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Synthesis and Crystal Structures of $(C_5H_7N_3Br)_3CuBr_4$ and $(C_5H_8N_3)CuBr_2$: An Isolated Tetrahedral $CuBr_4^{3-}$ Anion

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Introduction

Recently, a great effort has been devoted to the self-assembly of organic and inorganic molecules in the solid state, because it extends the range of designing new solids with desired physical and chemical properties.[1] One important approach is the use of organic counterions as templating agents to link the metal ions.[2] Hydrogen bonding between the organic cation and the metal layer is an important issue in understanding the organic−inorganic hybrid materials, which influences both the alignment and spacing of the nearest-neighbor metal sheets or chains. Despite some recent progress, the ability to predict and control the supramolecular assembly of molecules remains an elusive goal, and much more work is required to understand the intermolecular forces that determine the patterns of molecular packing in the solid state. In an effort to prepare new organic/inorganic composite solids, we have found that protonated 2,6-diaminopyridine and its derivatives can crossed-link copper halide complexes through Cu−Br⋯H−N interactions. The synthesis and structural characterization of mononuclear $(C_5H_7N_3Br)_3CuBr_4$ and polymeric $(C_5H_8N_3)CuBr_2$ form the subject of this report. The complex $(C_5H_7N_3Br)_3CuBr_4$ contains a unique, tetrahedral $CuBr_4^{3-}$ anion which is stabilized by extensive N−H⋯Br and C−H⋯Br hydrogen bonding.

Experimental Section

Starting Material. The reagents $CuBr_2$ (99%), aqueous HBr (48%), and 2,6-diaminopyridine (98%) were purchased from Aldrich Chemical Co. and used as received.

Preparations. $CuBr_2$ (0.022 g, 0.1 mmol) in 2.5 mL of H_2O was added to a solution of 2,6-diaminopyridine (0.022 g, 0.2 mmol) in 2.5 mL of HBr (48%). Slow evaporation of the aqueous solution at room temperature for 1 week gave colorless and brown crystals. The crystals were filtered, washed with ethanol, and then dried under vacuum. The crystals were separated manually. Qualitatively, about 40% of the crystals were colorless and 60% were brown. The colorless crystals were characterized as $(C_5H_7N_3Br)_3CuBr_4$ and the brown ones as $(C_5H_8N_3)CuBr_2$ by X-ray crystallography. Anal. Calcd for $(C_5H_7N_3Br)_3CuBr_4$ ($C_{15}H_{21}Br_7CuN_9$; MW = 950.32): C, 18.96; H, 2.23; N, 13.27. Found: C, 18.72; H, 2.48; N, 12.89. ^1H NMR (DMF-d_7): 6.17 (d, 1H, C*H*), 7.60 (br, 4H, N*H*$_2$), 7.87 (d, 1H, C*H*), 13.21 (br, 1H, N*H*) ppm. Anal. Calcd for $(C_5H_8N_3)CuBr_2$ ($C_5H_8Br_2CuN_3$; MW = 333.50): C, 18.01; H, 2.24; N, 12.60. Found: C, 18.27; H, 2.26; N, 12.05. ^1H NMR (DMSO-d_6): 5.90 (d, 2H, C*H*), 7.19 (s, 4H, N*H*$_2$), 7.31 (t, 1H, C*H*),11.95 (s, 1H, N*H*) ppm.

X-ray Crystallography. The diffraction data of **1** and **2** were collected on a Siemens CCD diffractometer, which was equipped with graphite-monochromated Mo Kα ($\lambda_\alpha = 0.71073$ Å) radiation.[3] Data reduction was carried out by standard methods with use of well-established computational procedures.[4]

A colorless crystal of **1** was mounted on the top of a glass fiber with epoxy cement. A hemisphere data collection method was used to scan the data points at $4.48° < 2\theta < 49.96°$. The structure factors were obtained after Lorentz and polarization corrections. The positions of the heavier atoms, including the copper and bromide atoms, were located by the direct method. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. The final residuals of the refinement were R1 = 0.0559 and wR2 = 0.1179. The X-ray crystallographic procedures for **2** were similar to those for **1**. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1.

Results and Discussions

The resulting salts of colorless $(C_5H_7N_3Br)_3CuBr_4$, **1**, and brown $(C_5H_8N_3)CuBr_2$, **2**, were crystallized from the reaction mixture prepared by adding $CuBr_2$ to the HBr solution of 2,6-diaminopyridine. The crystals of **1** and **2** show distinctly different colors and were separated manually. The structure of **1** was solved in the monoclinic space group $P2_1/c$ with each molecule occupying a general position within the unit cell. The structure (Figure 1) consists of a tetrahedral $CuBr_4^{3-}$ anion linked by three 2,6-diamino-5-bromoaminopyridinium cations through extensive intermolecular N−H⋯Br and C−H⋯Br interactions. The pyridine rings of the original 2,6-diaminopyridine have undergone bromination during the synthesis process. The bromination occurred in the 3-position, which is ortho and para to the NH_2 substituents in the 2- and 6-positions, respectively. Bond distances and angles in the brominated cations are normal, with average distances of C−Br = 1.88 Å, C−C = 1.37 Å, and C−N = 1.35 Å. The formation of the brominated cations was accompanied by reduction of the Cu(II) ion to Cu(I) and by oxidation of the carbon atoms attached to the bromide atoms, as evidenced by the structural result that each resulting salt contains three monovalent cations and one anion. The existence of three protonated 2,6-diaminopyridine cations was verified with the fact that all three hydrogen atoms in question can be found in the difference Fourier map. Complex **1** is ESR inactive and shows distinctive ^1H NMR peaks in DMF-d_7 solvent, supporting the proposition of a diamagnetic Cu(I) center. Halogenation of the pyridine rings of the substituted pyridinium cations has been frequently observed.[5] For example, bromination of the 3-chloroanilinium cation has been reported recently in the complexes $(C_6H_3BrClNH_3)Br$, $(C_6H_3BrClNH_3)_2CuBr_3$, and $(C_6H_3Br_2ClNH_3)CuBr_3$.[5e] Direct halogenation of 2,6-diaminopyridine has been reported,[5f−h] and dichlorination of 2,6-diaminopyridine ligand was found in the complex bis(2,6-diamino-3,5-dichloropyridinium) tetrachlorocuprate(II).[5d]

As far as the geometry of the $CuBr_4^{3-}$ anion is concerned, the Cu−Br lengths are in the range from 2.436(2) to 2.515(2) Å and the Br−Cu−Br angles vary within the range from 103.41-

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(1) (a) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311. (b) Desiraju, G. R. *Chem. Commun.* **1997**, 1475.

(2) (a) Mitzi, D. B. *J. Chem. Soc., Dalton Trans.* **2001**, 1. (b) Mitzi, D. B. *Prog. Inorg. Chem.* **1999**, *48*, 1. (c) Chesnut, D. J.; Hagrman, D.; Zapf, P. J.; Hammond, R. P.; LaDuca, R., Jr.; Haushalter, R. C.; Zubieta, J. *Coord. Chem. Rev.* **1999**, *190−192*, 737.

(3) *SMART/SAINT/ASTRO*, release 4.03; Siemens Energy & Automation, Inc.: Madison, WI, 1995.

(4) Sheldrick, G. M. *SHELXTL PLUS*, release 4.1; Siemens Analytical X-ray Instruments Inc.: Karlsruhe, Germany, 1991.

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Table 1. Crystal Data for $(C_5H_7N_3Br)_3CuBr_4$, **1**, and $(C_5H_8N_3)CuBr_2$, **2**

complex	**1**	**2**
empirical formula	$C_{15}H_{21}Br_7CuN_9$	$C_5H_8Br_2CuN_3$
fw	950.32	333.50
space group	*P*2(1)/*c*	*C*2/*m*
a, Å	8.179(1)	17.122(2)
b, Å	24.347(2)	6.492(1)
c, Å	13.760(3)	8.720(1)
α, deg	90	90
β, deg	101.907(1)	90.947(2)
γ, deg	90	90
V, $Å^3$	2681.4(3)	969.1(2)
Z	4	4
D_{calcd}, g/cm^3	2.354	2.286
F(000)	1792	632
μ(Mo Kα), mm^{-1}	11.269	10.443
temp, °C	25	25
R indices $[I > 2\sigma(I)]^{a,b}$	R1 = 0.0559, wR2 = 0.1179	R1 = 0.0436, wR2 = 0.1196
R indices (all data)	R1 = 0.0740, wR2 = 0.1281	R1 = 0.0459, wR2 = 0.1223

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (ap)^2 + (bp)]$, $p = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$. $a = 0.0362$, $b = 19.5966$ for **1**; $a = 0.0682$, $b = 2.6636$ for **2**.

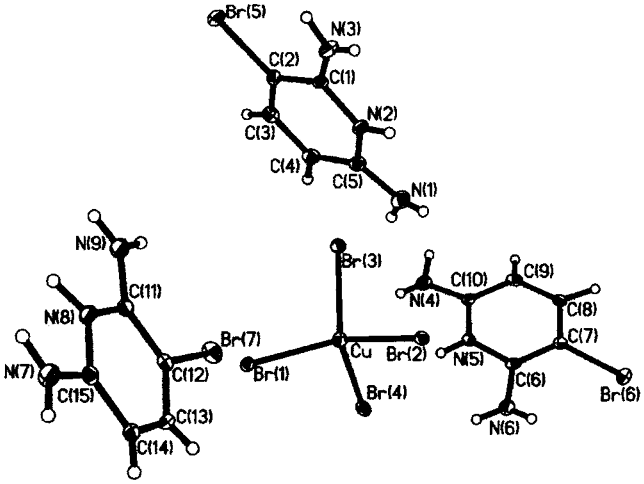

Figure 1. ORTEP diagram of $(C_5H_7N_3Br)_3CuBr_4$. Thermal ellipsoids are shown at the 50% probability level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $(C_5H_7N_3Br)_3CuBr_4$

	Distances		
Cu−Br(1)	2.436(2)	Cu−Br(3)	2.491(2)
Cu−Br(2)	2.504(2)	Cu−Br(4)	2.515(2)
	Angles		
Br(1)−Cu−Br(3)	108.87(6)	Br(1)−Cu−Br(2)	120.89(6)
Br(3)−Cu−Br(2)	103.41(6)	Br(1)−Cu−Br(4)	106.28(6)
Br(3)−Cu−Br(4)	112.67(6)	Br(2)−Cu−Br(4)	104.84(6)

(6)° to 120.89(6)° (Table 2). These bond distances and angles are in marked contrast to those of the Cu^{2+} ion in tetrahedral coordination. For example, the Cu−Br distances of the isolated tetrahedral $CuBr_4^{2-}$ anion in $(3\text{-MAP})_2CuBr_4$ (3-MAP = 2-amino-3-methylpyridinium)[6] are in the range from 2.358(3) to 2.411(3) Å and the bond angles are in the range from 94.73(9)° to 141.6(1)°. Noticeably, the Cu−Br distances in $CuBr_4^{3-}$ are all longer than those in $CuBr_4^{2-}$. The larger range for the Br−Cu−Br angles in $CuBr_4^{2-}$ ion is due to the fact that it has an orbitally degenerate state $^2T_2$ and is subjected to a rather large Jahn−Teller force that leads to a compressed tetrahedron. There are no important interactions between the $CuBr_4^{3-}$ anions, the nearest nonbonded Cu•••Br distance is 6.588 Å, and the shortest Br•••Br contact is 4.236 Å, which is longer than the sum of van der Waals radii (3.90 Å) of the bromide anions. However, a significant Br••• Br contact, which is 3.618 Å, is found between the $CuBr_4^{3-}$ anion and one of the cations. There is also a short van der Waals contact between the ring bromide atoms with a distance of 3.756 Å. These Br•••Br short contacts can be attributed to the nonuniformity of the electrostatic potential on the bromide atom.[7] The presence of these short Br•••Br contacts is mediated by the extensive hydrogen-bonding capability of the 2,6-diamino-5-bromoaminopyridinium cations and by the *π*−*π* stacking interactions of the pyridine rings (vide infra).

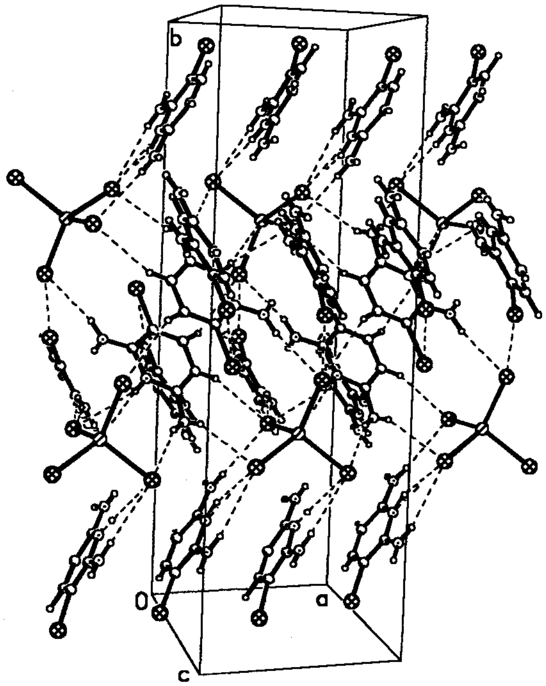

Figure 2. Packing diagram of $(C_5H_7N_3Br)_3CuBr_4$.

Although monomeric species including the linear CuX_2^- anion[8] and the planar triangular CuX_3^{2-} anion[9] are known, isolated tetrahedral CuX_4^{3-} anions have never been reported, probably due to the high charge density that would be produced.[5] Complex **1** is thus the first one containing an isolated tetrahedral CuX_4^{3-} anion. The packing diagram of complex **1** (Figure 2) shows that the molecules pack into layers of discrete $CuBr_4^{3-}$ anions that are separated by layers of the cations. The cations

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(5) (a) Willett, R. D. *Acta Cryst.* **1988**, *C44*, 450. (b) Grigereit, T. E.; Ramamrishna, B. L.; Place, H.; Willwtt, R. D.; Pellacani, G. C.; Manfredini, T.; Menabue, L.; Bonamartini-Corradi, A.; Battaglia, A. *Inorg. Chem.* **1987**, *26*, 2235. (c) Place, H.; Willett, R. D. *Acta Cryst.* **1987**, *C43*, 1497. (d) Willett, R. D.; West, D. X. *Acta Cryst.* **1987**, *C43*, 2300. (e) Willett, R. D. *Inorg. Chem.* **2001**, *40*, 966. (f) Boudakian, M. M. *J. Fourine Chem.* **1981**, *18*, 497. (g) Chen, T. K.; Flowers, W. T. *J. Chem. Soc., Chem. Commun.* **1980**, 1139. (h) Mutterer, W. *Helv. Chim. Acta* **1976**, *59*, 222. (i) Luque, A.; Sertucha, J.; Lezama, L.; Tojo, T.; Roman, P. *J. Chem. Soc., Dalton Trans.* **1997**, 847.

(6) Coffey, T. J.; Landee, C. P.; Robinson, W. T.; Turnbull, M. M.; Winn, M.; Woodward, F. M. *Inorg. Chim. Acta* **2000**, *303*, 54.

(7) (a) Lieberman, H. F.; Davey, R. J.; Newsham, D. M. T. *Chem. Mater.* **2000**, *12*, 490. (b) Desiraju, G. R.; Parthasarathy, R. *J. Am Chem. Soc.* **1989**, *111*, 8725. (c) Lommerse, J. P. M.; Stone, A. J.; Taylor, R. Allen, F. H. *J. Am. Chem. Soc.* **1996**, *C43*, 1497.

(8) (a) Healy, P. C.; Engelhardt, L. M.; Patrick, V. A.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 2541. (b) Levy, A. T.; Olmstead, M. M.; Patten, T. E. *Inorg. Chem.* **2000**, *39*, 1628.

(9) Aandersson, S.; Jagner, S. *Acta Chem. Scand. A* **1987**, *41*, 230.

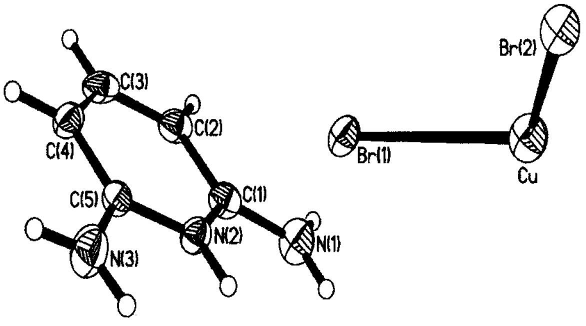

Figure 3. ORTEP diagram of $(C_5H_8N_3)CuBr_2$. Thermal ellipsoids are shown at the 50% probability level.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $(C_5H_8N_3)CuBr_2$

	Distances		
Br(1)−Cu	2.4975(8)	Br(2)−Cu	2.5078(8)
	Angles		
CuA−Br(1)−Cu	79.62(4)	CuB−Br(2)−Cu	82.11(4)
Br(1A)−Cu−Br(1)	100.38(4)	Br(1)−Cu−Br(2)	114.32(2)
Br(2B)−Cu−Br(2)	97.89(4)	Br(1A)−Cu−Br(2)	115.42(2)

are planar and form alternating layers between the sheets of the anions. The ions are linked not only through Br···Br contacts but also through extensive N−H···Br and C−H···Br hydrogen bonds by means of interactions among the bromide atoms of the $CuBr_4^{3-}$ anion and the C−H and N−H hydrogen atoms of the cations, which are in the range from 2.384 to 3.011 Å. The high charge density on the $CuBr_4^{3-}$ anion is most possibly annulled through these N−H···Br and C−H···Br hydrogen bondings. Noticeably, the bromide atoms of one cation do not interact with the hydrogen atoms of the other. Two sets of face to face noncovalent interactions between π systems of the pyridines of the cations are observed. In the first set of $\pi-\pi$ stacking interactions, the rings which involve N(5) and N(8) atoms are eclipsed. The dihedral angle between the rings is 6.3°, and the interplanar distance is 3.813 Å. In the other set of stronger interactions, the rings which involve N(2) atoms are staggered. The dihedral angle and the interplanar distance are 0° and 3.665 Å, respectively. The strengths of the $\pi-\pi$ stacking interactions in this complex are thus subject to the steric hindrance.

The structure of **2** was solved in the monoclinic space group *C*2/*m*, which consists of anionic chains of doubly edge sharing copper(I) metal centers through bromide atoms. The asymmetric unit of the anion of **2**, Figure 3, consists of a single $CuBr_2$ moiety and a protonated 2,6-diaminopyridine cation, which under the appropriate symmetry operations yields a polymeric chain. The tetrahedral Cu(I) metal center is achieved by means of four bridging bromide atoms. In the anion, the Cu−Br distances of the bridging Br−Cu−Br linkage are 2.4975(8) and 2.5078(6) Å, which are longer than those reported for the linear dibromocuprate anions[8] (Table 3). The acute Cu−Br−Cu angles of 79.62(4)° and 82.11(4)° lead to a short Cu···Cu distance of 3.198 Å. The four Br−Cu−Br angles of 100.38(4)°, 114.32(2)°, 115.42(2)°, and 97.89(4)° show some distortions from ideal tetrahedral geometry. The $\{[CuBr_2]^n\}^{n-}$ linear chains are linked into two-dimensional structure through the N−H···Br interactions (2.582−2.951 Å), which are formed between adjacent chains through the bridging bromide atoms and the amine hydrogen atoms and the pyridine nitrogen atoms of the protonated 2,6-diaminopyridine compounds (Figure 4). The cations are planar (mean deviation = 0.00 Å) and perpendicular to the molecular chains (vs the plane formed by the Cu atoms). Infinite chains of edge-sharing Cu(I)−Br tetrahedra have been found in the complex $Cu(NH_3)_4(CuBr_2)_2$.[10] For comparison it is noted that, in $(LH)CuBr_2$ (L = 2-aminopyrimidine), each copper(I) ion in the chain completes its tetrahedral coordination sphere by coordinating to one pyrimidinium cation and to one bromide ion.[11]

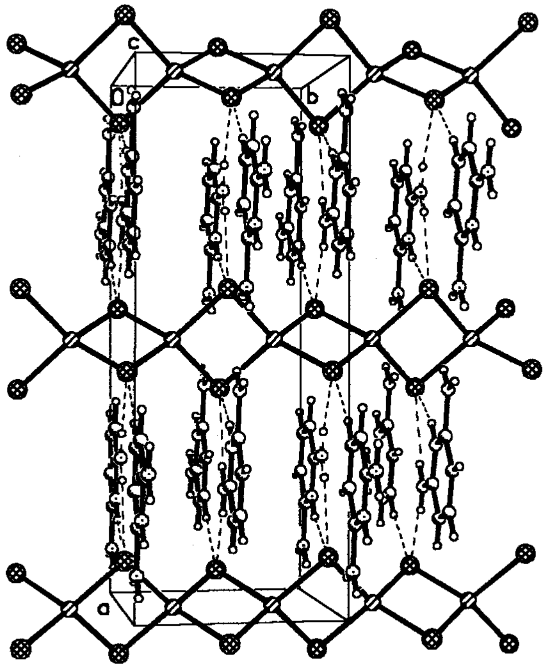

Figure 4. Packing diagram of $(C_5H_8N_3)CuBr_2$.

In summary, two new complexes of monomeric $(C_5H_7N_3Br)_3CuBr_4$, **1**, and polymeric $(C_5H_8N_3)CuBr_2$, **2**, have been structurally characterized. Complex **1** appears to be the first one containing the $CuBr_4^{3-}$ anion. In both complexes three N−H···Br hydrogen bondings are used to link the metal units to the protonated 2-aminopyridine. Two are through the amine hydrogen atoms, and the other is through the pyridine hydrogen atom. To be incorporated into metal-based solid phases as ligands serving to buttress the inorganic layer, the molecular planes of 2,6-diaminopyridinium groups in **2** are positioned in a direction perpendicular to the planes of the molecular sheets containing the cations.

Acknowledgment. We wish to thank the National Science Council of the Republic of China for support.

Supporting Information Available: X-ray crystallographic files in CIF format for complexes **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[10] Baglio, J. A.; Vaughan, P. A. J. *Inorg. Nucl. Chem.* **1970**, *32*, 803.

[11] Pon, G.; Willett, R. D.; Prince, B. A.; Robinson, W. T.; Turnbull, M. M. *Inorg. Chim. Acta* **1997**, *255*, 325.