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Communication

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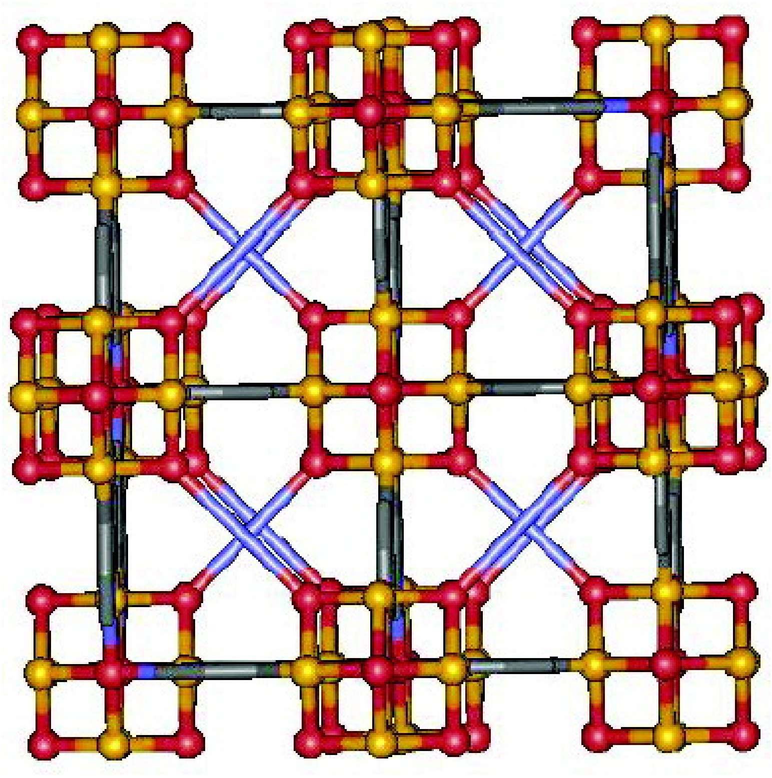

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A Twelve-Connected Cu_6S_4 Cluster-Based Coordination Polymer

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Metal−organic frameworks are of great current interest because of the possibilities for various applications and intriguing topological terms.[1] The classification of structures by Wells lays the foundation for the general understanding of inorganic solids as well as metal−organic frameworks.[2] Of the structural types commonly found in metal−organic frameworks, the majority are based on three-, four-, and six-connected topologies in which d- and f-block ions act as nodes.[1] Examples of five-, seven-, and eight-connected metal−organic coordination frameworks are extremely rare.[3,4] It appears that for the majority of metal−organic framework structures, there are well-known prototypes in metallic or binary inorganic solids. The following topological metal−organic frameworks have been reported: diamond, α-Po, boracite, $CdSO_4$, CaB_6, feldspar, NbO, perovskite, Pt_3O_4, PtS, pyrite, quartz, rutile, sodalite, $SrSi_2$, tungsten bronze, CsCl, and fluorite.[5] Up to now, a connectivity larger than eight has not been observed in the metal−organic frameworks, probably due to the limited coordination numbers of metal centers and steric hindrance of the organic ligands.[4] On the other hand, many important metals, such as copper, silver, and gold, have face-centered cubic (fcc) lattices with connectivity as large as twelve. Recently, metal clusters with substituted single metal atoms have been used as nodes for high-connected metal−organic frameworks.[5] Compared with d- or f-block ions, metal-cluster-based nodes generally have larger sizes and more coordination sites but smaller steric hindrance when coordinated by organic ligands.

We have been interested in developing Cu(I) and Cu(I,II) complexes under hydrothermal conditions and established that Cu(II) ions not only can be reduced to Cu(I) in the presence of N-containing ligands but also they often play a catalytic role in hydro(solvo)thermal ligand reactions.[6] On the basis of our effort to develop copper complexes, we synthesized a novel complex $[Cu_3(pdt)_2(CN)]$ (**1**) (pdt = 4-pyridinethiolate) which has a three-dimensional twelve-connected coordination framework with Cu_6S_4 clusters as nodes.

The hydrothermal reaction of $Cu(MeCO_2)_2$, (4-pyridylthio)acetic acid, NH_4SCN, and NaOH in a molar ratio of 2:1:0.8:1.2:1300 at 170 °C for 120 h afforded black block crystals of **1** in 35% yield, based on NH_4SCN. The product was characterized by X-ray single-crystal structural analysis, the IR spectrum, and the elemental analysis.[7] The infrared spectrum of **1** shows a medium peak at 2129 cm^{-1}, attributed to the C≡N vibration of the cyanide groups, and a series of peaks at 1684, 1449, 1614, and 1402 cm^{-1} due to the pdt groups. The TGA trace of **1** (Figure S1) shows that **1** is thermally stable up to 205 °C in air. A slight weight increase and subsequent mass loss (4.8%) in the range of 210−350 °C indicates addition of oxygen and removal of cyanide. The decomposition of the pdt groups starts at 430 °C and is not finished up to 700 °C.

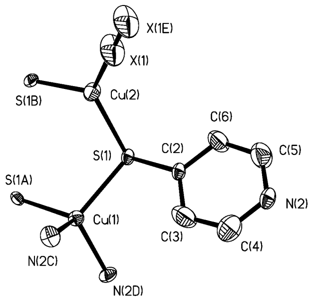

Figure 1. View of the coordination environment of copper in **1**. Selected bond lengths (Å) and angles (°): Cu(1)−N(2c) 2.056(5); Cu(1)−S(1) 2.3053(15); Cu(2)−X(1) 1.876(6); Cu(2)−S(1) 2.2434(9); X(1)−X(1e) 1.161(13); N(2c)−Cu(1)−N(2d) 107.5(3); N(2c)−Cu(1)−S(1) 110.08(8); S(1)−Cu(1)−S(1a) 108.98(8); X(1)−Cu(2)−S(1) 126.22(4); X(1)−Cu(2)−S(1b) 126.22(4); S(1)−Cu(2)−S(1b) 107.55(7); Cu(2)−S(1)−Cu(1) 108.56(4). Symmetry codes: (a) $-x + 1, -y + 1, z$; (b) $-x + 1, y, -z$; (c) $x + {}^1/_2, -y + {}^1/_2, -z + {}^1/_2$; (d) $-x + {}^1/_2, y + {}^1/_2, -z + {}^1/_2$; (e) $x, -y, z$.

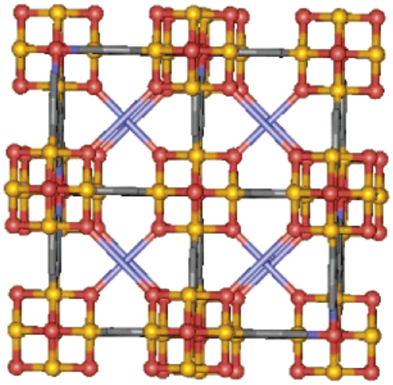

Figure 2. View of the three-dimensional twelve-connected framework in **1**.

The single-crystal X-ray structural analysis[8] reveals that **1** has a three-dimensional twelve-connected face-centered cubic topological framework, and the starting materials, (4-pyridylthio)acetic acid and SCN^- anion, have been converted into pdt and cyanide by the cleavage of S−C bonds. Compound **1** crystallizes in the tetragonal noncentrosymmetrical space group $I\bar{4}2m$, and there are two crystallographically independent Cu(I) sites, one cyanide and one pdt (Figure 1). The indistinguishable C and N atoms of cyanide occupy the same sites and are labeled as X(1). The X(1)−X(1e) distance of 1.160(12) Å is typical for the cyanide group.[9] The Cu(1) site has a tetrahedral geometry and is coordinated to two S and two N atoms from four pdt ligands; the Cu(2) site has a trigonal coordination geometry, coordinated to one X atom from the cyanide group and two S atoms from pdt ligands. Compound **1** is EPR silent, indicating that both Cu(1) and Cu(2) are monovalent.

Compound **1** has a three-dimensional uninodal twelve-connected framework in which the nodes are Cu_6S_4 clusters and the connectors are pyridine rings of pdt and cyanide groups (Figure 2). The Cu_6S_4 cluster in **1** shows approximate T_d symmetry with six Cu(I) ions arranged to form a Cu_6 octahedron and four μ_3-S atoms distributed at the centers of trigonal faces, as found in the hexanuclear complex $Cu_6(4\text{-pyridinethione})_4Cl_6$.[10] The adjacent Cu···Cu distances are 3.69 and 3.75 Å in the Cu_6 octahedron. Each Cu_6S_4 cluster is

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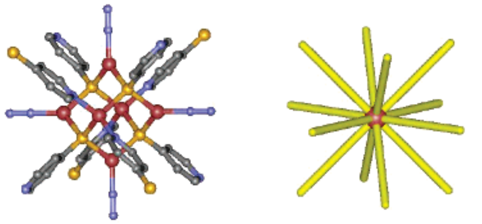
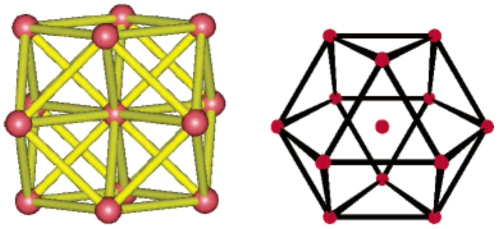


Figure 3. Perspective (left) and simplified (right) views of the twelve-connected Cu_6S_4 cluster.

Scheme 1. Schematic View of the Augmented Face-Centered Cubic Lattice Net in **1** Showing Twelve-Connection (left) and a Cuboctahedral Coordination Figure (right)



connected to twelve adjacent Cu_6S_4 clusters via four cyanide groups and eight pyridine rings, as shown in Figure 3. The distances between the centers of the Cu_6S_4 clusters linked by pyridine rings and cyanide are 10.6 and 10.2 Å, respectively. The net, when idealized, simply corresponds to a cubic closest-packed array of spheres, namely, a face-centered cubic lattice, as shown in Scheme 1. The Schläfli symbol for the idealized net is $3^{24}{\cdot}4^{36}{\cdot}5^{6}$. It may also be described as an augmented face-centered cubic lattice, and the three-letter symbol proposed by O'Keeffe is fcu.[11] Each Cu_6S_4 cluster has a cuboctahedral coordination figure which is enclosed by twelve adjacent Cu_6S_4 clusters. Calculation by PLATON reveals that there is no free void in **1**, which is consistent with a cubic closest-packed structure.

Interestingly, the synthesis of **1** relies on subtle control over various hydrothermal parameters, particularly the starting materials, temperature, and the pH value. Hydrothermal reactions of Cu(II), cyanide, and pdt ligands did not form **1**, but hydrothermal treatment of Cu(I), cyanide, and pdt ligands produced a powder of **1**, indicating that slow synthesis of pdt via sulfation of (4-pyridylthio)-aceto is critical for growing single crystals of **1**. Besides, a similar hydrothermal reaction at a lower temperature could not produce **1**. Furthermore, the initial pH value (slightly basic, pH 8−9) is also important for the formation of **1**. The formation mechanism of **1** is not clear. However, the existence of sulfate ions in the filtrate allows us to speculate that there are at least two steps in the formation of **1**. The first step probably is a redox reaction involving Cu(II) and SCN^-, generating Cu(I), cyanide, and sulfate ions.

The formation of cyanide by oxidation of thiocyanate was documented by Schug and co-workers, and their studies also revealed that sulfur atoms of SCN^- are converted to sulfate.[12] The second step is the assembly of Cu(I), cyanide, and (4-pyridylthio)-aceto via coordination interactions to form **1**, which is concomitant with the cleavage of S−C bonds of (4-pyridylthio)aceto to generate the pdt ligands. The cleavage of S−C bonds in (4-pyridylthio)-aceto is possibly due to steric hindrance caused by the coordination of the S atom to Cu(I) at the relatively high reaction temperature.

To sum up, a twelve-connected face-centered cubic coordination polymer has been successfully produced by using Cu_6S_4 clusters as nodes, and this further demonstrates that the replacement of d- or f-block ions with metal clusters as nodes is a feasible route to synthesize highly connected metal−organic frameworks.

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Supporting Information Available: Crystallographic data in CIF format and an additional figure. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Anal. Calcd for $C_{11}H_8Cu_3N_3S_2$: C, 30.23; H, 1.85; N, 9.62. Found: C, 30.14; H, 1.90; N, 9.57. IR data (KBr, cm^{-1}): 3419m, 3044w, 2457w, 2129m, 1684s, 1649w, 1614m, 1449w, 1402s, 1376m, 1262m, 1133s, 957m, 863m, 629m, 535s.

(8) Crystal data for **1** $C_{11}H_8Cu_3N_3S_2$: tetragonal, $I\bar{4}2m$, $M_r = 436.94$, $a = 10.2175(5)$ Å, $c = 15.4618(15)$ Å, $V = 1614.17(19)$ Å^3, $Z = 4$, $D_c = 1.798$ g cm^{-3}, $\mu = 4.162$ mm^{-1}, $T_{min} = 0.4612$, $T_{max} = 0.5052$, $F(000) = 856$, $R1 = 0.0359$, $wR2 = 0.0959$, $S = 1.038$. The absolute structure has been determined with the Flack parameter of 0.05(4).

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