*Inorg. Chem.* **2001,** *40,* 966−971

# Bromination of the 3-Chloroanilinium Cation: Structure of a Novel Two-Dimensional Copper(I) Bromide Lattice Prepared via In-Situ Redox Processes

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*Received June 27, 2000*

The prolonged reactions of 3-chloroaniline with $CuBr_2$ in HBr solution yielded three crystalline compounds involving brominated anilinium cations. The first, $(C_6H_3BrClNH_3)Br$, is the bromide ion salt of the 6-bromo-3-chloroanilinium cation. The compound is monoclinic, space group $P2_1/c$, with $a = 10.520(4)$, $b = 8.4238(13)$, $c = 10.502(4)$ Å and $\beta = 108.55(1)°$ with $Z = 4$. The compound with stoichiometry $(C_6H_3BrClNH_3)_2CuBr_3$, contains the 4-bromo-3-chloroanilinium cation. It is triclinic, space group $P$-1, with $a = 8.217(2)$, $b = 14.496(4)$, $c = 16.993(4)$ Å, $\alpha = 77.46(2)$, $\beta = 86.00(3)$, $\gamma = 89.22(2)°$ with $Z = 4$. Finally, the third compound contains the dibrominated cation, 4,6-dibromo-3-chloroanilinium, with stoichiometry $(C_6H_3Br_2ClNH_3)CuBr_2$. It is orthorhombic, space group $Pnma$, with $a = 7.2177(2)$, $b = 29.7188(3)$, and $c = 10.9309(2)$ Å with $Z = 8$. The latter two salts contain Cu(I) species, obtained by the reduction of the original Cu(II) ions during the bromination process. The first of these two Cu(I) salts contain $Cu_2Br_6^{4-}$ dimers in which two $CuBr_4$ tetrahedra share edges. The last compound contains a unique two-dimensional lattice composed of corner shared $Cu_2Br_6$ species.

## Introduction

A major focus in our laboratory has been on the elucidation structure/property relations in hybrid organic/inorganic copper(II) chloride materials. This has included investigations of compounds with novel magnetic properties,[1] thermochromic[2] and piezochromic[3] responses, dynamic Jahn−Teller behavior,[4] and other novel phase transition phenomena.[5] The continuing interest in these studies is a result of a combination of the varied stereochemistry of the Cu(II) ion, the bridging capability of the spherical chloride ion, and the wide variety of size, shape, and hydrogen bonding abilities of the organic counterions. In an attempt to extend the success of our investigations with the copper(II) chloride salts to the corresponding bromide compounds, an additional factor has frequently come into play. Associated with the increased redox activity of the copper(II) bromide system relative to the copper(II) chloride systems, reduction of copper(II) to copper(I) has been observed.[6]

In this paper, we report the crystal structure of two new copper(I) bromide salts obtained serendipitously through the latter redox process. We had investigated the Jahn−Teller distortion in $(C_6H_7NCl)_8CuCl_{10}$, where $(C_6H_7NCl)^+$ is the 3-chloroanilinium cation.[7] The compound was initially reported to contain a $CuCl_6^{4-}$ anion with a compressed octahedral geometry.[8] Our detailed temperature-dependent diffraction study, as well as an EXAFS and EPR study in another laboratory,[9] conclusively showed that the “compressed” coordination geometry was really the superposition of two normal elongated octahedra. To extend the study, an attempt to prepare the analogous bromide salt was begun.

In this process, three different substituted anilinium cations were obtained by the bromination of the 3-chloroanilinium cation by $CuBr_2$. One of the cations was isolated as the simple bromide salt; the other two were obtained as copper(I) bromide salts with novel structural characteristics. The first compound, which contains the monobrominated 6-bromo-3-chloroanilinium cation, $A6^+$, was isolated as the A6Br salt. The next compound, which contains the 4-bromo-3-chloroanilinium cation, $A4^+$, has stoichiometry $A4_4Cu_2Br_6$. The final compound contains the dibrominated 4,6-dibromo-3-chloroanilinium cation, $A46^+$. It

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**Table 1.** Crystal Data and Structure Refinement Parameters

| | A6Br | $A4_2Cu_2Br_6$ | $A46_2Cu_2Br_4$ |
|---|---|---|---|
| empir formula | $C_6H_6Br_2ClN$ | $C_{12}H_{12}Br_5Cl_2CuN_2$ | $C_6H_5Br_4ClCuN$ |
| space group | $P2_1/c$ | $P$-1 | *Pnma* |
| $a$/Å | 10.520(4) | 8.217(2) | 7.2177(2) |
| $b$/Å | 8.4238(13) | 14.496(4) | 29.7188(3) |
| $c$/Å | 10.502(4) | 16.993(4) | 10.9309(2) |
| $\alpha$/deg | 90 | 77.46(2) | 90 |
| $\beta$/deg | 108.55(1) | 86.00(3) | 90 |
| $\gamma$/deg | 90 | 89.22(2) | 90 |
| $V$/Å$^3$ | 882.3(5) | 1971.0(9) | 2344.69(8) |
| $Z$ | 4 | 4 | 8 |
| $\rho_{calcd}$/mg m$^{-3}$ | 2.163 | 2.420 | 2.888 |
| $T$/K | 298 | 298 | 298 |
| $\mu$/mm$^{-1}$ | 9.42 | 11.51 | 15.68 |
| $F$(000) | 544 | 1344 | 1872 |
| radiation, $\lambda$/Å | 0.71073 (Mo K$\alpha$) | 0.71073 (Mo K$\alpha$) | 0.71073 (Mo K$\alpha$) |
| reflns measd/ unique | 3738/1262 | 8438/5330 | 8435/1709 |
| merging $R$ | 0.087 | 0.063 | 0.288 |
| %$T$: max./min | 0.694/0.285 | 0.562/0.190 | 0.417/0.124 |
| $R_1{}^a$ ($I > 2\sigma$) | 0.0334 | 0.0706 | 0.0679 |
| $wR_2{}^b$ ($I > 2\sigma$) | 0.0723 | 0.1607 | 0.1219 |

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

**Table 2.** Atomic Coordinates (× $10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × $10^3$) for 4-Br-3-Cl-anilinium Bromide

| | $x$ | $y$ | $z$ | $U$(eq)$^a$ |
|---|---|---|---|---|
| Br(1) | 8582(1) | 1553(1) | 785(1) | 37(1) |
| Br(2) | 8873(1) | 6609(1) | 375(1) | 40(1) |
| Cl | 3823(1) | 5758(2) | 2410(2) | 44(1) |
| N | 8671(5) | 4522(6) | 2768(5) | 27(1) |
| C(6) | 7391(5) | 6340(5) | 988(5) | 29(1) |
| C(3) | 5185(5) | 5983(6) | 1841(5) | 29(1) |
| C(2) | 6373(5) | 5189(6) | 2523(5) | 27(1) |
| C(5) | 6199(5) | 7098(7) | 338(6) | 34(1) |
| C(1) | 7458(4) | 5388(5) | 2088(5) | 25(1) |
| C(4) | 5107(5) | 6920(6) | 755(5) | 33(1) |

[a] $U$(eq) is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table 3.** Atomic Coordinates (× $10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$ × $10^3$) for (4-Br-3-Cl-anilinium)$_2$CuBr$_3$

| | $x$ | $y$ | $z$ | $U$(eq)$^a$ |
|---|---|---|---|---|
| Cu(1) | 3407(3) | 5228(1) | 5255(2) | 55(1) |
| Br(1) | 2635(2) | 6892(1) | 5161(1) | 37(1) |
| Br(2) | 1248(2) | 4081(1) | 5830(1) | 37(1) |
| Br(3) | 4269(2) | 5205(1) | 3804(1) | 38(1) |
| Cu(2) | 1569(3) | 360(1) | 4749(1) | 54(1) |
| Br(4) | 3761(2) | −506(1) | 4171(1) | 37(1) |
| Br(5) | 2309(2) | 1967(1) | 4848(1) | 37(1) |
| Br(6) | 725(2) | −396(1) | 6201(1) | 38(1) |
| N(11) | −4351(16) | 7464(9) | 13729(8) | 47(4) |
| C(11) | −3601(19) | 7838(10) | 12919(9) | 36(4) |
| C(12) | −3224(18) | 8762(10) | 12671(10) | 37(4) |
| C(13) | −2500(20) | 9094(10) | 11916(11) | 40(4) |
| C(14) | −2080(20) | 8516(11) | 11417(11) | 44(4) |
| C(15) | −2490(20) | 7550(11) | 11670(13) | 59(5) |
| C(16) | −3240(20) | 7221(10) | 12398(11) | 48(5) |
| Cl(13) | −2082(8) | 10309(3) | 11621(3) | 78(2) |
| Br(14) | −1041(3) | 8921(2) | 10385(1) | 75(1) |
| N(21) | −788(15) | 5994(8) | 6189(7) | 38(3) |
| C(21) | −231(19) | 6191(9) | 6937(10) | 34(4) |
| C(22) | 270(20) | 5462(11) | 7533(12) | 58(5) |
| C(23) | 820(20) | 5678(11) | 8193(11) | 51(5) |
| C(24) | 790(20) | 6566(12) | 8325(11) | 49(5) |
| C(25) | 330(20) | 7307(11) | 7708(11) | 46(5) |
| C(26) | −230(20) | 7108(11) | 7028(11) | 44(5) |
| Cl(23) | 1463(11) | 4751(4) | 8942(4) | 120(3) |
| Br(24) | 1577(3) | 6882(2) | 9256(1) | 73(1) |
| N(31) | 4234(14) | −1593(8) | 6162(7) | 35(3) |
| C(31) | 4780(18) | −2163(10) | 6892(9) | 31(4) |
| C(32) | 5492(19) | −1740(10) | 7425(10) | 39(4) |
| C(33) | 6020(20) | −2304(12) | 8127(11) | 50(5) |
| C(34) | 5870(20) | −3266(10) | 8301(10) | 40(4) |
| C(35) | 5140(20) | −3700(10) | 7754(11) | 50(5) |
| C(36) | 4670(20) | −3151(10) | 7052(10) | 49(5) |
| Cl(33) | 6946(7) | −1761(3) | 8805(3) | 73(2) |
| Br(34) | 6550(3) | −4058(1) | 9253(1) | 74(1) |
| N(41) | 663(16) | 8179(8) | 3695(7) | 41(3) |
| C(41) | 1463(16) | 8202(10) | 2874(9) | 30(4) |
| C(42) | 1740(20) | 7387(11) | 2652(10) | 43(4) |
| C(43) | 2500(20) | 7395(11) | 1903(12) | 49(5) |
| C(44) | 2941(19) | 8268(10) | 1377(10) | 41(4) |
| C(45) | 2670(20) | 9097(11) | 1647(11) | 51(5) |
| C(46) | 1870(20) | 9077(11) | 2383(10) | 45(4) |
| Cl(43) | 2857(8) | 6353(3) | 1585(4) | 88(2) |
| Br(43) | 4009(3) | 8327(2) | 367(1) | 71(1) |

[a] $U$(eq) is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

has stoichiometry $A46_2Cu_2Br_4$. $A4_2Cu_2Br_6$ contains two crystallographically independent bibridged $Cu_2Br_6{}^{4-}$ dimers formed by edge sharing of copper bromide tetrahedra. This species was only recently discovered in our laboratory.[10] In $A46_2Cu_2Br_4$, an extended two-dimensional $(Cu_2Br_4)_n{}^{n-}$ network is built up by corner sharing of the above $Cu_2Br_6{}^{4-}$ dimer units. In this structure, the templating effect of the $A46^+$ cation imposes an open framework on the two-dimensional structure.

## Experimental Section

**Synthesis.** An attempt to prepare the Br analogue to $A_8CuCl_{10}$ (where A = $C_6H_4ClNH_3{}^+$, the 3-chloroanilinium cation) was undertaken using a thermal gradient technique. A procedure similar to that reported for the preparation of the chloride salt was employed.[8] In 1991, a sealed tube was prepared which contained a dilute HBr solution with an excess amount of approximate 10:1 ratio of 3-chloroaniline:$CuBr_2$. This was placed in the thermal gradient device, in which the bottom portion of the tube (containing the excess solid) was kept a constant temperature of approximately 45 °C. The upper portion of the tube was cooled with a flow of room temperature compressed air. The tube was left undisturbed (read "forgotten") until September, 1999 when the device was moved to a new location. It was observed that a large crystalline mass was present in the opaque purple solution. Removal and drying of the crystals revealed that they were colorless, indicating that they could not be a copper(II) bromide salt. Upon microscopic examination, three distinctly shaped crystals were observed: hexagonal rods, flat plates, and multifaceted polyhedra. Qualitatively, about 60% of the crystals were of the polyhedral variety, with about 30% of the platelets and 10% of the rods. A suitable crystal of each type was separated out and mounted for X-ray data collection as described below.

**X-ray Diffraction.** Data for the compounds were collected at room temperature on a Bruker 3-circle platform diffractometer equipped with a CCD detector maintained near −54 °C and the c-axis fixed at 54.74°. The frame data were acquired with the SMART[11] software at 295 K using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) from a fine-focus tube. Initial cell constants were determined from reflections obtained from 60 10-s frames. Final values of the cell parameters were obtained from least squares refinement of the positions of all observed reflections. A complete hemisphere of data is scanned on omega (0.3°) with a run time of 10-s per frame at the detector resolution of 512 × 512 pixels. A total of 1271 frames are collected in three sets and a final set of 50 frames, identical to first 50 frames, are also collected to determine crystal decay. The frames were then processed on a SGI-Indy/Indigo 2 workstation by using the SAINT software[12] to give the hkl file corrected

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(11) SHELXTL 5.10 (PC−Version), *Program library for Structure Solution and Molecular Graphics*; Bruker AXS Inc.: Madison, WI, 1997.

**Table 4.** Atomic Coordinates (× $10^4$) and Equivalent Isotropic Displacement Parameters ($A^2 \times 10^3$) for (4,6-diBr-3-Cl-anilinium)$CuBr_2$

| atom | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Cu(1) | 397(3) | 7500 | 8550(2) | 83(1) |
| Cu(2) | 838(2) | 7500 | 10910(2) | 70(1) |
| Br(1) | 1986(2) | 7500 | 6632(1) | 59(1) |
| Br(2) | 1080(1) | 6789(1) | 9820(1) | 66(1) |
| Br(3) | −1932(2) | 7500 | 12307(1) | 68(1) |
| N | 589(11) | 6793(2) | 4542(8) | 61(2) |
| C(1) | 1087(11) | 6329(3) | 4248(9) | 54(2) |
| C(2) | 1286(12) | 6205(3) | 3057(9) | 57(2) |
| C(3) | 1749(12) | 5766(3) | 2761(8) | 53(2) |
| Cl | 1968(4) | 5613(1) | 1251(2) | 68(1) |
| C(4) | 2018(13) | 5457(3) | 3701(10) | 59(2) |
| Br(4) | 2644(2) | 4852(1) | 3343(1) | 75(1) |
| C(5) | 1834(13) | 5574(3) | 4903(8) | 56(2) |
| C(6) | 1367(12) | 6016(3) | 5190(8) | 49(2) |
| Br(6) | 1083(2) | 6202(1) | 6831(1) | 68(1) |

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

**Table 5.** Bond Lengths (Å) and Angles (deg) for 4-Br-3-Cl-anilinium Bromide

| | | | |
|---|---|---|---|
| Br(2)−C(6) | 1.881(5) | C(5)−C(6)−Br(2) | 119.8(4) |
| Cl−C(3) | 1.729(5) | C(1)−C(6)−Br(2) | 121.7(4) |
| N−C(1) | 1.446(6) | C(4)−C(3)−Cl | 121.0(4) |
| C(2)−C(1) | 1.368(7) | C(2)−C(3)−Cl | 118.4(4) |
| C(3)−C(2) | 1.398(7) | C(1)−C(2)−C(3) | 118.4(5) |
| C(3)−C(4) | 1.368(8) | C(2)−C(1)−C(6) | 121.4(4) |
| C(5)−C(4) | 1.361(8) | C(2)−C(1)−N | 118.2(5) |
| C(6)−C(5) | 1.379(7) | C(4)−C(5)−C(6) | 121.2(5) |
| C(6)−C(1) | 1.389(7) | C(4)−C(3)−C(2) | 120.7(5) |
| | | C(6)−C(1)−N | 120.4(5) |
| | | C(5)−C(6)−C(1) | 118.4(5) |
| | | C(5)−C(4)−C(3) | 119.9(5) |

for Lp/decay. The absorption correction was performed using the SADABS[13] program. The structures were solved by the direct method using the SHELX-90[14] program and refined by least-squares method on F2, SHELXL-93,[15] incorporated in SHELXTL V 5.03.[16,17] The crystals used for the diffraction study showed no appreciable decomposition during data collection. Intensity statistics for all three compounds clearly indicated centric structures, so the structure solutions were pursued in the space groups $P2_1/c$ (multifaceted crystals), *P*-1 (platelets), and *Pnma* (hexagonal rods), respectively, utilizing the direct methods subroutine TREF in the XS routine in the SHELXTL program package. The resultant E-map revealed the position of the heavy atoms and most of the C and N atoms. The remaining C and N atoms were located on subsequent difference Fourier maps. All non-hydrogen atoms are refined anisotropically. Refinement of the site occupancy factors for the ring bromine atoms indicated that bromination was essentially complete in all cases ($0.98 \le \mathrm{SOF} \le 1.00$). Hydrogen atoms positions were generated with the HADD instruction in the XP routine of SHELXTL V 5.03. The R1 values for the Cu(I) salts are relatively high. This is presumably due to the X-ray fluorescence of these compounds. Table 1 summarizes the most important structural and refinement parameters. Atomic coordinates are given in Tables 2−4 and a list of important distances and angles in the three compounds are given in Tables 5−7.

**Table 6.** Bond Lengths (Å) and Angles (deg) for (4-Br-3-Cl-anilinium)$_2$$CuBr_3$[a]

| | | | |
|---|---|---|---|
| Cu(1)−Br(2) | 2.449(3) | C(24)−Br(24) | 1.895(17) |
| Cu(1)−Br(1) | 2.460(3) | C(25)−C(26) | 1.36(2) |
| Cu(1)−Br(3) | 2.524(3) | | |
| Cu(1)−Br(3)#1 | 2.561(3) | N(31)−C(31) | 1.430(16) |
| Cu(1)−Cu(1)#1 | 2.815(5) | C(31)−C(32) | 1.37(2) |
| | | C(31)−C(36) | 1.401(19) |
| Cu(2)−Br(4) | 2.451(3) | C(32)−C(33) | 1.39(2) |
| Cu(2)−Br(5) | 2.458(2) | C(33)−C(34) | 1.37(2) |
| Cu(2)−Br(6) | 2.526(3) | C(33)−Cl(33) | 1.748(18) |
| Cu(2)−Br(6)#2 | 2.560(3) | C(34)−C(35) | 1.40(2) |
| Cu(2)−Cu(2)#2 | 2.802(4) | C(34)−Br(34) | 1.885(15) |
| | | C(35)−C(36) | 1.36(2) |
| N(11)−C(11) | 1.462(19) | | |
| C(11)−C(12) | 1.348(19) | N(41)−C(41) | 1.494(19) |
| C(11)−C(16) | 1.40(2) | C(41)−C(42) | 1.33(2) |
| C(12)−C(13) | 1.36(2) | C(41)−C(46) | 1.390(19) |
| C(13)−C(14) | 1.34(2) | C(42)−C(43) | 1.38(2) |
| C(13)−Cl(13) | 1.757(14) | C(43)−C(44) | 1.42(2) |
| C(14)−C(15) | 1.41(2) | C(43)−Cl(43) | 1.727(17) |
| C(14)−Br(14) | 1.874(18) | C(44)−C(45) | 1.39(2) |
| C(15)−C(16) | 1.33(2) | C(44)−Br(43) | 1.858(18) |
| | | C(45)−C(46) | 1.37(2) |
| N(21)−C(21) | 1.465(19) | | |
| C(21)−C(26) | 1.37(2) | Br(2)−Cu(1)−Br(1) | 114.93(11) |
| C(21)−C(22) | 1.38(2) | Br(2)−Cu(1)−Br(3) | 112.74(10) |
| C(22)−C(23) | 1.34(2) | Br(1)−Cu(1)−Br(3) | 102.08(9) |
| C(23)−C(24) | 1.35(2) | Br(2)−Cu(1)−Br(3)#1 | 104.67(9) |
| C(23)−Cl(23) | 1.742(17) | Br(1)−Cu(1)−Br(3)#1 | 109.90(10) |
| C(24)−C(25) | 1.40(2) | Br(3)−Cu(1)−Br(3)#1 | 112.78(10) |
| Cu(1)−Br(3)−Cu(1)#1 | 67.22(10) | C(23)−C(24)−Br(24) | 123.4(14) |
| | | C(25)−C(24)−Br(24) | 117.7(12) |
| Br(4)−Cu(2)−Br(5) | 114.61(10) | C(26)−C(25)−C(24) | 119.4(15) |
| Br(4)−Cu(2)−Br(6) | 112.75(10) | C(25)−C(26)−C(21) | 119.5(15) |
| Br(5)−Cu(2)−Br(6) | 101.97(10) | | |
| Br(4)−Cu(2)−Br(6)#2 | 103.67(10) | C(32)−C(31)−C(36) | 119.3(14) |
| Br(5)−Cu(2)−Br(6)#2 | 111.06(9) | C(32)−C(31)−N(31) | 119.4(13) |
| Br(6)−Cu(2)−Br(6)#2 | 113.15(9) | C(36)−C(31)−N(31) | 121.2(13) |
| Cu(2)−Br(6)−Cu(2)#2 | 66.85(9) | C(31)−C(32)−C(33) | 118.6(14) |
| | | C(34)−C(33)−C(32) | 122.3(15) |
| C(12)−C(11)−C(16) | 119.6(16) | C(34)−C(33)−Cl(33) | 119.1(13) |
| C(12)−C(11)−N(11) | 120.9(15) | C(32)−C(33)−Cl(33) | 118.6(13) |
| C(16)−C(11)−N(11) | 119.5(13) | C(33)−C(34)−C(35) | 119.1(15) |
| C(11)−C(12)−C(13) | 120.0(15) | C(33)−C(34)−Br(34) | 123.7(13) |
| C(14)−C(13)−C(12) | 121.7(14) | C(35)−C(34)−Br(34) | 117.2(11) |
| C(14)−C(13)−Cl(13) | 120.4(14) | C(36)−C(35)−C(34) | 118.6(14) |
| C(12)−C(13)−Cl(13) | 117.9(13) | C(35)−C(36)−C(31) | 121.9(15) |
| C(13)−C(14)−C(15) | 118.5(17) | | |
| C(13)−C(14)−Br(14) | 123.9(12) | C(42)−C(41)−C(46) | 123.6(16) |
| C(15)−C(14)−Br(14) | 117.6(14) | C(42)−C(41)−N(41) | 118.3(13) |
| C(16)−C(15)−C(14) | 120.3(17) | C(46)−C(41)−N(41) | 118.1(15) |
| C(15)−C(16)−C(11) | 119.8(14) | C(41)−C(42)−C(43) | 119.0(15) |
| C(26)−C(21)−C(22) | 121.2(16) | C(42)−C(43)−C(44) | 119.7(16) |
| C(26)−C(21)−N(21) | 118.7(13) | C(42)−C(43)−Cl(43) | 120.5(13) |
| C(22)−C(21)−N(21) | 120.1(14) | C(44)−C(43)−Cl(43) | 119.7(16) |
| C(23)−C(22)−C(21) | 118.0(16) | C(45)−C(44)−C(43) | 119.0(17) |
| C(22)−C(23)-C(24) | 123.0(17) | C(45)−C(44)−Br(43) | 119.0(11) |
| C(22)−C(23)−Cl(23) | 117.6(13) | C(43)−C(44)−Br(43) | 121.8(14) |
| C(24)−C(23)−Cl(23) | 119.2(14) | C(46)−C(45)−C(44) | 120.3(15) |
| C(23)−C(24)−C(25) | 118.5(16) | C(45)−C(46)−C(41) | 118.2(16) |

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

## Discussion

All three compounds contain cations in which the phenyl rings have undergone bromination during the synthesis process. Three different brominated cations were found in the crystallographic studies: A4$^+$, the 4-bromo-3-chloroanilinium cation; A6$^+$, the 6-bromo-3-chloranilinium cation; A46$^+$, the 4,6-dibromo-3-chloroanilinium cation. The formation of these brominated cations was accompanied by reduction of the Cu(II) ions to Cu(I), as evidenced by the structural results for two of the reported compounds. Crystallization of the A4$^+$ and A6$^+$ salts presumably occurred early during the process, while the formation of

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

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

(14) SADABS, Program for absorption correction for area detectors; Bruker AXS Inc.: Madison, WI, 1996.

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

(16) Sheldrick, G. M. SHELXL-97, *Program for the Refinement of Crystal Structure*; University of Göttingen: Germany, 1997.

(17) SHELXTL 5.10 (PC-Version), *Program library for Structure Solution and Molecular Graphics*; Bruker AXS Inc.: Madison, WI, 1997.

**Table 7.** Bond Lengths (Å) and Angles (deg) for (4,6-diBr-3-Cl anilinium)$CuBr_2$

| | | | |
|---|---|---|---|
| Cu(1)−Br(1) | 2.390(2) | Br(2)#2-Cu(1)−Br(2) | 110.31(9) |
| Cu(1)−Br(1)#1 | 2.470(2) | Br(2)−Cu(2)−Br(2)#2 | 120.66(9) |
| Cu(1)−Br(2) | 2.5766(15) | Br(2)−Cu(2)−Br(3) | 110.75(5) |
| Cu(1)−Cu(2) | 2.599(3) | Br(2)−Cu(2)−Br(3)#3 | 109.39(5) |
| Cu(2)−Br(2) | 2.4336(14) | Br(3)−Cu(2)−Br(3)#3 | 92.18(7) |
| Cu(2)−Br(3) | 2.515(2) | Cu(1)−Br(1)−Cu(1)#4 | 123.29(8) |
| Cu(2)−Br(3)#3 | 2.528(2) | Cu(2)−Br(2)−Cu(1) | 62.41(6) |
| Br(1)−Cu(1)#4 | 2.470(2) | Cu(2)−Br(3)−Cu(2)#5 | 166.92(9) |
| Br(3)−Cu(2)#5 | 2.528(2) | | |
| | | C(2)−C(1)−C(6) | 120.4(8) |
| N−C(1) | 1.459(11) | C(2)−C(1)−N | 119.6(9) |
| C(1)−C(2) | 1.362(13) | C(6)−C(1)-N | 120.0(9) |
| C(1)−C(6) | 1.402(13) | C(1)−C(2)-C(3) | 120.4(9) |
| C(2)−C(3) | 1.384(12) | C(4)−C(3)-C(2) | 118.8(9) |
| C(3)−C(4) | 1.391(14) | C(4)−C(3)-Cl | 121.4(7) |
| C(3)−Cl | 1.720(9) | C(2)−C(3)-Cl | 119.7(7) |
| C(4)−C(5) | 1.366(14) | C(5)−C(4)-C(3) | 122.0(8) |
| C(4)−Br(4) | 1.897(9) | C(5)−C(4)-Br(4) | 117.6(8) |
| C(5)−C(6) | 1.394(12) | C(3)−C(4)-Br(4) | 120.5(8) |
| C(6)−Br(6) | 1.888(8) | C(4)−C(5)-C(6) | 118.6(8) |
| | | C(5)−C(6)-C(1) | 119.7(8) |
| Br(1)−Cu(1)-Br(1)#1 | 114.05(9) | C(5)−C(6)-Br(6) | 121.0(7) |
| Br(1)−Cu(1)-Br(2) | 112.38(6) | C(1)−C(6)-Br(6) | 119.2(7) |
| Br(1)#1−Cu(1)−Br(2) | 103.53(6) | | |

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

the $A46^+$ occurred in the latter stages. The three different brominated cations are illustrated in Figure 1. In the $A6^+$ cation, bromination occurred in the 6 position, para to the Cl substituent. In contrast, for the other monobrominated species, $A4^+$, bromination occurred in the 4 position, para to the ammonium substituent. Finally, for the $A46^+$ cation, bromination occurred at both the 4 and 6 positions. Bond distances and angles in the cations are not unusual, with average distances of C−C = 1.38, C−N = 1.46, C−Cl = 1.73, and C−Br = 1.88 Å.

The A6Br salt consists of alternate layers of $A6^+$ cations and $Br^-$ anions. The organic layers are composed of facial stacks of the phenyl rings. The organic and bromide ion layers are held together by a well-defined N−H···Br hydrogen bonding network, as illustrated in Figure 2. Each $NH_3^+$ group forms three strong hydrogen bonds to the lattice bromide ion, with distances ranging from 3.237 to 3.325 Å. There is also a short van der Waals contact between the ring bromine atom and the lattice bromide ion, with a distance of 3.623 Å. This is considerably shorter than the sum of the van der Waals radii of 3.90 Å.

The compound $A4_2Cu_2Br_6$ contains the novel and only recently reported[10] Cu(I) halide species, the bibridged $Cu_2Br_6^{4-}$ dimer. One of the two independent dimers in the triclinic cell is illustrated in Figure 3 and a view of the asymmetric unit is given in Figure 4. As is seen in these figures, the dimeric unit is formed by the edge sharing of two $CuBr_4$ tetrahedra. As anticipated, the bridging Cu−Br distances (2.543 Å, average) are significantly longer than the terminal distances (2.455 Å, average). Angular distortions of the Cu coordination sphere are not too severe, with Br−Cu−Br angles ranging from 102 to 115°. Each dimer sits on a center of inversion, so that the bridging unit is required to be planar. Because of the high charge on the dimeric unit, extensive hydrogen bonding interactions occur. Each of the four crystallographically independent $NH_3^+$ groups forms five short N−H···Br contacts in the range of 3.2−3.3 Å.

In contrast to the previously reported structure containing the $Cu_2Br_6^{4-}$ dimer anion, the bridging geometry here is more nearly symmetrical, with the bridging Cu−Br distances differing by less than 0.04 Å (compared to nearly 0.24 Å in the previous report). This presumably is due to the cations' ability to form short hydrogen bonding to all the bromide ions, not just the terminal bromide ions as in the previous report. In addition, the Cu−Br−Cu bridging bond angle is much more acute (67.0°, average) than in the previous report (86.7°), and the Cu coordination shows much less severe distortion from ideal tetrahedral geometry. Thus the Cu−Cu distances are only 2.812 and 2.802 Å for Cu(1)−Cu(1) and Cu(2)−Cu(2), respectively.

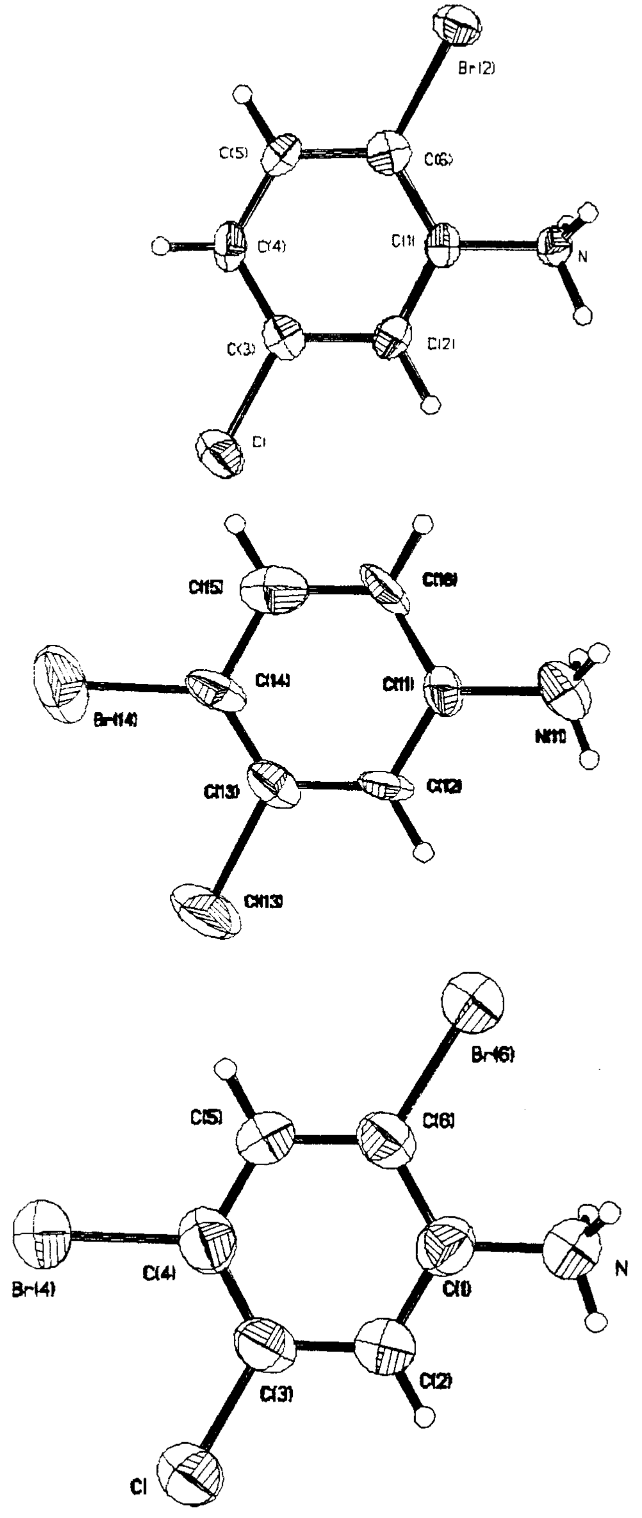

**Figure 1.** Illustration of the brominated cations. (top) $A6^+$, 6-bromo-3-chloroanilinium; (middle) $A4^+$, 4-bromo-3-chloroanilinium; (bottom) $A46^+$, 4,6-dibromo-3-chloroanilinium. Thermal ellipsoids shown at 50% probability level.

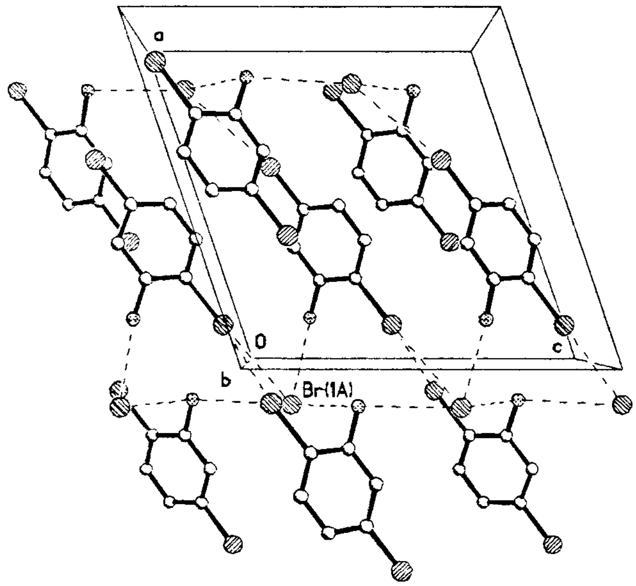

**Figure 2.** Illustration of the hydrogen bonding and short Br−Br contacts in A6Br.

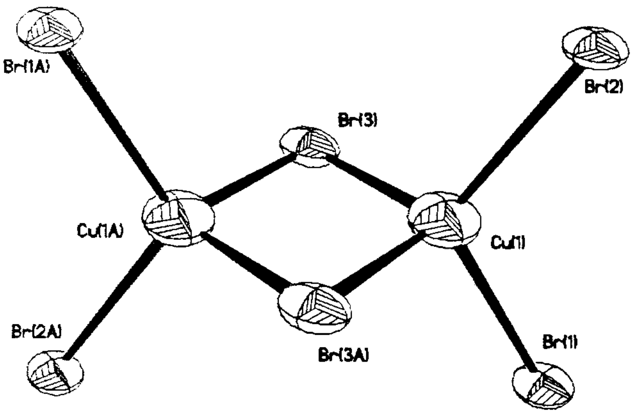

**Figure 3.** The $Cu_2Br_6^{4-}$ anion in $(A4)_2CuBr_3$. Thermal ellipsoids shown at 50% probability level.

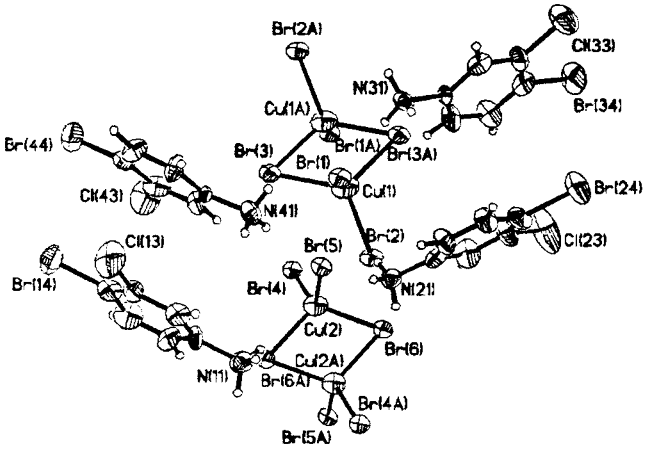

**Figure 4.** The asymmetric unit in $(A4)_2CuBr_3$. Thermal ellipsoids shown at 50% probability level.

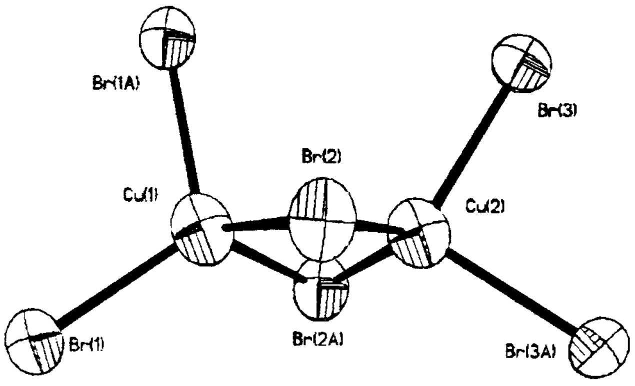

**Figure 5.** The $Cu_2Br_6^{4-}$ grouping in $(A46)_2CuBr_2$. Thermal ellipsoids shown at 50% probability level.

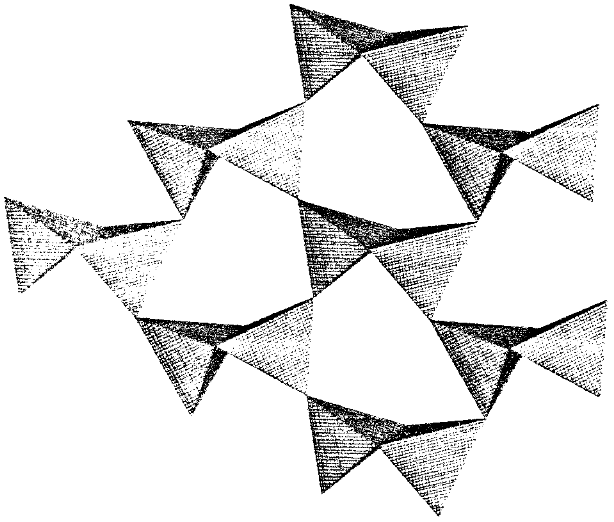

**Figure 6.** Polyhedral representation of the layer in $(A46)_2CuBr_2$.

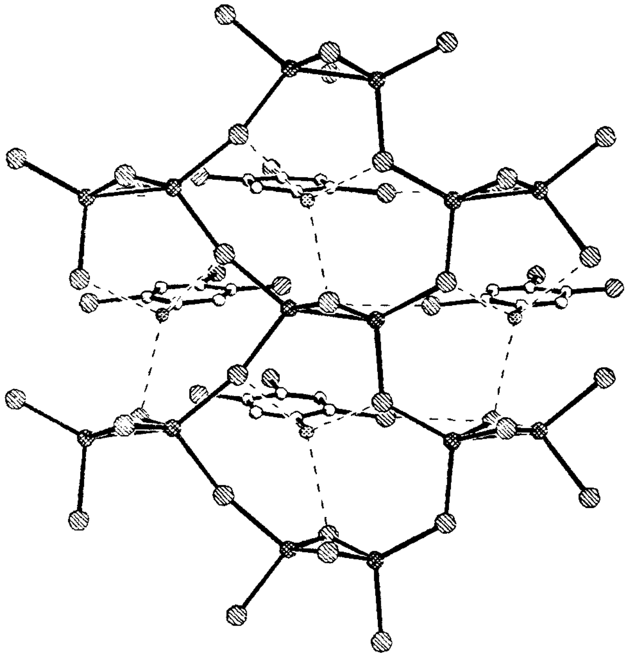

**Figure 7.** Illustration of the templating effect of the $A46^+$ cation on the anionic layer in $(A46)_2CuBr_2$.

The $A46_2Cu_2Br_4$ compound is the most interesting of the series. It contains the dibrominated cation, illustrating the reactivity of the 3-chloroanilinium cation to bromination by $CuBr_2$. The dominant feature of the structure is the formation of a unique two-dimensional Cu/Br network based the $Cu_2Br_6$ dimers found in the previous structure. These $Cu_2Br_6$ dimer units lie on mirror planes, but with the bridging $Cu_2Br_2$ units sitting athwart the mirror plane. Thus, as seen in Figure 5, the $Cu_2Br_2$ bridging moiety is not planar, but has a substantial fold, with a fold angle of 27.8°. Surprisingly, the $Cu_2Br_2$ bridging framework is quite asymmetric, with Cu(1)−Br(2) = 2.577(2) Å but Cu(2)−Br(2) = 2.434(1) Å, a difference of more than 0.14 Å. The short Cu(2)−Br(2) distance, coupled with the extremely acute Cu(1)−Br(2)-Cu(2) angle of 62.41(6)°, leads to the very short Cu(1)−Cu(2) contact of 2.599(3) Å. This is 0.2 Å shorter than the distances in the isolated $Cu_2Br_6^{4-}$ dimer in $A4_2Cu_2Br_6$.

Each of the “terminal” bromide ions in the dimers is shared with a different adjacent dimer and, in so doing, defines the open two-dimensional framework shown in Figure 6. This structure contains six-membered rings of alternating edge and corner shared tetrahedra, with a ring diameter of 5.0−5.5 Å. The templating nature of the cation can be seen in Figure 7. Each cation sits above (and below, because of the network lies on a mirror plane) the “holes” in the two-dimensional framework, and each cation hydrogen bonds to three of the bromide ions in the framework: two bromide ions involved in the corner sharing of the tetrahedra and one bromide ion involved in edge sharing.

**Acknowledgment.** The use of the Single Crystal X-ray Diffraction Laboratory of the University Research Office at the University of Idaho is greatly appreciated.

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

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