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Notes

Dimeric Cu(I) Bromide Species Consisting of Two Edge-Shared Tetrahedra: Crystal Structure of $(C_8H_{14}N_2)_2Cu_2Br_6$

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Introduction

One of the current interests in our laboratory has been the synthesis of extended anionic copper(I) halide systems, especially two-dimensional networks. Several synthetic strategies can be employed. One approach utilized extensively in crystal engineering is the use of small synthons or building blocks to develop higher order oligomers and extended structures. A second approach is the use of organic counterions as templating agents based on their shape and their hydrogen-bonding capabilities.

In the attempt to synthesize these anionic networks, it is desirable to identify possible synthons. The stereochemistry of copper(I) halides appears to be relatively well-defined; linear two-coordinate species, trigonal planar three-coordinate species, and tetrahedral four-coordinate species are the dominant geometries observed, although distortions, both angular and radial, can be rather severe in the last species. This regularity in coordination geometry is not surprising, given the d^{10} configuration of the central Cu(I) cation and the spherical nature of the coordinating halide anions. Anionic copper(I) halides are known to form a number of oligomeric and polymeric species.[1] It is possible for the oligomers to serve as such synthons to build extended structures. Known monomeric species include the linear CuX_2^- anion[2] and the planar triangular CuX_3^{2-} anion.[3] Isolated tetrahedral CuX_4^{3-} anions do not appear to be known probably because of the high charge density that would be produced. Nevertheless, conceptually, it is an important synthon for higher oligomers. Two types of dimers based on triangular species have been previously reported: $Cu_2X_4^{2-}$anions formed by edge sharing of two of the triangular anions[4] and $Cu_2X_5^{3-}$ anions formed by corner sharing of two such anions.[5] For X = I, two compounds containing $Cu_2I_6^{4-}$ anions formed by the edge-sharing of two CuX_4 tetrahedra have been reported.[6] Higher oligomers are generally formed by edge, corner, or face sharing of either triangular CuX_3^{2-}or tetrahedral CuX_4^{3-} species. These include trimeric (edge sharing of triangular and tetrahedral species),[7a] tetrameric (edge sharing of triangular species),[7b,c] pentameric (face sharing of tetrahedral species),[8] and hexameric complexes (more complex structures).[9] Several one-dimensional networks are also known involving primarily edge sharing or face sharing of tetrahedral species.[4d,10] Interestingly, the extended structures proposed by Subramanian and Hoffmann[1] all contain edge-shared tetrahedral species.

Subramanian and Hoffmann[1] have discussed the factors that enter into the formation of oligomeric and polymeric anionic Cu(I) halide species. In the examination of the known structures, one significant structural feature is the existence of short (2.6−2.9 Å) Cu−Cu contacts with acute Cu−X−Cu bond angles. Examples in which a halide ion bridges two, three, four, or five Cu(I) ions are known. This feature has been rationalized by Subramanian and Hoffmann in terms of the localization of sp_α lone pairs on the halide ions upon formation of the Cu−X bonds. One consequence of this lone pair formation, not fully appreciated previously, is the ability of organoammonium cations to hydrogen-bond to the halide ions. This can help reduce the charge density on the halide ions, thus giving the possibility of formation of new oligomers. In addition, it should be possible to use the structural features of the organic cations to template new extended anionic copper(I) halide salts. Using this concept, we recently synthesized the first two-dimensional Cu(I) halide anionic network utilizing a bulky organic cation as a template.[11]

For neutral CuX complexes with coordinating ligands, several recurring structural motifs have been identified, primarily by White[12] and co-workers and by Holt[13] and co-workers. The same progress has not been made with the anionic systems, and it is of interest to find new synthons and to establish structural motifs that can be used to predict (or postulate) possible solid-state structures. In an attempt to further exploit these techniques, we have undertaken the synthesis of anionic copper(I) halide lattices

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Table 1. Crystal Data and Structure Refinement for (m-Xylylenediaminium)$_2$Cu$_2$Br$_6$

formula	$C_8H_{14}Br_3CuN_2$
fw	441.48
temp (K)	293(2)
λ (Å)	0.710 73
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	9.077(2)
b (Å)	15.102(3)
c (Å)	9.709(2)
β (deg)	97.87(3)
V (Å^3)	1318.4(5)
Z	4
ρ_{calc} (Mg/m)	2.224
μ (mm^{-1})	10.716
R1 ($I > 2\sigma(I)$)[a]	0.0373
wR2 (all data)[b]	0.1157

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

utilizing bulky multifunctional organic cations as counterions. In this paper, we report the isolation of a dimeric copper(I) bromide synthon obtained as part of this effort.

Experimental Section

Synthesis. A total of 5 mmol m-xylylenediamine (Aldrich, 99%) was added to 5 mmol of CuBr in 60 mL of ethanol that had been acidified by the addition of 1.5 mL of concentrated HBr. The light-brown solution was stirred at room temperature. Colorless crystals were separated during stirring. The volume of the solution was increased with 30 mL more of ethanol, and the solution was warmed to 50 °C and stirred for 5 min. The colorless crystals that separated upon cooling were removed by filtration. A second crop came from the mother liquor in 12 h. A single crystal with dimensions of 0.15 mm × 0.25 mm × 0.4 mm was mounted for structure determination.

X-ray Diffraction. Data were collected on a Bruker three-circle platform diffractometer equipped with a CCD detector using the SMART[14] software at 295 K using Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The data were processed using the SAINT software,[15] and absorption corrections were performed using the SADABS[16] program. The structures were solved by the direct method using the SHELX-90[17] program and refined by the least-squares method on F^2, SHELXL-93,[18] incorporated in SHELXTL, version 5.03.[19] The crystal used for the diffraction study showed no appreciable decomposition during data collection. Table 1 summarizes the most important structural and refinement parameters, while a list of important distances and angles is given in Table 2. Figure 1 illustrates the molecular species.

Discussion

The structure consists of centrosymmetric bibridged Cu$_2$Br$_6^{4-}$ anions and m-xylylene diammonium cations. As illustrated in Figure 1, the anion can be visualized as two fused CuBr$_4^{3-}$ tetrahedra forming a dimeric copper(I) halide moiety. This edge-shared arrangement of two tetrahedra forms the basis for a synthon to be utilized in the design and synthesis of extended anionic Cu(I)−X structures.

Table 2. Cu and Br Bond Lengths [Å] and Angles [deg] for (m-Xylylenediammonium)$_2$Cu$_2$Br$_6$[a]

Br(1)−Cu	2.4669(13)	Br(3)−Cu#1	2.4308(15)
Br(2)−Cu	2.5033(14)	Br(3)−Cu	2.6698(17)
Cu#1−Br(3)−Cu	86.29(5)	Br(3)#1−Cu−Br(3)	93.71(5)
Br(3)#1−Cu−Br(1)	113.29(5)	Br(1)−Cu−Br(3)	110.97(5)
Br(3)#1−Cu−Br(2)	112.16(6)	Br(2)−Cu−Br(3)	117.28(5)
Br(1)−Cu−Br(2)	108.90(5)		

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

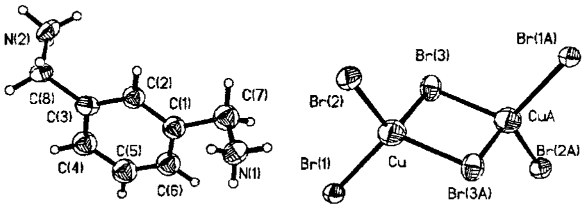

Figure 1. Illustration of the structure of (m-xylylenediammonium)$_2$Cu$_2$-Br$_6$. Thermal ellipsoids shown at 50% probabilities.

In this structure, the bridging Cu−X−Cu linkage shows significant asymmetry with Cu−Br distances of 2.431(2) and 2.670(2) Å. The terminal bonds show a much smaller spread (2.467(2) and 2.503(1) Å), averaging 0.07 Å shorter than the average bridging bond distance. The barely acute Cu−Br−Cu angle of 86.29(5)° leads to an unusually long Cu−Cu contact of 3.492 Å. Because of the smaller than tetrahedral Br−Cu−Br angle (93.7(5)°) in the bridging framework, significant angular distortions from ideal tetrahedral geometry occur. The trans Br−Cu−Br angle is also less than the ideal tetrahedral angle; all the rest are greater than ideal (up to 117.2(5)°).

The m-xylylenediammonium dication has approximate C_2 symmetry, with the C−N bonds nearly perpendicular to the plane of the xylylene moiety. This minimizes the repulsive interactions between the ring hydrogen atoms and the methylene hydrogen atoms. Each −NH$_3$ moiety participates in four N−H···Br hydrogen bonds: one short bond of ~3.25 Å and three longer bonds of ~3.5 Å. The short bonds are to the terminal bromine atoms, with N(1) forming a short bond to Br(2) and N(2) to Br(1). Each −NH$_3$ group forms one hydrogen bond to a bridging Br atom.

It is instructive to compare the structure reported here with the structures of the two Cu$_2$I$_6^{4-}$ anions previously reported. The anion in [(py)$_2$CH$_2$]$_2$Cu$_2$I$_6$, where (py)$_2$CH$_2^{2+}$ is the dipyridinemethane cation,[6a] has a geometry remarkably similar to the geometry of the Cu$_2$Br$_6^{4-}$ anion reported in this study. The bridging Cu−X−Cu angles are 86.67(3)° in the iodide salt, compared to 86.29(5)° for the Br salt. Similarly, the bridging geometry is asymmetric, with a difference of 0.169(2) Å compared to 0.239(3) Å in the Br salt. In contrast, the Cu$_2$I$_6^{4-}$ anions in Tl$_4$Cu$_2$I$_6$ have a very different structure,[6b] with symmetric bridges and very acute Cu−I−Cu angles of 60.77(4)°. This difference is presumably due to the difference in the nature of the electrostatic interactions and the hardness associated with the two different cations. The Tl$^+$ ions are tightly bound on the triangular faces of the CuI$_4$ tetrahedra. These "hard" interactions compress the dimer, forcing the Cu−I−Cu angles to be acute. In the (py)$_2$CH$_2^{2+}$ salt, a much softer lattice exists. Each dication in this salt wraps around one of the terminal iodine atoms of the dimer. The asymmetric nature of this interaction leads to the asymmetric bridging in the dimer.

The edge-shared Cu$_2$X$_6^{4-}$ dimer can be recognized as a useful synthon for developing extended structures. While two- and three-coordinate Cu(I)−X species are more common for monomeric and dimeric species than four-coordinate geometries because of electrostatic charge considerations, this will not be

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(14) *SMART, Software for the CCD Detector System*, version 4.045; Bruker AXS, Inc.: Madison, WI, 1996.

(15) *SAINT, Software for the CCD Detector System*, version 4.035; Bruker AXS, Inc.: Madison, WI, 1996.

(16) *SADABS, Program for Absorption Correction for Area Detectors*; Bruker AXS, Inc.: Madison, WI, 1996.

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(19) *SHELXTL, Program Library for Structure Solution and Molecular Graphics*, PC version 5.10; Bruker AXS, Inc.: Madison, WI, 1997.

the case for extended systems. Here the existence of bridging (sharing) reduces the X/Cu ratio and so reduces electrostatic repulsions between the halide ions. Similarly, the use of hydrogen-bonding counterions can also be effective in reducing electrostatic repulsions and thus favors the formation of four-coordinate species, as observed in this report.

Examination of the known extended structures shows that the Cu_2X_6 synthon can be recognized in many of them. The $(CuX_2)_n^{n-}$ chains in the (paraquat)CuX_2 structures[20] consist of infinite X synthons. The linear systems of stoichiometry ACu_2X_3 usually assume a structure that results from the fusion to a pair of $(CuX_2)_n^{n-}$ chains. The recently reported ACu_4Cl_6 structure (where A^{2+} is the paraquat cation)[10f] can be visualized as Cu_6Cl_{10} oligomers fused into chains with the Cu_2Cl_6 synthons.

Supporting Information Available: An X-ray crystallographic file in CIF format for the compound (*m*-xylylenediaminium)Cu_2Br_6. This material is available free of charge via the Internet at http://pubs.acs.org.

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