

# Communications

## In Situ Formed Guanidinium Cations as Templates To Direct Fabrication of Honeycomb-like CuCN Networks

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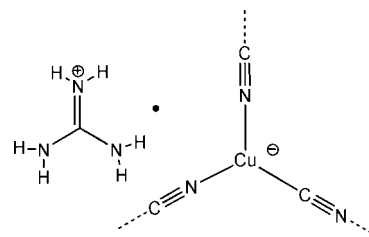
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**ABSTRACT:** The solvothermal reaction of CuSCN and 1,2-bis(diphenylphosphino)ethane (dppe) in mixed solvents acetonitrile/*n*-hexane/ (methanol or ethanol) gave a honeycomb-like guanidinium cyanocuprate  $[\text{C}(\text{NH}_2)_3]^+ \cdot [\text{Cu}_2(\text{CN})_3]^-$ . The in situ formed cations  $\text{C}(\text{NH}_2)_3^+$  act as templates to direct the formation of the CuCN network in which multiple weak  $\text{N}-\text{H} \cdots \text{N}/\text{C}$  hydrogen interactions potentially exist between the cations  $\text{C}(\text{NH}_2)_3^+$  and the  $\{\text{CuCN}\}_6$  rings.

Guanidinium cation  $\text{C}(\text{NH}_2)_3^+$  is a good candidate as a building block in constructing intriguing and functional hydrogen-bonded networks for its six hydrogen atoms being used as pair of hydrogen bonds to hydrogen accepting atoms.<sup>1</sup> Surely, a number of interesting hydrogen-bonded networks involving the cation have been found and studied, for example, the rosette ribbon network,<sup>1d</sup> rosette network,<sup>1e</sup> sodalite-like network,<sup>1f,g</sup> SrSi<sub>2</sub>-related network,<sup>1h</sup> and boracite-like network.<sup>1i</sup> Another very interesting application of the cation is that it can be used as a template to direct the fabrication of inorganic open-framework materials.<sup>2</sup> Harrison and co-workers have elegantly exploited the cation to generate an extensive family of open-framework solids including zinc phosphates<sup>2a</sup> (or zincophosphate),<sup>2b</sup> aluminophosphate,<sup>2c</sup> vanadium(V) phosphate,<sup>2d</sup> zincocarbonate,<sup>2e</sup> and zinc selenite.<sup>2f</sup> In these guanidinium salts, the  $\text{N}-\text{H} \cdots \text{O}$  hydrogen bonds [ $\text{N}-\text{H}$  from  $\text{C}(\text{NH}_2)_3^+$ , and  $\text{O}$  from the frameworks] abundantly exist and play an important role in implementing the template function of cation  $\text{C}(\text{NH}_2)_3^+$  to the inorganic open-frameworks.

Hydro(solvo)thermal in situ synthesis has been developed rapidly, not only for its advantage in the crystal engineering of complexes but also for the possible application in organic syntheses.<sup>3</sup> Many interesting hydro(solvo)thermal in situ reactions have been discovered, especially in some reactions happened with difficulty under traditional conditions, for example, dehydrogenative carbon-carbon coupling,<sup>4</sup> hydroxylation of aromatic rings,<sup>5</sup> cycloaddition of organic nitriles with ammonia,<sup>6</sup> and transformation sulfur from inorganic sulfur to organic sulfur.<sup>7</sup> However, the discovery of new hydro(solvo)thermal in situ reactions is still a great challenge due to their unpredictable results. Herein, as our continuing research of the sulfur transformation from inorganic sulfur to organic sulfur,<sup>7</sup> we found that the in situ yielded guanidinium cation under solvothermal conditions could act as a template to direct the formation of honeycomb-like CuCN network.

### Scheme 1. Structure Illustration of 1

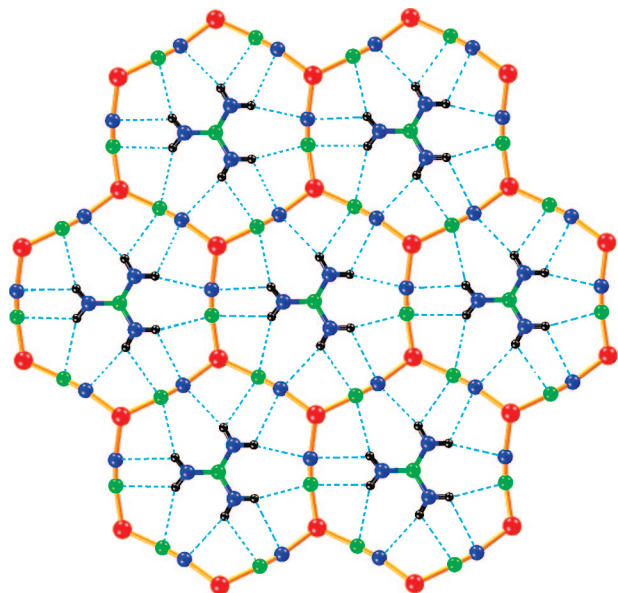


Solvothermal reactions of CuSCN and 1, 2-bis(diphenylphosphino)ethane (dppe) in mixed solvents acetonitrile/*n*-hexane/ (methanol or ethanol) yielded  $[\text{C}(\text{NH}_2)_3][\text{Cu}_2(\text{CN})_3]$  (**1**) (Scheme 1).<sup>8</sup> Except for **1**, the product was also mixed with some unknown white microcrystalline phase, which was not successfully determined by single-crystal diffraction. Compound **1** crystallizes in monoclinic space group *C2/c*, and is composed of honeycomb-like CuCN networks which contain ions  $\text{C}(\text{NH}_2)_3^+$  in hexagonal  $\{\text{CuCN}\}_6$  rings. The formation of ions  $\text{C}(\text{NH}_2)_3^+$  was also verified by FT-IR spectrum, showing the characteristic absorption of guanidinium at 3427(s), 3325(m), 3268(m), and 1674(s).<sup>2d</sup> Although the generation of **1** was intricate and the mechanism was not clear, CuCN should be yielded by decomposing the CuSCN, in which the sulfur was transferred to dppe. This was documented by the formation of 1,2-bis(diphenylthiophosphiny)ethane (dppeS<sub>2</sub>), found in the filtrate as our previous study.<sup>7c</sup> The cations  $\text{C}(\text{NH}_2)_3^+$  probably in situ come from the solvent acetonitrile because the product was not found in the syntheses with mixed solvents *n*-hexane/(methanol or ethanol) (*v/v* = 1:1) or pure methanol or ethanol in the absence of acetonitrile. On the other hand, we also tried to synthesize compound **1** by the direct reactions from CuCN and guanidinium  $\text{C}(\text{NH}_2)_3\text{Cl}$ . Unfortunately, no products of **1** were obtained even though great effort was made by using  $\text{C}(\text{NH}_2)_3\text{Cl}$ . It may be partially caused by the existing competition between the  $\text{CN}^-$  and

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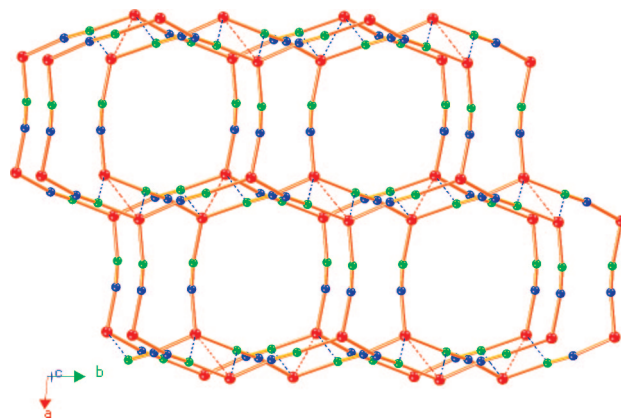
**Figure 1.** The CuCN honeycomb-like network with  $C(NH_2)_3^+$  guests. Red, blue, green and dark spheres representing Cu, N, C and H atoms, respectively. Cyan broken line represents N–H...N/C weak hydrogen bonds.

$Cl^-$  anions, which yield byproduct but not **1**.<sup>10</sup> On the other hand, it may be due to the relative difficulty by the direct synthesis of **1**.

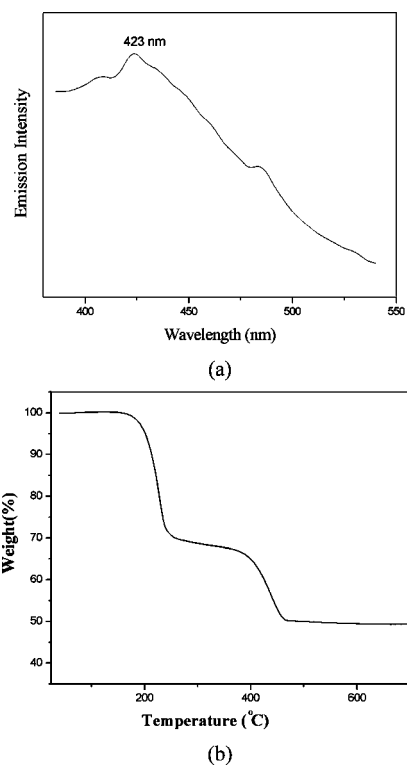
The asymmetrical unit of **1** contains one copper(I) atom, 1.5 cyanide groups, and 0.5  $C(NH_2)_3^+$  ion. Each copper(I) atom adopts triangular coordination geometry, and is coordinated by three N/C donors of  $CN^-$  anions. The Cu–C/N bonds distances range from 1.945(2) to 1.988(2) Å, and C≡N bonds distances of  $CN^-$  anions range from 1.139(3) to 1.144(5) Å. The C–N bonds of the  $C(NH_2)_3^+$  ion from 1.351(5) to 1.361(3) Å are reasonable. Similar to other CuCN compounds  $M[Cu_2(CN)_3] \cdot H_2O$  ( $M = K^+$ ,<sup>11a</sup>  $Rb^+$  and  $Cs^+$ <sup>11b</sup>),  $[Cu(H_2O)_4] \cdot [Cu_4(CN)_6]$ ,<sup>11c</sup>  $[(\kappa-ET)_2] \cdot [Cu_2(CN)_3]$  ( $\kappa-ET =$  bis(ethylenedithio)-tetrathiafulvalene),<sup>11d</sup>  $[PPh_4][Cu_2(CN)_3]$ ,<sup>11e</sup> and  $[H_3O][Cu_2(CN)_3] \cdot H_2O$ ,<sup>11f</sup> the copper(I) atoms are linked by anions  $CN^-$  forming the anionic honeycomb-like networks, as shown in Figure 1. The diameter of  $\{CuCN\}_6$  rings is about 9.93 Å [average values of the longest  $Cu \cdots Cu$  distances (9.91–9.97 Å) between one copper(I) atom with the other copper(I) atoms in the  $\{CuCN\}_6$  rings], which is significantly different from other compounds containing  $\{CuCN\}_6$  rings without templates. For example, in  $[Cu(H_2O)_4] \cdot [Cu_4(CN)_6]$ ,<sup>11b</sup> the  $\{CuCN\}_6$  ring is long and narrow with a dimension of  $11.7 \times 6.8$  Å. However, the atoms of the  $\{CuCN\}_6$  ring are not on a plane, and the  $\{CuCN\}_6$  ring is distorted and adopts a cyclohexane-like conformation.<sup>11b</sup>

Notably, the distances between the central carbon atom of  $C(NH_2)_3^+$  and the copper(I) atoms of the  $\{CuCN\}_6$  ring are almost equal, ranging from 4.93 to 4.98 Å (about the value of the radius of the  $\{CuCN\}_6$  ring), indicating that the planar triangle  $C(NH_2)_3^+$  ions are at the center of the  $\{CuCN\}_6$  rings (Figure 1). Synchronously, the distances between H atoms of  $C(NH_2)_3^+$  and the C/N atoms of the  $\{CuCN\}_6$  ring range from 2.5949(1) to 2.8140(1) Å, and the N–H...N/C angles range from 110.888(5) to 164.743(8)°, which are analyzed by OLEX software.<sup>12</sup> These structural data show that the weak N–H...N/C hydrogen bonds potentially exist in compound **1**.<sup>13</sup> Although each N–H...N/C hydrogen bond is weak, the synergy of the interactions between  $C(NH_2)_3^+$  ions and 12 N/C atoms is believed to be strong. Such multiple N–H...N/C hydrogen bonds possibly add to the stabilization of the whole systems and for implementing the template function of the cations. The existence of guanidinium template functionality may be important in the fabrication of the  $\{CuCN\}_6$  rings in the complicated in-situ reaction.

The adjacent honeycomb-like CuCN layers stack along  $c$  axis (Figure 2), are extended via weak Cu–C/N bonds (2.554 Å, which



**Figure 2.** The packing style of the honeycomb-like CuCN layers along the  $c$  axis. Red, blue, and green spheres represent Cu, N, and C atoms, respectively. Blue broken line represents Cu(I)–C/N weak bonds, red broken line represents the short Cu(I)–Cu(I) distance. The  $C(NH_2)_3^+$  cations are omitted for clarity.



**Figure 3.** (a) The solid-state emission spectrum of **1** ( $\lambda_{ex} = 290$  nm); (b) the thermogravimetry curve of **1**.

is much longer than the Cu–C/N bonds in **1** (1.945(2) to 1.988(2) Å)). If the weak Cu–C/N bonds are considered, the whole network can be rationalized as a diamond network.<sup>11f</sup> The Cu(I)–Cu(I) distance between adjacent layer is 2.735 Å, which is less than the sum of the van der Waals radii of Cu(I) (2.8 Å). Therefore, the potential interlayer Cu(I)–Cu(I) interactions may exist according to the literature.<sup>10b,11f,14</sup> However, the short Cu(I)–Cu(I) interlayer distance is more probably caused by the weak Cu–C/N bonds support.

As shown in Figure 3a, compound **1** shows an intense emission band maximized at 423 nm in the solid state upon photoexcitation ( $\lambda_{ex} = 290$  nm). According to the literature,<sup>10b</sup> the emission may be tentatively assigned to be from a metal-to-ligand charge transfer (MLCT, copper(I) center to the unoccupied  $\pi^*$  orbital of  $CN^-$ ) excited state.

Thermogravimetric analysis of compound **1** is given in Figure 3b. The compound is stable until around 180 °C and a total weight of 30.2% is lost from 180 to 260 °C, which corresponds to the removal of all  $C(NH_2)_3^+$  and  $1/3 CN^-$  anions (calculated 32.4%) and CuCN is probably formed. Then the resulting CuCN further decomposes at about 385 °C, and a total weight of 50.4% is lost at about 470 °C, which corresponds to the removal of the other  $2/3 CN^-$  anions (calculated 52.0%) and the yield of copper element.<sup>15</sup>

In summary, an interesting honeycomb-like guanidinium cyanocuprate was solvothermally in situ synthesized and structurally characterized. It represents the first example of in situ formed guanidinium template. The in situ formed guanidinium ions and the synergy of the N–H···N/C weak hydrogen bond interactions seem to be important in the formation of the CuCN network. Further systematic study of the template functionality of guanidinium ions in the cuprous pseudohalogen network by directly employed varied guanidinium salt, and the mechanism of in situ formed guanidinium are being carried out.

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**Supporting Information Available:** X-ray crystallographic data for **1** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) Synthesis of **1**: A mixture of CuSCN (0.0488 g, 0.4 mmol), dppe (0.0400 g, 0.4 mmol), and mixed acetonitrile/*n*-hexane/methanol or ethanol (5 mL/3 mL/2 drops) was stirred for 1 min in air, then transferred and sealed in a 15 mL Teflon-lined reactor, which was heated in an oven for 72 h at 180 °C and then slowly cooled to room temperature at a rate of 10 °C/h. Yellow needle-like crystals were obtained and washed with acetonitrile in 20% yield based on CuSCN. Elemental analysis (%) calcd for  $C_4H_6N_6Cu_2$ : H 2.28, C 18.11, N 31.68%; found 2.15, C 18.17, 31.82%; IR (KBr,  $cm^{-1}$ ): 3427s, 3325m, 3268m, 2091m, 1674s, 1515w, 1368w, 616m.
- (9) Single-crystal X-ray diffraction data collection for **1** was performed on a Bruker Smart Apex CCD diffractometer (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) by using frames of 0.38 oscillation ( $4.56 < 2\theta < 50^\circ$ ). The structures were solved by direct methods, and all non hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares methods on  $F^2$  by using the SHELXTL program.<sup>16</sup> The hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Crystal data for **1**:  $C_4H_6N_6Cu_2$ , monoclinic, space group  $C2/c$ ,  $M_r = 265.23$ ,  $a = 14.8770(15)$ ,  $b = 8.5545(8)$ ,  $c = 7.4081(7)$  Å,  $\beta = 118.7780(10)^\circ$ ,  $V = 826.35(14)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{calcd} = 2.132$  g  $cm^{-3}$ ,  $\mu = 5.096$  mm<sup>-1</sup>,  $F(000) = 520$ ,  $T = 293(2)$  K;  $R_1 = 0.0292$ ,  $wR_2 = 0.0788$  for all data.
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