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Novel Copper(I) Halide Polymers: Structures of Cu_2Br_2(2,3-dimethylquinoxaline) and (2,3-Di(bromomethyl)quinoxalinium)$CuBr_2$. The Continuing Saga of Copper(II) Bromide Reactivity with Organoamines

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Introduction

The design of low dimensional coordination polymers involving Cu(I) and/or Cu(II) halides is one of the current crystal engineering goals in our laboratory.[1,2] One particular interest is in the development of rectangular two-dimensional magnetic systems. One strategy is to build one-dimensional halide structures that are bridged by nonchelating bidentate ligands.[3] To this end, the reaction of copper(II) halides with 2,3-dimethylquinoxaline (henceforth, dmq) was undertaken with the goal of obtaining systems analogous to the pyrazine complexes, but with larger interlayer spacing due to the additional bulk of the dmq ligand. As frequently is observed in our syntheses with copper(II) halides, chemical processes involving reduction of Cu(II) occur, and these are often accompanied by halogenation of the organic species.[4] The three solid materials, two bromide and one chloride containing compounds, isolated in our study are all Cu(I) complexes. In addition, bromination of the methyl groups of the dmq molecule was found to occur in one of the compounds isolated. These results give further evidence for these processes. Structural analysis of the two bromide compounds is reported. The first of these compounds, (dmq)Cu_2Br_2, complements recent structural studies of such systems obtained by more conventional synthetic routes.[5] The copper halide framework in the second compound, (dBrmqH)$CuBr_2$, where $dBrmqH^+$ is the 2,3-di(bromomethyl)quinoxalinium cation, mirrors the structural characteristics of the paraquat salts of copper(I).[6]

Experimental Section

Syntheses. (dmq)Cu_2Br_2 (1). Anhydrous copper(II) bromide (1.03 g, 4.62 mmol) was added to 30 mL of 95% ethanol. The mixture was warmed, and the copper salt dissolved upon the addition of 5 mL of distilled water to give a green/black solution. The 2,3-dimethylquinozaline (0.722 g, 4.56 mmol) was dissolved in 30 mL of warm 95% ethanol. The warm copper solution was then added to the warm, colorless dmq solution to give a reddish brown solution. Upon evaporation of the solvent, reddish brown crystals began to form. The crystals were collected by filtration and allowed to air dry. Yield: 0.577 g, 56%. Elemental Analysis: Calcd. C, 26.98; H, 2.26; N, 6.29; Br, 35.90; Found C, 26.96; H, 2.19; N, 6.24; Br, 35.92. IR (KBr): 3009.4 w, 1553.1 w, 1487.5 m, 1396.5 m, 1379.1 m, 1332.1 m, 1198.5 m, 1175.9 m, 1136.1 m, 1001.6 m, 957.8 m, 836.3 m, 771.9 s. A crystal with dimensions approximately 0.16 × 0.07 × 0.03 mm was selected for the diffraction study.

(dBrmqH)$CuBr_2$ (2). 0.5 mmol of $CuBr_2$ (0.112 g) and 0.5 mmol of dmq (0.079 g) were dissolved in 50 mL of 95% ethanol, 5 mL of water, and 5 mL of 1M HBr. The solution was heated to ~70 °C and evaporated to dryness at that temperature. A few red, nearly opaque platelets were able to be separated out from the solid mass. A crystal with dimensions approximately 0.28 × 0.11 × 0.08 mm was selected for the diffraction study.

(dmq)Cu_2Cl_2 (3). Copper(II) chloride dihydrate (0.748 g, 4.39 mmol) was added to 30 mL of 95% ethanol. The copper salt dissolved to give a green solution. The 2,3-dimethylquinozaline (0.708 g, 4.71 mmol) was dissolved in 30 mL of warm 95% ethanol. The copper solution was then added to the warm, colorless dmq solution to give an emerald green solution. Upon evaporation of the solvent, reddish brown crystals began to form. The crystals were collected by filtration and allowed to air dry. Yield: 0.244 g, 31%. Elemental Analysis: Calcd. C, 33.72; H, 2.83; N, 7.86; Cl, 19.90; Found C, 34.24; H, 2.90; N, 7.94; Cl, 19.50. IR (KBr): 3019.8 w, 1545.5 w, 1490.1 m, 1396.2 m, 1376.4 m, 1331.4 m, 1195.9 m, 1177.2 m, 1136.6 m, 999.9 m, 958.9 m, 834.5 m, 771.3 s.

Elemental analyses were carried out by Desert Analytical (Phoenix, Arizona). The IR measurements were made on a Perkin−Elmer FT-1000 instrument.

X-ray Diffraction. Data were collected on a Bruker three-circle platform diffractometer equipped with a CCD detector, using the SMART[7] software, at −70 °C for **1** and 22 °C for **2**, and Mo K radiation ($\lambda = 0.71073$ Å). The data were processed using the SAINT[8] software,

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(4) (a) Willett, R. D. *Inorg. Chem*. **1987**, *26*, 3423. (b) Place, H.; Willett, R. D. *Acta Crystallogr*. **1988**, *C43*, 34. (c)Willett, R. D. *Acta Crystallogr*. **1988**, *C43*, 450. (d) Willett, R. D.; West, D. X. *Acta Crystallogr*. **1987**, *C43*, 2300.

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10.1021/ic010280z CCC: $20.00

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

	1	**2**
empirical formula	$C_{10}H_{10}Br_2Cu_2N_2$	$C_{10}H_9Br_4CuN_2$
Fw	445.10	540.37
cryst syst; space group	triclinic, *P*−1	monoclinic, *C*2/*c*
color, habit	orange plate	yellow needle
crystal dim, mm	0.16 × 0.07 × 0.03	0.28 × 0.11 × 0.08
a (Å)	8.1225(10)	24.384(11)
b (Å)	8.9171(11)	10.031(5)
c (Å)	9.3516(12)	11.934(6)
α (°)	117.063(2)	−
β (°)	91.017(2)	101.654(9)
γ (°)	103.174(2)	−
V (Å^3)	581.50(13)	2859(2)
Z	2	8
D_{calc} (Mg m^{-3})	2.542	2.511
μ (mm^{-1})	10.497	12.687
T (°C)	−70(2)	22(2)
λ (Å)	0.71073	0.71073
θ_{max}(°)	25.00	25.00
rfxns	2051	2252
final *R* indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0326$, $wR_2 = 0.0755$	$R_1 = 0.0410$, $wR_2 = 0.1027$
R indices (all data)^a	$R_1 = 0.0455$, $wR_2 = 0.0802$	$R1 = 0.0940$, $wR_2 = 0.1348$

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected Bond Lengths and Angles for **1** and **2**

Bond Lengths

1		**2**	
Cu(1)−Br(2)	2.4584(9)	Cu(1)−Br(1)	2.5049(18)
Cu(1)−Br(1)	2.4823(9)	Cu(1)−Br(1)#2	2.5681(16)
Cu(1)−Cu(2)	2.7236(10)	Cu(1)−Br(2)	2.4752(18)
Cu(2)−Br(2)	2.3872(9)	Cu(1)−Br(2)#1	2.4520(18)
N(1)−Cu(2)	1.991(4)	C(11)−Br(3)	1.956(7)
Cu(1)−N(4)#1	2.023(4)	C(12)−Br(4)	1.958(8)

Bond Angles

1		**2**	
Cu(1)−Br(2)−Cu(2)	68.38(3)	Br(1)−Cu(1)−Br(2)	108.33(6)
Br(1)−Cu(1)−Br(2)	112.30(3)	Br(1)−Cu(1)−Br(1)#2	100.81(6)
Br(2)−Cu(2)−Br(1)#2	115.24(3)	Br(1)−Cu(1)−Br(2)#1	112.35(6)
Cu(1)−Br(1)−Cu(2)#2	93.05(3)	Br(2)−Cu(1)−Br(2)#1	110.34(7)
Br(2)−Cu(1)−Br(1)#2	100.00(3)	Br(2)−Cu(1)−Br(1)#2	106.62(5)
Br(1)−Cu(1)−Br(1)#2	86.95(3)	Cu(1)−Br(1)−Cu(1)#2	77.13(6)
		Cu(1)−Br(2)−Cu(1)#1	69.66(7)

symmetry transformations:
#1 $x, y, z + 1$;
#2 $-x - 2, -y - 1, -z + 1$

#1 $-x, -y, -z$;
#2 $-x, y, -z + 0.5$

and absorption corrections were performed using the SADABS[9] program. The structures of the bromide compounds were solved by the direct method using the SHELX-90[10] program and refined by the least-squares method on F^2 using SHELXL-97,[11] incorporated in SHELXTL, version 5.10.[12] The crystals used for the diffraction study showed no appreciable decomposition during data collection. Crystals of the chloride compound were invariably twinned, and it was impossible to obtain a satisfactory structure solution. Table 1 summarizes the most important structural and refinement parameters, while a list of important distances and angles is given in Table 2. Figures 1 and 2 illustrate the molecular species.

Results and Discussion

The reaction of the Cu(II) halides with dmq to form compounds **1** and **3** proceeded spontaneously with the slow formation of red−brown crystals over a period of several hours to days, depending on temperature. Their IR spectra were virtually identical, indicating that the interaction of the dmq molecules with the copper halide was very similar in the two compounds. Unfortunately, the inherent twinning of the chloride crystals (compound **3**) precluded obtaining a definitive crystal structure. However, it was clearly not isomorphous with the bromide crystals (compound **1**). The formation of **2** occurred under more extreme conditions, and limited attempts to obtain pure samples of the material were unsuccessful.

The structure observed in **1** is closely related to the crystal chemistry of a series of copper(I) halides that have recently been reported. These studies have elucidated and elaborated upon a number of basic structural types. In the study by Graham et al.,[5] a number of basic structural types for copper(I) halide coordination polymers have been elucidated and elaborated upon. One of these is the so-called stairstep polymer (type **1a**, Chart 1).[13] With nonchelating bidentate ligands, such as pyrazine or quinoxaline, these polymers become linked together into two-

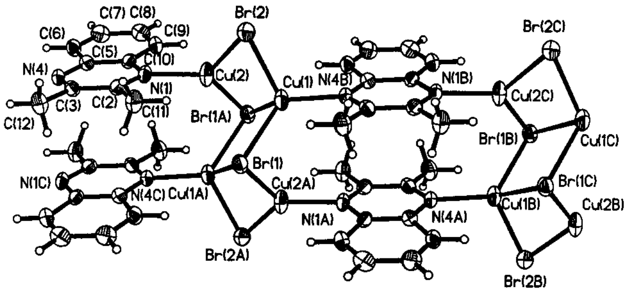

Figure 1. Illustration of the chain of tetramers in **1**. Thermal ellipsoids shown at the 50% level.

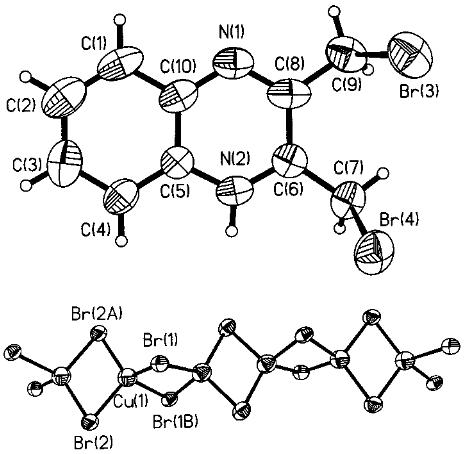

Figure 2. (a) Illustration of the brominated cation in **2**. (b) Illustration of the $(CuBr_2)_n^{n-}$ chain in **2**. Thermal ellipsoids shown at the 50% level.

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(8) *SAINT−Plus*, Version 6.02, Data Reduction Software for the SMART System; Bruker AXS Inc.: Madison, WI, 1999.

(9) *SADABS*, Version 2.01, Bruker/Siemens Area Detector Absorption Software; Bruker AXS Inc.: Madison, WI, 1999.

(10) Sheldrick, G. M. *SHELXS-90*, Program for the Solution of Crystal Structure,; University of Göttingen: Germany, 1986.

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(12) *SHELXTL 5.10* (PC−Version), Program Library for Structure Solution, Refinement and Molecular Graphics; Bruker AXS Inc.: Madison, WI, 1998.

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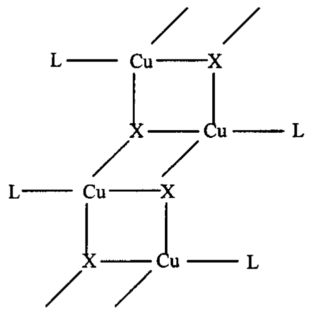
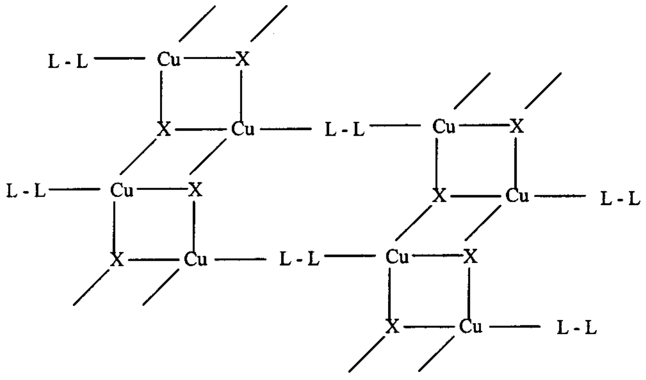
Chart 1



(a) Stair step polymer



dimensional sheets (type **1b**).[5a,14] Two notable exceptions to this are the structures of Cu_2I_2(pyrazine)[14a] and Cu_2I_2(4,4′-bipyridine)[5b] in which the bidentate ligands bridge Cu_2I_2 groups to form a chain structure (type **2a**, Chart 2). The structure of compound **1** is an interesting variant of these structure types. Compound **1** forms a ribbon structure consisting of Cu_4Br_4 tetramers linked by pairs of dmq ligands, as shown in Figure 1. These ribbons are readily identified as slices from the parent two-dimensional structure in type **1b**. The ribbons are shown schematically in type **2b**. Conversely, the structure of **1** can be viewed as a dimer of the chain structure in type **2a**.

In **1**, the centrosymmetric Cu_4Br_4 tetramers are in the stair-step conformation. The ribbons extend in the [001] direction. The inner copper atoms (Cu(1)) are four coordinate, and the outer copper atoms (Cu(2)) are three coordinate. This structure distorts the coordination geometry around Cu(1), with the Cu(1)−Br(2) bond notably elongated to 2.843(1) Å, which is roughly 0.37 Å longer than the other two Cu−Br bonds for that copper atom. The trigonal geometry on Cu(2) also induces a short Cu(1)−Cu(2) interaction of 2.724(1) Å. The presence of two distinct coordination geometries for the copper(I) ions is in contrast to the type **1a** and **1b** structures, where only tetrahedral geometry is found, and to type **2a**, where only trigonal geometry occurs.

The stepped Cu_4X_4 core (as contrasted to a cubane-like core) has been found in several other systems, although never incorporated into a chain type structure. Included in this list are the $Cu_4Br_4(\phi_3P)_4$[15] and $Cu_4I_4(\phi_3P)_4$[16] structures, $Cu_4Br_4(\phi_2PCH_2P\phi_2)_2$,[17] and an iodide compound with a bidentate ligand.[18] A variant occurs in $[Cu(bpy)_2Br]_2Cu_4Br_6$,[19] where the Cu_4Br_4 core is augmented by the coordination of two bromide ions and two bromine atoms from the Cu(II) complex to the four Cu(I) atom core.

Each pair of bridging dmq ligands is related by a center of inversion, so they stack in a parallel fashion, with a strong overlap of the conjugated ring system. The interligand distance is 3.331(6) Å. Because of the bulk of the methyl groups, they extend in opposite sides of the stacked pairs. It is likely the presence of these methyl groups leads to the formation of a ribbon structure rather than a two-dimensional sheet structure. The dmq molecule from the next dimer pair stack such that the methyl groups on one ligand overlap the phenyl group on the adjacent ligand. This led to an interligand distance of 3.515(6) Å.

The structural analysis of **2** revealed that bromination of the methyl groups had occurred during the crystallization of this compound. The organic dmq molecule has been monobrominated on each of the methyl groups to yield 2,3-di(bromomethyl)quinoxaline (henceforth, dBrmq). The solid phase consists of bibridged $(CuBr_2)_n^{n-}$ chains hydrogen bonded by the monoprotonated $(dBrmqH)^+$ cations. This is illustrated in Figure 2a. In the solid state, these bromine atoms lie out of the plane of the molecule, with N−C−C−Br torsional angles of 111.9(7) and −72.1(7)° for Br(3) and Br(4), respectively. Each cation forms a N−H···Br hydrogen bond to Br(1), with a N···Br distance of 3.21(1) Å.

The Cu(I) ions have a distorted tetrahedral geometry. These tetrahedra are linked together by edge sharing to form chains running parallel to the *c* axis (Figure 2b). Crystallographically, the chains have C_2 symmetry. A salient feature is a pronounced dimerization of the chains, with the Cu−Cu distances alternating between 2.814(2) and 3.163(2) Å. This dimerization is induced by the N−H···Br hydrogen bonding documented above. Thus, the Cu−Br(2)−Cu angle (69.65(7)°) is more acute than the Cu−Br(1)−Cu angle (77.14(6)°).

Two systems containing $(CuBr_2)_n^{n-}$ chains similar to those in **2** have been recently reported. These chains are formed for $X = Cl^-$, Br^-, and I^-, with the paraquat dication.[6] A compound with the 4-methylpyridinium cation has been reported which contains both isolated $CuBr_4^{2-}$ cations and the chain.[20] Thus, it is a type I Robin and Day mixed valence system. This is in contrast to $(Me_{4-n}Et_nN)Cu_2X_4$ ($X = Cl^-$, Br^-), where type III Robin and Day $[Cu(I)Cu(II)X_4]_n^{n-}$ chain systems are found.[21] Finally, in $(Et_2NH_2)_2(Cu_3Br_8)$ $(CuBr_2)$, bibridged Cu(II) chains exist with $(CuBr_2)_n$ stoichiometry.[22]

A number of examples of halogenation of organic species in the presence of copper(II) halides have been observed in structural studies in our laboratory. Most of these have involved halogenation of activated pyridinium cations, such as various 2-aminopyridinium derivatives.[2e−i] Recently, the bromination

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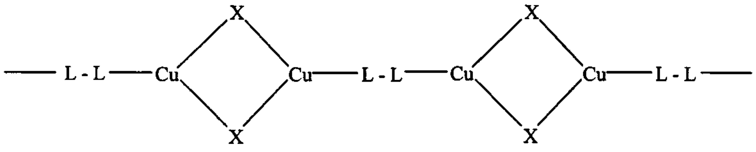
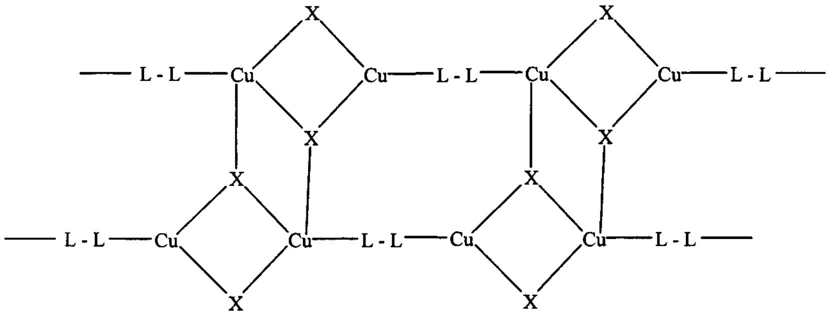
[22] Fletcher, R.; Livermore, J.; Hansen, J. J.; Willett, R. D. *Inorg. Chem.* **1983**, *22*, 330.

Chart 2



(a) Chain structure



(b) Ribbon structure

of the phenyl ring in the 3-chloroanilinium cation was observed.[2a] The result reported here is the first example we have observed involving saturated hydrocarbon substitution. This type of reaction, however, is not unknown. Kosower et al. observed chlorination of the hydrocarbon backbone in a bis-dione molecule.[23] The bromination of a methyl group on an acetyl derivative of an activated phenolic system is another example.[24] A plausible mechanism for the reaction involves an analogy to the alkylation of activated enolate complexes.[25] Upon coordination of one of the quinoxaline nitrogen atoms to the Cu(II) ion, the exo C−CH_3 bonds attain a greater emamine character, allowing a Br^- anion to displace one the hydrogen atoms.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the two polymorphs of $(C_7H_{11}N_2)_2CuCl_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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