Inorg. Chem. **1999,** *38,* 2663−2671

Solid State Coordination Chemistry of the Copper Halide- and Pseudo-Halide-Organoamine System, Cu-X-[(bis-2,3-(2-pyridyl)pyrazine)] (X = Cl, Br, CN): Hydrothermal Synthesis and Structural Characterization

Douglas J. Chesnut, Anakarin Kusnetzow, Robert R. Birge, and Jon Zubieta*

Department of Chemistry, Syracuse University, Syracuse, New York 13244-4100
W. M. Keck Center for Molecular Electronics, Syracuse University, Syracuse, New York 13244-4100

Received January 29, 1999

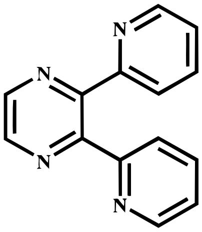
The compounds [Cu_3Cl_3(bipypy)] (**1**), [CuBr(bipypy)]$_2$ (**2**), [Cu_2Br_2(bipypy)] (**3**), and [$Cu_3(CN)_3$(bipypy)] (**4**) were prepared from mixtures of the copper halide salts and the ligand bis-2,3-(2-pyridyl)pyrazine (bipypy) in hydrothermal media. The series of compounds includes molecular, one- and two-dimensional species and demonstrates a trend in increasing complexity. The synthetic conditions, methods of structural characterization and descriptions of the structures of compounds **1**−**4** are presented. Crystal data for $C_{14}H_{10}Cl_3Cu_3N_4$ (**1**), orthorhombic, $Pna2_1$, $a = 18.6778(5)$ Å, $b = 5.1046(2)$ Å, $c = 16.6257(2)$ Å, $Z = 4$; for $C_{28}H_{20}Br_2Cu_2N_8O_2$ (**2**), triclinic, $P\bar{1}$, $a = 7.795(1)$ Å, $b = 8.857(1)$ Å, $c = 11.1268(2)$ Å, $\alpha = 72.2(1)°$, $\beta = 83.050(1)°$, $\gamma = 73.832(1)°$, $Z = 1$; for $C_{14}H_{10}Br_2Cu_2N_4$ (**3**), monoclinic $C2/c$, $a = 10.884(2)$ Å, $b = 16.713(4)$ Å, $c = 9.307(2)$ Å, $\beta = 113.199(5)°$, $Z = 4$; and for $C_{17}H_{10}Cu_3N_7$ (**4**), monoclinic, $P2_1/n$, $a = 12.8549(2)$ Å, $b = 9.0875(1)$ Å, $c = 16.0023(2)$ Å, $Z = 4$.

Introduction

Exploitation of the physical properties of inorganic solid-state materials results in applications ranging from heavy construction to microcircuitry.[1] A powerful synthetic approach for influencing the self-assembly of the microstructures of solid-state inorganic materials employs organic components as integral members of hierarchical structures. The incorporation of organic components to form composite materials results in synergistic interactions between the organic and inorganic substructures. [2−8]

Often novel solid phase microstructures can be achieved by incorporation of what may be considered remarkably fragile organic components.[9] One experimentally facile method of introducing such organic components into composite materials is a manifestation of the so-called *chimie douce* techniques, hydrothermal synthesis.[10,11] An advantage of *chimie douce* methods is the ability to isolate metastable, kinetic phases whereas traditional high-temperature techniques result in the formation of thermodynamically favored phases. Not only does the use of hydrothermal media allow for the retention of the structural integrity of organic constituents, but the elevated temperature and pressure regimes required effectively modify the solvent properties of water.[12−14]

Chart 1



bis-2,3-(2-pyridyl)pyrazine (bipypy)

There exists a formidable body of literature describing an array of anionic copper halide and psuedo-halide structures linked through extensive networks of hydrogen bonds with neutral and protonated organoamines.[15,16] Typically, the anionic substructures of such composite materials are of low dimensionality, with $[(en)_2Cu]_2[Cu_7Cl_{11}]$[17] (en = ethylenediamine) and several copper cyanide compounds[18] providing notable exceptions. Our recent efforts to employ large, aromatic organoamines as templates for multidimensional framework materials resulted in the formation of unusual isostructural one-dimensional

---

(1) Cheetham, A. K. *Science* **1994**, *264*, 794.
(2) Mann, S. *J. Chem. Soc., Dalton Trans.* **1997**, 3953.
(3) Mann, S.; Ozin, G. A. *Nature (London)* **1996**, *382*, 313.
(4) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck J. S. *Nature* **1992**, *359*, 710.
(5) (a) Smith, J. V. *Chem. Rev.* **1988**, *88*, 149. (b) Occelli, M. L.; Robson, H. C. *Zeolite Synthesis*; American Chemical Society: Washington, DC, 1989.
(6) (a) Haushalter, R. C.; Mundi, L. A. *Chem. Mater.* **1992**, *4*, 31. (b) Khan, M. I.; Meyer, L. M.; Haushalter, R. C.; Schweitzer, C. L.; Zubieta, J.; Dye, J. L. *Chem. Mater*. **1996**, *8*, 43.
(7) Mann, S. *Nature* **1993**, *365*, 499.
(8) Hagrman, D.; Zubieta, C.; Rose, D. J.; Zubieta, J.; Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 873.
(9) Sogomonian, V.; Chen, Q.; Haushalter, R. C.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 223.
(10) Gopalakrishnan, J. *Chem. Mater.* **1995**, *7*(7), 1265.
(11) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993**, *257*, 1558.
(12) Hoffman, M. M.; Conradi, M. S. *J. Am. Chem. Soc.* **1997**, *119*, 3811.
(13) Ohtaki, H.; Radnai, T.; Yamaguchi, T. *Chem. Soc. Rev.* **1997**, 41.
(14) Sweeton, F. H.; Mesmer, R. E.; Baes, C. F., Jr. *J. Sol. Chem.* **1974**, *3*(3), 191.
(15) Geiser, U.; Willet, R. D.; Lindbeck, M.; Emerson, K. *J. Am. Chem. Soc.* **1986**, *108*, 1173.
(16) Pons, G.; Willet, R. D.; Prince, B. A.; Robinson, W. T.; Turnbull, M. M. *Inorg. Chim. Acta* **1997**, *255*, 325 and references therein.
(17) DeBord, J. R. D.; Lu, Y.; Warren, C. J.; Haushalter, R. C.; Zubieta, J. *Chem. Commun.* **1997**, 1365.
(18) Williams, R. J.; Larson, A. C.; Cromer, D. T. *Acta Crystallogr.* **1972**, *B28*, 858.

10.1021/ic990132x CCC: $18.00

Table 1. Crystallographic Data for Compounds **1**−**4**

	1	**2**	**3**	**4**
chemical formula	$C_{14}H_{10}Cl_3Cu_3N_4$	$C_{28}H_{10}Br_2Cu_2N_8O_2$	$C_{14}H_{10}Br_2Cu_2N_4$	$C_{17}H_{10}Cu_3N_7$
fw	531.23	787.42	521.16	502.94
space group (No.)	$Pna2_1$ (33)	$P\bar{1}$ (2)	$C2/c$ (15)	$P2_1/n$ (14)
a (Å)	18.6778(5)	7.7950(1)	10.884(2)	12.8549(2)
b (Å)	5.1046(2)	8.857(1)	16.713(4)	9.0875(1)
c (Å)	16.6257(2)	11.1268(2)	9.307(2)	16.0023(2)
α (deg)	90	72.2(1)	90	90
β (deg)	90	83.050(1)	113.199(5)	110.476(1)
γ (deg)	90	73.832(1)	90	90
V (Å^3), Z	1585.14(8), 4	701.94(2), 1	15556.0(6), 4	1751.26(4), 4
T (K)	115	115	115	115
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	2.226	1.863	2.225	1.908
μ (cm^{-1})	44.97	44.04	78.68	36.27
R, R_w[a]	0.0684, 0.1158	0.0316, 0.0823	0.0344, 0.0873	0.0404, 0.0790

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(FF_o^2)^2]]^{1/2}$.

ribbons of $[Cu_3X_3(bpy)_2]$ (bpy = 2,2′-bipyridyl) where X = Br or I.[19] Higher dimensionality appears to be precluded by passivation of the Cu(I) sites by coordinated bpy. Furthermore, the use of bpy for the same purpose with systems incorporating the psuedo-halide, cyanide, resulted in the formation of conformationally flexible $[(bpyCu)_2CN]^+$ cations entrained within the two-dimensional anionic copper−cyanide structure of $[(bpyCu)_2CN][Cu_5(CN)_6]$[20] and intercalated in $[(bpyCu)_2CN]_2$-$[Cu_5(CN)_7]\cdot{}^1/_6H_2O$.[21]

In an attempt to encourage the self-assembly of phases of higher dimensionality from copper halide and pseudo-halide organoamine systems, bpy has been replaced with bis-2,3-(2-pyridyl)pyrazine (bipypy), shown in Chart 1. It was felt that the potential of multiple chelation sites in an ambidentate ligand would allow linkage of metal centers through the organoamine bridges. In addition to such chaining, it was proposed that the bipypy ligand would not be constrained to a planar conformation and subsequently allow for the interconnection of chains and propagation of the microstructure in two or three dimensions. Here we report the synthesis and structural characterization of $[Cu_3Cl_3(bipypy)]$ (**1**), $[CuBr(bipypy)]_2$ (**2**), $[Cu_2Br_2(bipypy)]$ (**3**), and $[Cu_3(CN)_3(bipypy)]$ (**4**) from the reaction of simple CuX salts and the bipypy ligand in hydrothermal media.

Experimental Section

Synthesis. All reagents were obtained from Aldrich and used without further purification. All compounds were synthesized in 23 mL Parr acid digestion bombs from the reaction of the simple CuX salts with bipypy at 170 ± 5 °C and autogenous pressure in hydrothermal media.

Synthesis of $[Cu_3Cl_3(bipypy)]$ (1). Compound **1** was prepared as brown platelike crystals from the successive addition of $CuCl_2\cdot 2H_2O$ (52 mg, 0.31 mmol), CuCl (28 mg, 0.28 mmol), bipypy (65 mg, 0.28 mmol), and H_2O (8.00 g, 0.444 mol) to an acid digestion vessel which was then sealed. The reaction vessel was then placed in an oven for 79.5 h at 170 ± 5 °C after which it was removed from the oven and allowed to stand for ca. 24 h. The vessel was then opened for inspection of the contents and a mass of reflective brown crystals and red brown powder were observed under a nearly opaque dark brown solution. A brittle, brown platelike crystal of dimensions 0.43 × 0.11 × 0.09 mm was chosen for structural determination via a single-crystal X-ray diffraction experiment. The powdery nature of the red brown phase precluded attempts at structural characterization. Attempts to prepare **1** in the absence of $CuCl_2\cdot 2H_2O$ resulted only in dark brown, viscous solutions, as did attempts using only $CuCl_2\cdot 2H_2O$ as the metal halide source.

Synthesis of $[CuBr(bipypy)]_2$ (2). Compound **2** was prepared as brown platelike crystals by the successive addition of CuBr (51.7 mg, 0.360 mmol), bipypy (77.4 mg, 0.330 mmol), and H_2O (5.00 mL, 0.278 mol) to an acid digestion bomb which was then sealed. The vessel was placed in an oven for 64.5 h at 170 ± 5 °C after which the vessel was removed from the oven and allowed to stand for ca. 5 h. The vessel was then opened for examination of the contents. A mass of very dark red, nearly black, and clear crystalline solids were observed as masses surrounding a scattering of long light brown platelike crystals. Both solid phases were observed to be under a clear and colorless solution. A single crystal of the brown phase of dimensions 0.46 × 0.10 × 0.04 mm was chosen for structural determination via a single-crystal X-ray diffraction experiment. The crystals of the red phase were of poor morphology and characterization was not attempted.

Synthesis of $[Cu_2Br_2(bipypy)]$ (3). Compound **3** was prepared as dark red, nearly black, crystals by the successive addition of CuBr (51.7 mg, 0.360 mmol), bipypy (77.4 mg, 0.33 mmol), and H_2O (5.00 mL, 0.278 mol) to an acid digestion vessel which was then sealed and placed in an oven for 60.5 h at 185 ± 5 °C. The vessel was then removed from the oven and allowed to stand for ca. 4 h prior to being opened for examination of the contents. A mass of tan powder and extremely dark red, nearly black, crystals were observed under a clear and colorless solution. A single crystal of the dark red phase of dimensions 0.60 × 0.40 × 0.40 mm was chosen for structural determination via a single crystal X-ray diffraction experiment. Subtle variations in reaction times, temperatures, and cooling rates may have individually or collectively resulted in the different products under apparently similar preparation conditions for compounds **2** and **3**.

Synthesis of $[Cu_3(CN)_3(bipypy)]$ (4). Compound **4** was prepared as clear red wine colored solids from the successive addition of CuCN (120.4 mg, 1.344 mmol), KCN (82.1 mg, 1.26 mmol), bipypy (78.9 mg, 0.337 mmol), and H_2O (5.00 mL, 0.278 mol) to an acid digestion bomb which was then sealed. The reaction vessel was then placed in an oven for 64.5 h at 170 ± 5 °C. The vessel was then removed from the oven and allowed to stand for ca. 5 h prior to being opened for examination of the contents. A mass of clear red wine colored plate like crystals in 85 mg yield were observed under a clear and colorless solution. A single crystal of dimensions 0.50 × 0.20 × 0.02 mm was chosen for structural determination via a single-crystal X-ray diffraction experiment. (IR, KBr pellet (cm^{-1}): 2137, 2125, 2100).

FTIR Spectroscopy. Fourier transform infrared spectra of compounds **2** and **4** were obtained using a Nicolet Nic-Plan IR Microscope coupled to a Nicolet Magna IR 750. Single crystals of the compounds were selected based on thickness and lack of impurities, i.e., inclusions. Spectra of compounds **1** and **3** were not obtained due to the nearly opaque nature of the crystals nor was a spectrum collected using standard KBr pellet methods due to the heterogeneous nature of the reaction products. Crystals of compounds **2** and **4** were mounted on CaF_2 windows (4000−1100 cm^{-1}), and the images were focused using a 32× IR objective lens. Transmission spectra were collected and averaged (516 scans) at a resolution of 2 cm^{-1}; area scanned was 10 μm in diameter. The detector used to collect the data was a liquid N_2

---

(19) Hammond, R. P.; Zubieta, J. Unpublished results.

(20) Chesnut, D. J.; Zubieta, J. *Chem. Commun.* **1998**, 1707.

(21) Chesnut, D. J.; Kusnetzow, A.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1998**, *24*, 4081.

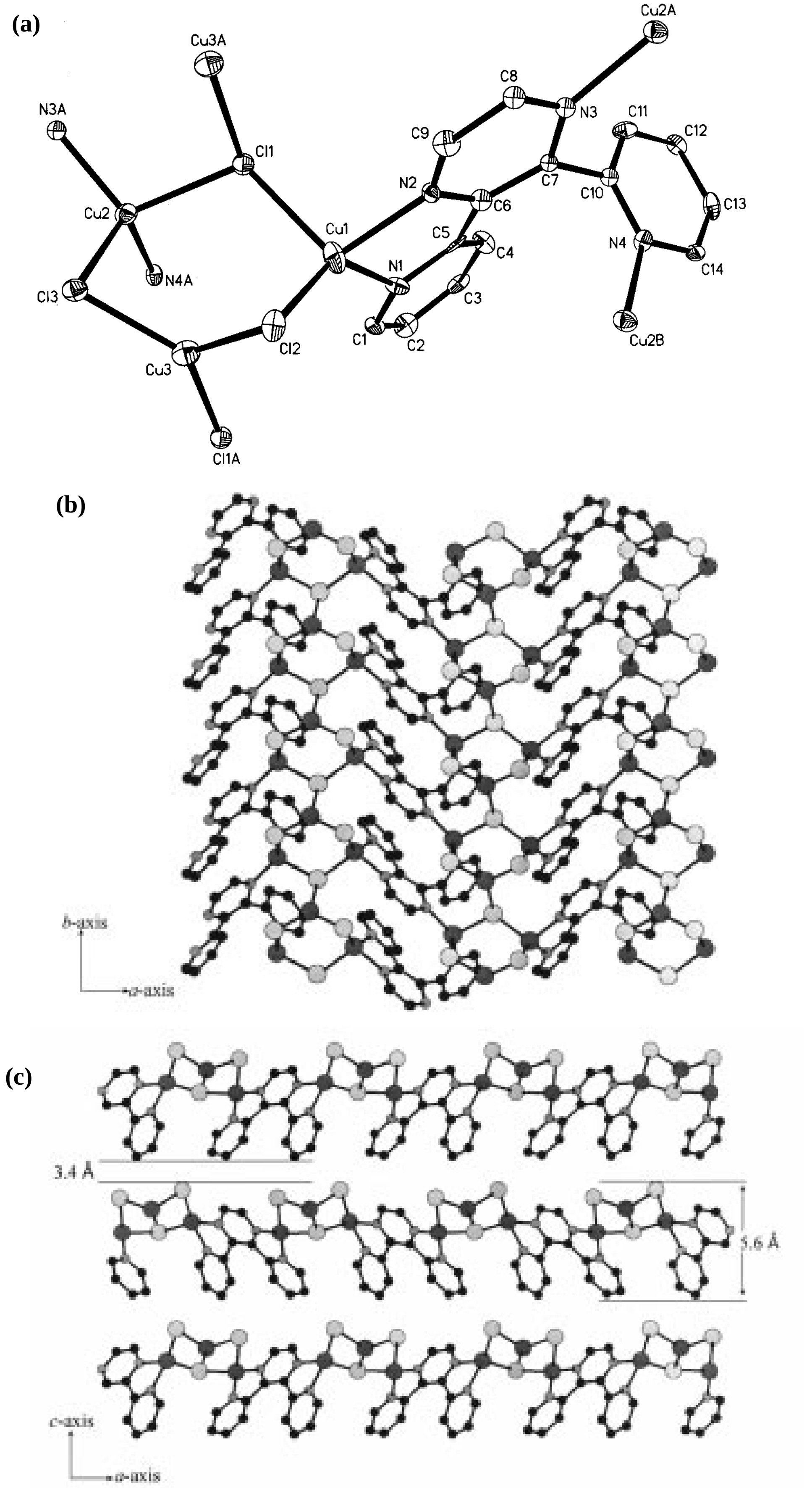


Figure 1. (a) The metal−ligand coordination geometries of compound **1** (atoms are represented as 50% thermal ellipsoids); (b) a layer of compound **1** viewed perpendicular to the crystallographic *ab* plane showing the chains of $\{Cu_3Cl_3\}$ rings and the rows of bipypy ligand molecules; (c) stacking of the layers of compound **1** along the crystallographic *b* axis with the layer thickness and interlayer spacing indicated when viewed perpendicular to the crystallographic *ac* plane. Hydrogen atoms have been omitted for clarity. Small black circles, small light gray circles, large light gray circles, and large dark gray circles denote C, N, Cl, and Cu atoms, respectively.

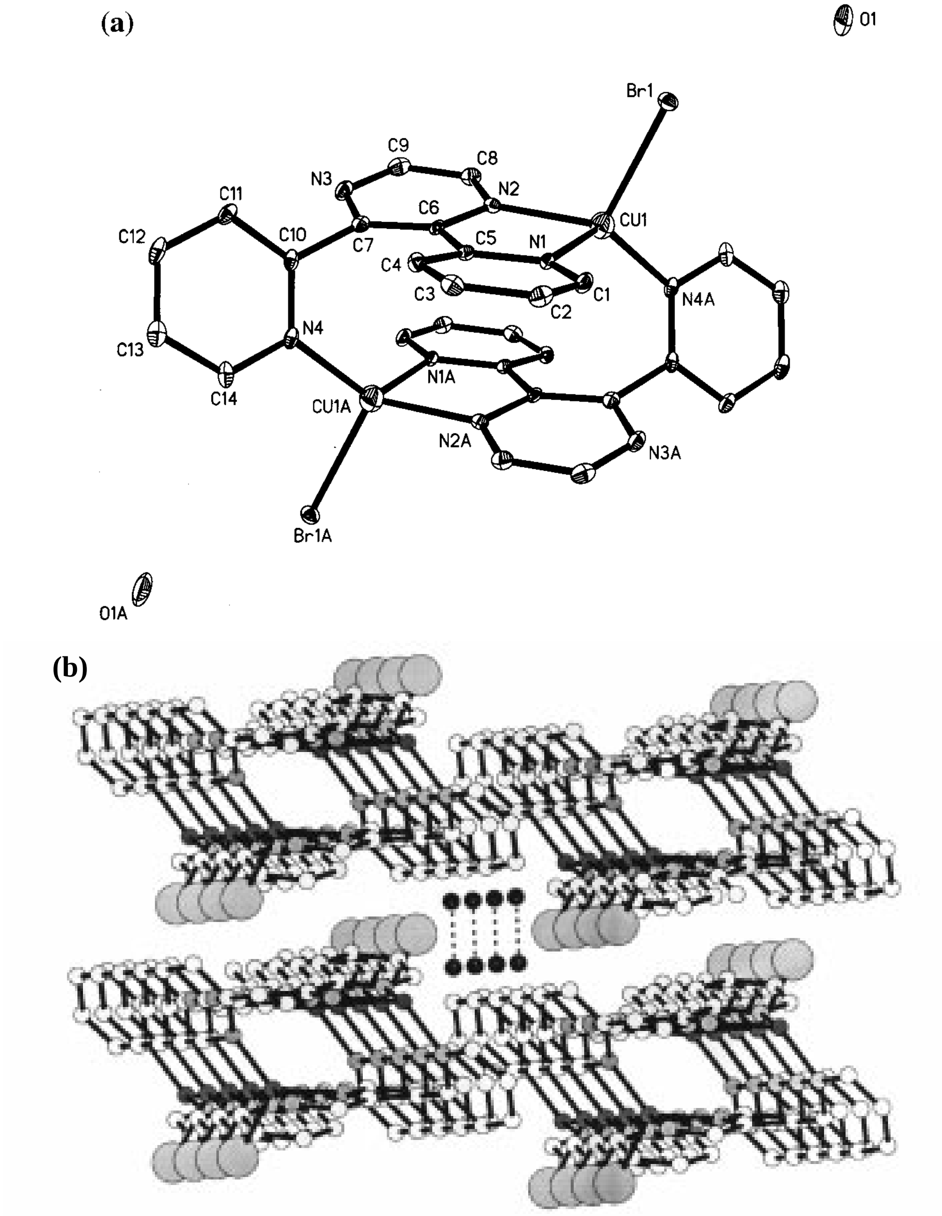


Figure 2. (a) A view of compound **2** showing the labeling of the Br, C, Cu, N, and O atoms marked (atoms are represented as 50% thermal ellipsoids); (b) the crystal packing of compound **2** viewed oblique to the crystallographic *ac*-plane showing the "band" of water, hydrogen bonded pairs of water are noted by the light gray dashed lines. van der Waals contacts between water molecules and Br atoms are for each successive rank of $[CuBr(bipypy)]_2$ dimers and pair of hydrogen bonded water molecules. Hydrogen atoms omitted for clarity. Large light gray circles, small empty circles, dark gray circles, small light gray circles, and black circles denote Br, C, Cu, N, and O atoms, respectively.

cooled MCT-A detector. The OMNIC 3.1 software package was used to collect and process all data.[22]

X-ray Crystallographic Studies. Structural measurements for compounds **1**−**4** were performed on a Siemens SMART CCD diffractometer with graphite monochromated Mo Kα radiation [λ(Mo Kα) = 0.710 73 Å]. The data were collected at 150 ± 3 K using slow ω scans with narrow frames. Crystallographic data for compounds **1**−**4** are listed in Table 1. Empirical absorption corrections using the SADABS software were applied to all compounds.[23] The structures were solved by direct methods.[24] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions with exception of protons of waters of crystallization of compound **2**. Neutral atom scattering factors were taken from the *International Tables*.[25] All structure solution and refinement calculations were performed using

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **1**

Cu1−N1	2.080(9)	Cu1−N2	2.081(8)
Cu1−Cl2	2.228(3)	Cu1−Cl1	2.512(3)
Cu2A−N3	2.022(8)	Cu2−N4A	2.026(9)
Cu2−Cl3	2.386(3)	Cu2−Cl1	2.438(3)
Cu3−Cl3	2.250(3)	Cu3−Cl1	2.261(3)
N1−Cu1−N2	78.4(3)	N1−Cu1−Cl2	133.9(3)
N2−Cu1−Cl2	122.5(3)	N1−Cu1−Cl1	108.7(3)
N2−Cu1−Cl2	102.7(2)	Cl2−Cu1−Cl1	105.6(1)
N3A−Cu2−N4A	124.2(3)	N3−Cu2−Cl3	104.5(3)
N4A−Cu2−Cl3	109.7(3)	N3−Cu2−Cl1	107.1(2)
N4A−Cu2−Cl1	104.2(2)	Cl3−Cu2−Cl1	106.0(1)
Cl3−Cu3−Cl1A	133.1(1)	Cl3−Cu3−Cl2	110.1(1)
Cl1A−Cu3−Cl2	116.4(1)	Cu3A−Cl1−Cu2	102.2(1)
Cu3A−Cl1−Cu1	117.2(1)	Cu2−Cl1−Cu1	114.8(1)
Cu1−Cl2−Cu3	89.9(1)	Cu3−Cl3−Cu2	85.1(1)

---

(22) *OMNIC 3.1*; Nicolet Instrument Corporation: Madison, WI, 1992−1996.

(23) Sheldrick, G. M., Ed. *SADABS: Program for Empirical Absorption Corrections*; University of Göttingen: Germany, 1986.

(24) Sheldrick, G. M. *SHELXTL: Structure Determination Programs*, Version 5.0 PC; Siemens Analytical X-ray Instruments: Madison, WI, 1994.

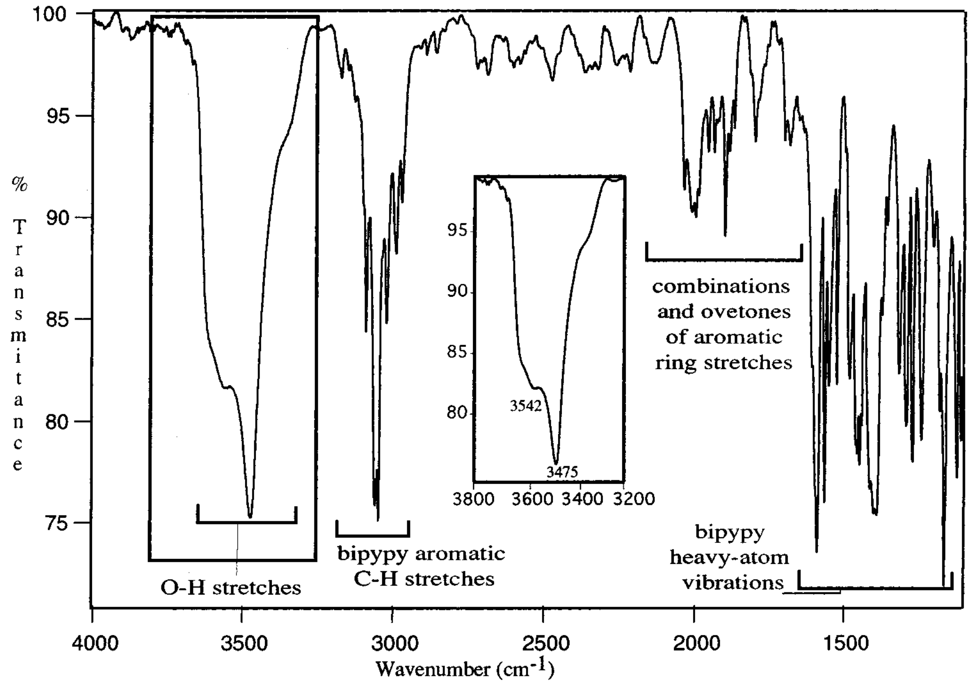


Figure 3. Infrared spectrum of compound **2** from 4000 to 1100 cm^{-1}. Inset shows the region from 3800 to 3200 cm^{-1}.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound **2**

Cu1−N4A	1.985(2)	Cu1−N2	2.040(2)
Cu1−N1	2.068(2)	Cu1−Br1	2.4460(4)
N4A−Cu1−N2	126.33(9)	N4A−Cu1−N1	124.48(9)
N2−Cu1−N1	79.15(9)	N4A−Cu1−Br1	106.45(6)
N2−Cu1−Br1	108.54(6)	N1−Cu1−Br1	109.21(6)

the SHELXTL crystallographic software package.[24] All graphics were prepared using the SHELXTL and Crystalmaker software packages.[24,26]

The cyano groups of compound **4** were crystallographically disordered. The positions of the N atoms and the C atoms of the cyano groups were modeled with each position having an occupancy of 50% of each atom type. The temperature factors were then simultaneously refined.

Results and Discussion

Synthesis. Conventional synthetic methods such as crystallization from saturated solutions have afforded numerous structurally interesting solid state compounds from halocuprate-protonated organoamine systems. Such methods have rarely yielded solid-state materials where in the organoamine is incorporated as a member of the micro- and macrostructure in other than a hydrogen bonding role. The exploitation of hydrothermal reaction methods to prepare compounds **1**−**4** demonstrates the utility of such methods in preparing new solid-state structures.

Initial explorations of the hydrothermal chemistry of bipypy with copper halides were not promising. Reaction conditions and reagent concentrations similar to those used to prepare $[(en)_2Cu]_2[Cu_7Cl_{11}]$ merely resulted in the formation of black, malodorous oils. However, by decreasing the concentrations of reactants to those reported in the Experimental Section, compounds **1**−**4** were prepared as crystalline materials amenable to structural characterization via single-crystal X-ray diffraction experiments.

While attempts to synthesize a homologous series led to the preparation of compounds **1**−**3**, efforts to prepare the copper iodide analogues proved unsuccessful, yielding only dark, viscous oils with offensive odors.

As the psuedo-halide cyanide has proved a useful ligand for linking metal centers in solid-state composite materials, hydrothermal reactions of CuCN, KCN, and bipypy were carried out. Compound **4** was the sole crystalline product observed from these studies.

Descriptions of the Structures. The structure of $[Cu_3Cl_3(bipypy)]$ (**1**), a two-dimensional network, was somewhat unaniticipated since the bipypy ligand adopts monodentate modes as well as the anticipated bidentate geometry. In compound **1**, every N donor of the bipypy ligand ligates to Cu sites. Thus each bipypy molecule is bonded to three Cu atoms: two via monodentate coordination through a pyrazyl N atom and a pyridyl N atom and one via the bidentate chelation of the remaining pyrazyl and pyridyl N atoms, as shown in Figure 1a. Selected bond lengths and angles for compound **1** are listed in Table 2.

There are three crystallographically unique Cu atoms participating in a $\{Cu_3Cl_3\}$ ring. The Cu1 site adopts a distorted tetrahedral coordination geometry with two N donors provided by the chelating bipypy ligand and with two chlorine atoms, Cl1 and Cl2 of the $\{Cu_3Cl_3\}$ ring, constituting the remainder of the coordination sphere.

Chlorine atoms Cl1 and Cl2 bridge the Cu sites in μ_3 and μ_2 modes, respectively. The μ_3 bridging mode of Cl1 constrains the atom to a distorted trigonal planar geometry with the Cu−Cl1−Cu bond angles ranging from 102.2(1)° to 117.2(1)°. In contrast, the Cu1−Cl2−Cu3 bond angle is acute at 86.9(1)°. The third Cl atom of the $\{Cu_3Cl_3\}$ ring, Cl3, also participates in μ_2 bridging of Cu atoms with a bond angle of 85.1(1)°.

The Cu2 site also exhibits tetrahedral geometry through coordination to two N and two Cl donors. One N atom is drawn from a pyridyl ring of one bipypy molecule and the second N atom is drawn from a pyrazine ring of a second bipypy molecule.

---

(25) Macgillary, C. H., Rieck, G. D., Eds. *International Tables for Crystallography*; Kynoch Press: Birmingham, England, 1962; Vol. III.

(26) Palmer, D. C. *Crystalmaker*^{2}, Version 2.1.6; Apple Computer, Inc.: Cupertino, CA, 1994−1997.

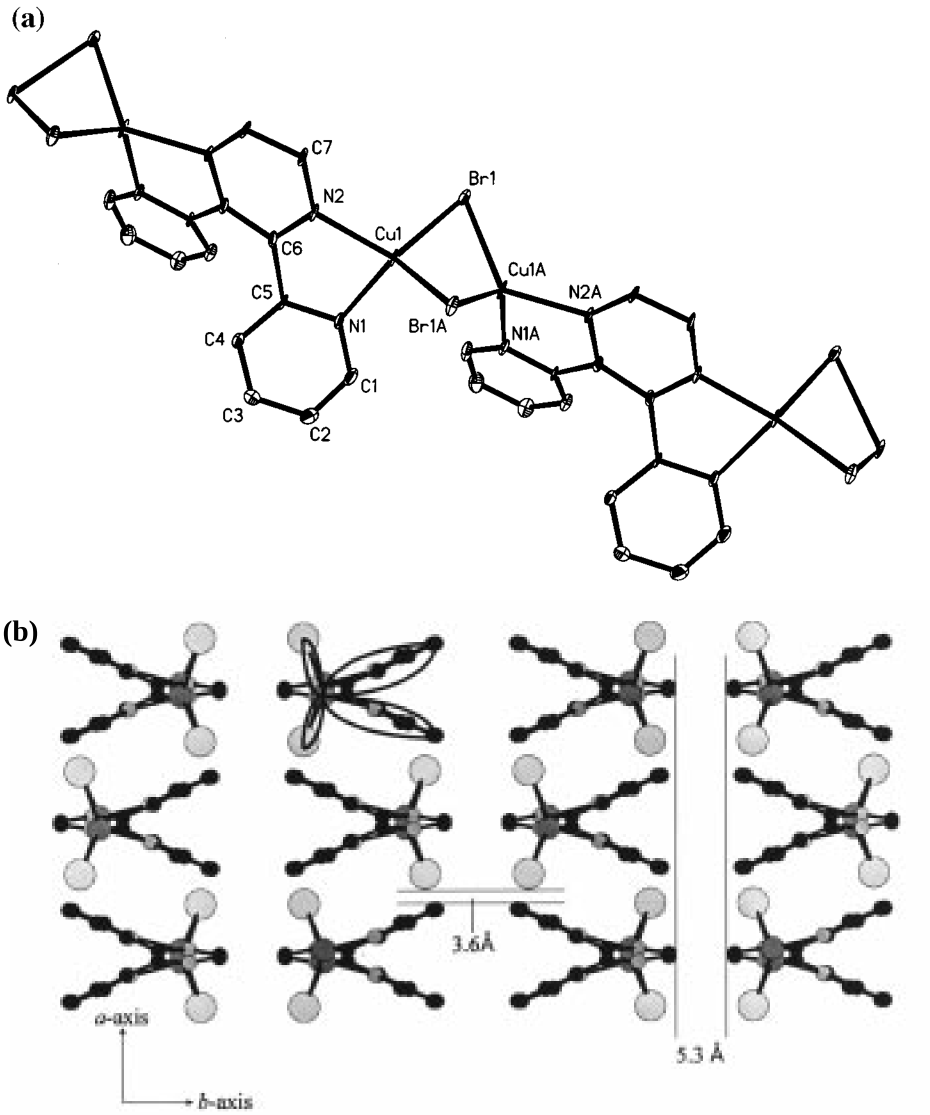


Figure 4. (a) A view of the composite inorganic−organic chain of compound **3** with the Br, Cu, and N atoms of two asymmetric units indicated (atoms are represented as 50% thermal ellipsoids); (b) crystal packing of compound **3** viewed parallel to the crystallographic *c* axis, the interchain spacing within rows and the interrow spacings are noted. The thick black curved lines denote the degree of distortion of the four-leafed clover motifs described in the text. Hydrogen atoms have been omitted for clarity. Large light gray circles, small black circles, small dark gray circles, and small light gray circles denote Br, C, Cu, and N atoms, respectively.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound **3**

Br1−Cu1	2.4546(7)	Br1−Cu1A	2.4618(6)
Cu1−N2	2.053(3)	Cu1−N1	2.054(3)
Cu1−Br1A	2.4168(6)		
Cu1−Br1−Cu1A	62.8(2)	N2−Cu1−N1	80.4(1)
N2−Cu1−Br1	109.5(7)	N1−Cu1−Br1	126.38(7)
N2 Cu1−Br1A	127.22(8)	N1−Cu1−Br1A	107.76(7)
Br1−Cu1−Br1A	106.39(2)		

The Cu3 site coordinates exclusively to chloride atoms. Two of the Cl atoms bonded to Cu3, Cl2 and Cl3, derive from the same {Cu_3Cl_3} ring containing Cu3 while the third is from an adjacent {Cu_3Cl_3} ring. The Cu3 site exhibits a distorted trigonal pyramidal coordination geometry with Cl−Cu3−Cl bond angles ranging from 110.1(1)° to 133(3)°.

This latter bridging interaction between {Cu_3Cl_3} rings provided by Cl1 leads to inorganic chains constructed from {Cu_3Cl_3} rings. The chains propagate parallel to the crystallographic *b* axis and are linked through the bidentate chelation of each bipypy ligand molecule to one Cu atom of one {Cu_3Cl_3} ring of one chain and the monodentate coordination of the two remaining N atoms of the ligand molecule to individual Cu atoms of two separate {Cu_3Cl_3} rings of an adjacent metal halide chain, as shown in Figure 1b. This pattern generates a layered structure with distinct organic and inorganic surfaces.

The layers stack along the crystallographic *c* axis with the organic face of one layer oriented toward the inorganic face of the adjacent layer. The layers are separated by ca. 3.4 Å, as shown in Figure 1c. The individual layers are ca. 5.6 Å in depth. The organic and inorganic portions of adjacent layers are staggered from layer to layer. Alignment of the compositionally equivalent layer sections does occur for every second layer. The Cl2 and Cl3 ligands project from each layer toward the region defined by two sets of bipypy ligands linking the rows of {Cu_3Cl_3} rings of a subsequent layer.

Although [CuBr(bipypy)]$_2$ (**2**) was prepared in an attempt to isolate the heavier homologues of the Cl derivative **1**, it is not structurally analogous to compound **1**. Compound **2** is a dimeric molecular species, with terminal bromide ligands exclusively. Each organoamine ligand molecule is bonded in a monodentate

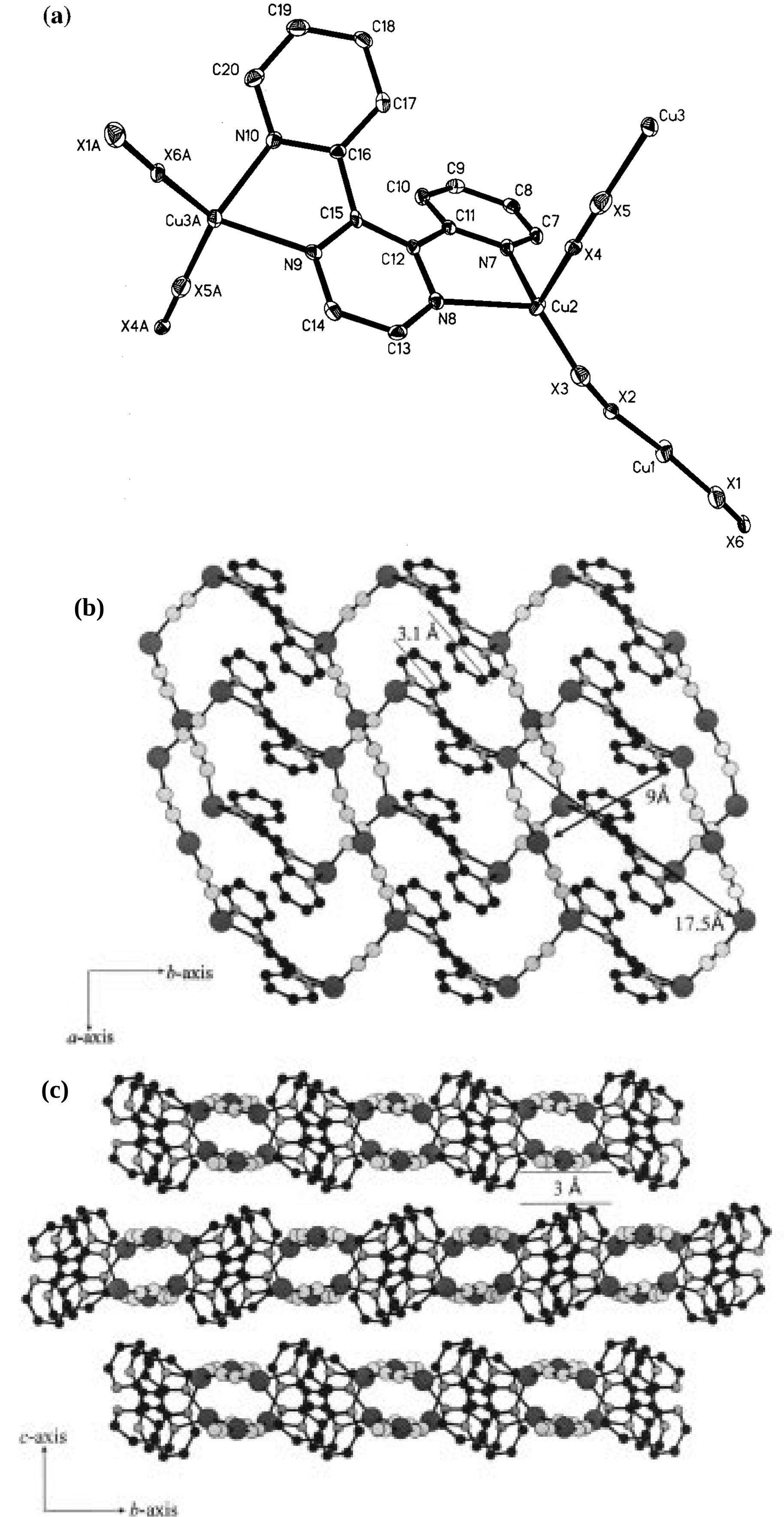


Figure 5. (a) View of the asymmetric unit of compound **4** with the cyanide atoms marked as X due to the disorder of the sites; symmetry equivalents have been included to complete the coordination spheres (atoms are represented as 50% thermal ellipsoids); (b) the interdigitation of two neutral sheets composed of fused $\{Cu_8(CN)_6(pyr)_2\}$ rings of compound **4** to form a layer with the interpyridyl ring distance between bipypy pyridyl rings indicated; the layer is viewed parallel to the crystallographic *c* axis; (c) the crystal packing of compound **4** when viewed parallel to the crystallographic *a* axis, the staggering of the inorganic−organic components of the composite material is clearly visible as is the inlayer spacing. Small black circles, large dark gray circles, small light gray circles, and larger light gray circles denote C, Cu, N, and cyanide atoms (X), respectively.

fashion to one Cu atom, and chelates in a bidentate fashion to the second Cu site, as shown in Figure 2a. The distorted tetrahedral geometries are consisitent with the formal Cu(I) oxidation states. The major distortion from idealized geometry is the N1−Cu1−N2 bond angle of 79.15(9)°. Selected bond lengths and angles for compound **2** are compiled in Table 3.

The molecules of $[CuBr(bipypy)]_2$ are oriented to provide a border for a region containing the waters of crystallization, which are associated as pairs into a flat "band" in a zigzag pattern, with O···O separations of ca. 3 Å, as shown in Figure 2b. The separation between pairs is ca. 5.8 Å. Hydrogen bonding appears to be significant between adjacent water molecules in the water band. Two distinct absorptions assigned as the terminal (O−H) stretch at 3542 cm^{-1} and as (O···H−O) at 3475 cm^{-1} can be resolved in the IR spectrum of compound **2** (Figure 3).[27] The molecules can be distinguished by their orientations relative to the water band. One group directs the edges of the pyridyl rings toward the water band, while the second projects terminal Br atoms toward two different water bands (Figure 2b). The O···Br distance of ca. 3.3 Å suggests only weak van der Waals contacts.[28]

The structure of $[Cu_2Br_2(bipypy)]$ (**3**) consists of a one-dimensional organic−inorganic chain of alternating bipypy ligand molecules and $\{Cu_2Br_2\}$ rings (Figure 4a). Each ligand molecule is chelated in a bidentate fashion to two Cu atoms, one from each of two different $\{Cu_2Br_2\}$ rings. Each Cu(I) center exhibits severely distorted tetrahedral coordination geometry defined by the N atoms from the chelated ligand and two Br atoms. The degree of distortion is evidenced by the N1−Cu1−N2 bond angle of 80.5(1)°. Each Br atom participates in μ_2 bridging between the Cu atoms of one $\{Cu_2Br_2\}$ ring, with a Cu1−Br1−Cu1A bond angle of 62.80(2)°. The nonplanarity of the $\{Cu_2Br_2\}$ rings results in a short Cu to Cu distance of ca. 2.56 Å. Despite the short distance between the Cu(I) centers, the d^{10} valence electronic configuration of such species would preclude direct bonding interactions between the metal centers.[29] Selected bond lengths and angles for compound **3** are tabulated in Table 4.

Figure 4b shows that when the structure of **3** is viewed parallel to the crystallographic *c* axis, the cross sections of the chains form severely distorted four-leafed clovers. Two arms of each four-leafed clover are composed of portions of the bipypy ligand and two are composed of the Br atoms of the $\{Cu_2Br_2\}$ rings. The chains pack to form rows of aligned four-leafed clover stacks separated by ca. 3.6 Å. The separation between rows is ca. 5.3 Å. The chain components of each row are positioned such that the organic arms of the four-leafed clovers formed by the chains do not interact within a row but are oriented toward each other across the row to row separation.

The structure of $[Cu_3(CN)_3(bipypy)]$ (**4**) exhibits each bipypy ligand chelated to two Cu atoms in the bidentate fashion previously described for compound **3** (Figure 5a). In contrast to compound **3**, the bipypy molecules of compound **4** are not members of a simple chain structure, but rather link Cu sites to form a 28-membered ring (Figure 5b).

Each Cu atom chelated by a bipypy ligand is also coordinated by two cyano ligands in a distorted tetrahedral geometry, with two acute angles, N8−Cu2−N7 and N9−Cu3−N10 bond angles of 77.9(1)° and 77.6(1)°, respectively, and two obtuse angles, X3−Cu2−N8 of 125.5(1)° and X5A−Cu3−N10 of 131.3(1)°. A third Cu atom displays nearly linear coordination geometry to two cyano groups (Table 5). There are three crystallographically unique cyano moieties in the structure and three distinct C≡N stretches can be resolved in the IR spectrum of compound **4** at 2137, 2125, and 2100 cm^{-1}.[30]

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound **4**

Cu1−C(N)2	1.843(3)	Cu1−C(N)1	1.854(4)
Cu2−C(N)3	1.891(4)	Cu2−C(N)4	1.971(3)
Cu2−N7	2.093(3)	Cu2−N8	2.153(3)
Cu3−C(N)5	1.917(4)	Cu3−C(N)6	1.967(3)
Cu3−N10	2.094(3)	Cu3−N9	2.181(3)
C(N)1−C(N)6	1.162(4)	C(N)2−C(N)3	1.163(4)
C(N)4−C(N)5A	1.153(5)		
C(N)2−Cu1−C(N)1	172.7(2)	C(N)3−Cu2−C(N)4	124.6(1)
C(N)3−Cu2−N7	111.5(1)	C(N)4−Cu2−N7	105.0(1)
C(N)3−Cu2−N8	126.5(1)	C(N)4−Cu2−N8	100.5(1)
N7−Cu2−N8	77.9(1)	C(N)5−Cu3−C(N)6	120.8(1)
C(N)5−Cu3−N10	131.3(1)	C(N)6−Cu3−N10	98.4(1)
C(N)5−Cu3−N9	104.6(1)	C(N)6−Cu3−N9	117.4(1)
N10−Cu3−N9	77.6(1)		

The 28-membered rings of compound **4** are composed of eight Cu atoms, six cyano groups, and two N atoms and two C atoms of the pyrazyl ring of the bipypy molecule. The ring can be formulated as $\{Cu_8(CN)_6(pyr)_2\}$ (pyr = pyrazyl). The Cu atoms are distributed in two linearly coordinated sites on opposing edges and in six tetrahedral coordination sites with three to each of the remaining sides. A parallelogram of dimensions, 9 Å × 17.5 Å is roughly outlined by the $\{Cu_8(CN)_6(pyr)_2\}$ unit with the pyr components "denting" two corners. Each $\{Cu_8(CN)_6(pyr)_2\}$ ring is fused to six adjacent rings to form a neutral sheet. The sheets dispose the pyridyl rings of the bipypy ligands such that they project from the same face of a given sheet, forming a hydrophobic region.

Two such sheets can be seen to interdigitate their pyridyl rings when overlaid (Figure 5c) with the hydrophobic faces oriented toward each other to form layers. Adjacent pyridyl rings from separate sheets are oriented face to face with a separation of ca. 3.1 Å, a distance consistent with a π-stacking interaction.[31] A layer formed by the overlay of two sheets is divided from adjacent layers by ca. 3 Å. The "organic" pyridyl groups of one layer are staggered in such a fashion that the organic domains are aligned with the inorganic copper cyanide portions of the adjacent layers (Figure 5c).

Observations and Conclusions

The use of the bipypy molecule as a potential bridging ligand allowed the preparation of a series of new copper halide and pseudo-halide compounds from hydrothermal media. Not only were novel one- and two-dimensional solid-state inorganic−organic composite phases synthesized and structurally characterized, but an unusual neutral molecular dimer was also observed.

The low reagent concentrations required for the isolation of the halide phases of this study, compared to those required for the synthesis of the $[Cu_3X_3(bpy)_2]$ phases, provide a useful experimental observation. However, the synthetic conditions for the cyano compound **4** were more similar to other copper organoamine−cyanide phases prepared from hydrothermal conditions than those employed for the halide phases of this study.

---

(27) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrophotometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1991; pp 110−111.

(28) Müller, U. *Inorganic Structural Chemistry*; John Wiley & Sons: New York, 1993; p 31.

(29) Pykkö, P.; Runeberg, N.; Fernando, M. *Chem. Eur. J.* **1997**, *3*(9), 1451.

(30) Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; Academic Press: New York, 1976; pp 226−271.

(31) Wright, J. D. *Molecular Crystals*; Cambridge University Press: New York, 1987; Chapter 3.

The initial expectation that the bipypy ligand would participate in bidentate chelation through both potential chelation sites proved to be naive. Compound **1** and the binuclear compound **2** exhibited both chelating and monodentate coordination modes, while the N3 site of the ligand remains unligated in **2**. All nitrogen sites of the ligand in compound **1** were coordinated to metal centers, thus bridging the three metal sites. In contrast, the doubly chelated mode expected for the bipypy ligand was observed in compounds **3** and **4**.

The demonstrated preference for the structurally characterized phases to form hydrophobic and hydrophilic regions may rationalize the observation of only molecules, one-dimensional, and two-dimensional archetypes. The formation of hydrophobic regions for each structure may prevent the continued condensation which drives structure genesis.[32] The binuclear species **2** would then represent the ultimate result of interrupted self-assembly of potentially higher dimensional structure types.

Acknowledgment. Funding for this work was through NSF Grant CHE9617232, NIH Grant GM34548, and the W. M. Keck Foundation.

Supporting Information Available: Listings of crystal data and collection parameters, atomic positional parameters, aniosotropic thermal parameters, and all bond lengths and angles for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990132X

---

(32) Zapf, P. J.; Hammond, R. P.; Haushalter, R. C.; Zubieta, J. *Chem. Mater.* **1998**, *10*, 1366.