Hydrothermal Syntheses, Structures, and Properties of [Cu_3Cl_2CN(pyrazine)] and Copper(I) Halide Pyrazine Polymers

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Crystals of copper halide and pseudohalide compounds with pyrazine are synthesized under hydrothermal conditions. The title compound, [Cu_3Cl_2CNPz] (**1**) (Pz = pyrazine), is a new copper compound exhibiting an unusual -(Cu_3Cl_2)- polymeric stair structural motif and three-coordinate cyanide. Compound **1** crystallizes in the monoclinic space group $P2_1/m$, with $a = 3.6530(7)$ Å, $b = 17.160(3)$ Å, $c = 6.9800(14)$ Å, $\beta = 90.58(3)°$, and $Z = 2$. In addition, the series of complexes [Cu_2X_2Pz] for X = Cl (**2**), Br (**3**), and I (**4**) are also crystallized under hydrothermal conditions. The inorganic polymer [Cu_2Br_2Pz] (**3**) belongs to the triclinic space group $P\bar{1}$, with $a = 6.9671(14)$ Å, $b = 7.849(2)$ Å, $c = 8.099(2)$ Å, $\alpha = 71.69(3)°$, $\beta = 70.71(3)°$, $\gamma = 85.43(3)°$, and $Z = 2$. The structure of **3**, is similar to the recently reported structure for [Cu_2Cl_2Pz] (**2**) (Kawata, S.; Kitagawa, S.; Kumagai, H.; Iwabuchi, S.; Katada, M. *Inorg. Chim. Acta* **1998**, *267*, 143). The third member of the series, [Cu_2I_2Pz], is found to be isostructural on the basis of X-ray powder diffraction results. The lattice parameters are refined from indexed reflections to $a = 7.115(10)$ Å, $b = 8.321(19)$ Å, $c = 8.378(17)$ Å, $\alpha = 71.1(3)°$, $\beta = 67.3(1)°$, and $\gamma = 83.0(2)°$. Electronic spectra show that compounds **1**−**4** have optical band gaps in the range 2.2−2.4 eV. The infrared and Raman spectra as well as the thermal properties of all compounds are presented.

Introduction

There is a well-recognized and rapidly growing class of materials based on the supramolecular assembly of metal, ligand, and anion systems.[1,2] Interest in crystal engineering and the design of new architectures for functional materials has led to studies of the roles of the metal (coordination geometry), the ligand (functionality and steric and electronic properties), and the anion (size and coordinating ability) in the structures formed.[3,4] The first goal has been to determine what topology (i.e., 1-, 2-, or 3-dimensional structure type) is formed for a given set of components.[5,6] Topology is important because properties are highly related to structure. For example, open 3-dimensional nets might function as zeolite[7−10] or mineral mimics[11−15] whereas lower dimensional solids (with layers or chains) often exhibit interesting anisotropic magnetic or electronic properties.[16]

Halides and pseudohalides have been of interest both for their structure-directing abilities and for their novel properties. For example, metal halides form a variety of structure types, such as the metal halide amine perovskites that have tunable electronic, optical, and magnetic properties.[17] Recently, the perovskite $(C_6H_5C_2H_4NH_3)_2SnI_4$ was reported to have promising semiconductor properties for thin-film field effect transistor applications.[18] Another class of metal halide rich amines, with stoichiometries such as $Ag_2I_4(C_8H_{12}N)$, $Ag_6I_8(C_8H_{12}N)$, and $Ag_{44}I_{53}(C_{11}H_{30}N_3)_3$, are known to form rapid ion conductors.[19]

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With similar bonding properties, cyanide is of interest for its ability to act as a mediator for the electronic interaction between metal ions,[20,21] often resulting in interesting magnetic coupling[22] (particularly for the Prussian blue type materials).[23−26] In addition to magnetism, cyanometalate framework structures exhibit features ranging from reversible oxygen binding[27] to chiral networks for catalysis.[28] Copper is one of the prototypical linking metals[29] and, along with cadmium, has been of interest for designing new cyanometalates because of the number of new mineral-like structures that have been discovered.[4,11,30,31]

We have been interested in using hydrothermal synthesis to discover new coordination compounds and explore the interplay between anion and ligand on the structures formed for simple copper frameworks. Hydrothermal synthesis has advantages such as ideal crystal growth conditions (important for structural studies) and the potential for forming metastable phases.[32−34] Molecular assemblies of copper halides[35−37] and copper cyanides[38−43] formed by room-temperature solution routes have been long studied, yet new compounds have been synthesized under hydrothermal conditions.[44−53] Until now, there are no examples of mixed halide−cyanide bridged metal polymers. Using hydrothermal synthesis, we have isolated single crystals of $[Cu_3Cl_2CNPz]$ (**1**) (Pz = pyrazine), which has unusual structural features in metal geometry and ligand coordination and has not yet been synthesized by room-temperature solution routes.

Here we present the synthesis, structure, and properties of $[Cu_3Cl_2CNPz]$ and compare it with the related copper halide pyrazine compounds. We have determined that the compounds $[Cu_2X_2Pz]$ where X = Br (**3**) and I (**4**) both exhibit the commonly found copper halide “stair” polymer structure as seen for X = Cl (**2**).[54] By contrast, the $[Cu_3Cl_2CNPz]$ structure has five-membered -(Cu_3Cl_2)- rings that form the step in this novel stair polymer. Another striking feature in this compound is μ_3-CN coordination. The vibrational spectroscopy of this compound is of particular interest, as there is only one other known compound that has just three-coordinate cyanide with no terminal or linearly bridging CN.

Experimental Section

General Information. The CuX salts (X = Cl, Br, I) and pyrazine were purchased from Aldrich and used without further purification. The copper salts were stored in a glovebox. Deionized water was used for all hydrothermal syntheses. Reactions were performed in 23 mL Teflon-lined stainless steel Parr bombs at 150 °C under autogenous pressure.

Vibrational Spectroscopy. Fourier transform infrared spectra of compounds **1**−**4** were obtained using a Perkin-Elmer 1760 FTIR spectrometer. Single crystals were ground with KBr to form pellets, and spectra were recorded from 4000 to 400 cm^{-1}. Raman spectra were obtained using a Nicolet 760 FT Raman spectrometer with a laser power ranging between 0.17 and 0.24 W for 16−48 scans. In the case of **1**, the sample was ground with KBr to prevent thermal decomposition in the laser.

X-ray Diffraction. Single-crystal X-ray diffraction studies of $[Cu_3Cl_2CNPz]$ and $[Cu_2Br_2Pz]$ were performed on a Bruker CCD 1000 diffractometer with Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The structures were solved and refined with SHEXTL software, version 5. The non-hydrogen atoms were located by direct phase determination and full-matrix least-squares refinement on F^2. Hydrogen atoms were generated theoretically and refined isotropically. The unit cell parameters with data collection details are included in Table 1. Final atomic coordinates and temperature factors and selected bond lengths and angles are reported in Tables 2 and 3.

Phase determinations of polycrystalline samples by X-ray powder diffraction were performed on a Philips MPD-3040 X-ray powder diffractometer with Cu Kα radiation from 5 to 70° in 2θ, with a step size of 0.02 and count times of 1 s, at a power of 40 kV/50 mA. Lattice parameters were calculated using a least-squares refinement.[55]

Thermal Analysis. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) data for $[Cu_2X_2Pz]$ (X = Cl, Br, I) were obtained on an SDT 2960 TA instrument from 10 to 800 °C with a scanning rate of 10 °C/min under flowing nitrogen. The TGA and DTA data for $[Cu_3Cl_2CNPz]$ (**1**) were obtained using an SDT 2960 TA instrument coupled with a mass spectrometer for evolved gas analysis. The scan was run from 10 to 1500 °C at a rate of 20 °C/min under nitrogen.

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Table 1. Crystallographic Data for **1** and **3**

	[$C_5H_4Cl_2Cu_3N_3$] (**1**)	[$C_4H_4Br_2Cu_2N_2$] (**3**)
fw	367.62	366.99
space group	$P2_1/m$	$P\bar{1}$
a (Å)	3.6530(7)	6.9671(14)
b (Å)	17.160(3)	7.849(2)
c (Å)	6.9800(14)	8.099(2)
α (deg)		71.69(3)
β (deg)	90.58(3)	70.71(3)
γ (deg)		85.43(3)
V (Å^3)	435.4(2)	396.75(14)
Z	2	2
T (K)	296	296
λ (Å)	0.710 73	0.710 73
d_{calcd} g/cm^3	2.832	3.072
μ (mm^{-1})	7.83	15.35
final R ($I > 2\sigma(I)$): R1[a], wR2[b]	0.0595, 0.166	0.0732, 0.2048

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR1 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Positional Parameters and U(eq)[a] Values for **1**

	x	y	z	U(eq)
Cu(1)	0.4565(4)	0.6760(1)	0.2492(2)	0.034(1)
Cu(2)	1.1074(6)	0.75	−0.1336	0.051(1)
Cl	0.9290(6)	0.6422(2)	0.0347(3)	0.031(1)
N(1)	0.4732(23)	0.5708(5)	0.4033(11)	0.032(2)
N(2)	0.2747(39)	0.75	0.6169(18)	0.057(3)
C(1)	0.5742(29)	0.5671(6)	0.5841(15)	0.033(2)
C(2)	0.3941(26)	0.5027(6)	0.3188(14)	0.032(2)
C(3)	0.3503(39)	0.75	0.4546(25)	0.050(4)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ vector.

Electronic Spectroscopy. The diffuse reflectance UV−visible absorption spectra were obtained from 250 to 800 nm, using a Cary UV−visible spectrophotometer.

Synthesis of [Cu_3Cl_2CNPz] (1). Method a. Compound **1** was first synthesized by the reaction of $Cu(NO_3)_2{\cdot}H_2O$ (0.462 g, 2 mmol) and pyrazine (0.204 g, 2.6 mmol) with chloranilic acid (0.288 g, 1.4 mmol) and hydrochloric acid (0.2 mL) in 6 mL of water. The $Cu(NO_3)_2{\cdot}H_2O$ and chloranilic acid were combined in water with gentle heating. The hydrochloric acid and pyrazine were added to the mixture upon transfer to a Teflon cup. The reaction mixture was heated at 150 °C for 4 h and then cooled to room temperature at a rate of 0.6 °C/min. Large, yellow crystals suitable for single-crystal X-ray diffraction analysis were mechanically separated from the amorphous green powder. The matted powder stuck to the filter paper, and the loose large crystals were easily removed. It was possible to isolate bulk crystals of **1** on the basis of density differences. The product was placed in a separatory funnel containing approximately 3 mL of $CHBr_3$ ($d = 2.89$ g/mL), and $CHCl_3$ ($d = 1.47$ g/mL) was slowly added until the yellow crystals ($d = 2.83$ g/mL) sank to the bottom (~0.25 mL). The crystals were drained into a beaker and then filtered and washed with acetone.

Method b. Compound **1** could also be synthesized by the reaction of CuCl (0.1 g, 1 mmol), KCN (0.0195 g, 0.3 mmol), and pyrazine (0.024 g, 0.3 mmol) in 5 mL of H_2O. The reaction mixture was heated to 150 °C for 4 h and then slowly cooled to room temperature at a rate 0.1 °C/min. The resulting powder pattern matched the pattern calculated from single-crystal X-ray data.[56] IR data (KBr; cm^{-1}): 2067 (m), 1529 (br), 1481 (w), 1416 (vs), 1370 (w), 1161 (m), 1120 (s), 1049 (vs), 804 (vs). Raman data (cm^{-1}): (3072 (w), 2057 (vs), 1593 (w), 1025.9 (s), 642 (w), 158 (w). Anal. Calcd for $C_5H_4N_3Cl_2Cu_3$: C, 16.26; H, 1.08; N, 11.38. Found: C, 16.75; H, 1.15; N, 11.21.

Synthesis of [Cu_2Cl_2Pz] (2). Compound **2** was synthesized by the reaction of CuCl (0.1 g, 1 mmol), pyrazine (0.041 g, 0.5 mmol), and 5 mL of HCl (0.36 M). After 5 h at 150 °C, the reaction vessel was cooled at 0.6 °C/min to room temperature. The products, large orange single crystals of [Cu_2Cl_2Pz] and the secondary phase [$CuCl_2Pz$] (green crystals), were filtered off in air and washed with acetone. Large crystals were mechanically isolated for optical, vibrational, and thermal characterization. IR data (KBr; cm^{-1}): 1945 (w), 1729 (w), 1476 (m), 1417 (vs), 1160 (m), 1115 (m), 1055 (m), 804 (s), 493 (w), 451 (s). Raman data (cm^{-1}): 3070.16 (w), 1590.81 (vs), 1213 (w), 1024 (s), 651 (s), 128 (w). Anal. Calcd for $C_4H_4N_2Cl_2Cu_2$: C, 17.27; H, 1.44; N, 10.07. Found: C, 17.40; H, 1.48; N, 10.24.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **1**[a]

Cu(1)−C(3)	1.956(13)	Cu(1)−N(1)	2.102(8)
Cu(1)−Cl	2.362(3)	Cu(1)−Cl^1	2.489(3)
Cu(1)−Cu(1)^2	2.539(3)	Cu(2)−N(2)^3	1.850(12)
Cu(2)−Cl	2.288(3)	N(2)−C(3)	1.17(2)
C(3)−Cu(1)−N(1)	100.8(4)	C(3)−N(2)−Cu(2)^5	174.4(10)
N(1)−Cu(1)−Cl	95.5(2)	C(1)−N(1)−Cu(1)	122.7(8)
N(1)−Cu(1)−Cl^1	97.2(2)	N(2)−C(3)−Cu(1)	139.5(3)
C(3)−Cu(1)−Cu(1)^2	49.5(2)	N(1)−Cu(1)−Cu(1)^2	149.2(2)
Cl−Cu(1)−Cu(1)^2	104.22(3)	Cl^1−Cu(1)−Cu(1)^2	103.48(6)
N(2)^3−Cu(2)−Cl^2	125.49(7)	N(2)^3−Cu(2)−Cl	125.49(9)
Cl^2−Cu(2)−Cl	107.86(9)	Cu(2)−Cl−Cu(1)	109.78(11)
Cu(2)−Cl−Cu(1)^4	84.24(14)	Cu(1)−C(3)−Cu(1)^2	80.9(7)

[a] Symmetry transformations used to generate equivalent atoms: (1) $x - 1, y, z$, (2) $x, {}^3/_2 - y, z$, (3) $x + 1, y, z - 1$, (4) $x + 1, y, z$, (5) $x - 1, y, z + 1$.

Synthesis of [Cu_2Br_2Pz] (3). Compound **3** was synthesized by the reaction of CuBr (0.173 g, 1.2 mmol), pyrazine (0.0481 g, 0.6 mmol), and 8 mL of HBr (0.26 M). After 5 h at 150 °C, the reaction vessel was cooled at 0.2 °C/min to room temperature. The yellow crystals of [Cu_2Br_2Pz] were filtered off in air and washed with acetone. IR data (KBR; cm^{-1}): 1650 (br, w), 1476 (m), 1417 (s), 1385 (w), 1356 (w), 1159 (m), 1117 (m), 1054 (m), 804 (s), 451(s). Raman data (cm^{-1}): 3063 (w), 1590 (s), 1213 (w), 1023 (s), 648 (m), 118 (w). Anal. Calcd for $C_4H_4N_2Br_2Cu_2$: C, 13.04; H, 1.09; N, 7.61. Found: C, 13.22; H, 1.04; N, 7.39.

Synthesis of [Cu_2I_2Pz] (4). Compound **4** was synthesized by the reaction of a well stirred mixture of CuI (0.226 g, 1.2 mmol), pyrazine (0.048 g, 0.6 mmol), and 9 mL of HI (0.25 M). After 5 h at 150 °C, the reaction vessel was cooled at 0.6 °C/min to room temperature. The light yellow [Cu_2I_2Pz] crystals were filtered off in air and washed with acetone. IR data (KBR; cm^{-1}): 1477(w), 1417 (s), 1157 (w), 1120 (w), 1050 (m), 805 (m), 453 (m), 381 (m). Raman data (cm^{-1}): 3053 (w), 1590 (s), 1215 (m), 1022 (s), 906 (w), 643 (m), 141 (m), 111 (m). Anal. Calcd for $C_4H_4N_2I_2Cu_2$: C, 10.39; H, 0.87; N, 6.06; Cu, 27.71; I, 54.98. Found: C, 10.53; H, 0.77; N, 5.93. Lattice parameters (based on 21 reflections): $a = 7.115(10)$ Å, $b = 8.321(19)$ Å, $c = 8.378(17)$ Å, $\alpha = 71.1(3)°$, $\beta = 67.3(1)°$, $\gamma = 83.0(2)°$, $V = 432.9$ Å^3.

Room-Temperature Reactions. The syntheses of all compounds were compared with room-temperature reactions of CuX (X = Cl, Br, I, CN) and pyrazine in acetonitrile using standard Schlenk line techniques. Dry, degassed acetonitrile was used for these reactions.

Results and Discussion

Hydrothermal synthesis has recently been developed to prepare new coordination compounds.[32,57,58] New structures have been discovered in the hydrothermal reactions of well-studied, rather garden variety ligands, such as oxalate[59] and bipyridyl[46,60,61] or pyrazine as reported here. New copper halide compounds have been synthesized hydrothermally with less

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common organoamines: large, multifunctional ligands designed to create higher dimensional solids.[44,47] Frequently these compounds cannot be synthesized unless hydrothermal methods are used.[62,63] Hydrothermal synthesis has also been extended to copper cyanide polymers[44,50,51,53] as well as a new class of solid-state coordination complex materials where the coordination complexes act as subunits or bridges between metal oxide polyanion clusters.[64−70] We have found that compounds which tend to form difficult to characterize insoluble powders from solution[71] easily form beautiful crystals under hydrothermal conditions. In addition, we have discovered new compounds that so far can only be synthesized hydrothermally.

Syntheses. Copper halides and pseudohalides, although quite insoluble and unreactive in water at room temperature, are useful reagents under hydrothermal conditions. In our initial crystallization studies of [Cu_2X_2Pz] (X = Cl, Br, I), we found acidity and temperature to be important variables. The hydrothermal synthesis of [Cu_2Cl_2Pz] was relatively sensitive to stoichiometry and concentration, forming either [CuClPz][72] or [$CuCl_2Pz$].[73] By contrast, synthesis with X = Br or I formed the 2:2:1 stoichiometry ([Cu_2X_2Pz]) under a variety conditions. The room-temperature reaction of CuX and pyrazine under air-free conditions with acetonitrile as a solvent showed comparable results, where the 1:1:1 stoichiometry was formed for X = Cl and the 2:2:1 stoichiometry was formed for X = Br or I, independent of the starting stoichiometry.

In exploring the hydrothermal crystallization of copper inorganic−organic polymers, we discovered the new compound [Cu_3Cl_2CNPz] (**1**). Our original synthesis of **1** involved the reaction of $Cu(NO_3)_2$ and pyrazine under highly acidic solutions. While the formation of a Cu(I) compound was unanticipated, organoamines have been noted to be reducing under hydrothermal conditions.[50,74,75] Room-temperature reactions of Cu(II) with acidic solutions of pyrazine,[72,76] substituted pyrazines (e.g., 2,3-dimethylpyrazine),[77] and amines, such as 2-aminopyrimidine,[35] have also been reported to result in Cu(I) compounds. The nature of the redox chemistry is ill-defined in these examples, where solvent interaction,[76] halogenation of the ligand,[35] and the presence of other ligands (such as (2,6-dimethylphenyl)-glycinate)[72] as well as autoreduction[77] have been invoked to explain the formation of Cu(I).

Perhaps more surprising was the incorporation of cyanide in [Cu_3Cl_2CNPz]. The cleavage of pyrazine to yield CN^- has been observed under hydrothermal conditions in the reaction of CuO, pyrazine, and HNO_3 to synthesize [CuCNPz].[52] Although the hazards of forming cyanide under acidic conditions are averted by the insolubility of **1**, caution is advised for hydrothermal reactions of pyrazine in strong acidic solutions. We found a more direct route to **1** involving the reaction of CuCl, KCN, and pyrazine, also under hydrothermal conditions. Yellow needles of [Cu_3Cl_2CNPz] can be isolated from either method. In our hands, **1** could not be synthesized from room-temperature solution routes (acetonitrile solutions of CuCl, CuCN, and pyrazine in stoichiometric ratios). Rather than a mixed-ligand compound, a mixture of [CuCNPz], [CuClPz], and [Cu_2Cl_2Pz], was formed. Previous studies of Cu(I) have found that mixed-ligand complexes with halide and cyanide ions do not form under room-temperature conditions.[78] We believe this example to be unique for this reason. Attempts to form [Cu_3X_2CNPz] for X = Br or I as well as [Cu_3Cl_2CNL] for L = a bidentate amine such as 4,4′-bpy or phenazine have resulted in mixed-phase copper halide and copper cyanide compounds.

Descriptions of the Structures. Copper(I) halide complexes with nitrogen bases have long been of interest because of the diversity of structure types formed.[79−82] Typically, either discrete tetranuclear clusters[83] or polymers are produced.[82,84] The two common polymer frameworks are often termed the “chain” and the “stair”. The “chain” polymer has linear chains of -(CuX)- repeat units. These chains can form 2D sheets when pendant ligands are bidentate, by bridging copper atoms on adjacent chains (as seen in the polymer [CuClPz]).[72] Alternatively, the “stair” polymer has square -(Cu_2X_2)- units that form the step of a stair.[82,85−87] The [Cu_2X_2Pz] compounds all exhibit -(Cu_2X_2)- “stair” polymer structures cross-linked by pyrazine as shown in Figure 1. The single-crystal structure of [Cu_2Br_2Pz] is similar to that reported for [Cu_2Cl_2Pz].[54]

In addition to the structure-forming influence of the coordinated ligand, the halide can exert an influence on stoichiometrically identical compounds. For example, [$(C_6H_5)_3PCuX]_4$ exhibits a single “step” tetranuclear cluster structure for X = Br[88] and I,[89] but for X = Cl, it forms a cubane core.[90] As another example, in a more closely related series, [Cu_2X_2Phz] (Phz = phenazine), the -(Cu_2X_2)- stair polymer is formed for X = Cl and Br; however, X = I is distinct in forming a dimeric compound.[91] The X-ray powder diffraction pattern of [Cu_2I_2-

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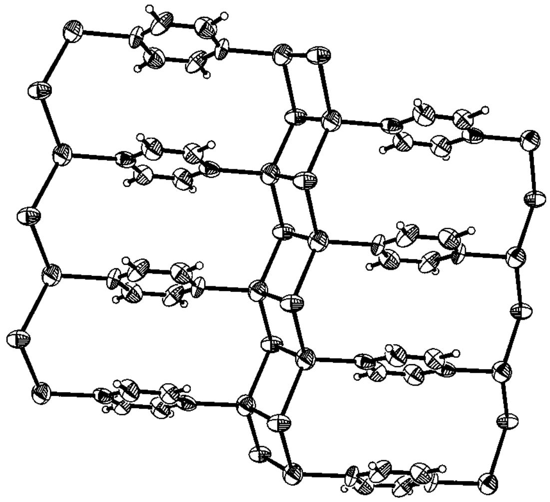

Figure 1. Structure of [Cu_2X_2Pz] (X = Cl, Br, I).

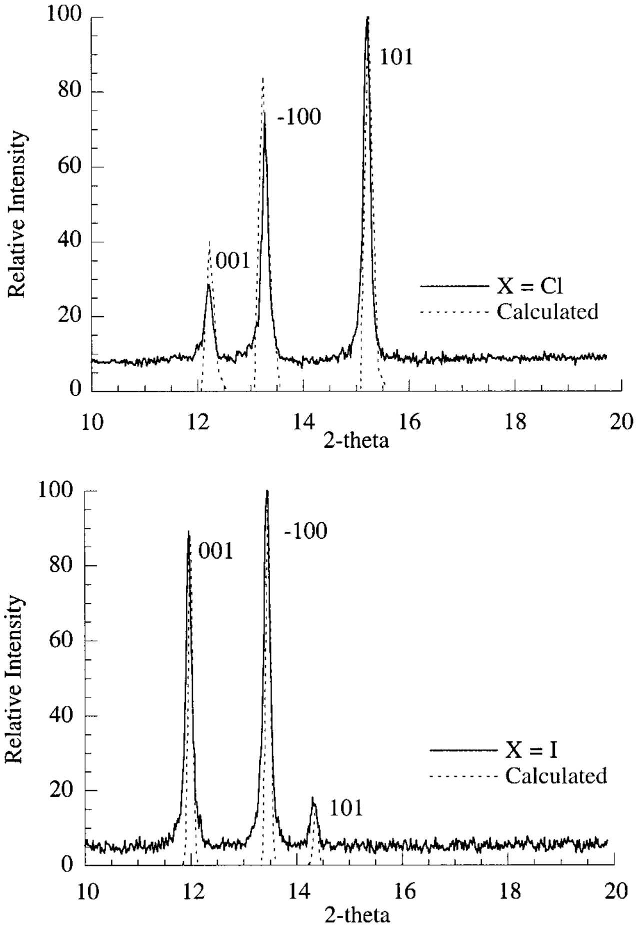

Figure 2. X-ray powder diffraction patterns for [Cu_2X_2Pz] (X = Cl, I).

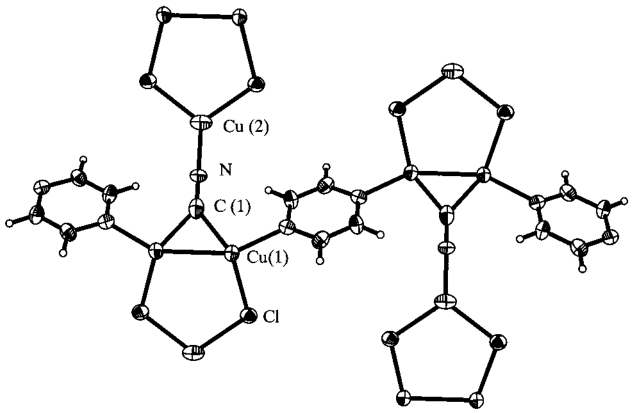

Figure 3. Structure of [Cu_3Cl_2CNPz].

Pz] was analogous to those of the chloride and bromide compounds. The pattern could be indexed on the basis of the [Cu_2Br_2Pz] pattern, and these reflections were used to refine the lattice parameters. The characteristic region of the diffraction pattern (10−20° in 2θ) for [Cu_2I_2Pz] along with the pattern calculated using refined lattice parameters is shown in Figure 2. For comparison, the same region for [Cu_2Cl_2Pz] is also included (with the corresponding calculated pattern). The shift to lower 2θ (larger d spacing) is primarily due to the increase in the cell volume as the halide becomes larger from Cl to I. In the triclinic crystal system, the (001) peak, for example, depends on the lattice constants according to $1/d^2 = 1/V^2(a^2b^2 \sin^2 \gamma)$. For [$Cu_2X_2Pz$], the d spacings are 7.16 Å for X = Cl, 7.28 Å for X = Br, and 7.36 Å for X = I. The intensities of these reflections also vary in a systematic way. Assuming the intensity of each reflection is proportional to $F_{hkl}{}^2$, the absolute intensities increase for all reflections from X = Cl to Br to I. The relative intensity of each reflection in the pattern, however, depends on the phase of the scattered wave for each atom in the unit cell. Those reflections that have halide atoms closer in phase to the resultant wave (relative to the pyrazine atoms) will vary most as the halide ion is changed. In this case, the contribution of the halide to the reflection intensity decreases from (001) to $(\bar{1}00)$ to (101). Therefore, the intensity of the (001) reflection becomes proportionately larger as the halide size increases (the $(\bar{1}00)$ reflection less so and the (101) reflection substantially less).

The structure has distinct -(Cu_3Cl_2)- five-membered rings that are connected along y by pyrazine and along z by cyanide (see Figure 3). Cu(I) halides can form a variety of cluster geometries including dimers, trimers, and tetramers.[92,93] Another compound with -(Cu_3Cl_2)- clusters, [$Cu_3Cl_2(DPM)_3$]Cl (DPM = bis(diphenylphosphino)methane),[94] has the more typical trigonal bipyramidal stereochemistry. In comparing bond lengths, we note that the Cu−Cl bonds are slightly shorter in **1** (2.362(3) and 2.489(3) Å) than in [$Cu_3Cl_2(DPM)_3$]Cl (2.438(4)−2.678(6) Å). An important difference is that [$Cu_3Cl_2(DPM)_3$]Cl has discrete molecular clusters, whereas **1** has fused rings that form a polymeric structure (see Figure 4), which to our knowledge has not been previously observed.

Cyanide was one of the original ligands identified as a "bifunctional rod" and successfully used to construct framework polymers.[4] In this context, it is notable that the number of examples which deviate from this paradigm is increasing. In general, μ_3-coordination is uncommon for pseudohalides, with the exception of thiocyanate.[95] Bond lengths for the first compound reported with three-coordinate cyanide, $CuCN{\cdot}NH_3$,[96] [Cu_3Cl_2CNPz], and the six other known compounds[114,115] with cyanide bound to three copper(I) atoms are listed in Table 4. Structurally, these compounds all posses a cyanide with the

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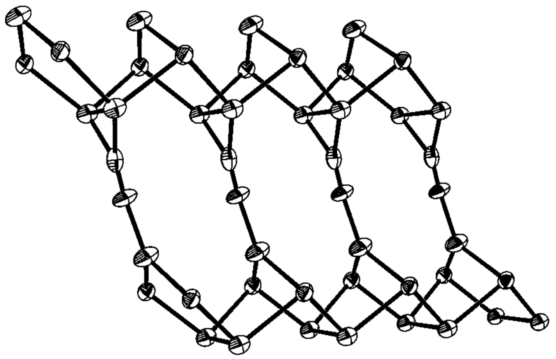

Figure 4. View of the -(Cu_3Cl_2)- stair (pyrazines omitted for clarity).

Table 4. Comparison of Bond Lengths (Å)in Cu(I) μ_3-Cyanide Compounds

compound	Cu−Cu	$Cu_2-\mu_2$-C	N−Cu	ref
[$(CuCN)_6(tetmen)_3$]	2.307	1.967 2.151		38
$CuCN\cdot NH_3$	2.418(2)	2.09(1) 2.13(1)	1.984(8)	96
[(CuCN)(phpip)]	2.534	2.013 2.347		38
[Cu_3Cl_2CNPz]	2.539(3)	1.956(13)	1.850(12)	this work
[$Cu_3(CN)_3H_2O$]	2.637(3)	1.93(2)	1.86(2)	114
[$Cu(NH_3)(py)Ag_{3-x}Cux(CN)_5\cdot py$]	2.641(1)	1.927(5)	2.059(5)	115
[$Me_2(C_6H_5)S$][$Cu_2(CN)_3$]	2.655(2)	1.959(9)	1.938(7)	103
[$(CuCN)_2$(butda)]	2.672	1.890 2.571		38

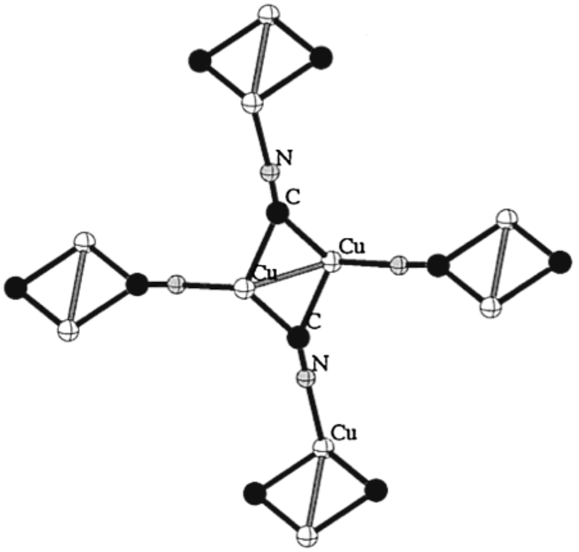

Figure 5. Structure of $CuCN\cdot NH_3$.

carbon bridging a copper dimer. The copper dimers all have short Cu(I)−Cu(I) bond lengths (2.42−2.66 Å). Although **1** is unique because it is not dimeric, it bears some structural resemblance in that the cyanide is bound to the base of the five-membered ring which is formed by a Cu−Cu bond. The copper bond in the ring has a length of 2.539(3) Å, well within the range expected for a copper−copper metal bond (2.37−2.65 Å).[97,98]

The third bond involving the cyanide occurs is a linear nitrogen−metal bond, typically to one end of another copper dimer, as illustrated for $CuCN\cdot NH_3$ (Figure 5). The soft d^{10} Cu(I) appears to be important for stabilizing the three-coordinate cyanide. All known examples of three-coordinate cyanide have the carbon end bound to a copper dimer, and more than half have the third bond to another Cu(I). Three-coordinate cyanide has also been observed for three other known structures where the third bond to cyanide is between N and Cu^{2+} ($Cu_5(CN)_6(dmf)_4$),[99] Cd^{2+} ([$Cd(H_2O)_3Cu(CN)_3$]CH_3CN),[100] or Sn^{4+} ([$CuCNMe_3SnCN\cdot 0.5bpy$]).[101]

The orientation of CN^- is still of some debate in these compounds because carbon and nitrogen are indistinguishable by X-ray diffraction. Linkage isomerism is well-known in cyanide-bridged systems.[20] One indication of the orientation is the metal−cyanide bond lengths. Usually, linearly bridged -(Cu−CN−Cu)- complexes have shorter Cu−C than Cu−N distances.[102] However, in the set of μ_3-CN compounds, the carbon is bonded to two Cu atoms, so the Cu−C bond length is longer than usual (generally on the order of 1.82 Å)[103] and in each case is also slightly longer than the N−Cu bond (see Table 4). Equivalent M−C and M−N bonds for linearly bridged compounds are often evidence for linkage isomerism or "head to tail" disorder of the CN. Another useful tool for determining bonding and isomerism is NMR spectroscopy. For example, although the structure of CuCN itself has never been determined by X-ray diffraction, from $^{63/64}$Cu NQR the cyanide was determined to be linearly bridged (Cu−CN−Cu), with linkage isomerism based on the multiplicity and breadth of the peaks.[104] Using doubly labeled $^{13}C^{15}N$, the Cu−C−N−Zn ordering scheme proposed in the structual study by Hoskins[4] was confirmed.[105] Cyanide disorder in [Cu_3Cl_2CNPz], however, is unlikely because the vibrational spectra show only one CN stretch (vide infra).

Vibrational Spectroscopy. Both [Cu_3Cl_2CNPz] and $CuCN\cdot NH_3$ are rare in having only μ_3-CN. The nine other compounds that exhibit three-coordinate cyanide also have terminal or linearly bridging CN^-. The frequency of free CN^- is 2080 cm^{-1}, and CN complexes normally exhibit a sharp band due to a CN stretch between 2200 and 2000 cm^{-1}.[106] Vibrational spectroscopy of **1** in this region shows a single IR absorption at 2067 cm^{-1} and a single Raman absorption at 2057 cm^{-1}. This is in contrast to the case of $CuCN\cdot NH_3$, which has a more complicated spectrum (see Table 5).[107] The linearly bridged CN in CuCN has a cyanide stretch at 2172 cm^{-1}.[116] Generally, σ donation from either carbon or nitrogen tends to raise ν(CN), while π back-bonding decreases ν(CN).[108,109] Increases in metal coordination number can also result in a decrease in ν(CN) on the order of 20−40 cm^{-1}.[110] Although the position of the CN stretch is the result of competing factors, the low frequency is

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Table 5. Cyanide Coordinations, Bond Lengths, and Stretching Frequencies

compound	CN coordn	C−N (Å)	freq (cm^{-1})
$[Cu_3Cl_2CNPz]$	Cu_2−CN−Cu (μ_3)	1.17(2)	2067 (IR) 2057 (Raman)
CuCN[116]	Cu−CN−Cu (μ_2)		2172 (IR)
$CuCN \cdot NH_3$[107]	Cu_2−CN−Cu (μ_3)	1.13(1)	2065 (IR) 2090 (IR) 2135 (IR)
$[Me_2(C_6H_5)S][Cu_2(CN)_3]$[103]	Cu_2−CN−Cu (μ_3)	1.16(12)	2084 (IR)
	Cu−CN−Cu (μ_2)	1.130(10)	2108 (IR)

Table 6. Raman Frequencies (cm^{-1}) for $[Cu_2X_2Pz]$

X = Cl	X = Br	X = I	assign[117]
3070	3063	3053	ν(CH)
1591	1590	1590	ν(ring)
1213	1213	1215	δ(CH)
1025	1024	1022	ν(ring)
651	648	644	δ(ring)

consistent with the long C−N bond length and indicates that back-bonding is important.

The vibrational spectra of $[Cu_2X_2Pz]$ (**2**−**4**) are dominated by pyrazine peaks. There are no coincident pyrazine peaks between the infrared and the Raman spectra, in agreement with the centrosymmetric, bidentate coordination seen in the X-ray crystallography studies. The low-frequency pyrazine peak in the infrared spectrum (417 cm^{-1} for free pyrazine) is considered to be most sensitive to the pyrazine binding mode and shifts to higher frequencies upon metal coordination.[111] This peak occurs at 451 cm^{-1} in the spectra of all compounds reported here, which is low for symmetrically bridging coordinated pyrazine (typically closer to 470 cm^{-1}).[72] While certain peaks are essentially invariant, there are consistent, subtle shifts in both the infrared and the Raman spectra. For example, in the Raman spectra (see Table 6 with assignments[117]), each compound exhibits peaks at 1590 and 1213 cm^{-1}, while the other peaks slowly decrease in frequency from X = Cl to Br to I. The pyrazine peaks for $[Cu_3Cl_2CNPz]$ are closest in frequency to those for$[Cu_2Cl_2Pz]$, as one might expect.

Electronic Spectroscopy. Diffuse reflectance spectra of $[Cu_3Cl_2CNPz]$ and $[Cu_2X_2Pz]$ (**2**−**4**) show that all compounds absorb strongly in the UV and visible regions, with absorbance falling off sharply at longer wavelengths. The shapes of the electronic spectra suggest that a continuum of electronic states are involved; however, no electrical properties have been measured. Compounds with metal−metal bonding between homoatomic d^{10} cations have been noted to exhibit a sharp absorption edge with a red shift in the UV−visible region and are often conductors or semiconductors.[112] Here, the optical band gaps for these compounds all fall within the semiconductor region; for example, the absorption edge for $[Cu_3Cl_2CNPz]$ corresponds to a band gap of 2.25 eV. For the series $[Cu_2X_2Pz]$ (**2**−**4**), the absorption edge shifts to higher energy down the series X = Cl, Br, I (2.19, 2.30, 2.36 eV, respectively). No d−d transitions are expected for Cu(I), and complexes with pyridine and related ligands typically exhibit MLCT bands at ∼300−500 nm,[113] as seen here. The absorption spectra of copper pyrazine compounds have been shown to be influenced by substituents on the pyrazine ring.[72] In principle, the electronic transitions can be associated with either metal-to-ligand or anion-to-ligand (or metal) charge transfers. However, if the transitions originated with the anions, the opposite trend in energies would be expected. The stacking distance between pyrazine rings increases down this series (Cl, Br, I), weakening the π interaction. It is reasonable that the loss of stabilization of the π orbitals of pyrazine (as the overlap decreases) results in an increase in the energy gap between metal and ligand.

Thermal Stability. The thermal stability of compounds **1**−**4** was determined using TGA and DTA. The thermal analysis data for the $[Cu_2X_2Pz]$ (**2**−**4**) all show a two-step weight loss corresponding to a loss of the organic ligand (Pz). For X = Cl, this occurs at 238 °C with a loss of 29.1% (calculated to be 28.8%) and a corresponding endothermic peak, followed by almost complete loss of the remaining metal halide at 576 °C. The decomposition for X = Br showed a loss of pyrazine at 218 °C (observed 22.2%, calculated 21.7%) and metal halide loss at 531 °C. For X = I, the pyrazine loss was at 212 °C (observed 17.49%, calculated 17.35%) with a broad decomposition around 580 °C. These values agree with previous studies of Cu(I) pyrazine thermal properties which also showed an initial loss of pyrazine around 200 °C.[76]

$[Cu_3Cl_2CNPz]$ also showed a similar two-step TGA-DTA weight loss. There is an endotherm at 264.7 °C corresponding to a weight loss of 22.2% (calculated for pyrazine 21.77%). The loss of pyrazine was confirmed by a peak in the mass spectrum at m/z 80 mass units. The second weight loss had no distinct thermal transition (occurring broadly near 640 °C), and corresponded to 58.3 wt %.

Conclusions

Hydrothermal synthesis provides access to new compounds through the unusual temperature region for water, as well as ideal crystallization conditions. In particular, hydrothermal routes are ideal for the crystallization of the series $[Cu_2X_2Pz]$ (X = Cl, Br, I) and, thus far, such a route is the only method for forming the mixed halide−cyanide compound $[Cu_3Cl_2CNPz]$. Structurally, $[Cu_3Cl_2CNPz]$ and the $[Cu_2X_2Pz]$ series exhibit very distinct polymeric structures. The $[Cu_3Cl_2CNPz]$ structure provides a new example of three-coordinate cyanide and has an unusual copper−chloride polymeric stair. The cyanide stretch in the vibrational spectrum is shifted to a low frequency, consistent with the long C−N bond length. This compound should provide a useful standard for comparing new three-coordinate cynide compounds. Although the structures are quite different, these copper halides and pseudohalides are quite similar in their optical and thermal properties, reflecting the copper−halide polymer backbone.

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Supporting Information Available: The two X-ray crystallographic files in CIF format are available free of charge via the Internet at http://pubs.acs.org.

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