

A 3-D Noninterpenetrating Diamondoid Network of a Decanuclear Copper(I) Complex

Jian-Kai Cheng,[†] Yu-Biao Chen,[†] Ling Wu,[‡] Jian Zhang,[†] Yi-Hang Wen,[†] Zhao-Ji Li,[†] and Yuan-Gen Yao^{*†}

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China, and Department of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, P. R. China

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The solvothermal reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with pyridine-4-thiol and ethanol yielded a novel photoluminescent 3-D polymeric complex with an interesting decorated diamondoid network that is constructed of decanuclear copper(I) cluster units and μ_4 -Cl ligands. The in situ generation of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ implies the spontaneous occurrence of desulfurization and redox reactions in the present system.

Coordination polymers have attracted wide interest because they provide a novel route to new functional materials that might find applications in molecular recognition, catalysis, gas storage, separation, optics, magnetism, electrical conductivity, and ion exchange.¹ One of the most effective approaches to polymeric frameworks is hydro(solvo)thermal assembly by incorporating appropriate metal ions (connectors) with multifunctional bridging ligands (linkers).² However, the hydro(solvo)thermal reaction is often accompanied by many interesting processes such as metal redox, ligand oxidative coupling, hydrolysis, desulfurization, alkylation, and substitution reactions,^{3–5} making the assembly products very difficult to predict. A great deal of work on hydro-

(solvo)thermal synthesis with O- or N-donor ligands has been reported, but there has been relatively little effort on organosulfur ligands,⁶ because of their much more complicated reactivity.

The design and synthesis of new coordination architectures for functional materials has led to the study of the respective and joint contributions of metals (coordination geometry) and ligands (functionality, steric and electronic properties) to the overall molecular properties.^{7,8} Copper is one of the prototype linking metals,⁹ and new copper(I) halides or chalcogenides have been of great interest for their rich photoluminescent properties¹⁰ and intriguing topology.¹¹ Thiopyridine ligands and their derivatives contain both N and S donors that are inclined to bind soft acids such as Cu(I) and Ag(I) via various S coordination modes ($\eta_1, \mu_2, \mu_3, \mu_4, \mu_5$).¹² Nevertheless, the reactions of copper salts with thiopyridine ligands are liable to result in uncharacterized precipitates under conventional

* To whom correspondence should be addressed. E-mail: yyg@fjirsm.ac.cn.

[†] Chinese Academy of Sciences.

[‡] Fuzhou University.

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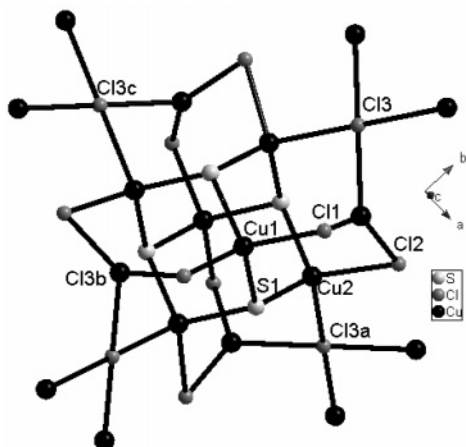
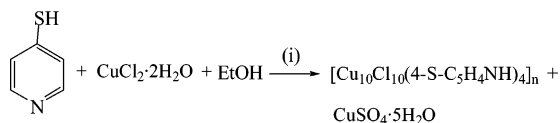


Figure 1. Molecular structure of **1** with atom labeling (pyridine rings are omitted for clarity). Symmetry codes: $a = 1.25 - y, 0.75 + x, -0.25 + z$; $b = -x, 1.5 - y, z$; $c = -1.25 + y, 0.75 - x, -0.25 + z$.

Scheme 1^a



^a Conditions: 160 °C, 60 h.

(solution) or hydrothermal conditions. Although it was previously reported that the reactions of pyridine-2-thiol with Cu(I) and Ag(I) ions can lead to soluble species,¹² only two analogues of pyridine-4-thiol have been reported by our group.^{5a,6c} Recently, we have been investigating this interesting reaction system of copper(II) salts with pyridine-4-thiol and observed some surprising processes such as redox, desulfurization, halogenation, alkylation, and ligand-coupling reactions.^{5a,6c,13}

On the other hand, rare examples of metal–organic polymeric structures constructed from multinuclear metal clusters have been reported, especially for copper(I) clusters.^{14,15} They are obtained mainly from Cu⁺ precursors. Few efforts have been directed toward the fabrication of cluster species via the reduction of Cu²⁺ to Cu⁺. Hererin, we reported a novel luminescent 3-D diamondoid polymeric copper(I) complex with decanuclear copper(I) clusters, [Cu₁₀Cl₁₀(4-S-C₅H₄NH)₄]_n, (**1**). The solvothermal synthesis¹⁶ of **1** from CuCl₂·2H₂O and pyridine-4-thiol in ethanol involves in the in situ desulfurization of organic sulfur and redox reactions (Scheme 1).

Single-crystal X-ray diffraction analysis¹⁷ of **1** reveals the formation of a 3-D framework with decanuclear copper(I) clusters. There exist three kinds of copper(I) atoms, three

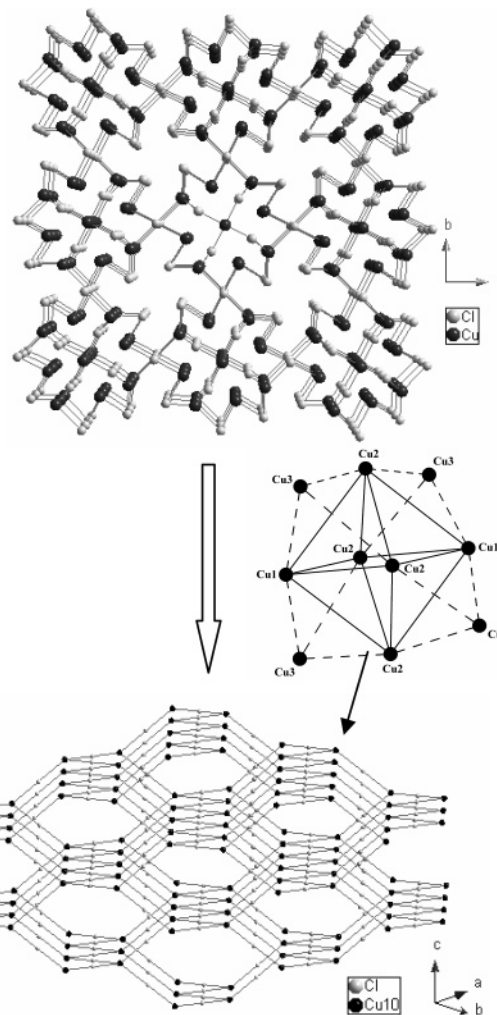


Figure 2. View of the 3-D network of **1** (heterocyclic ligands are omitted for clarity).

kinds of chloride atoms, and one pyridine-4-thiol molecule in each crystallographically asymmetric independent unit (Figure 1). Three independent copper(I) centers display different coordination modes: Cu(μ_2 -Cl)₂(μ_4 -Cl), CuS₂(μ_2 -Cl)₂, and CuS₂(μ_2 -Cl)(μ_4 -Cl). Cu1 and Cu2 exhibit a distorted tetrahedral geometry, whereas Cu3 exhibits a distorted trigonal-planar geometry. The sulfur atom from the neutral pyridine-4-thiol acts as a μ_3 -bridge. The CuCl distances are in the range of 2.229(3)–2.611(1) Å, and the CuS distances are in the range of 2.257(2)–2.304(2) Å. These values are comparable to those found in our previously reported complex [Cu₆Cl₆(S-4-C₅H₄NH)]_{5a}.

It is notable that the decanuclear unit Cu₁₀Cl₁₀ is four-connected to other units via four μ_4 -Cl atoms, resulting in a 3-D framework (Figure 2). In other words, heterocyclic ligands play an accessory role in the construction of the 3-D network. Moreover, if the Cu₁₀Cl₁₀ unit is simplified to a four-connected node and, accordingly, μ_4 -Cl becomes a two-connected linker, the overall topology can be described as a four-connected diamondoid network (Figure 2). Compared to most previously reported interpenetrating diamondoid networks,^{1c,18} the present structure is the first example of 3-D noninterpenetrating four-connected diamondoid network based on multinuclear cuprous chloride units. Ten

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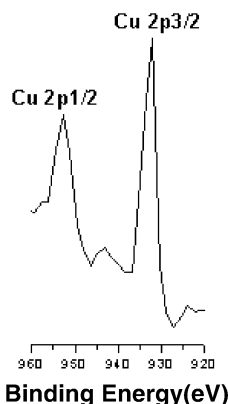


Figure 3. High-resolution XPS spectrum of Cu in **1**.

copper(I) atoms in $\text{Cu}_{10}\text{Cl}_{10}$ unit exhibit a regular array in which six Cu atoms form an octahedron and the other four Cu atoms are located at the capping sites of the four faces of the octahedron as a tetrahedral array (Figure 2). The $\text{Cu}\cdots\text{Cu}$ distances fall in the range between 3.030(2) and 3.407(2) Å, slightly shorter than those found in the comparable Cu_{10} cluster reported by Wu et al.¹⁹

During the reaction, blue crystals of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ were synchronously obtained as the byproducts. This prompts us to speculate that the desulfurization process is followed by the oxidation of S^{2-} to S^{6+} and the reduction of Cu^{2+} to Cu^+ . The low yield of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ indicates that only a small amount of pyridine-4-thiol undergoes the desulfurization reaction. This case is different from the desulfurization reaction of heterocyclic ligands reported by Dong et al.²⁰ The results here provides a model reaction to simulate the transformation of organic sulfur into inorganic sulfate under geothermic condition and a possible approach to a solution of the problem of pollution of organic sulfur complexes.

No signal was found in the ESR spectrum, which confirms that all copper atoms in **1** are Cu^{I} . This was also shown by X-ray photoelectron spectroscopy (XPS) measurements of **1**. The spin-orbit components ($^2\text{p}_{3/2}$ and $^2\text{p}_{1/2}$) of the Cu 2p peak were well deconvoluted by two curves at approximately 932.2 and 952.1 eV with a spin-orbit separation of 19.9 eV (Figure 3), confirming the presence of Cu^{I} in complex

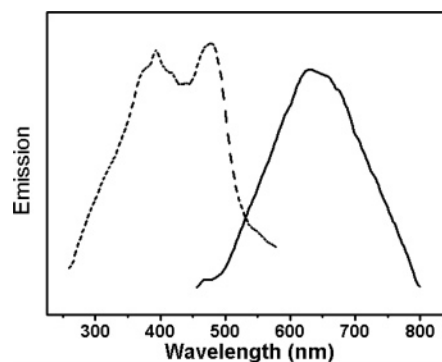
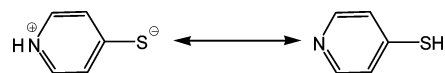


Figure 4. Emission spectrum (solid line, maximum 627 nm) and excitation spectrum (dotted line, maximum 380 nm) of **1** in the solid state at room temperature.

1. The typical shake-up lines of Cu^{II} were not observed, indicating that the chemical state of Cu in the title complex is not a bivalent oxidation state. This conclusion is consistent with the results of the single-crystal X-ray analysis, which shows that the heterocyclic ligands in complex **1** are not negative but neutral. In other words, the heterocyclic ligands in **1** are the isomers of pyridine-4-thiol:



1 is stable in air and insoluble in water and almost all organic solvents; no additional measurements in solution could be carried out. Interestingly, **1** shows strong photoluminescence in the solid state, with an intense emission at 627 nm upon excitation at 380 nm at room temperature (Figure 4). According to the results for similar copper(I) thiolate clusters and copper(I) halides,¹⁰ the emission can be assigned to originate from a mixture of LMCT ($\text{S} \rightarrow \text{Cu}$) and metal-centered (ds/dp) states modified by Cu–Cu interactions within decanuclear copper(I) clusters.

In summary, we have successfully synthesized a novel photoluminescent 3-D polymeric complex based on decanuclear copper(I) clusters. Redox reaction and desulfurization of organic sulfur have been observed. This is interesting for the development of a new strategy to construct diverse polymeric copper(I) complexes via an in situ solvothermal redox reaction. It also provides a new method for transforming organic sulfur into inorganic sulfate.

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Supporting Information Available: Crystallographic data in CIF format. XPS survey spectrum of complex **1**. High-resolution XPS spectrum of Cu in **1**. Diagrams showing the octagonal $\text{Cu}_{10}\text{Cl}_{10}$ clusters and diamondoid Cu_6S_4 clusters in **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (16) A mixture of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.363 g, 2.0 mmol), pyridine-4-thiol (0.115, 1 mmol), and ethanol (16 mL) was sealed in a 25-mL Teflon-lined reactor. The reactor was heated in an oven to 160 °C for 60 h and then cooled to room temperature at a rate of 5 °C·h⁻¹. Red prismatic crystals were obtained. Anal. Calcd (%) for $\text{Cu}_5\text{Cl}_5\text{C}_{10}\text{H}_{10}\text{N}_2\text{S}_2$: C 16.74, H 1.41, N 3.91, S 8.94. Found: C 16.78, H 1.50, N 4.03, S 8.79. IR (cm⁻¹): 3440 (vs), 2085 (w), 1643 (vs), 1518 (w), 1385 (w), 1335 (w), 1045 (m).
- (17) Crystal data for $\text{Cu}_5\text{Cl}_5\text{C}_{10}\text{H}_{10}\text{N}_2\text{S}_2$ (**1**): Tetragonal, space group *I*4-(1)/*a*, $M_r = 717.27$, $a = 17.5832(4)$ Å, $b = 17.5832(4)$ Å, $c = 12.1881(6)$ Å, $V = 3768.2(2)$ Å³, $Z = 8$, $F(000) = 2768$, $D_c = 2.529$ g cm⁻³, R_1 (wR2) = 0.0559 (0.1001), and $S = 1.063$ for 1045 reflections with $I > 2\sigma(I)$.
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