Inorg. Chem. **2005**, *44*, 1175–1177

Inorganic Chemistry
Communication

# Transformation of Inorganic Sulfur into Organic Sulfur: A Novel Photoluminescent 3-D Polymeric Complex Involving Ligands in Situ Formation

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Received October 29, 2004

The reaction of CuSCN with acetonitrile and methanol under solvothermal conditions yielded a novel 3-D polymeric photoluminescent complex containing dodecanuclear copper(I) clusters with methyl mercaptide. The synthesis involves in situ generation of ligands, which provides a model reaction to simulate the transformation of inorganic sulfur into organic sulfur under geothermic conditions.

Transformation of inorganic sulfur into organic sulfur under natural anoxic and geothermic conditions or in an organism catalyzed by anaerobic bacteria has always been an active area of research.[1] Hydro(solvo)thermal techniques, creating high-pressure and high-temperature conditions, similar to natural geothermic environments, have proved to provide a promising method to prepare highly stable infinite metal−ligand frameworks accompanied by many interesting phenomena such as metal redox, ligand oxidative coupling, hydrolysis, and substitution.[2,3] The reactivity of some organic compounds under hydro(solvo)thermal conditions can be reinforced by catalysis from solvent molecules.[4,5] Understanding the reaction mechanisms is an exciting challenge to chemists as, in most cases, the precise mechanisms are not clear.[6]

On the other hand, structures of metal-containing macrocyclic clusters have attracted considerable interest in the field of supramolecular coordination chemistry.[7] Many examples of such structures have been synthesized by normal solution methods.[8−10] However, rare examples of metal−organic polymeric structures constructed from multinuclear metal clusters have been reported, especially copper(I) clusters.[11,12] Herein, we report a novel photoluminescent 3-D polymer, $\{[Cu(\mu_3\text{-}SCH_3)_2(CN)]_2[Cu_{10}(\mu_3\text{-}SCH_3)_4(\mu_4\text{-}SCH_3)_2]\}_n$, that was solvothermally synthesized[13] by the reaction of CuSCN with methanol and acetonitrile involving in situ ligand formation that converted inorganic sulfur into organic sulfur.

The crystal structure[14] of the title complex shows that there are six copper(I) atoms, one cyanide ion, and five methyl mercaptide ions in one crystallographically asymmetric independent unit (Figure 1). C−S bond lengths are 1.819−1.835 Å, close to those in other mercaptanes.[15] There exist three different kinds of Cu(I) coordination geometry: CuS3, CuS2N, and CuS2C. All Cu(I) atoms display a distorted

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(13) A mixture of CuSCN (0.121 g, 1.0 mmol), methanol (5.0 mL), and acetonitrile (5.0 mL) was stirred for 10 min in air and then transferred to and sealed in a 25-mL Teflon-lined reactor. The reactor was heated in an oven to 140 °C for 72 h and then cooled to room temperature at a rate of 5 °C·h$^{-1}$. Yellow rhombic crystals were obtained. Anal. Calcd for $C_6H_{15}Cu_6NS_5$: H 2.35, C 11.21, N 2.18%. Found: H 2.13, C 11.32, N 2.01%. IR data (KBr, cm$^{-1}$): 2919 s, 2826 w, 2128 s, 1417 m, 1306 m, 956 s, 689 w, 463 w. **Caution!** *Reactions under high pressure are potentially vigorous and explosive and should be handled with care.*

(14) Crystal data for $C_6H_{15}Cu_6NS_5$ (**1**): triclinic, space group $P\bar{1}$, $M_r$ = 642.73, $a$ = 8.5509(8) Å, $b$ = 9.1618(8) Å, $c$ = 11.8131(11)Å, $\alpha$ = 74.2620(10)°, $\beta$ = 111.9290(10)°, $\gamma$ = 65.2030 (10)°, $V$ = 805.85(13) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 2.649 g cm$^{-3}$, $\mu$ = 8.398 mm$^{-1}$, $F$(000) = 624, $T$ = 296(2) K; R1 = 0.0449, wR2 = 0.1129, GOF = 1.091 for all data. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo Kα, $\lambda$ = 0.71073 Å).

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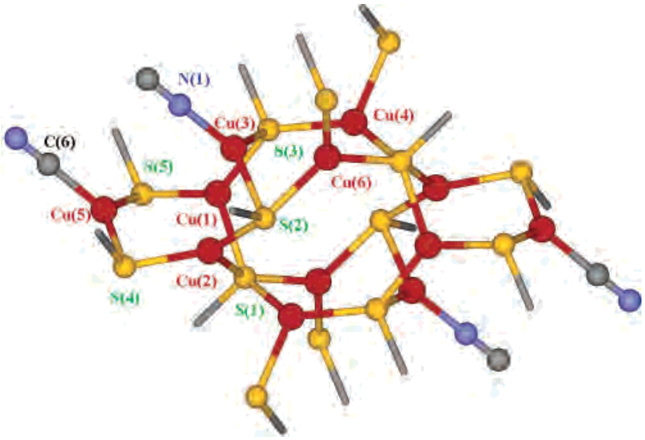


**Figure 1.** Dodecanuclear copper(I) cluster like a finger ring containing $\mu_3$-S and $\mu_4$-S atoms.

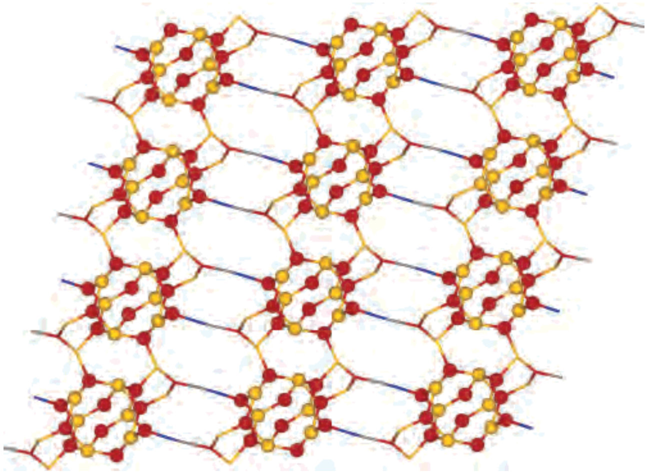


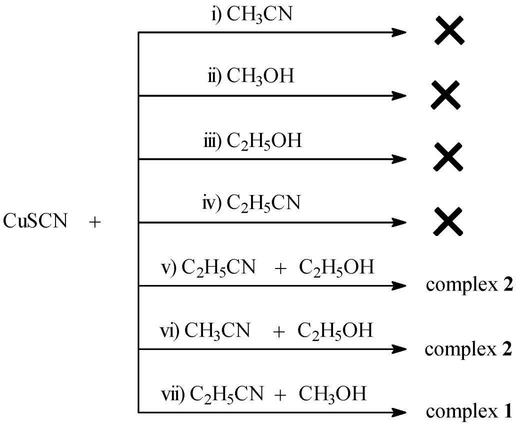
**Figure 2.** View of the 2-D layer along the (011) crystal plane. Methyl groups have been omitted for clarity. (Red = Cu, yellow = S, blue = N, gray = C).

trigonal-planar geometry. Sulfur atoms in methyl mercaptide ions adopt two different kinds of bridging modes: S(1) in $\mu_4$-S, and S(2), S(3), S(4), and S(5) in $\mu_3$-S. To our knowledge, the $\mu_4$-S bridging mode is rare and mainly occurs in silver complexes[16] but scarcely in copper(I) complex.[15] Cu(1), Cu(2), and Cu(3) atoms bridged by three sulfur atoms compose a triangle (Cu−Cu−Cu internal angles, 56.4−64°) with Cu···Cu separations of 2.720, 2.815, and 2.936 Å, respectively, which indicate simultaneous Cu−Cu bonds and weak Cu···Cu interactions. Ligand-supported metal bonds link Cu(3) and Cu(1) and Cu(3) and Cu(4) with bond lengths of 2.720 and 2.703 Å, respectively.

Intriguingly, a crystallographically asymmetric independent unit grows by inversion to form the decanuclear copper cluster [$Cu_{10}(\mu_3\text{-}SCH_3)_4(\mu_4\text{-}SCH_3)_2$], like a finger ring, with two decorated side units [$Cu(\mu_3\text{-}SCH_3)_2(CN)$] and all methyl groups protruding outside the finger ring. Every dodecanuclear copper cluster is connected to two adjacent clusters by four cyanide ions and to another two clusters by four $\mu_3$-$SCH_3$ units along the *a* axis, which results in a 2-D network (011 crystal plane, Figure 2). $\mu_3$-$SCH_3$ links the adjacent 2-D layers to built a 3-D framework. A parallelogram with dimensions of 8.551 Å × 9.162 Å × 12.837 Å constructed by eight neighboring copper clusters, one of which occupys one vertex of the parallelogram, was mainly filled by the methyl of the mercaptide ion. No solvent molecule was found in the cavity.

The notable feature of **1** is the in situ generation of new ligands $-SCH_3$ and −CN−. The only source of S atoms is CuSCN, via S−CN bond dissociation. The $-CH_3$ group can come from either $CH_3CN$ or $CH_3OH$, whereas −CN− can come from either $CH_3CN$ or CuSCN. To understand the elementary mechanism of the reaction, some contrastive experiments under the same conditions were performed, as illustrated in Scheme 1.

**Scheme 1**



No title complex was obtained in reactions i−iv, implying that the S−C(N) bond of CuSCN is not apt to dissociate in a single solvent. In reaction vii, the product was characterized to be complex **1**. As is the case for in $CH_3CN$ + $CH_3OH$, the residual solution smells pungently. Pale bar complex **2**[17] was crystallized in reactions v and vi. Unfortunately, the structure could not be solved because of the poor reflection data, even though great efforts were made to attain good single crystals. From the results of the above reactions, it is unambiguously believed that the sulfur atom in methyl mercaptide ion comes from thiocyanate ion and methyl from methanol rather than acetonitrile. However, the presence of nitrile is essential.

Furthermore, we replaced CuSCN with $M(SCN)_n$ (M = Ag, Ni, Co, Zn; $n = 1, 2$) and confirmed that copper(I) ions are crucial for the reaction, as no similar products could be found for the other metals.

We propose a possible mechanism for the in situ ligand formation as follows: The coordination of a nitrile molecule to CuSCN weakens the S−C(N) bond. Subsequently, $CH_3OH$ attacks $Cu(CH_3CN)_x$S−CN to form a new S−C($H_3$) bond, methyl mercaptide, completing the transformation of inorganic sulfur into organic sulfur (Scheme 2). The IR

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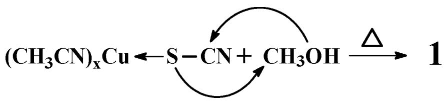
[16] (a) Su, W.-P.; Hong, M.-C.; Weng, J.-B.; Cao, R.; Lu, S.-F. *Angew. Chem., Int. Ed.* **2000**, *39*, 2911. (b) Hong, M.-C.; Su, W.-P.; Cao, R.; Zhang, W.-J.; Lu, J.-X. *Inorg. Chem.* **1999**, *38*, 600. (c) Su, W.-P.; Cao, R.; Hong, M.-C.; Chen, J.-T.; Lu, J.-X. *Chem. Commun.* **1998**, 1389.

[17] Crystal data for complex **2** at 293 K: orthorhombic, $a = 14.4565(14)$ Å, $b = 15.0251(15)$ Å, $c = 4.6796(5)$ Å, $V = 1016.46(13)$ Å$^3$. Elemental analysis: H 2.94, C 17.64, N 4.12%.

**Scheme 2**



spectrum of **1** shows a peak at 2128 $cm^{-1}$ assigned to the stretching vibration of the $CN^-$ species,[18] which is agreement with the crystallographic results. Rationally, we can speculate that complex **2** should contain $-SC_2H_5$.

**1** is stable in air and insoluble in water and most organic solvents; no additional measurements in solution could be performed. Interestingly, **1** shows strong photoluminescence in the solid state, with an emission maximum at 570 nm upon excitation at 390 nm at room temperature (Figure 3). In comparison to Cu(I) clusters with chalcogen ligands, the emission is tentatively assigned to originate from a mixture of LMCT (S → Cu) and metal center $3d^94s^1$ modified by Cu−Cu interactions.[19] Unlike in **1**, no photoluminescence was observed in **2**. The possible reason is that the relative bulky ligand ($-SC_2H_5$) prevents the formation of a Cu−Cu bond that is essential to the MMLCT.

In conclusion, we solvothermally synthesized a novel potoluminescent 3-D polymeric complex based on dodecanuclear copper(I) clusters with in situ ligand formation. A strategy for exploring the reaction mechanism was evolved. The reaction provides a model for understanding the essence of the transformation of an inorganic compound into an organic group under natural conditions. Further studies on other members of this cluster motif involving different solvents or inorganic salts are in progress.

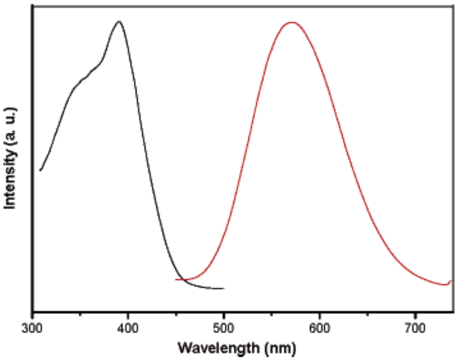


**Figure 3.** Emission spectrum (red line, maximum 570 nm) and excitation spectrum (black line, maximum 390 nm) of **1** in the solid state at room temperature.

**Acknowledgment.** The authors gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (No. 29901004 & 20271031) and the Natural Science Foundation of Guangdong Province of China (No. 021240).

**Supporting Information Available:** Crystallographic data in CIF format. Figures showing parallelogram constructed by eight adjacent Cu(I) clusters, 3-D network of polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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