Investigations of the Copper Bromide−2,2′-Dipyridyl System: Hydrothermal Synthesis and Structural Characterization of Molecular $Cu_3Br_4(C_{10}H_8N_2)_2$, One-Dimensional $CuBr_2(C_{10}H_8N_2)$, and Two-Dimensional $[Cu_2(OH)_2(C_{10}H_8N_2)_2][Cu_4Br_6]$

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The hydrothermal reactions of $CuBr_2$, CuBr, and 2,2′-dipyridyl have resulted in the synthesis of three new compounds. $Cu_3Br_4(C_{10}H_8N_2)_2$ (**1**) is a molecular phase; $CuBr_2(C_{10}H_8N_2)$ (**2**) is a one-dimensional chain structure; and $[Cu_2(OH)_2(C_{10}H_8N_2)_2][Cu_4Br_6]$ (**3**) crystallizes in a two-dimensional sheet structure. All three compounds were characterized by single-crystal X-ray diffraction. Crystal data for **1**, triclinic, space group $P\bar{1}$ (No. 2) with $a = 10.604(2)$ Å, $b = 11.642(2)$ Å, $c = 11.688(2)$ Å, $\alpha = 61.965(5)°$, $\beta = 68.965(5)°$, $\gamma = 69.523(5)°$, $Z = 2$; **2**, monoclinic, space group $C2/c$ (No. 15) with $a = 16.766(4)$ Å, $b = 9.287(2)$ Å, $c = 7.392(2)$ Å, $\beta = 110.536(6)°$, $Z = 4$; **3**, monoclinic, space group $P2_1/n$ (No. 14) with $a = 10.907(3)$ Å, $b = 6.0677(13)$ Å, $c = 21.620(5)$ Å, $\beta = 90.542(4)°$, $Z = 4$.

Introduction

The recent characterization of $[(H_2N(CH_2)_2NH_2)_2Cu]Cu_7Cl_{11}$,[1] which has a novel three-dimensional copper halide framework, has provoked our interest in the hydrothermal synthesis of other anionic copper halide framework structures which are templated by bulky organic ligands. This approach has been successfully applied to the synthesis of a wide range of organically templated transition metal-oxide frameworks such as molybdenum phosphates,[2] vanadium phosphates,[3] cobalt phosphates,[4] and vanadium oxides.[5] One aspect of our investigation has focused on the reactions of CuBr, $CuBr_2$, and 2,2′-dipyridyl under mild hydrothermal conditions. While the reaction of CuBr with 2,2′-dipyridyl has previously been studied under ambient conditions,[6] only the 1:1 adduct was formed.

Table 1. Crystal Data and Structure Refinement for $Cu_3Br_4(C_{10}H_8N_2)_2$ (**1**), $CuBr_2(C_{10}H_8N_2)$ (**2**), and $[Cu_2(OH)_2(C_{10}H_8N_2)_2][Cu_4Br_6]$ (**3**)

	1	**2**	**3**
empirical formula	$Cu_3Br_4C_{20}H_{16}N_4$	$CuBr_2C_{10}H_8N_2$	$Cu_3Br_3C_{10}H_9N_2O$
fw	822.26	379.54	603.54
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)
a (Å)	10.604(2)	16.766(4)	10.907(3)
b (Å)	11.642(3)	9.287(2)	6.0677(13)
c (Å)	11.688(3)	7.392(2)	21.620(5)
α (deg)	61.965(5)		
β (deg)	68.346(5)	110.536(6)	90.542(4)
γ (deg)	69.523(5)		
V (Å^3)	1156.1(4)	1077.9(5)	1430.8(6)
Z	2	8	4
ρ_{calc} (g/cm^3)	2.363	2.339	2.802
T (K)	120	120	120
λ (Å)	0.710 73	0.710 73	0.710 73
μ (mm^{-1})	9.664	9.403	12.785
wR2[a]	0.0947	0.0890	0.0786
R1[b]	0.0582	0.0423	0.0622

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

As a result of our investigations, several new compounds have been prepared displaying a wide range of structure types. We report the synthesis and structural characterization of three new phases, $Cu_3Br_4(C_{10}H_8N_2)_2$ (**1**), $CuBr_2(C_{10}H_8N_2)$ (**2**), and $[Cu_2(OH)_2(C_{10}H_8N_2)_2][Cu_4Br_6]$ (**3**), obtained from the reaction of CuBr and $CuBr_2$ with 2,2′-dipyridyl (Table 1).

Experimental Section

All syntheses were conducted using reagent grade CuBr, $CuBr_2$, CuO, and 2,2′-dipyridyl, purchased from Aldrich Chemical Co. and used without further purification. All hydrothermal reactions were performed in 23-mL polyfluoroethylene-lined stainless steel Parr bombs under autogenous pressure.

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Table 2. Atomic Coordinates and Isotropic Thermal Displacement Parameters (Å^2) for $Cu_3Br_4(C_{10}H_8N_2)_2$ (**1**)

	x	y	z	U_{eq}^{a}
Br(1)	−0.09707(5)	1.05894(5)	0.31448(5)	0.0215(1)
Br(2)	0.03669(5)	0.80920(5)	0.09581(5)	0.0200(1)
Br(3)	0.28521(5)	0.97978(5)	0.10122(6)	0.0210(1)
Br(4)	0.35120(6)	0.54164(5)	0.26071(6)	0.0254(2)
Cu(1)	−0.29493(6)	1.25878(6)	0.33664(6)	0.0161(2)
Cu(2)	0.03747(7)	1.02502(7)	0.10912(7)	0.0248(2)
Cu(3)	0.26068(8)	0.76484(7)	0.16395(7)	0.0260(7)
C(1)	−0.3034(5)	1.4693(5)	0.0512(5)	0.020(1)
C(2)	−0.2754(6)	1.5836(5)	−0.0582(6)	0.022(1)
C(3)	−0.1922(6)	1.6528(5)	−0.0556(5)	0.021(1)
C(4)	−0.1389(5)	1.6022(5)	0.0543(5)	0.020(1)
C(5)	−0.1713(5)	1.4858(5)	0.1607(5)	0.017(1)
C(6)	−0.1192(5)	1.4241(5)	0.2827(5)	0.014(1)
C(7)	−0.0209(5)	1.4682(5)	0.2959(6)	0.021(1)
C(8)	0.0229(5)	1.4010(5)	0.4133(6)	0.021(1)
C(9)	−0.0269(5)	1.2903(5)	0.5118(5)	0.019(1)
C(10)	−0.1214(5)	1.2490(5)	0.4908(5)	0.019(1)
C(11)	−0.4600(5)	1.2961(5)	0.5970(5)	0.021(1)
C(12)	−0.5699(6)	1.2850(6)	0.7092(6)	0.026(1)
C(13)	−0.6781(5)	1.2336(6)	0.7238(6)	0.024(1)
C(14)	−0.6724(5)	1.1983(5)	0.6244(5)	0.019(1)
C(15)	−0.5596(5)	1.2122(5)	0.5146(5)	0.015(1)
C(16)	−0.5437(5)	1.1765(5)	0.4032(5)	0.014(1)
C(17)	−0.6422(5)	1.1246(5)	0.3990(5)	0.019(1)
C(18)	−0.6155(6)	1.0917(5)	0.2923(6)	0.022(1)
C(19)	−0.4936(6)	1.1102(5)	0.1932(6)	0.021(1)
C(20)	−0.4009(5)	1.1602(5)	0.2038(5)	0.018(1)
N(1)	−0.2536(4)	1.4207(4)	0.1595(4)	0.0169(9)
N(2)	−0.1673(4)	1.3156(4)	0.3786(4)	0.0142(8)
N(3)	−0.4530(4)	1.2575(4)	0.5033(4)	0.0147(8)
N(4)	−0.4257(4)	1.1938(4)	0.3072(4)	0.0163(9)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates and Isotropic Thermal Displacement Parameters (Å^2) for $CuBr_2(C_{10}H_8N_2)$ (**2**)

	x	y	z	U_{eq}^{a}
Br(1)	0.40751(2)	0.39085(4)	0.04996(5)	0.179(1)
Cu(1)	$^{1}/_{2}$	0.57377(7)	$^{1}/_{4}$	0.153(2)
N(1)	0.4273(2)	0.7412(3)	0.1056(4)	0.146(6)
C(1)	0.3525(2)	0.7329(4)	−0.0407(5)	0.200(8)
C(2)	0.3044(2)	0.8578(5)	−0.1253(5)	0.208(8)
C(3)	0.3360(3)	0.9886(5)	−0.0545(6)	0.265(9)
C(4)	0.4137(3)	0.9966(5)	0.0925(6)	0.229(8)
C(5)	0.4596(3)	0.8734(4)	0.1711(5)	0.171(8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

$Cu_3Br_4(C_{10}H_8N_2)$, 1. The hydrothermal reaction of $CuBr_2$ (0.223 g, 1.0 mmol), CuBr (0.143 g, 0.1 mmol) and 2,2′-dipyridyl (0.243 g, 1.6 mmol) in 5 mL of H_2O in a mole ratio of 1:1:1.6:278, at 170 °C for 3 days, resulted in the formation of black crystals of **1** in an approximate yield of 75% based on Cu(I).

$CuBr_2(C_{10}H_8N_2)$, 2. The hydrothermal reaction of $CuBr_2$ (0.446 g, 2.0 mmol), CuBr (0.143 g, 0.1 mmol) and 2,2′-dipyridyl (0.243 g, 1.6 mmol) in 5 mL of H_2O in a mole ratio of 2:1:1.6:278, at 170 °C for 3 days resulted in the formation of brown-black plates of **2** in a total yield of approximately 30% based on Cu(I).

$[Cu_2(OH)_2(C_{10}H_8N_2)_2][Cu_4Br_6]$, 3. Black plates of **3** (total yield approximately 90% based on Cu(I)) and a minor product of an unidentified phase of thin aqua-blue plates were initially prepared by reacting $CuBr_2$ (0.224, 1.0 mmol), CuBr (0.143 g, 0.1 mmol), CuO (0.080, 1.0 mmol), and 2,2′-dipyridyl (0.243 g, 1.6 mmol) in 5 mL of H_2O in a mol ratio of 1:1:1:1.6:278, at 170 °C for 3 days. **3** could also be prepared as a minor product of black needles (approximately 10% yield based on Cu(I)), in an unidentified, polycrystalline, chrome-green matrix from the reaction of CuBr (0.430 g, 3.0 mmol) and 2,2′-dipyridyl (0.156 g, 1.0 mmol) in 5 mL of water in a mole ratio of 3:1:278 at 170 °C for 3 days.

Table 4. Atomic Coordinates and Isotropic Thermal Displacement Parameters (Å^2) for $[Cu_2(OH)_2(C_{10}H_8N_2)_2][Cu_4Br_6]$ (**3**)

	x	y	z	U_{eq}^{a}
Br(1)	0.87839(4)	0.14182(8)	0.23599(2)	0.0180(1)
Br(2)	0.55072(4)	0.15862(8)	0.14447(2)	0.0197(1)
Br(3)	0.80916(4)	0.64991(8)	0.11240(2)	0.0199(1)
Cu(1)	0.58892(5)	−0.40845(10)	−0.04239(3)	0.0162(2)
Cu(2)	0.71309(6)	−0.08625(12)	0.18149(3)	0.0310(2)
Cu(3)	0.72118(6)	0.38212(11)	0.18282(3)	0.0286(2)
O(1)	0.5211(3)	−0.3445(5)	0.0378(2)	0.0188(7)
N(1)	0.7126(3)	−0.1707(6)	−0.0414(2)	0.0155(8)
N(2)	0.6908(3)	−0.5137(7)	−0.1124(2)	0.0163(9)
C(1)	0.7104(5)	0.0053(8)	−0.0046(2)	0.019(1)
C(2)	0.8050(5)	0.1606(8)	−0.0036(2)	0.022(1)
C(3)	0.9017(4)	0.1289(8)	−0.0430(2)	0.023(1)
C(4)	0.9051(4)	−0.496(8)	−0.0816(2)	0.020(1)
C(5)	0.8079(4)	−0.2000(8)	−0.0803(2)	0.016(1)
C(6)	0.7970(4)	−0.3970(8)	−0.1200(2)	0.016(1)
C(7)	0.8853(4)	−0.4671(9)	−0.1610(2)	0.023(1)
C(8)	0.8648(5)	−0.6560(9)	−0.1959(2)	0.029(1)
C(9)	0.7552(5)	−0.7680(9)	−0.1895(2)	0.027(1)
C(10)	0.6707(5)	−0.6925(8)	−0.1469(2)	0.021(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $Cu_3Br_4(C_{10}H_8N_2)_2$ (**1**)

Br(1)−Cu(1)	2.5753(9)	Br(1)−Cu(2)	2.4336(10)
Br(2)−Cu(2)	2.5924(10)	Br(2)−Cu(2)#1[a]	2.4624(10)
Br(2)−Cu(3)	2.5873(10)	Br(3)−Cu(2)	2.4669(10)
Br(3)−Cu(3)	2.3359(10)	Br(4)−Cu(3)	2.2904(10)
Cu(1)−N(1)	2.067(4)	Cu(1)−N(2)	1.984(4)
Cu(1)−N(3)	2.045(4)	Cu(1)−N(4)	1.986(4)
Cu(1)−Br(1)−Cu(2)	126.88(3)	Cu(2)−Br(2)−Cu(2)#1	80.58(3)
Cu(2)−Br(2)−Cu(3)	72.88(3)	Cu(2)#1−Br(2)−Cu(3)	129.51(3)
Cu(2)−Br(3)−Cu(3)	79.62(3)	Br(1)−Cu(1)−N(1)	106.52(12)
Br(1)−Cu(1)−N(2)	87.86(12)	Br(1)−Cu(1)−N(3)	125.96(12)
Br(1)−Cu(1)−N(4)	91.71(12)	N(1)−Cu(1)−N(2)	80.8(2)
N(1)−Cu(1)−N(3)	127.4(2)	N(1)−Cu(1)−N(4)	102.9(2)
N(2)−Cu(1)−N(3)	96.3(2)	N(2)−Cu(1)−N(4)	176.2(2)
N(3)−Cu(1)−N(4)	80.9(2)	Br(1)−Cu(2)−Br(2)	117.26(3)
Br(1)−Cu(2)−Br(2)#1	116.14(4)	Br(1)−Cu(2)−Br(3)	107.33(3)
Br(2)−Cu(2)−Br(3)	98.95(3)	Br(2)#1−Cu(2)−Br(2)	99.42(3)
Br(2)#1−Cu(2)−Br(3)	116.69(3)	Br(2)−Cu(3)−Br(3)	102.64(3)
Br(2)−Cu(3)−Br(4)	111.96(3)	Br(3)−Cu(3)−Br(4)	145.39(4)

[a] Symmetry transformation used to generate equivalent atoms: #1, $-x, -y + 2, -z$.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for $CuBr_2(C_{10}H_8N_2)$ (**2**)

Br(1)−Cu(1)	2.4224(7)	Cu(1)−N(1)	2.033(3)
Br(1)−Cu(1)−Br(1)#1[a]	90.94(3)	Br(1)−Cu(1)−N(1)	94.50(9)
Br(1)−Cu(1)−N(1)#1	174.11(9)	N(1)#1−Cu(1)−N(1)	80.2(2)

[a] Symmetry transformation used to generate equivalent atoms: #1, $-x + 1, y, -z + {}^{1}/_{2}$.

Crystal Structure Determination. Crystallographic data for all three compounds were collected using a Siemens P4 diffractometer (Mo Kα radiation; $\lambda = 0.710\,73$ Å) equipped with the SMART system.[7] All three data sets were corrected for Lorentz and polarization effects, and absorption corrections were made using SADABS.[7] Structure solutions and refinements were carried out using the SHELXL96 software package. [7] All three structures were solved using direct methods and all of the non-hydrogen atoms were located from the initial solution or

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(7) (a) *SMART Sofware Reference Manual*; Siemens Analytical X-ray Instruments Inc.: Madison, WI. (b) Sheldrick, G. M. *SADABS. Program for Empirical Absorption Correction*; University of Göttingen: Germany. (c) Sheldrick, G. M. *SHELXL96: Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, **1996**.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for $[Cu_2(OH)_2(C_{10}H_8N_2)_2][Cu_4Br_6]$ (**3**)[a]

Br(1)−Cu(3)	2.5200(9)	Br(1)−Cu(2)	2.5523(9)
Br(1)−Cu(2)#2	2.6334(10)	Br(1)−Cu(3)#1	2.6038(9)
Br(2)−Cu(2)	2.4409(9)	Br(2)−Cu(3)	2.4401(9)
Br(3)−Cu(2)#3	2.4333(9)	Br(3)−Cu(3)	2.4304(9)
Cu(1)−O(1)	1.930(3)	Cu(1)−O(1)#4	1.923(3)
Cu(1)−N(1)	1.975(4)	Cu(1)−N(2)	1.992(4)
Cu(3)−Br(1)−Cu(2)	68.19(3)	Cu(3)−Br(1)−Cu(3)#1	111.80(2)
Cu(2)−Br(1)−Cu(3)#1	71.68(3)	Cu(3)−Br(1)−Cu(2)#2	71.70(3)
Cu(3)#1−Br(1)−Cu(2)#2	76.07(3)	Cu(2)−Br(1)−Cu(2)#2	112.46(2)
2			
Cu(3)−Br(2)−Cu(2)	71.26(3)	Cu(3)−Br(3)−Cu(2)#3	83.14(3)
Br(3)#5−Cu(2)−Br(2)	120.97(3)	Br(3)#5−Cu(2)−Br(1)	109.49(3)
Br(2)−Cu(2)−Br(1)	109.18(3)	Br(3)#5−Cu(2)−Br(1)#1	99.89(3)
Br(2)−Cu(2)−Br(1)#1	108.97(3)	Br(1)−Cu(2)−Br(1)#1	107.31(3)
Br(3)−Cu(3)−Br(2)	117.57(3)	Br(3)−Cu(3)−Br(1)	113.68(3)
Br(2)−Cu(3)−Br(1)	110.27(3)	Br(3)−Cu(3)−Br(1)#2	100.80(3)
Br(2)−Cu(3)−Br(1)#2	104.13(3)	Br(1)−Cu(3)−Br(1)#2	109.21(3)
O(1)#4−Cu(1)−O(1)	82.25(14)	O(1)#4−Cu(1)−N(1)	174.3(2)
O(1)−Cu(1)−N(1)	96.39(14)	O(1)#4−Cu(1)−N(2)	98.2(2)
O(1)−Cu(1)−N(2)	165.56(14)	N(1)−Cu(1)−N(2)	81.8(2)
Cu(1)#4−O(1)−Cu(1)	97.75(14)		

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

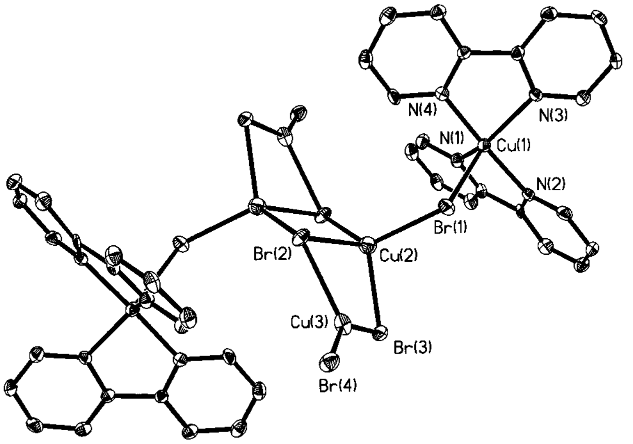

Figure 1. ORTEP drawing for the centrosymmetric dimer structure of **1**, showing 50% probability ellipsoids and the atom labeling scheme. Hydrogen atoms have been removed for clarity.

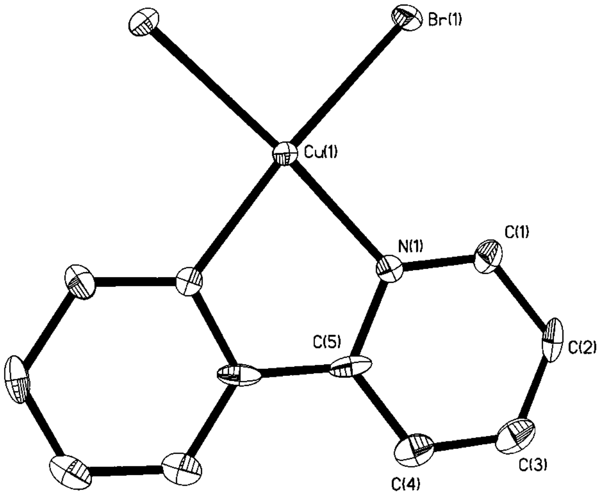

Figure 2. ORTEP drawing for the basic structure of **2**, showing 50% probability ellipsoids and the atom labeling scheme. Hydrogen atoms have been removed for clarity.

from subsequent electron density difference maps during the initial course of the refinement. After locating all of the non-hydrogen atoms the models were refined against F^2, first using isotropic and finally anisotropic thermal displacement parameters, until the value of Δ/σ_{max} was less than 0.001. The positions of the hydrogen atoms were then calculated and fixed, and a final cycle of refinements was performed, until Δ/σ_{max} was again less than 0.001 (Tables 2-7).

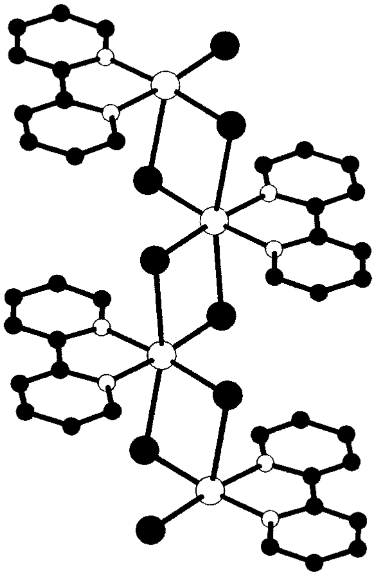

Figure 3. View of the one-dimensional chain structure of **2**, showing the long semicoordinate Cu−Br bonds (in Å) which join adjacent units.

Results and Discussion

While the application of the hydrothermal technique to synthetic crystal growth has been established for some time,[8] it is only recently that the method has begun to be used in the routine preparation of inorganic materials [9] such as oxomolybdenum phosphates,[2] oxovanadium phosphates,[3] and metal−organophosphonate systems.[10] Hydrothermal reactions conducted under mild conditions (i.e., at 110−260 °C under autogenous pressure) allow for the self-assembly of the product from soluble molecular precursors. The reduced viscosity of

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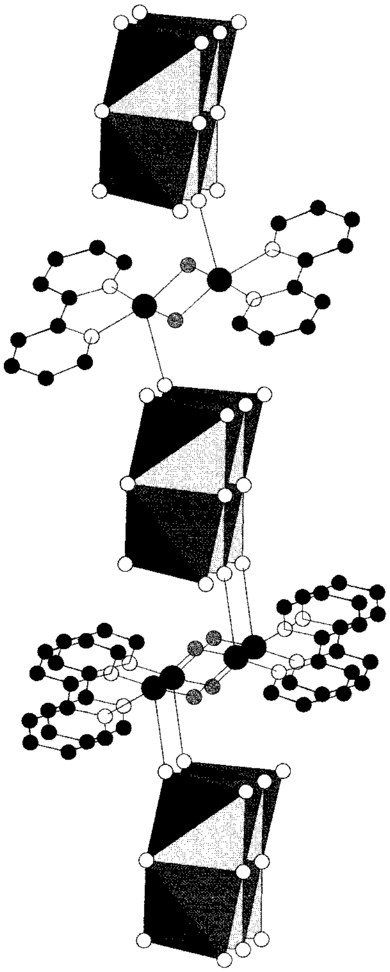

Figure 4. View of the two-dimensional sheets found in the **3** structure. The structure consists of one-dimensional $[Cu_4Br_6]^{2-}$ chains, shown as space-filling polyhedra, which are cross-linked by $[Cu_2(OH)_2(C_{10}H_8N_2)_2]^{2+}$ units via long semicoordinate Cu−Br bonds (in Å). The hydrogen atoms have been removed for clarity.

the solvent under these conditions leads to an increased rate of solvent extraction and crystal growth from the solution, while minimizing the problems associated with differential solubilities of the precursors. As a result, a large number of simple precursors may be employed, as well as a variety of organic and inorganic templating (i.e., structure-directing) agents, from which those of appropriate shape and size may be selected for efficient crystal packing during the process of crystallization.[11,12] The application of this technique to the synthesis of novel molecular clusters was recently demonstrated by the isolation of a series of compounds from the V−O-trisalkoxide system.[13,14] Although reactions of copper halides with organic ligands have been studied extensively, for example the large body if ongoing work by Willet and co-workers,[15] this research has primarily dealt with the chemistry of these materials under ambient conditions. As a result of our interest in the application of the hydrothermal method in the preparation of organically templated copper halide solid phases, the chemistry of 2,2′-dipyridyl with copper(I) and copper(II) bromide was investigated.

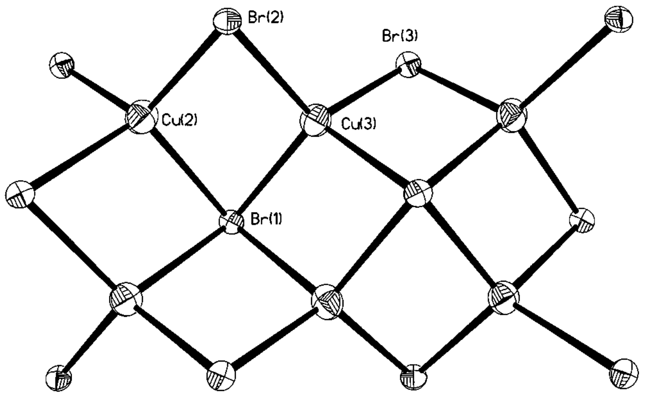

Figure 5. ORTEP drawing of the double chain of edge-sharing $CuBr_4$ tetrahedra in the $[Cu_4Br_6]^{2-}$ chains **3**, showing 50% probability ellipsoids and the atom labeling scheme.

$Cu_3Br_4(C_{10}H_8N_2)_2$ (**1**) crystallizes as a mixed valence, centrosymmetric dimer, resulting in the hexanuclear cluster shown in Figure 1. Each dimer contains one crystallographically unique divalent copper ion, Cu(1), and two monovalent copper ions, Cu(2) and Cu(3), occurring in a five-, four-, and 3-fold coordinate site, respectively. The divalent Cu(1) is in a distorted trigonal bipyramidal coordination, with axial Cu−N bonds of 1.984(4) and 1.986(4) Å and longer equatorial Cu−N bonds of 2.044(5) and 2.067(5) Å, in addition to an equatorial Cu−Br bond of 2.5753(9) Å. The monovalent Cu(2) site is tetrahedrally coordinated with Cu−Br bonds ranging from 2.4336(10) to 2.5924(10) Å, while Cu(3) is trigonally coordinated to two bridging and one terminal bromine atom (Br(2), Br(3), and Br(4), respectively). The Cu(3)−Br(2) and Cu(3)−Br(3) bonds are 2.5873(10) and 2.3359(10) Å, while the terminal Cu(3)−Br(4) bond is 2.2904(10) Å. As expected the shortest (i.e., strongest) Cu(3)−Br bond is to the terminal Br(4). The assignment of the formal oxidation states of the copper atoms was confirmed by calculating bond valence sums for the copper atoms using the software program STRUM OR.[16] The valence sums for Cu(1), Cu(2), and Cu(3) were calculated as 2.2, 1.1, and 1.1 respectively, confirming the assignment made above.

Figure 2 shows the fundamental building block for the structure of $CuBr_2(C_{10}H_8N_2)$ (**2**). Each copper(II) site is coordinated by two nitrogen atoms of a single dipyridyl ligand (Cu−N = 2.033(3) Å), and two bromine atoms (Cu−Br = 2.4224(7) Å). The square planar motifs are then stacked stepwise to form one-dimensional chains via long, semicoordinate Cu−Br bonds (Cu−Br = 3.137(1) Å), as illustrated in Figure 3. This results in a distorted 4+2 octahedral coordination geometry for the Cu(II) center, a common geometry in copper(II) halide species.[17] The orientation of the $CuBr_2(C_{10}H_8N_2)$ molecules alternates with each step, such that one-half of the dipyridyl groups lie on each side of the chain (see Figure 3), with gaps of approximately 6.7 Å between adjacent dipyridyl ligands. The chains are then aligned so that the dipyridyl units in one chain are directed toward the gaps in the adjacent chain.

The two-dimensional sheets of the $[Cu_2(OH)_2(C_{10}H_8N_2)_2][Cu_4Br_6]$ (**3**) structure consist of one-dimensional chains of edge sharing $CuBr_4$ tetrahedra which are cross-linked by planar [Cu2-

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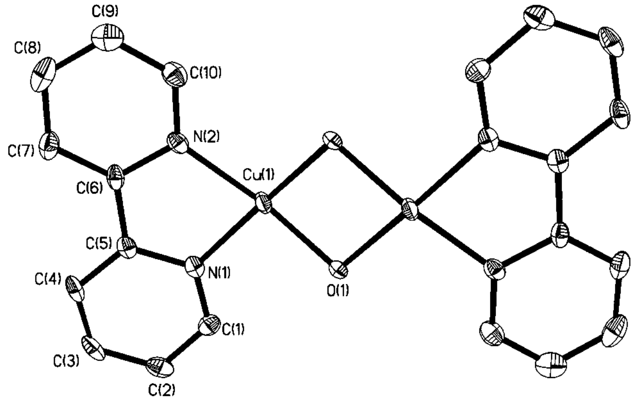

Figure 6. ORTEP drawing of the centrosymmetric $[Cu_2(OH)_2(C_{10}H_8N_2)_2]^{2+}$ units in **3**, showing 50% probability ellipsoids and the atom labeling scheme. Hydrogen atoms have been removed for clarity.

$(OH)_2(C_{10}H_8N_2)_2]^{2+}$ units (see Figure 4). The one-dimensional $[Cu_4Br_6]^{2-}$ chain has previously been observed,[18] and consists of a double chain of edge-sharing $CuBr_4$ tetrahedra (see Figure 5) running parallel to the *b* axis. These tetrahedra are highly distorted, with Cu−Br bond distances ranging between 2.4304(9) and 2.6334(10) Å and tetrahedral bond angles varying from 99.89(3) to 120.97°. The divalent copper center, Cu(1) located within the centrosymmetric $[Cu_2(OH)_2(C_{10}H_8N_2)_2]^{2+}$ unit, is coordinated to the two nitrogen atoms of the dipyridyl ligand (Cu−N = 1.975(4) and 1.992(4) Å) and to two bridging hydroxide ligands (Cu−O = 1.923(3) and 1.930(3) Å) as shown in Figure 6. Although it was not possible to locate the proton of the bridging hydroxide group during the structure refinement, its presence is required to balance the charge of the crystal structure and can be deduced from a calculation of the bond valence sum around the oxygen atom ($\sum s_{ij} = 1.01$ for the oxygen using only the two Cu−O bonds). The Cu(II) ion also has a long semi-coordinate Cu−Br bond (Cu−Br = 3.070(1) Å) linking it to an adjacent $[Cu_4Br_6]^{2-}$ chain, resulting in a [4+1] geometry (see Figure 4). As the two Cu(II) sites in each $[Cu_2(OH)_2(C_{10}H_8N_2)_2]^{2+}$ unit are linked to different $[Cu_4Br_6]^{2-}$ chains, the result is a cross-linking of the one-dimensional chains to form two-dimensional sheets.

The variety of structure types (i.e., molecular, one-dimensional, and two-dimensional) obtained from our preliminary study of the hydrothermal reactions of copper bromides with 2,2′-dipyridyl suggests that a rich field of diverse structural types is accessible by exploiting this technique. Further work in this are is in progress, including an extension to the iodides, and the use of other organic templating agents such as 1,2-diaminopropane and ethylenediamine.

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

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