Inorg. Chem. **2008**, *47*, 2255−2257

Inorganic Chemistry

Communication

Two Cuprous Cyanide Polymorphs: Diamond Net versus 3,4-Connected Net

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Received December 11, 2007

Hydrothermal reactions generated two cuprous cyanide polymorphs with similar hexagonal $[Cu_2(CN)_3]^-$ layers but different supramolecular arrays.

Polymorphism and supramolecular isomerism are receiving more and more attention in the crystal engineering of coordination polymers because the control over polymorphs and supramolecular isomers lies at the very heart of the concept of crystal engineering.[1–4] However, the rational design and controlled synthesis of supramolecular isomers and polymorphs, in particular polymorphs, remain a challenge in coordination polymers. The structural chemistries of CuCN-based compounds are diverse, which provides a good chance to study polymorphism and supramolecular isomerism.[5–11] For CuCN itself, there exist two high- and low-temperature polymorphs, and their interconversion via an isolable intermediate phase has been demonstrated.[12] In the contribution, we report two temperature-controlled polymorphs, $H_5O_2[Cu_2(CN)_3]$ (**1** and **2**), both of which are constructed by hexagonal $[Cu_2(CN)_3]^-$ layers.

Hydrothermal treatment of a mixture of $CuCl_2$, $K_3[Fe(CN)_6]$, tetrazole, and acetonitrile at 160 °C/170 °C resulted in a solution, from which initial pale-yellow crystals of **1** and **2** were grown by slow evaporation of the solvent. Further study reveals that **1** and **2** are also available in the absence of $K_3[Fe(CN)_6]$. Thus, it is reasonable to deduce cyanide ligands coming from acetonitrile via in situ C−C bond cleavage rather than from $[Fe(CN)_6]^{3-}$ ions. The formation of cyanide via hydrothermal in situ C−C bond cleavage of acetonitrile has been observed recently.[13] Polymorphs **1** and **2** are separable, as confirmed by powder X-ray diffraction patterns. The IR spectra show intense stretching absorptions of cyanides at 2112 and 2092 cm^{-1} for **1** and at 2114 and 2096 cm^{-1} for **2**, respectively. A series of absorption bands in the range of 3000–3600 cm^{-1} in **1** and **2** are associated with hydrogen-bonded water molecules, and the difference of these bands indicates different structural motifs of water molecules in **1** and **2**.

X-ray crystallography reveals that **1** is a three-dimensional (3-D) diamondlike microporous framework constructed by hexagonal $[Cu_2(CN)_3]^-$ layers via Cu^I−Cu^I interactions.[14] **1** crystallizes in monoclinic space group *C*2/*c*, and the asymmetric unit consists of one crystallographically independent Cu^I center, one and a half cyanides, and one water molecule. The C and N sites of CN groups are disordered. The Cu center shows a trigonal geometry, coordinated by three X (C or N) atoms from three cyanides.

The charge balance requires protonation of water molecules in the form of $(H_5O_2)^+$. Each Cu center is connected to three adjacent Cu centers via linearly coordinated cyanides to generate a hexagonal anionic $[Cu_2(CN)_3]^-$ layer. The basic units in the layer are 18-membered $Cu_6(CN)_6$ rings, and the

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(14) Crystal data for **1**: $C_3H_5Cu_2N_3O_2$, monoclinic, space group *C*2/*c*, $M_r = 242.18$, $a = 13.7386(18)$ Å, $b = 8.0167(10)$ Å, $c = 7.2151(9)$ Å, $\beta = 113.971(2)°$, $V = 726.12(16)$ Å^3, $Z = 4$, $D_c = 2.215$ g/cm^3, $\mu = 5.796$ mm^{-1}, $F(000) = 472$, $T_{min} = 0.4574$, $T_{max} = 0.8013$, $2\theta_{max} = 54°$, $S = 1.190$, R1 = 0.0549, wR2 = 0.1450. Crystal data for **2**: $C_3H_5Cu_2N_3O_2$, monoclinic, space group $P2_1/c$, $M_r = 242.18$, $a = 12.0108(16)$ Å, $b = 8.3037(11)$ Å, $c = 7.5441(10)$ Å, $\beta = 95.773(2)°$, $V = 748.59(17)$ Å^3, $Z = 4$, $D_c = 2.149$ g/cm^3, $\mu = 5.622$ mm^{-1}, $F(000) = 472$, $T_{min} = 0.4310$, $T_{max} = 0.7663$, $2\theta_{max} = 54°$, $S = 1.183$, R1 = 0.0605, wR2 = 0.1764. CCDC Nos. 669718 and 669719.

10.1021/ic702394w CCC: $40.75

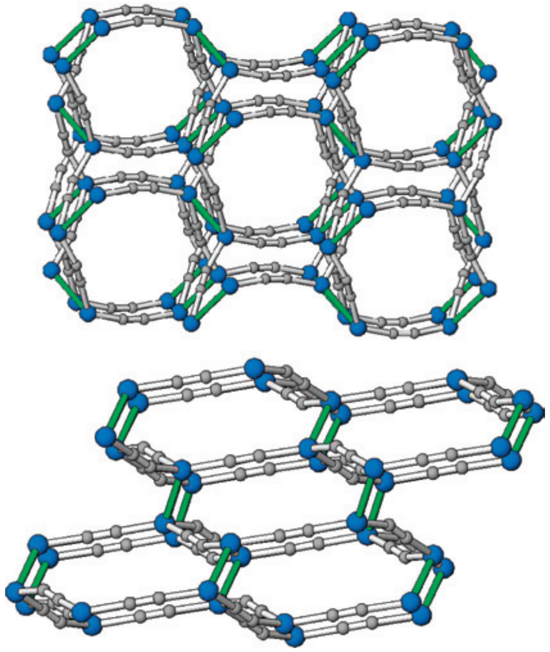

Figure 1. View of the 3-D diamondlike framework showing 1-D channels (a) and $Cu^{I}-Cu^{I}$ interactions (b) in **1**. Color code: blue balls, Cu; gray balls, C and N atoms; $Cu^{I}-Cu^{I}$ interactions, green line.

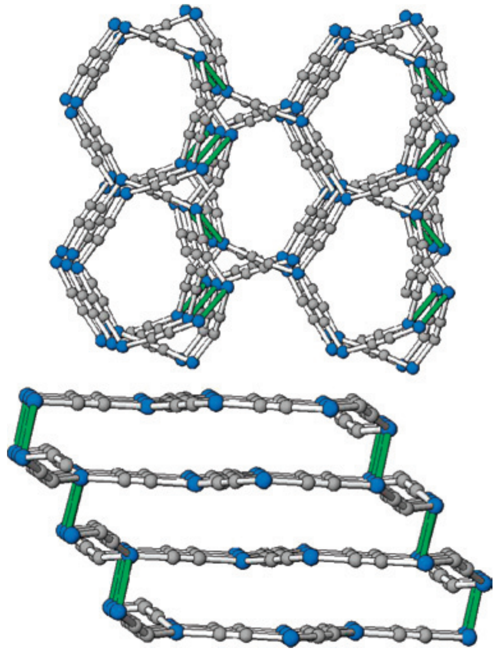

Figure 2. View of the 3-D 3,4-connected framework showing 1-D channels (a) and $Cu^{I}-Cu^{I}$ interactions (b) in **2**. Color code: blue balls, Cu; gray balls, C and N atoms; $Cu^{I}-Cu^{I}$ interactions, green line.

diagonal Cu···Cu distances in a $Cu_6(CN)_6$ ring are 9.4, 9.4, and 10.5 Å. All of the $Cu_6(CN)_6$ rings within one layer have identical orientations. Interestingly, there exist Cu−Cu interactions between adjacent layers with $Cu^{I}-Cu^{I}$ distances of 2.86 Å. The $[Cu_2(CN)_3]^-$ layers are extended via Cu−Cu interactions into a 3-D diamondlike framework with 1-D channels filled by protonated water molecules (Figure 1). Each water molecule has two neighboring water molecules with O···O distances of 2.80 and 3.13 Å. The O···O distance of 3.13 Å indicates a very weak hydrogen bond or no hydrogen bond, and thus the protonated water molecules can be approximately described as existing in an isolated $H_5O_2^+$ dimer.

Compound **2** crystallizes in space group $P2_1/c$ and the asymmetric unit consists of two Cu^{I} centers, three cyanides, and two water molecules. The C and N sites in CN groups in **2** possibly are ordered because our attempted refinement by application of 50% C and 50% N occupancies resulted in a much larger *R* index and very poor anisotropic temperature factors. Both Cu centers show trigonal geometry. The Cu(1) atom is coordinated by one C atom and two N atoms, while the Cu(2) atom is coordinated by one N atom and two C atoms. Similar to **1**, the hexagonal anionic $[Cu_2(CN)_3]^-$ layers are formed, but the 18-membered $Cu_6(CN)_6$ ring in the hexagonal layer of **2** is a little distorted, as indicated by diagonal Cu···Cu distances of 8.3, 10.2, and 10.9 Å. Besides, the $Cu_6(CN)_6$ rings within one $[Cu_2(CN)_3]^-$ layer in **2** have two different orientations. The shortest Cu(2)···Cu(2) distance of 3.83 Å eliminates $Cu^{I}-Cu^{I}$ interaction. However, the interlayer Cu(1)−Cu(1) distance of 3.027 Å indicates ambiguous $Cu^{I}-Cu^{I}$ interactions, which extend hexagonal $[Cu_2(CN)_3]^-$ layers into a 3-D 3,4-connected microporous framework with short Schläfli symbol $(6^3)_{Cu2}(6^5\cdot8)_{Cu1}$ (Figure 2). The protonated water molecules reside in the channels. The neighboring O(1w)···O(2w) distances of 2.87 and 2.93 Å indicate normal hydrogen bonds, which extend protonated water molecules into a zigzag water chain.

Five CuCN compounds with similar $[Cu_2(CN)_3]^-$ layers have been documented, and they are $NEt_4[Cu_2(CN)_3]$,[10] $K[Cu_2(CN)_3]\cdot H_2O$,[7] $[Cu(H_2O)_4][Cu_4(CN)_6]$,[8] $H_3NCH_2CH_2NH_3[Cu_4(CN)_6]\cdot 2H_2O$[9] and $NH_4[Cu_2(CN)_3]\cdot H_2O$.[11] It is meaningful to compare the $[Cu_2(CN)_3]^-$ layer itself, short interlayer Cu···Cu distances, and supramolecular arrays in **1** and **2** as well as the five related compounds. The $[Cu_2(CN)_3]^-$ layers in $NBt_4[Cu_2(CN)_3]$, $K[Cu_2(CN)_3]\cdot H_2O$, $[Cu(H_2O)_4][Cu_4(CN)_6]$, $H_3NCH_2CH_2NH_3[Cu_4(CN)_6]\cdot 2H_2O$, and $NH_4[Cu_2(CN)_3]\cdot H_2O$ are similar to that in **2**, as indicated by two different orientations of $Cu_6(CN)_6$ rings within one $[Cu_2(CN)_3]^-$ layer. The short interlayer Cu···Cu distances are 6.389 Å in $NEt_4[Cu_2(CN)_3]$, 2.953 and 3.798 Å in $K[Cu_2(CN)_3]\cdot H_2O$, 3.523 and 3.607 Å in $[Cu(H_2O)_4][Cu_4(CN)_6]$, 3.634 and 3.687 Å in $H_3NCH_2CH_2NH_3[Cu_4(CN)_6]\cdot 2H_2O$, and 3.060 and 3.816 Å in $NH_4[Cu_2(CN)_3]\cdot H_2O$. If we take a Cu···Cu distance of 3.1 Å as the upper limit of the Cu−Cu interaction, the 3-D supramolecular arrays are formed by $[Cu_2(CN)_3]^-$ layers via Cu−Cu interactions in $K[Cu_2(CN)_3]\cdot H_2O$, $NH_4[Cu_2(CN)_3]\cdot H_2O$, **1**, and **2**.

A thermogravimetric analysis (TGA) trace of **1** performed at 10 °C/min in air shows a continuous weight loss of 44.9% in the range of 100–490 °C, indicating the removal of water and cyanides. The remaining weight percentage of 55.1% at 490 °C is in agreement with the theoretical value of elemental Cu. The weight increase of 13.5% for **1** was observed in the range of 490–580 °C, which indicates the oxidization of Cu into CuO. The TGA curve of **2** is similar to that of **1** but is somewhat hysteretic. Polymorphs **1** and **2** show strong blue photoluminescent emission with maxima in the range of 472 and 469 nm, with an 80 nm red shift compared with the emission band of CuCN. According to related literature, the emissions in **1** and **2** are assigned as cuprophilicity-assisted Cu-centered 3d → (4p, 4s) transitions.

Acknowledgment. This work was financially supported by NSFC (Grants 20401011 and 20771069), FANEDD (Grant 200422), and NECT (Grant 05-0270).

Supporting Information Available: Crystal structural data for **1** and **2** and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

IC702394W