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Hydrothermal synthesis of the fist two-dimensional folded layer formed by a cyano-bridged one-dimensional chain joined by Cu(I)–Cu(I) bonding

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Two cyano-bridged polymers, $[Cu_3(CN)_3(phen)]_n$ (1) and $[Cu(CN)(phen)]_n$ (2) (phen = 1,10-phenphralonine), were synthesized by the hydrothermal reaction of $Cu(NO_3)_2\cdot 3H_2O$, $K_3[Fe(CN)_6]$ and phen and were characterized structurally by X-ray, IR and ERSC methods. Compound 1 shows a two-dimensional folded coordination network by Cu(I)–CN–Cu(I) and Cu(I)–Cu(I) interaction, while compound 2 exhibits an infinite helix chain by Cu(I)–CN linkages. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: hydrothermal synthesis; chain; copper(I); cyano-bridged

INTRODUCTION

In the past decade, transition metal cyanides have become the focus of interest because of the large range of potential applications[1,2] in some fields, such as composite inorganic–organic zeolitic materials,[3,4] catalysts,[5] and high-Tc molecular-based magnets.[6,7] Of all the commonly studied transition metal cyanides, copper(I) cyanide attracts particular attention. In previous reports, copper(I) cyanide has been used via cyano-Gilman chemistry,[8] to construct multi-dimensional networks to form the open-framework materials[9–12] and as precursors for the preparation of superconducting materials.[13] Thus, enormous efforts are being made in the synthesis and characterization of copper(I) cyanides to explore their construction of networks and materials with novel functional properties.[14–16] Usually, copper(I) cyanides are synthesized through the reaction of Cu(CN) with organoamine ligands. However, recently, these types of complexes have been synthesized using redox reactions between copper salts and organoamines via hydrothermal method.[16,17] Originally, we intended to prepare mixed-metal Cu–Fe cyanide complexes by the hydrothermal reaction of 1,10-phen, $Cu(NO_3)_2$ and $K_3[Fe(CN)_6]$; however, unexpectedly, we obtained a variety of one- and two-dimensional materials, namely $[Cu_3(CN)_3(phen)]_n$ (**1**) and $[Cu(CN)(phen)]_n$ (**2**).

RESULTS AND DISCUSSION

Compound **1** was prepared as yellow-orange crystals in ca. 20–25% yield from the reaction of $Cu(NO_3)_2\cdot 3H_2O$, $K_3[Fe(CN)_6]$, phen and H_2O in the mole ratio 1 : 1:1.5 : 600 at 160 °C for 24 h. Element analysis and X-ray data showed the composition to be $[Cu_3(CN)_3(phen)]$. Compound **2,** as a red phase, cocrystallized with **1**, and was identified as [Cu(CN)(phen)]. In the reaction, we found that the yields of **1** and **2** showed a significant dependence on the reaction time. Within 15 h, compound **1** was the primary reaction product, but after 2 days compound **1** transformed completely into compound **2**, indicating that compound **1** is kinetically stable and compound **2** is thermodynamically stable. The characteristic peak cyano measurements were observed by IR for both complexes in the region of 2100–2160 cm^{-1}. Two characteristic peaks were observed by ESCA at 937.08 and 957.05 eV, respectively, indicating that compounds **1** and **2** both contain copper(I) centers (see Scheme 1), which suggests that $K_3[Fe(CN)_6]$ provides cyano groups for compound **1** and **2** in this reaction and copper(II) ions are reduced. This is explained through the use of the stability constants of $K_3[Fe(CN)_6]$ and CuCN. At room temperature, the stability constant of $K_3[Fe(CN)_6]$ ($\log \beta_6 = 42$) is much larger than that

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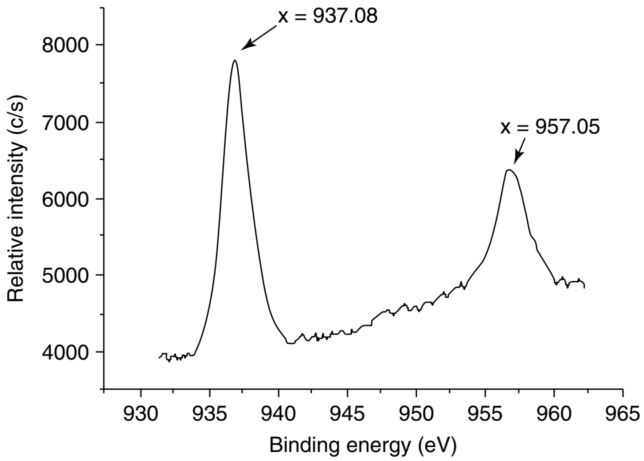

Scheme 1. Electronic energy plot for **1** and **2**.

of CuCN ($\log \beta_4 = 30.3$), indicating that it is very stable in solution. Because heating promotes hydrolysis of $Fe(H_2O)_6^{3+}$ ions in solution, CN^- anions are released slowly from $[Fe(CN)_6]^{3-}$ anions at high temperature. On the other hand, free CN^- anions from $[Fe(CN)_6]^{3-}$ ions in solution can bind to copper(I) ions, leading to formation of product, which also speeds decomposition of $[Fe(CN)_6]^{3-}$ anions.

As shown in Figure 1, the asymmetric unit of **1** contains three-coordinate $\{Cu(CN)_2\}$ (Cu2) sites, four-coordinate $\{Cu(CN)_3\}$ (Cu3) sites and three-coordinate {Cu(CN)(phen)} (Cu1) sites. The Cu1 atom presents a triangular planar geometry arising from two nitrogen atoms of a chelating phen ligand (N1 and N2) and one C atom from CN group (C13); the Cu1–N and Cu1–C13 distances are 1.985(7)–2.085(6) and 1.832(8) Å, respectively. The coordination geometry of the Cu3 atom can also be described as being coordinated with Cu2 atom, as a distorted tetrahedron geometry defined by three X^- ions provided by three CN^- ions [N–Cu3 (or C), 1.880(6)–1.690(7) Å; N–Cu3–N (or C), 112.4(3)–129.7(3)°] (X represents the C or N atoms of CN^-), whereas the Cu2 atom is coordinated to two cyano groups [N–Cu (or C), 1.830(7)–1.858(7) Å].

It is noteworthy that the twisted one-dimensional infinite chain forms through two CN^- ions of these three as the bridges to alternately link the tetrahedron geometry Cu3 and the three-coordinate Cu2 sites. The remaining CN^- ion projects from the chain and further coordinates to a $[Cu1(phen)^+]$ side arm. As shown in Fig. 2, the chain exhibits a novel A–A–B–B pattern [namely the two-coordinate (A) and three-coordinate sites (B) of the monovalent Cu ions repeat in this pattern],[18] which is different from those of related complexes,[16,19,20] such as $[Cu_3(CN)_3(2,2'\text{-bpy})]\cdot 0.1H_2O$,[19] $[Cu_3(CN)_3(phen)]$[19] and $[Cu_4(CN)_4(biquin)_2]$[16] (A–B–A–B pattern) (2, 2′-bpy = 2, 2′-bipyridine, phen = 1,10-1,10-phenanthroline, biquin = 2, 2′-biquinoline); $[Cu_3(CN)_3(biquin)_2]$ (A–C–C–A–C–C

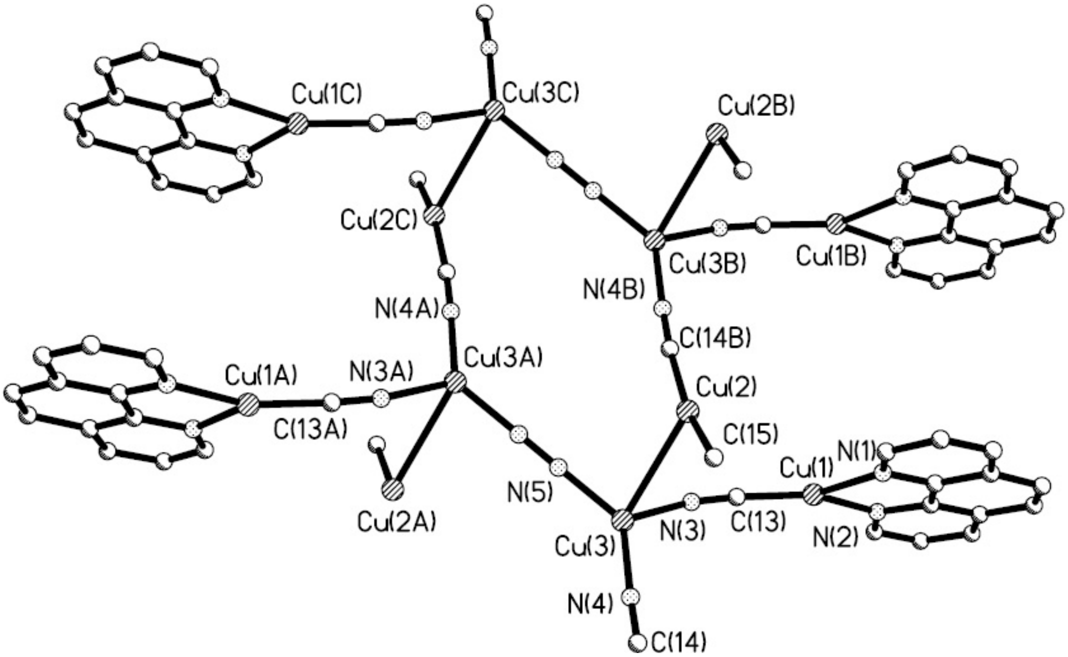

Figure 1. Part of two-dimensional sheet in compound **1** with 30% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu3–N5, 1.880(6); Cu3–N4, 1.912(9); Cu3–N3, 1.969(7); Cu3–Cu2, 2.8920(17); Cu2–C14, 1.830(7); Cu2–C15, 1.858(7); Cu1–C13, 1.832(8); Cu1–N2, 1.985(7); Cu1–N1, 2.085(6); N5–Cu3–N4, 129.7(3); N5–Cu3–N3, 117.8(3); N4–Cu3–N3, 112.4(3); N5–Cu3–Cu2, 82.1(3); N4–Cu3–Cu2, 127.2(2); N3–Cu3–Cu2, 61.4(2); C14–Cu2–C15, 161.6(4); C14–Cu2–Cu3, 117.6(3); C15–Cu2–Cu3, 78.9(3); C13–Cu1–N2, 151.7(3); C13–Cu1–N1, 125.2(3); N2–Cu1–N1, 82.4(3).

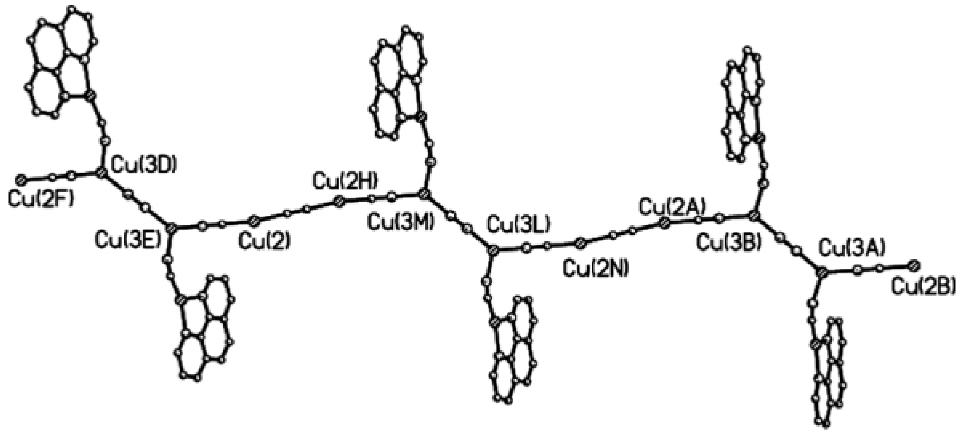

Figure 2. View of one-dimensional chain bridged by Cu–CN interaction with [Cu(CN)(phen)] groups.

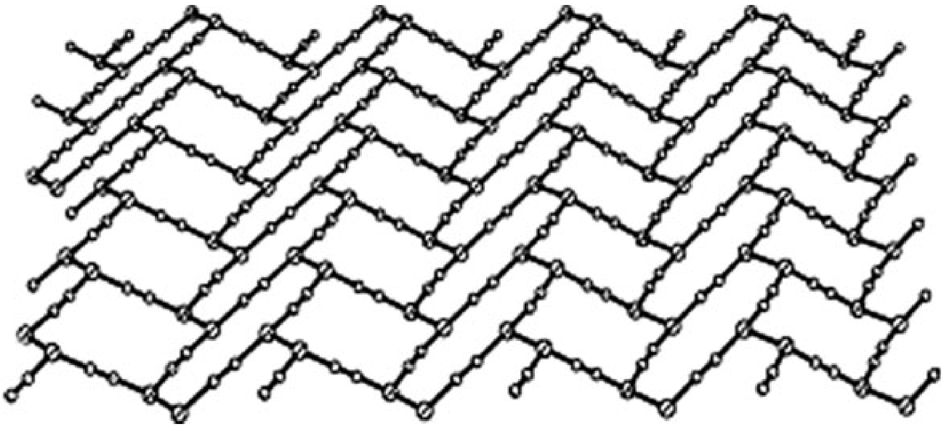

Figure 3. View of two-dimensional folded layer formed by cyano-bridged one-dimensional chains joined by Cu(I)–Cu(I) bonds along the ac plane.

pattern),[19] $[Cu_2(CN)_2(dpbp)]$ (A–C–A–C pattern)[19] (dpbp = 4, 4′-diphenyl-2,2′-bipyridine, C denotes the four-coordinate site) and [Cu(CN)(dmphen)] (C–C–C pattern)[20] (dmphen = 2,9-dimethyl-1,10-phenanthroline). In addition, one-dimensional infinite chains are held together by Cu–Cu interactions [Cu3–Cu2 2.8920(17) Å] resulting in two-dimensional infinite folded layers of hexagonal meshes with [Cu1(CN)(phen)] groups projecting from the chains. This is distinguished from a two-dimensional Cu–CN network for $[Cu_3(en)_2(CN)_4]\cdot 6H_2O$,[22] $K[Cu_2(CN)_3]\cdot H_2O$.[22] and $[\{Cu_2(bpy)_2(CN)\}Cu_5(CN)_6]$.[16] Furthermore, in the two-dimensional folded sheet, there is a dihedral angle of 27.9° between the two folded sides and the rings which present two different conformations of the chair type and hexagonal planar type (see Fig. 3). Owing to the interdigitation of the neighboring phen rings, two-dimensional layers stack in an orderly way on the c-axis leading to three-dimensional networks with large heart-like channels filled with the coordinated phen. Furthermore, weak face-to-face π–π interactions from the interdigitation of the phen rings of neighboring two-dimensional sheets play crucial roles in the formation and stabilization of the three-dimensional networks (Fig. 4). The distances of the phen rings from neighboring two-dimensional sheets is 3.49 Å.

The structure of **2** consists of an infinite helix chain formed by $\{Cu(phen)\}^+$ unit joined by CN^- groups. Although Cu–CN helix chain structures have been reported,[20], compound **2** exhibits a different space group, $P322_1$, compared with those of previously reported complexes, which contain the space groups $P3_1$.[20] The copper atom is bound to the cyanide carbon and nitrogen atoms and two nitrogen atoms from phen. The Cu–N (from CN) and Cu–N (from phen) distances of 1.866(6) and 2.051(6) Å are shorter than those of reported complexes[20] (see Fig. 5).

We now hope to extend this work to explore copper(I) and other transmetal or rare earth metals mixture complexes, and also their application properties, such as electronic conductance and catalysis.

EXPERIMENTAL SECTION

$[Cu_3(CN)_3(phen)]$ (**1**) and [Cu(CN)(phen)] (**2**) were prepared as yellow–orange lamellar crystals and red–black blocks

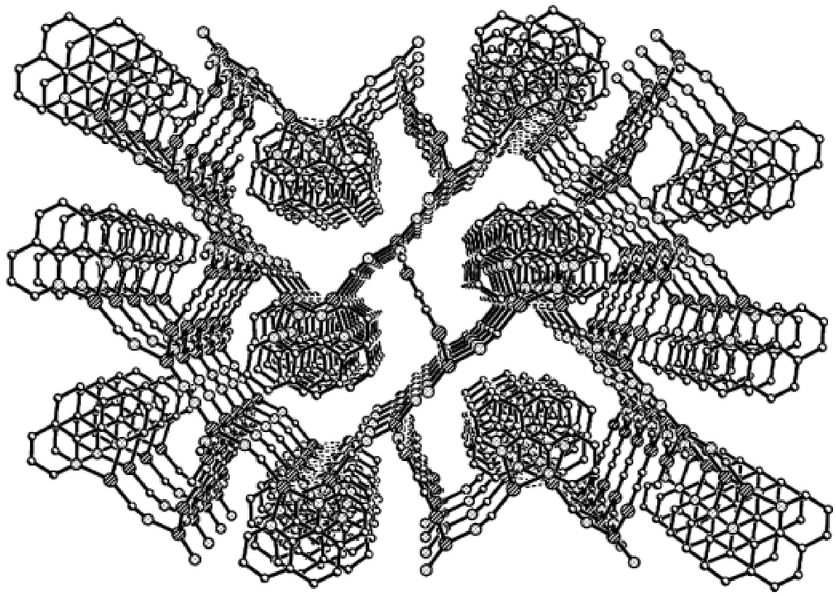

Figure 4. Packing diagram of part of compound **1**.

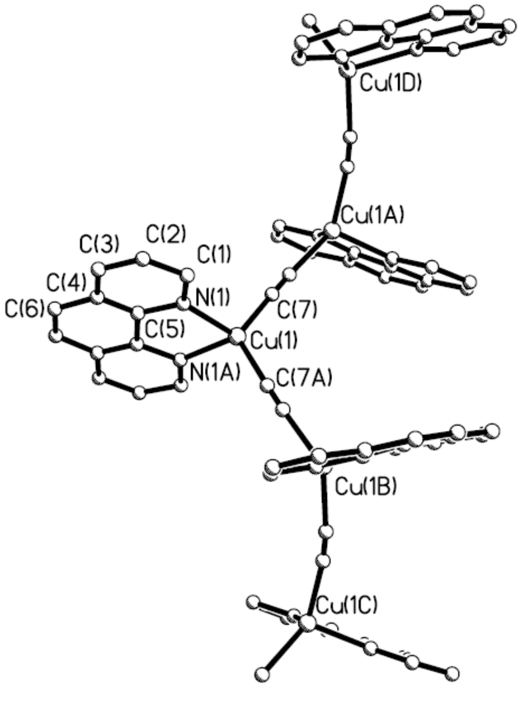

Figure 5. Part of **one-dimensional** infinite helix chain in compound **2** with 30% thermal ellipsoids. Selected bond distances (Å) and angles (deg): Cu1–C7, 1.866(6); Cu1–N2, 1.866(6); Cu–N2 (C2), 1.866(6); Cu–N1, 2.051(6); Cu1–N1, 2.051(6); N2–C7, 1.186(13); N2 (C2)–N2 (C2), 1186(13); C7–Cu1–N2, 124.7(4); N2–Cu1–N2(C2), 124.7(4); C7–Cu1–N1, 107.2(3); N2–Cu1–N1, 107.2(3); N2 (C2)–Cu1–N1, 114.9(3); C7–Cu1–N1, 114.9(3); N2–Cu1–N1, 114.9(3); N2–Cu1–N1, 107.2(3); N1–Cu1–N1, 78.8(4).

crystals, respectively, from the hydrothermal reaction of $Cu(NO_3)_2 \cdot 3H2O$ (1.25 g 5.0 mmol), $K_3[Fe(CN)_6]$ (0.82 g, 2.5 mmol) and phen (0.98 g, 5 mmol) and H_2O (20 ml, 1.11 mol) in a Parr acid digestion vessel of 23 ml volume and heated at 160 °C for 24 h. After cooling to room temperature, a mixture of lamellar yellow crystals of **1** and block-like red–back crystals of **2** was recovered in 46% total yield.

*Element analysis for **1**. Calcd (%)*

C 40.10, N 15.60, H 2.23. Found (%): C 39.86, N 15.68, H 2.17. IR (KBr) (cm^{-1}): 3441.36m, 2156.85w, 2140.31m, 2127.11m, 2112.40s, 1621.27w, 1509.74m, 1420.43m, 1384.36s, 843.82s, 723.74s; crystal data for lamellar yellow crystal $[Cu_3(CN)_3(phen)]$ (**1**): monoclinic, space group P21/C, $M = 448.9(6)$, $a = 9.602(2)$, $b = 23.373(6)$, $c = 6.888(17)$ Å, $\beta = 98.749(5)$, $V = 1528.0(6)$ Å^3, $Z = 4$, 3562 independent measured reflections, 2274 independent observed reflections [$I > 2\sigma(I)$, $2\theta_{\max} = 51.98°$]. A total of 208 parameters, F^2 refinement, $R = 0.0898$ (observed), $wR_2 = 0.230$.

*Element analysis for **2**. Calcd (%)*

C 57.36, N 15.44, H 3.68. Found (%): C 57.18, N 15.60, H 3.59. IR (KBr) (cm^{-1}): 3058.9m, 3033.8w, 2109.2s, 1620.5m, 1584.5m, 1569m, 1506.3m, 1493.2m, 1418.9s, 1139.9m, 842.6s, 727.9s; Crystal data for block-like red–back crystals [Cu(CN)(phen)] (**2**): monoclinic, space group: $P3(2)2_1$, $M = 272.6(6)$, $a = 9.043(3)$, $b = 9.043(3)$, $c = 11.625(8)$ Å, $\alpha = \beta = 90.0°$, $\gamma = 120.0°$, $V = 823.3(7)$ Å^3, $Z = 3$, 819 independent measured reflections, 2638 independent observed reflections [$I > 2\sigma(I)$, $2\theta_{\max} = 48.22°$]. A total of 78 parameters, F^2 refinement, $R = 0.0519$ (observed), $wR_2 = 0.1343$ (all data).

Crystallographic data for compound **1** and **2** have been deposited with the Cambridge Crystallogra-phic Data Centre as supplementary publication numbers. CCD numbers for **1** and **2**: 226 175 and 225 416, respectively. The data can be obtained from 12 Union Road, Cambridge CB2 1EZ (Tel: +44 1223 762 910 or +44 1223 336 408; Fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

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