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Hydrothermal Syntheses and Structures of Two Mixed-Valence Copper(I,II) 2-Pyrazinecarboxylate Coordination Polymers

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Replacement of linear ligand L in $Cu^{I}XL$ system (X = halide or pseudohalide; L = 4,4′-bipyridine or pyrazine) by neutral species $Cu(pzc)_2(H_2O)_x$ (pzc = 2-pyrazinecarboxylate) resulted in mixed-valence Cu(I,II) coordination polymers $[Cu_2(pzc)_2Br(H_2O)]_n$ (**1**) and $[Cu_3(pzc)_2(CN)_2(H_2O)_2{\cdot}2H_2O]_n$ (**2**). Complex **1** has two-dimensional (4,4) topological layer constructed by $[CuBr]_n$ chains and $Cu(pzc)_2(H_2O)$ species, while **2** has a three-dimensional framework formed by linkage of two-dimensional (6,3) layers via ligand-unsupported Cu(I)–Cu(I) interactions. The two-dimensional (6,3) layer in **2** is constructed by zigzag $[CuCN]_n$ chains and $Cu(pzc)_2(H_2O)_2$ species. Cyanides in **2** were produced by oxidative desulfation of SCN^- anions.

Introduction

There has been much research interest in metal coordination polymers because they have important implications for the development of new functional materials in molecular selection, ion exchange, electrical conductivity, catalysis, and novel magnetic propeties.[1] Interest in the area has led to studies of the roles of the metal ions (coordination geometry), the ligands (functionality and steric and electronic properties), and the anions (size and coordinating ability) in the formed structures. Halides and pseudohalides have been of interest for their structural diversity and novel properties.[2,3] For example, metal halides form a variety of structure types, among which perovskites have tunable electronic, optical, and magnetic properties.[2] Metal cyanides, especially the Prussian blue type materials, are of interest for interesting magnetic coupling.[3] In addition, metal cyanides exhibit features ranging from reversible oxygen binding to chiral networks for catalysis.[4]

We have been interested in developing mixed-valence Cu(I,II) complexes under hydrothermal conditions due to their superior electronic, optical, and magnetic properties[5] and found that not only Cu(II) ions can be reduced to Cu(I) in the presence of *N*-containing ligands but also Cu(II) ions often play a catalytic role in hydrothermal ligand reactions. Particularly, we established that Cu(II) ions under hydrothermal conditions can catalyze hydroxylation reaction of 1,10-phenanthroline and 2,2′-bipyridine, which is quite difficult to occur under routine synthetic conditions.[5] Considering that many Cu(I,II) complexes contain *N*-heterocycle and carboxylate ligands, we deduce that 2-pyrazinecarboxylate (pzc) is possibly a good ligand for mixed-valence Cu(I,II)complexes.[6,7] Besides, we note that the neutral species

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$Cu(pzc)_2(H_2O)_x$ ($x = 0, 1, 2$) can function as ligands because they possess all properties of linear *N*,*N*′ extra bidentate ligands such as 4,4′-bipyridine and pyrazine.[8] Furthermore, it is well-established that the hydrothermal reaction of copper halide/pseudohalide and 4,4′-bipyridine/pyrazine usually produces two-dimensional Cu(I) coordination polymers based on chainlike $[CuX]_n$ units (X = Cl, Br, I, CN).[9] Thus, we may expect the replacement of linear ligand L in the Cu^IXL system (L = 4,4′-bipyridine or pyrazine) by neutral species $Cu(pzc)_2(H_2O)_x$ will form mixed-valence Cu(I,II) coordination polymers. The expectation is realized in two mixed-valence copper(I,II) complexes $[Cu_2(pzc)_2Br(H_2O)]_n$ (**1**) and $[Cu_3(pzc)_2(CN)_2(H_2O)_2{\cdot}2H_2O]_n$ (**2**). Compound **1** shows a two-dimensional (4,4) topological layer constructed by linkage of crankshaft $[CuBr]_n$ chains by $Cu(pzc)_2(H_2O)$, while **2** has three-dimensional framework constructed by linkage of two-dimensional (6,3) layers via ligand-unsupported Cu(I)−Cu(I) interactions. The two-dimensional (6,3) layer is constructed by linkage of zigzag $[CuCN]_n$ chains by $Cu(pzc)_2(H_2O)_2$.

Experimental Section

Materials and Methods. All the starting materials were purchased commercially reagent grade. Elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 400−4000 cm−1 on a Nicolet 5DX spectrometer.

Syntheses. (a) $[Cu_2(pzc)_2Br(H_2O)]_n$ (1). A mixture of $CuBr_2$ (0.267 g, 1.2 mmol), Hpzc (0.065 g, 0.5 mmol), and water (7 mL) in a mole ratio of 2.4:1:780 was sealed in a 15 mL Teflon-lined stainless container, which is heated to 160 °C and held for 108 h. After cooling to room temperature, black block crystals of **1** were recovered in 62% yield based on Hpzc. Anal. Calcd for **1**, $C_{10}H_8BrCu_2N_4O_5$: C, 25.49; H, 1.71; N, 11.89. Found: C, 25.44; H, 1.77; N, 11.80. IR (KBr, $cm^{-}1$): 3428m, 3082w, 1628s, 1576w, 1419m, 1358s, 1281m, 1157m, 1044s, 891w, 852m, 791m, 738w, 537w.

(b) $[Cu_3(pzc)_2(CN)_2(H_2O)_2{\cdot}2H_2O]_n$ (2). A mixture of $Cu_2(OH)_2CO_3$ (0.3 mmol), Hpzc (0.3 mmol), NH_4SCN (0.6 mmol), and water (7 mL) in a mole ratio of 1:1:2:780 was stirred, to which two drops of aqueous solution of $HClO_4$ (2 M) were added. The resulting solution was transferred and sealed in a 15 mL Teflon-lined stainless container, which is heated to 180 °C and held for 120 h. After cooling to room temperature, brown block crystals of **2** (20% yield based Hpzc), colorless CuSCN,[10] and uncharacterized yellow powder were recovered. Anal. Calcd for **2,** $C_{12}H_{14}N_6Cu_3O_8$: C, 25.70; H, 2.52; N, 14.98. Found: C, 25.66; H, 2.56; N, 14.94. IR (KBr, $cm-^{1}$): 3436s, 2919w, 2348w, 2165s, 2079w, 1627s, 1411s, 1346m, 1174m, 1034mm, 861m, 7743m, 592w, 463w.

Table 1. Crystal Data and Structure Refinement Parameters for **1** and **2**

	complex **1**	complex **2**
empirical formula	$C_{10}H_8BrCu_2N_4O_5$	$C_{12}H_{14}Cu_3N_6O_8$
fw	471.19	560.91
temp (K)	298(2)	298(2)
λ (Å)	0.710 73	0.710 73
cryst syst	orthorhombic	monoclinic
space group	Pbca	*C*2/*c*
a (Å)	13.156(3)	7.0895(12)
b (Å)	7.7171(17)	9.5172(16)
c (Å)	26.148(6)	13.843(2)
β (deg)	90	100.527(3)
V ($Å^3$)	2654.7(10)	918.3(3)
Z	8	2
ρ_{calc} (g cm^{-3})	2.358	2.029
μ (mm^{-1})	6.244	3.499
F(000)	1832	558
cryst size (mm)	0.20 0.10 0.05	0.17 0.07 0.03
θ (deg)	1.56 to 28.34	2.99 to 26.00
reflcn	17271	2111
indep reflcn	3188	955
T_{max}/T_{min}	0.7454 and 0.3681	0.9023 and 0.5877
data/restraint/param	3188/0/199	955/12/92
goodness-of-fit on F^2	1.111	1.205
R1[a]	0.0560	0.0739
wR2[b]	0.1712	0.2038
largest peak and hole (e $Å^{-3}$)	1.418 and −0.824	0.889 and −0.827

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Crystallographic Studies. X-ray single-crystal diffraction data for complexes **1** and **2** were collected on a Bruker SMART APEX CCD diffractometer at 293(2) K using Mo Kα radiation ($\lambda \sim$ 0.710 73 Å) by the ω scan mode. The program SAINT was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.[11] All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms of pzc in **1** were generated theoretically onto the specific carbon atoms and refined isotropically with fixed thermal factors. Two hydrogen atoms of pzc in **2** were generated theoretically and refined isotropically with fixed thermal factors, while the third hydrogen atom cannot be generated theoretically because of the disorder of carboxylate group. The hydrogen atoms of water molecules in **1** and **2** were not found. The C/N atoms of the cyano group in **2** occupy the same sites and are indistinguishable. Further details for structural analysis are summarized in Table 1. Selected bond lengths and bond angles are shown in Table 2.

Results and Discussion

Description of Structures. Compound **1** crystallizes in orthorhombic space group *Pbca* and the asymmetric unit consists of 22 non-hydrogen atoms as shown in Figure 1. All atoms localize in general positions. There are two distinct copper ions, two pzc groups, one bromide, and one water molecule. The Cu(1) shows a distorted tetrahedral geometry coordinated by two nitrogen atoms from two pzc and two bromide ions. The Cu(1)−N distances are 1.992(5) and 2.008(5) Å, and Cu(1)−Br distances are 2.4939(13) and 2.7554(14) Å. The L−Cu(1)−L (L = N, Br) angles are in the range of 97.92(16)−143.9(3)°. The Cu(2) adopts a typical square-pyramidal coordination geometry, coordinated by two nitrogen and two oxygen atoms from two pzc ligands in equatorial plane and one water molecule at axial site. The Cu(2)−L (L = N, O) distances in the equatorial plane are

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Table 2. Selected Bond Lengths (Å) and Angles (deg)

Complex **1**[a]			
Cu(1)−Br(1)	2.4939(13)	Cu(2)−N(2a)	1.992(5)
Cu(1)−Br(1b)	2.7554(14)	Cu(2)−N(3)	2.008(5)
Cu(2)−O(1a)	1.947(5)	Cu(2)−O(1W)	2.231(6)
Cu(2)−O(4)	1.953(5)		
N(1)−Cu(1)−N(4)	143.9(3)	O(4)−Cu(2)−N(2)	96.8(2)
N(1)−Cu(1)−Br(1)	101.62(18)	O(1a)−Cu(2)−N(3)	97.7(2)
N(4)−Cu(1)−Br(1)	99.33(17)	O(4)−Cu(2)−N(3)	82.32(19)
N(1)−Cu(1)−Br(1b)	99.02(16)	N(2)−Cu(2)−N(3)	176.3(3)
N(4)−Cu(1)−Br(1b)	97.92(16)	O(1a)−Cu(2)−O(1W)	94.2(2)
Br(1)−Cu(1)−Br(1b)	115.63(4)	O(4)−Cu(2)−O(1W)	94.3(2)
O(1a)−Cu(2)−O(4)	171.5(2)	N(2a)−Cu(2)−O(1W)	92.6(2)
O(1a)−Cu(2)−N(2a)	82.7(2)	N(3)−Cu(2)−O(1W)	91.0(2)
Complex **2**[b]			
Cu(1)−O(1a)	1.964(10)	Cu(1)−O(1Wa)	2.393(11)
Cu(1)−O(1)	1.964(10)	Cu(2)−X(1c)	1.870(7)
Cu(1)−N(1a)	1.995(9)	Cu(2)-X(1)	1.870(7)
Cu(1)−N(1)	1.995(9)	Cu(2)−N(2)	2.164(8)
Cu(1)−O(1W)	2.393(11)	X(1)−X(1d)	1.162(15)
O(1a)−Cu(1)−O(1)	180.0(6)	O(1a)−Cu(1)−O(1Wa)	93.8(4)
O(1a)−Cu(1)−N(1a)	76.1(3)	O(1)−Cu(1)−O (1Wa)	86.2(4)
O(1)−Cu(1)−N(1a)	103.9(3)	N(1a)−Cu(1)−O(1Wa)	90.7(4)
O(1a)−Cu(1)−N(1)	103.9(3)	N(1)−Cu(1)−O(1Wa)	89.3(4)
O(1)−Cu(1)−N(1)	76.1(3)	O(1W)−Cu(1)−O(1Wa)	180.0(5)
N(1a)−Cu(1)−N(1)	180.0(5)	X(1c)−Cu(2)−X(1)	150.5(5)
O(1a)−Cu(1)−O(1W)	86.2(4)	X(1c)−Cu(2)−N(2)	104.7(2)
O(1)−Cu(1)−O(1W)	93.8(4)	X(1)−Cu(2)−N(2)	104.7(2)
N(1a)−Cu(1)−O(1W)	89.3(4)	X(1d)−X(1)−Cu(2)	175.7(10)
N(1)−Cu(1)−O(1W)	90.7(4)		

[a] Symmetry codes: (a) $x, -y + 1/2, z + 1/2$; (b) $-x + 3/2, y + 1/2, z$. [b] Symmetry codes: (a) $-x + 2, -y, -z$; (b) $-x + 2, y, -z$; (c) $x, -y, z$; (d) $-x + 3/2, -y + 1/2, -z + 1$.

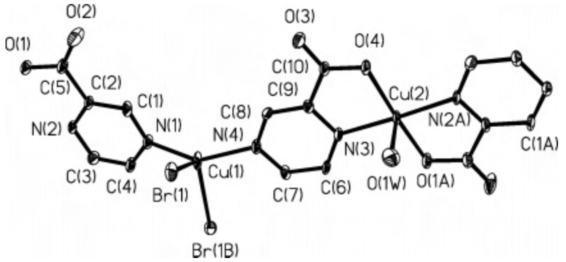


Figure 1. View of the coordination environments of copper atoms in **1** with 35% thermal ellipsoid probability.

in the range of 1.947(5)−2.008(5) Å. The axial longer Cu(2)−O(1w) distance of 2.228(6) Å may be attributed to strong Jahn−Teller effect of Cu(II) ion. The Cu(II) ion with d^9 configuration tends to form square pyramidal or elongated octahedral coordination geometry because of strong Jahn−Teller effect, but the Cu(I) ion with d^{10} configuration tends to form trigonal or tetrahedral coordination geometry. The coordination symmetry of copper ions in combination with charged balance indicates that in **1** Cu(1) is monovalent and Cu(2) is divalent.

In **1**, the alternate linkage of monovalent Cu(1) and bromide ions generates a crankshaft $[CuBr]_n$ chain as shown in Figure 2a. The adjacent Cu^I and Cu^I distance in the $[CuBr]_n$ chain is 4.475 Å. The $[CuBr]_n$ chains are further linked by $Cu^{II}(pzc)_2(H_2O)$ via Cu(1)−N coordination interactions that result in a two-dimensional layer with (4,4) topology, as shown in Figure 2b and Chart 1. Within the (4,4) topological layer, the four-connected nodes are provided by Cu(I) ions, while two-connected connectors are bromide ions and $[Cu^{II}(pzc)_2(H_2O)]$.

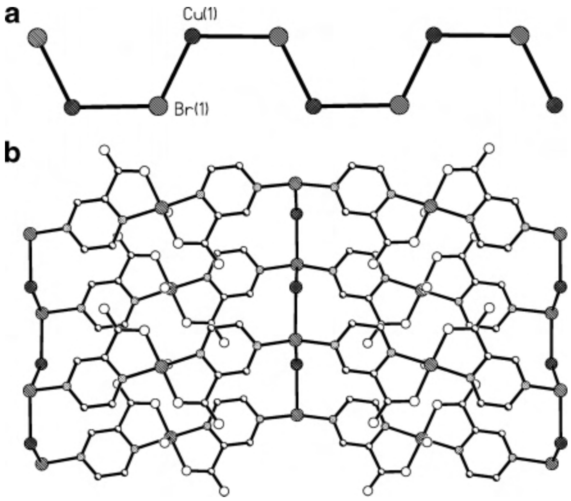
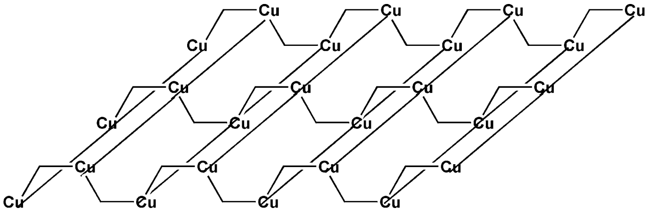


Figure 2. View of the crankshaft $[CuBr]_n$ chain (a) and the two-dimensional (4,4) layer (b) in **1**.

Chart 1. Schematic View of the (4,4) Topological Layer in **1**



Compound **2** crystallizes in monoclinic space group *C*2/*m* and the asymmetric unit consists of two crystallographically independent copper sites, one C/N site of cyanide, half pzc, and two water molecules as shown in Figure 3a. The C(2) and C(3) atoms localize general positions. The Cu(1) localizes at the crossing point of the C_2-axis and the mirror plane with site occupancy of 0.25. The crystallographic mirror plane passes through Cu(2), N(1), and N(2) sites and bisects the pzc ligand. This gives rise to Cu(2), N(1), and N(2) with site occupancy of 0.5 and disorder of the carboxyl group (Figure 3b). The crystallographic mirror plane also causes the disorder of O(1w). The two indistinguishable C/N atoms in the cyanide group occupy the same sites and thus are labeled X(1). The X−X distance is 1.162(15) Å, which is the typical C≡N bond length.[12] As shown in Figure 3c, Cu(1) adopts elongated octahedral coordination geometry, coordinated by two N and two O atoms in equatorial plane and two water molecules in axial positions. The Cu(1)−N and Cu(1)−O distances in equatorial plane are 1.964(10) and 1.995(9) Å, respectively. The axial longer Cu(1)−O(1w) distance of 2.393(11) Å is caused by strong Jahn−Teller effect of the Cu(II) ion. The Cu(2) has trigonal-planar geometry being surrounded by one pyrazine nitrogen atom and two C/N atoms from cyanide groups. The Cu(2)−N(2) and Cu−X(1) distances are 2.164(8) and 1.870(7) Å, respectively. In **2**, the alternate linkage of Cu(2) and cyanide ions generate zigzag $[Cu^I(CN)]_n$ chains, and the adjacent $[Cu^I(CN)]_n$ chains are further linked together by metalloligands

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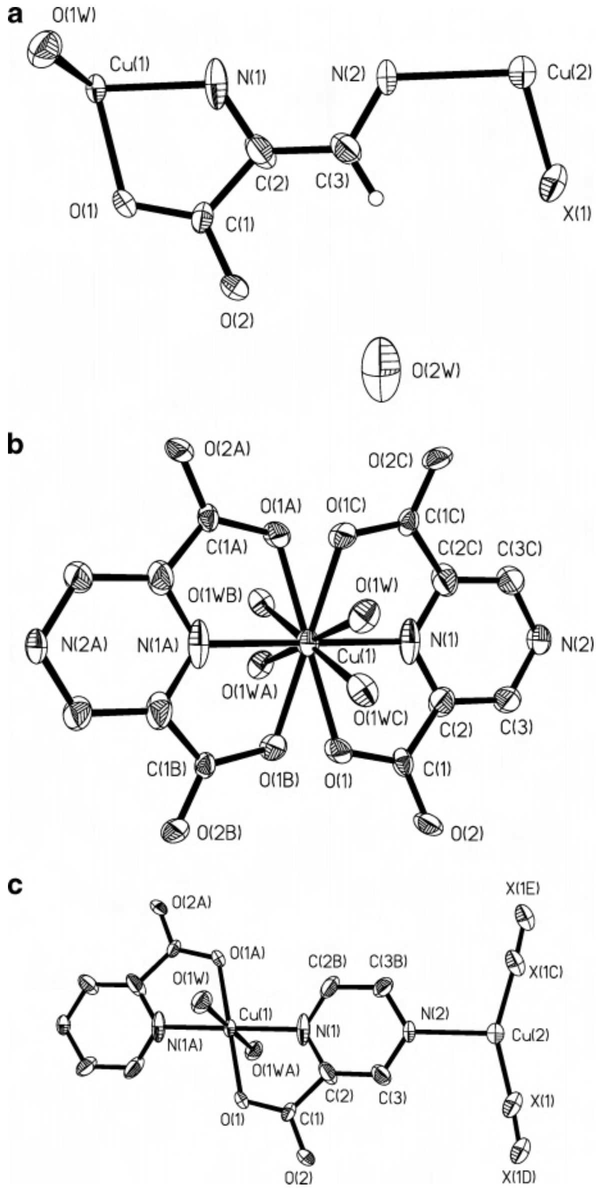

Figure 3. View of asymmetric unit (a), disordered carboxylate groups (b), and coordination environments of copper atoms (c) in **2** with 35% thermal ellipsoid probability.

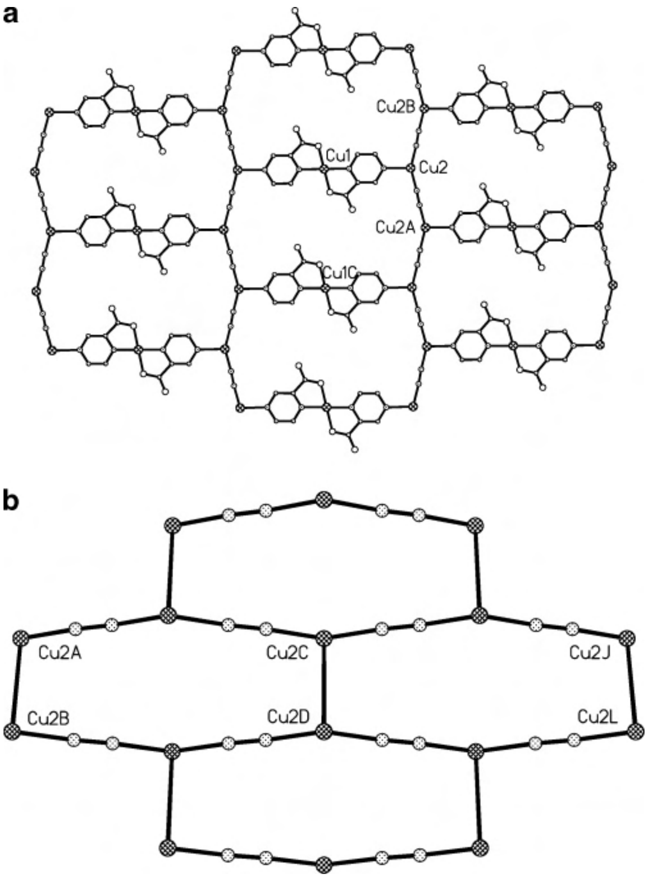

Figure 4. View of the two-dimensional (6,3) layer (a) and ligand-unsupported Cu(I)···Cu(I) interactions (b) in **2**.

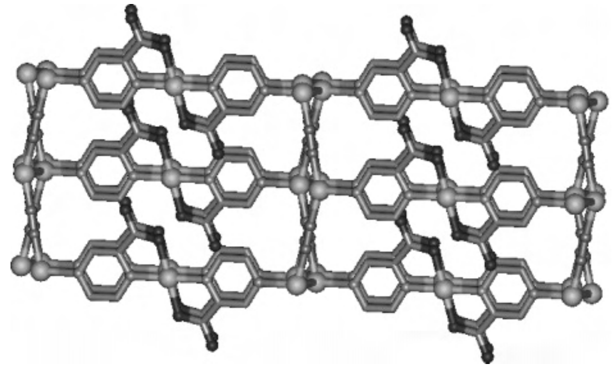

Figure 5. View of the three-dimensional framework of **2**.

$Cu^{II}(pzc)_2(H_2O)_2$ via Cu(2)−N(2) coordination interactions to result in a two-dimensional layer with (6,3) topology (Figure 4a). Within the (6,3) topological layer, the nodes are provided by monovalent Cu(2) ions while connectors are cyanides and $Cu^{II}(pzc)_2(H_2O)_2$. Actually, there are ligand-unsupported Cu(I)−Cu(I) bonding interactions with a Cu(2)···Cu(2) distance of 3.051(3) Å, as shown in Figure 4b. The adjacent two-dimensional (6,3) layers are linked together by ligand-unsupported Cu(I)−Cu(I) bonding interactions into a three-dimensional framework (Figure 5). Extensive attention has been focused on the attractive interactions between formally closed-shell d^{10} metal centers.[13,14] The term "cuprophilicity" has been coined to describe the Cu(I)−Cu(I) bonding interactions, which play an important role in optical and electronic properties of polynuclear Cu(I) complexes and have been recently confirmed by Ramam spectrum in dinuclear Cu(I) complexes.[15] However, most structurally characterized short Cu(I)−Cu(I) contacts in Cu^I complexes are associated with a ligand-bridge,[16] and only a few ligand-unsupported complexes have been reported.[17] The ligand-unsupported Cu(I)−Cu(I) distance 3.051(3) Å is slightly

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longer than those in clusterlike complexes [CuL][$CuCl_2$] {L = 1,1′-bis(2-pyridyl)octamethylferrocene; Cu···Cu distance, 2.810(2) Å}[17a] and $[CuL]_3$ {HL = 2-[3(5)-pyrazolyl]pyridine; Cu···Cu, 2.905(3) Å}[17b] but is close to those in complex $Cu_2(obpy)_2$ {Hobpy = 6-hydroxyl-2,2′-bipyridine; Cu···Cu, 2.986 and 2.993 Å}.[17c] However, the ligand-unsupported Cu(I)−Cu(I) distance in **2** is shorter than the Cu···Cu distance of 3.375 Å observed in complex $Cu_2(ophen)_2$ {Hophen = 2-hydroxyl-1,10-phenanthroline}.[4b]

IR Spectra. The $O-H_{water}$ stretching vibrations in the IR spectra of **1** and **2** are indicated by a broad band at 3442 and 3436 cm^{-}1, respectively. The antisymmetric and symmetric stretching vibrations of carboxyl groups in **1** are characterized by two strong peaks at 1628 and 1358 cm^{-}1, respectively. The corresponding antisymmetric and symmetric stretching vibrations of carboxyl groups in **2** are featured at 1627 and 1411 cm^{-}1. In addition, a strong peak at 2165 cm^{-}1 in **2** is typical of vibration absorption of cyanide.[18]

Synthesis Chemistry. The hydrothermal method has recently been adopted in the preparation of coordination complexes. There are a variety of hydrothermal parameters such as time, temperature, pH value, and molar ratio of reactants, and small changes in one or more of the parameters can have a profound influence on the final reaction outcome. The control over reaction temperature around 160 °C and a pH value below 2 are critical to the formation of **1**. For example, hydrothermal treatment of a mixture of $CuBr_2$ and Hpzc (2.4:1) at 160 °C resulted in crystals of **1** in single phase, while the same reaction at 170 °C produced crystals of **1** and an unexpected byproduct, $[Cu^I(pyrazine)Br]_n$.[9] In addition, similar reactions at a higher pH value formed mononuclear complex $Cu(pzc)_2$ or $Cu(pzc)_2(H_2O)_2$.[11] The decarboxylation mechanism of pzc at a higher temperature (170 °C) to form pyrazine ligand is not clear. However, we note that all reported hydrothermal decarboxylation reactions involve Cu(II) ions which possibly means that Cu(II) ions play a unique catalytic role in the hydrothermal decarboxylation procedure.[19]

As for the synthesis of **2**, influences of the starting materials and pH value are significant. Compound **2** is not available in the absence of NH_4SCN, which indicates that slow formation of cyanide via desulfation of SCN^- is critical in forming single crystals of **2**. Likewise, choosing insoluble $Cu(OH)_2CO_3$ as the Cu(II) source is helpful in decreasing the reaction speed to form single crystals of **2**. Furthermore, maintaining a weak basic condition (pH ≈ 8−9) is also important in the formation of **2**. The formation mechanism of **2** is not clear. However, the existence of sulfate ions in filtrate indicates that the redox reaction of Cu(II) and thiocyanate generating Cu(I), cyanide, and sulfate anions is a key step in the formation of **2**.

$$6Cu^{2+} + SCN^- + 8OH^- \rightarrow 6Cu^+ + CN^- + SO_4^{2-} + 4H_2O$$

The formation of cyanides by oxidation of thiocyanate anions was documented by Schug and co-workers, and their studies also revealed that sulfur atoms of SCN^- are converted into sulfate anions.[20] The redox reaction oxidation of Cu(II) and thiocyanate in **1** is something similar to Yao et al.’s recently reported hydrothermal oxidation of 4-pyridinethiol by Cu(II) to form Cu(I) and sulfate anion.[21]

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Note Added after ASAP: After this paper had been published on the Web (March 23, 2005), it was brought to our attention that the synthesis and structure of $[Cu_2(pzc)_2Br(H_2O)]_n$ was previously published by A. J. Jacobson and co-workers (*J. Solid State Chem.* **2000**, *152*, 174). We regret the omission. Due to a production error, the Web version posted on May 2, 2005, contained erroneous pagination. The Web version published on May 6, 2005, and the print version of the article are correct.

Supporting Information Available: Crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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