodes for 4-connected nodes,^[4,5] for example, 4.8^2 for 4^4 , 4.12^2 for NbO ($6^4 8^2$), and 4.14^2 for diamond (6^6).^[2c]

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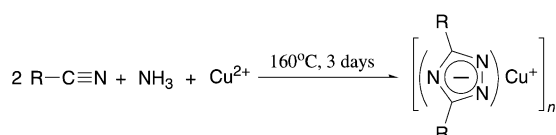
[**] This work was supported by NSFC (No. 20131020) and Ministry of Education of China via a Doctorate Program Fund (No. 20020558024) and a key project grant (No. 01134).



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On the other hand, novel coordination architectures with ligands generated in situ, (especially those that are inaccessible by direct preparation) are of great interest in coordination chemistry and organic chemistry for discovery of new organic reactions and understanding their mechanisms.^[6–10] Nitriles are of major importance in the syntheses of many products by addition to the nitrile carbon atom, and such processes usually require activation of RCN, for example, by ligation of a metal. Some compounds not usually accessible by pure organic chemistry have been obtained by metal-mediated reactions such as cycloadditions of tetrazoles and oxadiazolines.^[6–9]

In our continuing studies on hydrothermal ligand reactivity and new coordination architectures,^[10] we established the hydrolysis of 1,10-phenanthroline (phen) to 1*H*-1,10-phenanthroline-2-one in various copper complexes under hydrothermal conditions.^[10a,b] We then carried out an analogous reaction using copper(II) nitrate, phen, ammonia, and acetonitrile, which yielded a small quantity of pale-yellow crystals of [Cu(mtz)]_n (Hmtz = 3,5-dimethyl-1,2,4-triazole, **1**) and an unanalyzed mixture. As phen was not present in the product, we then used Cu(OH)₂ (or Cu₂(OH)₂CO₃), ammonia, and acetonitrile or butyronitrile to perform the reaction (Scheme 1) and obtained solid **1** or [Cu(ptz)]_n (**2**) (Hptz = 3,5-



Scheme 1. Hydrothermal synthesis of **1** (R = Me) and **2** (R = *n*Pr).

dipropyl-1,2,4-triazole), respectively, in moderate yield (up to 40%). Similar reactions performed with nitriles bearing pyridyl and phenyl groups yielded copper(II) complexes of 3,5-dipyridyl- and 3,5-diphenyltriazolate.^[11] The crystals of these compounds are stable toward air, and are insoluble in water and common organic solvents. However, their ready dissolution in aqueous HCl indicates that the triazole ligands can be liberated by acidification.

Based on the above observations, we suggest that the triazolates were derived from coupling of the nitriles and ammonia. The presence of Cu^I ions in the products indicates that Cu^{II} ions may act as an oxidant, in a similar manner as in our previous in situ hydrothermal reactions,^[10] to assist the elimination of protons in the cycloaddition to give the final ligands. In contrast to the metal-mediated reductive coupling of nitriles to generate diimino-, enediimido-, or bis(imino)-amines, and the addition of two nitriles with another species to produce metallocycles, all of which have already been reported,^[6,9] our one-pot, copper-mediated, hydrothermal reactions of nitriles and ammonia represent a novel, non-hydrazine synthetic route to 3,5-disubstituted 1,2,4-triazoles. 1,2,4-Triazole derivatives are of particular interest for their multifarious uses in agriculture, medicine, and industry. Continuous efforts have focused on the search for more efficient, simple, and green synthetic procedures for this

useful class of heterocycles, although many methods have been known for decades. However, most 1,2,4-triazoles are still prepared by multistep procedures, which usually involve the use of hydrazine derivatives as starting materials or conversion of other ring systems.^[12]

1,2,4-Triazoles are also unique ligands in coordination chemistry, especially in the synthesis of magnetic metal clusters, since they exhibit the coordination modes of both imidazoles and pyrazoles.^[13] However, no crystal structure of a binary metal triazolate has been reported to date. Crystallographic studies on **1** and **2**^[14] revealed that each triazolate binds in the μ₃-tridentate mode, and each Cu^I ion is coordinated in a trigonal-planar fashion (Cu⋯Cu 3.499(1) Å, Cu–N 1.963(1)–2.016(1) Å, and N–Cu–N 111.9(1)–134.3(1)° for **1**; Cu⋯Cu 3.422(1) Å, Cu–N 1.963(2)–1.973(3) Å, N–Cu–N 116.7(1)–121.6(1)° for **2**; see Supporting Information), and in each case a novel 3D 3-connected net results. A variety of intriguing 3D 3-connected nets were predicted by Wells decades ago,^[5] but they have rarely been documented in coordination polymers.^[2]

The framework of **1** consists of 1D helices in which the Cu^I ions are bridged by the triazolates in the imidazolate mode (Figure 1b). Each helical chain is further connected to four adjacent antiparallel chains through interchain Cu–N coordination bonds into a 3D net. The resulting 3-connected net (Figure 1a) for **1** can be symbolized as 4.8.16, which is unprecedented. This net is closely related to a series of other 3-connected nets such as 10³-a, 10³-d, 10³-f, 8²10-a, 8²10-b, and 4.14², since they all can be projected as a planar 4.8² net, but differs in the arrangement and type of helices.^[5] The network in **1** contains large 3D channels, which are fully occupied by an identical, translational net (see Supporting Information). A double-helical fragment (Figure 1c) of the entire structure may help to understand the interpenetration pattern in **1**. Note that the 4.8.16 net can be simplified as a 4.4.8₄.8₄.8₈ net based on 4-connected square-planar nodes (see Supporting Information). In other words, the topology of **1** can also be rationalized as a 4-connected net by considering dimeric {Cu₂(mtz)₂} subunits as 4-connected nodes. Of equal interest is that the 3-connected topological net in **2** exhibits a 4.12² net (Figure 2b) predicted by Wells,^[5] which had also not yet been documented in coordination networks. The 4.12² net can also be simplified to an NbO net (Figure 2c) if each {Cu₂(ptz)₂} subunit (Figure 2a) is considered as 4-connected node,^[4] an example distinct from the rarely observed, true 4-connected NbO nets.^[3a,b] Similar to other NbO nets, the network of **2** also contains channels, which are mainly occupied by the disordered propyl groups.

Very few 3D networks are based solely on square-planar nodes, since 2D square grids (4⁴) are favored when square-planar building blocks self-assemble into extended structures.^[1] The question arises why the similar dimeric building blocks in **1** and **2** extend not into a common 2D 4⁴ net but into 3D 4.4.8₄.8₄.8₈ and NbO nets. Examination of the related nets reveals differences in the dihedral angles between adjacent nodes in the networks based solely on square-planar nodes. These angles are all parallel for 4⁴, all perpendicular for NbO, all acute for 4.4.8₄.8₄.8₈, two parallel and two perpendicular for CdSO₄, and two parallel

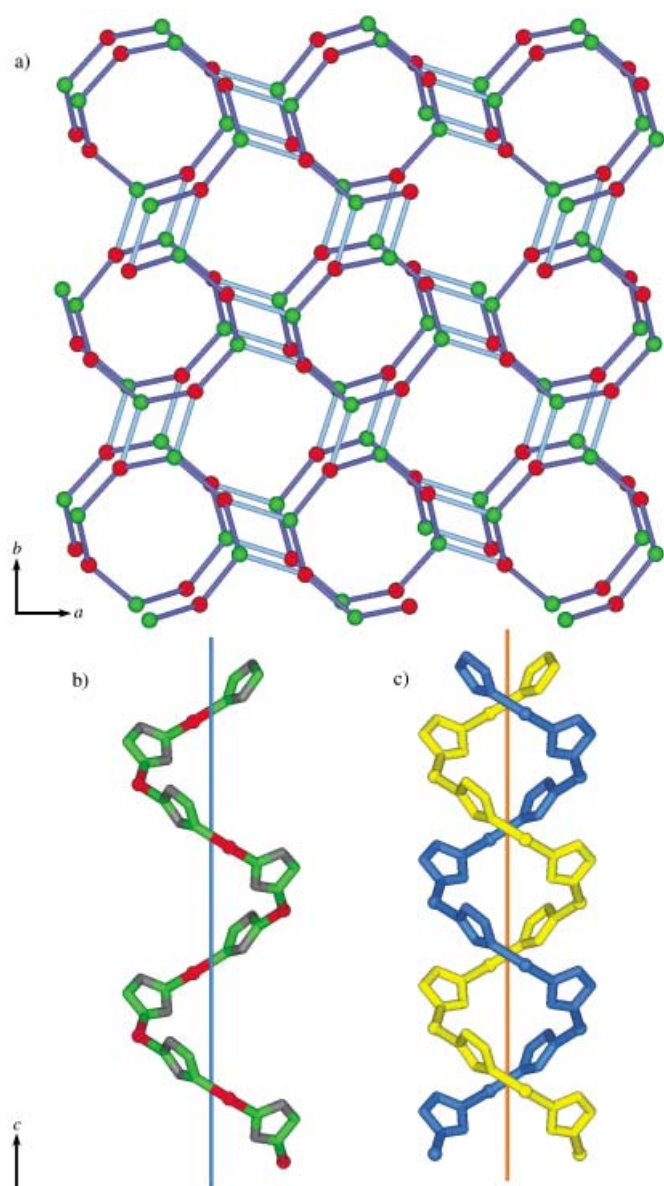


Figure 1. Compound 1: a) A single 4.8.16 net projected along the *c* axis, b) a single left-handed helical fragment, and c) a double helical fragment. For clarity, the methyl groups are omitted, and the triazolate groups are represented by green spheres in a).

and two acute for USF-1 networks.^[3g] These facts indicate that the topology of a network based solely on square-planar nodes depends strongly on the orientation of adjacent nodes; therefore, a specific network based solely on square-planar nodes can be assembled by control of the dihedral angles. A few structures have been successfully synthesized by directing rigid square-planar secondary building units (SBUs) with ligands of specific geometry.^[4c] In contrast, the ligands in both **1** and **2** are very similar except for the substituents, and the dihedral angles are about 30° in the case of methyl groups and 90° in the case of the larger propyl groups, respectively. Consequently, we may suggest that steric repulsion of the substituents of these triazolates may enforce the dihedral angles between adjacent square-planar nodes. Since all such

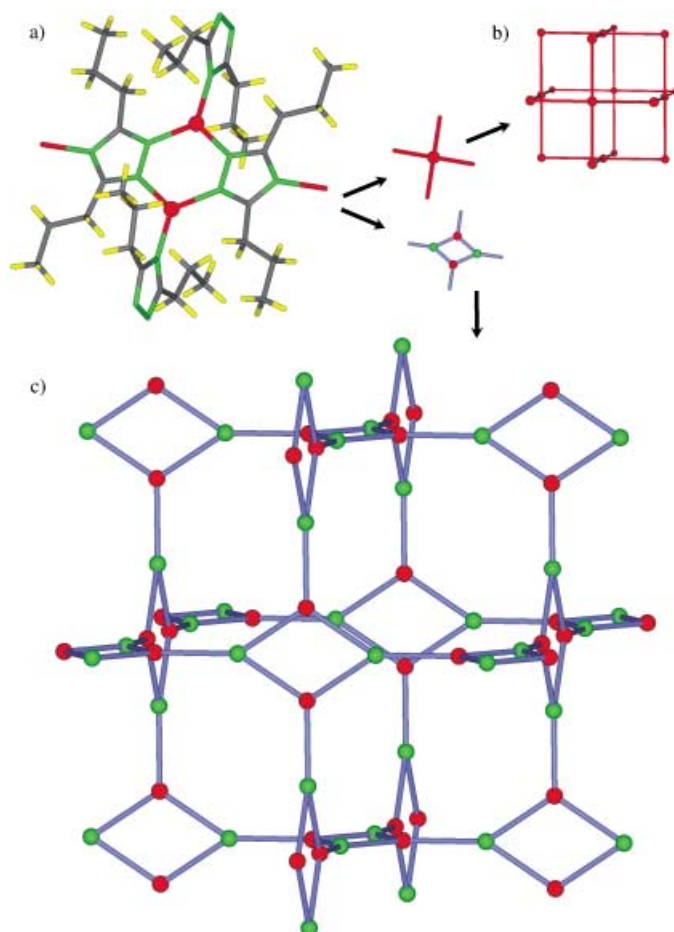


Figure 2. Compound 2: a) Definitions of the 3- and 4-connected nodes, b) the 4-connected NbO net, and c) the 3-connected 4.12² net.

4-connected nets can be augmented to related 3-connected nets, this work also illustrates an alternative strategy of using trigonal-planar building blocks to build such intriguing networks, rather than the usual methods involving square-planar units.

In summary, we have described two unprecedented copper(I) triazolate coordination polymers formed by unprecedented copper-mediated cycloadditions of nitriles and ammonia. These compounds form 3-connected networks with novel topologies that have implications for understanding the relationship between related nets, and the one-pot reaction may serve as a new synthetic approach for the synthesis of triazole derivatives.

Experimental Section

Synthesis of 1: a) Hydrothermal treatment of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (0.221 g, 1.0 mmol), aqueous ammonia (25 %, 3.0 mL), and butyronitrile (5.0 mL) at 160 °C for 3 days yielded pale-yellow needlelike crystals in 40 % yield based on $\text{Cu}_2(\text{OH})_2\text{CO}_3$. b) $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (0.221 g, 1.0 mmol) was replaced by $\text{Cu}(\text{OH})_2$ (0.098 g, 1.0 mmol), and the yield was 20 % based on $\text{Cu}(\text{OH})_2$.

Synthesis of 2: a) Hydrothermal treatment of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (0.221 g, 1.0 mmol), aqueous ammonia (25 %, 2.0 mL), and acetonitrile (2.0 mL) at 160 °C for 3 days yielded pale-yellow blocklike

crystals in 25% yield based on $\text{Cu}_2(\text{OH})_2\text{CO}_3$. b) $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (0.221 g, 1.0 mmol) was replaced by $\text{Cu}(\text{OH})_2$ (0.098 g, 1.0 mmol), and the yield was 10% based on $\text{Cu}(\text{OH})_2$.

Elemental analysis (%) calcd for **1** ($\text{C}_4\text{H}_6\text{CuN}_3$): C 30.09, H 3.79, N 26.32; Found: C 30.05, H 3.83, N 26.28. Calcd for **2** ($\text{C}_8\text{H}_{14}\text{CuN}_3$): C 44.53, H 6.54, N 19.48; Found: C 44.60, H 6.50, N 19.39. IR (KBr): **1**: $\tilde{\nu}$ = 3425m, 2960s, 2919s, 1487vs, 1415vs, 1366vs, 1332vs, 1090m, 1040m, 974m, 768s, 693m, 624 cm^{-1} m; **2**: $\tilde{\nu}$ = 3440m, 2959vs, 2930vs, 2873vs, 1496vs, 1461vs, 1354vs, 1274s, 1224s, 1079s, 901m, 825m, 746 cm^{-1} m.

Received: August 12, 2003 [Z52627]

Keywords: copper · cycloaddition · hydrothermal synthesis · N ligands · triazoles

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- [14] Crystal data for **1**: tetragonal, $P4_2/n$ (no. 86), $a = 13.470(2)$, $c = 6.142(2)$ Å, $V = 1114.6(5)$ Å³, $Z = 8$, $\rho_{\text{calcd}} = 1.903$ g cm⁻³, $F(000) = 640$, $\mu(\text{MoK}\alpha) = 3.796$ mm⁻¹, 7811 reflections measured, 1593 unique reflections ($R_{\text{int}} = 0.015$), final $R_1 = 0.0268$, $wR_2 = 0.0646$, $S = 1.082$ for all data; **2**: cubic, $Im\bar{3}$ (no. 204), $a = 14.923(2)$ Å, $V = 3323.2(8)$ Å³, $Z = 12$, $\rho_{\text{calcd}} = 1.294$ g cm⁻³, $F(000) = 1344$, $\mu(\text{MoK}\alpha) = 1.928$ mm⁻¹, 10034 reflections measured, 743 unique reflections ($R_{\text{int}} = 0.020$), final $R_1 = 0.0513$, $wR_2 = 0.1516$, $S = 1.154$ for all data. Data for **1** and **2** were collected with MoK α radiation ($\lambda = 0.71073$ Å) at 293 K on a Bruker SMART Apex CCD diffractometer by using frames of 0.3° oscillation ($4.3 \leq 2\theta \leq 60^\circ$ for **1** and $3.9 \leq 2\theta \leq 55.9^\circ$ for **2**). The structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares on F^2 using the SHELXTL program.^[15] CCDC-217202 and -217203 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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