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# Structure of Catalytically Related Species Involving Copper(II) Halides. III. 2-Amino-5-bromo-3-methylpyridinium 2-Amino-3-methylpyridinium Tetrabromocuprate(II)

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**Abstract.** $C_6H_8BrN_2^+.C_6H_9N_2^+.CuBr_4^{2-}$, $M_r = 680{\cdot}5$, monoclinic, $P2_1/a$, $a = 15{\cdot}913\,(5)$, $b = 7{\cdot}764\,(3)$, $c = 16{\cdot}297\,(5)$ Å, $\beta = 97{\cdot}33\,(2)°$, $V = 1996{\cdot}9\,(4)$ Å$^3$, $Z = 4$, $D_x = 2{\cdot}27$ g cm$^{-3}$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 110{\cdot}1$ cm$^{-1}$, $F(000) = 1284$, $T = 293$ K, 1719 unique reflections of which 1063 had $F \geq 3\sigma(F)$ were refined to a final $R = 0{\cdot}0593$ for the $3\sigma$ data set ($wR = 0{\cdot}0455$). The compound has nominal formula $(C_6H_8BrN_2)(C_6H_9N_2)CuBr_4$ consisting of a 2-amino-5-bromo-3-methylpyridinium cation, a 2-amino-3-methylpyridinium cation and a $CuBr_4^{2-}$ anion. The 5-bromo cations were formed by catalytic bromination of the substituted pyridinium rings by copper(II) bromide. The structure is such that nearly every second cation is the 5-bromo derivative, but this is replaced by the unbrominated cation about 22% of the time, which in turn causes disorder of the $CuBr_4^{2-}$ anion. The $CuBr_4^{2-}$ anion has geometry intermediate between square planar and tetrahedral with Cu—Br (average) 2·376 Å and Br—Cu—Br angles varying between 94·7 (1) and 131·5 (1)°.

**Introduction.** A series of quasi-planar copper bromide salts analogous to known copper chloride salts has been sought using 2-amino-*n*-methylpyridinium cations (where $n = 3$, 4, 5 or 6) in order to form the $Cu_mX_{2m+2}^{2-}$ cation (where $m = 3$ or 4) or related $Cu_mX_{2m}L_2$ oligomers ($X = Cl^-$ or $Br^-$). Frequently, crystals containing the $CuBr_4^{2-}$ anion are produced as the only product (Place & Willett, 1987). In the preparation of the 2-amino-3-methylpyridinium copper bromide salts, the only crystalline product turned out to contain the tetrabromide anion, and also had the unusual result of containing partially brominated cations. The catalytic activity of copper(II) halides is known (Hay, Blanchard, Endres & Austance, 1959; Rogic, Demmin & Hammond, 1976). The crystal structures (papers I and II of this series) of the catalytically active species and the phenoxide precursor for the catalytic oxidation of phenols by copper(II) chlorides have been reported (Willett & Breneman, 1983; Marengo-Rullàn & Willett, 1986).

**Experimental.** An aqueous solution of 1·0 *M* 2-amino-3-methylpyridine was added to a fourfold excess of 1·0 *M* $CuBr_2$ with sufficient 1·0 *M* HBr added to just dissolve any $Cu(OH)_2$ formed. Excess acid was avoided. The solution was warmed for about 3 h. The solution was allowed to evaporate very slowly over several weeks, yielding dark-brown-black plate-like crystals. A crystal approximately 0·1 × 0·15 × 0·05 mm was selected for data collection. Data were collected with an $\omega$ scan on a Nicolet *R3m/E* diffractometer system with Mo $K\alpha$ radiation and a graphite monochromator (Campana, Shepherd & Litchman, 1980). Agreement between equivalent reflections was 0·0659. The monoclinic cell and orientation matrix were defined by a least-squares refinement of 25 reflections in the 28–30° $2\theta$ range. The space group was $P2_1/a$ with systematic absences $h0l$, $h$ odd; $0k0$, $k$ odd. Empirical $\psi$-scan absorption corrections were applied assuming an ellipsoidal shaped crystal (min. transmission 0·193, max. transmission 0·347). Data were collected for $h \geq 0$, $k \geq 0$ and all $l$. (The max. values

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of *h*, *k* and *l* were 7, 8 and 14, respectively.) Three standards were monitored every 50 reflections with variation within counting statistics. Scan speeds ranged from 4·00 to 29·30° min$^{-1}$, with 1874 total reflections (out to $2\theta = 45°$), 1719 unique reflections and 1063 reflections with $F > 3\sigma(F)$. The structure was solved *via* direct methods yielding the Cu and Br positions on the $CuBr_4^{2-}$ anion. A subsequent difference map yielded the pyridinium rings and an additional large peak approximately 2 Å from one of the pyridinium rings. This was assigned as a Br atom. Refinement of the site occupancy factor, $S_{Br}$, for this Br atom, Br(5), yielded a value of 0·78. One of the Br atoms, Br(3), of the $CuBr_4^{2-}$ ion had an anomalously large thermal parameter, and a smaller but substantial peak was observed about 2·5 Å from the Cu ion. It was assumed that the position of Br(3) in the $CuBr_4^{2-}$ anion was dependent upon whether the nearest pyridinium ring was brominated. The site occupancy factor of Br(3) was set equal to $S_{Br}$ while the site occupancy factor for the Br ion at the alternate site, Br(3*x*), was set equal to $(1 - S_{Br})$. Final refinement on *F* for all observed reflections with anisotropic thermal parameters for the Cu and Br atoms in the $CuBr_4^{2-}$ anion and based on 128 least-squares parameters gave $R = 0.0593$ and $wR = 0.0455$ with av. $\Delta/\sigma = 0.091$ (*SHELXTL*; Sheldrick, 1984), where $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$, $g = 0.0012$. The goodness of fit was 1·610. H atoms were fixed at calculated positions ($r_{\text{C-H}} = r_{\text{N-H}} = 0.96$ Å) with isotropic thermal parameters approximately 20% larger than those of the corresponding heavy atom. The amino groups appeared to be disordered on the electron density maps, and were approximated as a tetrahedral $-NH_3$ moiety with 2/3 site occupancy factors for the H atom. The largest residual on the final difference map was 0·76 e Å$^{-3}$, the largest negative residual being −0·8 e Å$^{-3}$ near N(7). There was evidence of considerable disorder as might be anticipated from the partial bromination of one of the pyridine rings, and it proved impossible to refine the cations with anisotropic thermal parameters without them becoming non-positive definite. Scattering factors, corrected for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1974).

Final positional parameters are given in Table 1, with selected bond angles and distances in Table 2.* The final value of $S_{Br}$ was 0·79 (4).

**Discussion.** The structure consists of discrete $CuBr_4^{2-}$ anions, 2-amino-5-bromo-3-methylpyridinium cations and 2-amino-3-methylpyridinium cations (Fig. 1). The cations in this compound are unusual in that the pyridinium ring is partially brominated. This partial bromination has also been observed in bis(2-amino-5-bromo-6-methylpyridinium) octabromotricuprate(II) (Place, 1986). The difference in the structures of these

Table 1. *Positional* (×10$^4$) *and isotropic thermal parameters* (Å$^2$ ×10$^3$) *for* $C_{12}H_{17}N_4CuBr_5$

The equivalent isotropic *U* values of atoms refined anisotropically (designated by an asterisk) and defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

| | *x* | *y* | *z* | $U_{eq}/U_{iso}$ |
|---|---|---|---|---|
| Cu | 3231 (1) | 6742 (3) | 2624 (1) | 47 (1)* |
| Br(1) | 3428 (1) | 9266 (2) | 1810 (1) | 52 (1)* |
| Br(2) | 4696 (1) | 5989 (3) | 2963 (1) | 68 (1)* |
| Br(3) | 2686 (2) | 4011 (3) | 2248 (2) | 67 (1)* |
| Br(4) | 2244 (1) | 7846 (3) | 3445 (1) | 70 (1)* |
| Br(5) | 1284 (2) | 6227 (3) | 805 (2) | 56 (1)* |
| Br(3*x*) | 2223 (31) | 4876 (67) | 1815 (30) | 77 (20) |
| C(5) | 514 (11) | 7271 (19) | 3 (1) | 36 (5) |
| C(4) | −315 (11) | 7546 (20) | 153 (11) | 48 (5) |
| C(3) | −894 (11) | 8288 (21) | −376 (11) | 46 (5) |
| C(2) | −685 (11) | 8880 (20) | −1157 (10) | 34 (5) |
| N(1) | 147 (8) | 8592 (15) | −1288 (8) | 41 (4) |
| C(6) | 737 (11) | 7817 (20) | −735 (10) | 47 (6) |
| C(8) | −1807 (10) | 8558 (21) | −224 (10) | 62 (6) |
| N(7) | −1206 (8) | 9636 (17) | −1755 (8) | 55 (4) |
| N(11) | −661 (10) | 3962 (17) | 3578 (8) | 55 (5) |
| C(16) | −1072 (13) | 3355 (24) | 4231 (11) | 77 (7) |
| C(15) | −613 (11) | 2611 (24) | 4864 (12) | 74 (7) |
| C(14) | 256 (11) | 2396 (20) | 4881 (10) | 50 (6) |
| C(13) | 677 (11) | 2983 (21) | 4242 (10) | 48 (5) |
| C(12) | 182 (12) | 3827 (21) | 3580 (10) | 49 (6) |
| C(18) | 1629 (11) | 2776 (24) | 4225 (11) | 89 (7) |
| N(17) | 510 (8) | 4439 (18) | 2898 (9) | 64 (5) |

Table 2. *Bond angles* (°) *and bond distances* (Å) *in* $C_{12}H_{17}N_4CuBr_5$

| | | | |
|---|---|---|---|
| Cu—Br(1) | 2·413 (3) | Cu—Br(2) | 2·400 (3) |
| Cu—Br(3) | 2·340 (3) | Cu—Br(4) | 2·352 (3) |
| Cu—Br(3*x*) | 2·418 (48) | | |
| | | Br(5)—C(5) | 1·860 (16) |
| C(5)—C(4) | 1·389 (26) | C(5)—C(6) | 1·367 (24) |
| C(4)—C(3) | 1·313 (23) | C(3)—C(2) | 1·434 (24) |
| C(3)—C(8) | 1·520 (25) | C(2)—N(1) | 1·388 (23) |
| C(2)—N(7) | 1·333 (20) | N(1)—C(6) | 1·356 (20) |
| N(11)—C(16) | 1·401 (25) | N(11)—C(12) | 1·347 (25) |
| C(16)—C(15) | 1·320 (26) | C(15)—C(14) | 1·389 (25) |
| C(14)—C(13) | 1·388 (25) | C(13)—C(12) | 1·414 (23) |
| C(13)—C(18) | 1·528 (25) | C(12)—N(17) | 1·373 (23) |
| Br(1)—Cu—Br(2) | 97·7 (1) | Br(1)—Cu—Br(3) | 131·5 (1) |
| Br(2)—Cu—Br(3) | 98·9 (1) | Br(1)—Cu—Br(4) | 99·3 (1) |
| Br(2)—Cu—Br(4) | 131·2 (1) | Br(3)—Cu—Br(4) | 103·0 (1) |
| Br(1)—Cu—Br(3*x*) | 108·1 (12) | Br(2)—Cu—Br(3*x*) | 122·4 (12) |
| Br(5)—C(5)—C(4) | 119·9 (12) | Br(5)—C(5)—C(6) | 122·2 (13) |
| C(4)—C(5)—C(6) | 117·9 (15) | C(5)—C(4)—C(3) | 123·7 (17) |
| C(4)—C(3)—C(2) | 120·1 (17) | C(4)—C(3)—C(8) | 124·0 (16) |
| C(2)—C(3)—C(8) | 115·9 (14) | C(3)—C(2)—N(1) | 114·9 (14) |
| C(3)—C(2)—N(7) | 126·8 (16) | N(1)—C(2)—N(7) | 118·3 (15) |
| C(2)—N(1)—C(6) | 124·2 (14) | C(5)—C(6)—N(1) | 119·2 (16) |
| C(16)—N(11)—C(12) | 122·4 (14) | N(11)—C(16)—C(15) | 118·5 (18) |
| C(16)—C(15)—C(14) | 121·1 (19) | C(15)—C(14)—C(13) | 121·4 (15) |
| C(14)—C(13)—C(12) | 116·9 (16) | C(14)—C(13)—C(18) | 123·7 (15) |
| C(12)—C(13)—C(18) | 119·4 (16) | N(11)—C(12)—C(13) | 119·6 (16) |
| N(11)—C(12)—N(17) | 117·1 (14) | C(13)—C(12)—N(17) | 123·2 (17) |

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* Anisotropic thermal parameters, H-atom positions, hydrogen-bond lengths and a listing of observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43889 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

two compounds containing brominated pyridinium rings is that in this compound the crystal packs with nearly every second cation being brominated (Fig. 2). In the 2-amino-5-bromo-6-methylpyridinium salt, almost all cations are brominated, the site occupancy factor for Br being 74%, as compared to 39% for the present salt. For the brominated pyridinium ring in the 2-amino-5-bromo-3-methylpyridinium cation, the site occupancy factor for the bromination is 78% and no evidence is observed for incorporation of the brominated ring into the other cation site. For the 22% of the time when neither cation is brominated, the position of one Br atom on the $CuBr_4^{2-}$ anion is affected. This position is given in Table 1 as Br(3*x*).

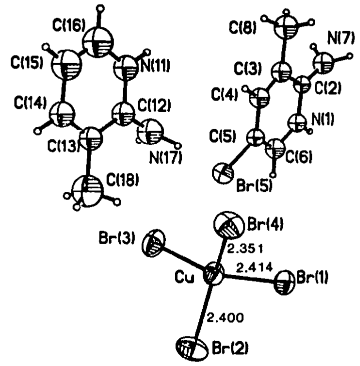

Fig. 1. Cations and anion of $C_{12}H_{17}N_4CuBr_5$. The Br(5) site is occupied.

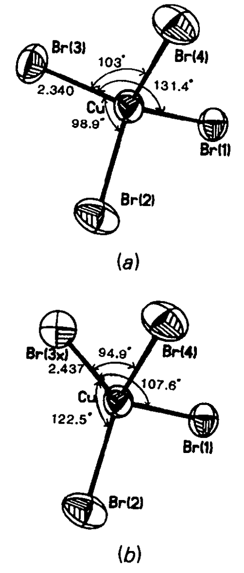

Fig. 2. Anion of $C_{12}H_{17}N_4CuBr_5$. (*a*) Br(5) site is occupied. (*b*) Br(5) site is vacant and Br(3) site becomes Br(3*x*).

Pyridine is normally resistant to electrophilic substitution. However, the amino group will activate the ring toward such substitution. In alkylpyridine systems, the ring N atom directs the position of substitution, but in an aminopyridine molecule the amino group directs the position of further substitution, either *ortho* or *para* to the amino group. 2-Aminopyridine is readily brominated to 2-amino-5-bromopyridine in the presence of $Br_2$ under mildly acidic conditions. In the bromination of the 2-amino-3-methylpyridinium cation observed here, a catalytic mechanism may be suggested using $CuBr_2$ as the brominating agent with the copper(II) ion being reduced to $Cu^I$ and subsequently air oxidized back to $Cu^{II}$.

The $CuBr_4^{2-}$ anion shows disorder, the position of Br(3) being dependent upon the presence of Br(5) on the cation (site occupancy 0·78). The $CuBr_4^{2-}$ anions have approximate $D_{2d}$ geometry intermediate between square planar and tetrahedral, the *trans* Br—Cu—Br angle being 131·3 (2)° and the Cu—Br distance being 2·376 (20) Å (average) for the anion when Br(5) is present. When Br(5) is absent and Br(3) becomes Br(3*x*), the anion apparently assumes a geometry closer to tetrahedral. However, the disorder of Br(3) and Br(3*x*) certainly implies the disorder of the rest of the atoms in the $CuBr_4^{2-}$ anion. This is evidenced by large and unusually anisotropic ellipsoids for Br(1), Br(2) and Br(4). Since this latter disorder was not treated in the refinement, discussion of the geometry of this disordered species is not meaningful.

The geometry of the $CuBr_4^{2-}$ ion in sites where the cation is brominated is within the range of other $CuBr_4^{2-}$ ions studied in this laboratory (Place & Willett, 1987) and other similar $CuCl_4^{2-}$ ions reported. Salts containing $CuCl_4^{2-}$ anions have been studied more extensively than those containing $CuBr_4^{2-}$ anions. The $CuCl_4^{2-}$ anion shows geometry ranging from square planar to nearly tetrahedral (Helmholz & Kruh, 1952; Harlow, Wells, Watt & Simonsen, 1974). The amount of distortion of the ion from square planar can be estimated by considering the dihedral angle formed between the *trans* Br—Cu—Br planes. This angle would be 0° for square planar and 90° for tetrahedral. In the $CuBr_4^{2-}$ ion in this salt (cation brominated) this angle is 65·4°. Other $CuBr_4^{2-}$ ions have shown dihedral angles ranging from 51·6 to 80·4° (Place & Willett, 1987).

The geometry of $CuX_4^{2-}$ ions in the solid state appears to be largely dictated by the strength of the hydrogen bonding and other electrostatic and steric interactions between the counterions and the halide ions (Willett, Haugen, Lebsach & Morrey, 1974; Harlow *et al.*, 1974; Battaglia, Bonamartini-Corradi, Marcotrigiano, Menabue & Pellacani, 1979). With strong hydrogen bonding (as evidenced by short nearly linear N—H··· interactions), a square-planar coordination is realized (Harlow *et al.*, 1974). As the hydrogen-bonding capabilities of the cations decrease, the anion distorts towards a more tetrahedral geometry. The distortion present in this salt lies well towards the tetrahedral end of the range of geometries normally observed, and is consistent with the limited extent of hydrogen bonding observed. However, it is not unknown for a $CuX_4^{2-}$ anion to assume two or more geometries in the same structure (Bloomquist & Willett, 1981) and it is known that pressure can cause significant distortion (Willett, Ferraro & Choca, 1974; Wang & Drickamer, 1973). Thus, the observed disorder and distortion when the brominated cation is replaced by the unbrominated one are readily rationalized.

The anions and cations are held together in the crystal lattice with hydrogen bonding between the Br atoms on the anion and the N atoms of the cations. The pyridinium N(1) atom is hydrogen bonded to Br(2) with N(11) hydrogen bonded to Br(1). There is also evidence of hydrogen bonding between the amine groups and the anion. There is a bifurcated hydrogen bond from N(7) to Br(1) and Br(5). N(17) shows hydrogen bonding to Br(1).

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# Structure of Dimethylformamide(dioxo)[*N*,*N'*-(1,3-propanediyl)bis(salicylideneiminato)]uranium(IV)

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**Abstract.** $[UO_2(C_{17}H_{16}N_2O_2)(C_3H_7NO)]$, $M_r$ = 623·45, orthorhombic, *Pbca*, $a = 12{\cdot}664\,(2)$, $b = 9{\cdot}563\,(2)$, $c = 35{\cdot}024\,(6)$ Å, $V = 4242\,(1)$ Å$^3$, $Z = 8$, $D_m$(by flotation) = 1·94, $D_x = 1{\cdot}952$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 73{\cdot}35$ cm$^{-1}$, $F(000) = 2368$, $T = 296\,(2)$ K, $R = 0{\cdot}037$ for 1600 observed reflections with $F_o \geq 6{\cdot}0\sigma(F_o)$. The U atom has a pentagonal bipyramidal coordination and the Schiff base the 'stepped' conformation. U—N distances [2·573 (2), 2·569 (8) Å] are much longer than U—O distances [2·240 (8), 2·253 (8), 2·417 (8) Å]. Bond angles at U are 71·2 (3), 74·0 (3) and 75·5 (3)° for N(1)—U—N(2), O(3)—U—O(5) and O(4)—U—O(5) respectively.

**Introduction.** Uranyl complexes with Schiff bases have been the subject of many investigations (Casellato, Vigato, Tamburini, Sitran & Graziani, 1984). The greatest attention has been given to polyhedra generated by bidentate or polydentate ligands with oxygen or nitrogen donor atoms (Casellato, Vidali & Vigato, 1976). A coordination number of 7 for the U atom seems to be the most common case (Cattalini, Croato, Degetto & Tondello, 1971). Most complexes exhibit a pentagonal bipyramidal geometry, with the uranyl oxygens at the axial position (Casellato, Vidali & Vigato 1976; Cattalini, Croato, Degetto & Tondello, 1971). In this report we present our results on the structure of such a complex of U with the Schiff base *N*,*N'*-(1,3-propanediyl)bis(salicylideneimine).

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