

Rb⁺, NH₄⁺ to one water molecule for the [N(CH₃)₄]⁺ and C(NH₂)₃⁺ cations. In the compound with ammonium and potassium cations disorder of one water molecule is present – as in ammonium tris(oxalato)gallate(III) trihydrate (Bulc, Golič & Šiftar, 1984).

There are no significant differences between the crystal structures of the complexes discussed, except for the disorder of the cations and water molecules. The disorder of the water molecules in the ammonium and potassium compounds could be expected, but the disorder of the monovalent cations in the above-mentioned compounds is unusual.

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Structures of Catalytically Related Species Involving Copper(II) Halides. VI. Tetrakis(3-aminopyridinium) Decabromodicuprate(I)dicuprate(II)

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Abstract. [C₅H₇N₂]₄[Cu₄Br₁₀], *M_r* = 1433.8, triclinic, *P* $\bar{1}$, *a* = 8.389 (5), *b* = 9.563 (2), *c* = 12.015 (3) Å, α = 98.04 (2), β = 91.61 (4), γ = 106.18 (4)°, *V* = 914.3 (6) Å³, *Z* = 1, *D_x* = 2.60 g cm⁻³, $\lambda(\text{Mo K}\alpha)$ = 0.71069 Å, μ = 131.6 cm⁻¹, *F*(000) = 670, *T* = 293 K, *R* = 0.0647 for 2368 unique observed reflections with *F* ≥ 3σ(*F*). The title compound contains mixed-valence binuclear copper(I)/copper(II) bromide species weakly linked together into tetranuclear units. The Cu^{II} ion assumes a square pyramidal coordination (two Br⁻ and two amino ligands in the equatorial positions and a Br⁻ in the axial position). The Cu^I ion is disordered between two positions; one with trigonal coordination, the other with tetrahedral coordination. The Cu^I and Cu^{II} ions are bridged by one Br⁻ ion, while the two Cu^I ions are bridged by two Br⁻ ions.

Introduction. In the past several years in this laboratory, we have been investigating the structural and magnetic properties of substituted aminopyridinium salts of copper(II) halides. This has resulted in the synthesis of a large number of oligomeric and poly-

meric species including a variety of planar, bibridged Cu_{*n*}X_{2*n*+2} oligomers (Willett, Grigereit, Halvorson & Scott, 1987), infinite bibridged (CuX₃)_{*n*} chains (Geiser, Gaura, Willett & West, 1987), as well as isolated CuX₄²⁻ anions (Place & Willett, 1988). Particularly with X = Br⁻, and occasionally with X = Cl⁻, the reaction process has led to the halogenation of the pyridine ring (Willett & West, 1987; Place & Willett, 1987). It has been surmised that this involves the reduction of copper(II) to copper(I) during the halogenation process and subsequent reoxidation by O₂. Indirect evidence for such a process can be inferred from the anaerobic recrystallization of (R₄N)CuCl₃ salts which have led to the isolation of several mixed-valence Cu^I/Cu^{II} species: a bibridged (Cu₂Cl₄)_{*n*} chain in (Et₄N)Cu₂Cl₄ (Willett, 1987), and isolated Cu₂Cl₆²⁻ and CuCl₂⁻ anions in (Bu₄N)₃Cu₃Cl₈ (Willett, Geiser & Ramakrishna, 1988). In this paper we report the crystal structure of a new mixed-valence Cu^I/Cu^{II} bromide salt obtained in an investigation of the 3-aminopyridine/CuBr₂/HBr system. In dilute HBr solution, the system yields (3-aminopyridinium)₂Cu₂Br₆·H₂O (Blanchette &

Willett, 1988), while in concentrated acid, (3-ammonio-pyridinium)CuBr₄ is obtained (Place, 1986).

Experimental. The salt was prepared by refluxing a 1:1 mixture of CuBr₂ and 3-aminopyridine in concentrated hydrobromic acid for several hours in a sealed system. Upon cooling, a purple mass settled out. Repeated warming and cooling cycles led to the formation of opaque purple platelets. Since both of the Cu^{II} salts discussed above also grow as opaque purple platelets, a crystal was mounted on a Syntex P2₁ diffractometer (upgraded to Nicolet P3F specifications) with Mo K α radiation and a graphite monochromator in order to identify it (Campana, Shepherd & Litchman, 1981). However, as it proved to be different from either of the copper(II) salts, a complete crystal-structure analysis was undertaken. Data-collection details are in Table 1. Structure solution *via* direct methods with *SHELXTL* package (Sheldrick, 1986) on a Data General Eclipse computer yielded Cu and Br positions. Remaining non-H atoms from resulting difference syntheses. H atoms constrained to idealized positions. The atom identified as the Cu^I ion was disordered between two sites, with 73 (1)% occupancy of site *A* and 27 (1)% occupancy of site *B*. No additional large electron density residuals or thermal parameters were observed, so no attempt was made to account for any induced disorder in neighboring atoms. Refinement details are also given in Table 1. Atomic scattering factors from *SHELXTL* package.

Discussion. Atomic parameters are given in Table 2.* The structure consists of isolated tetrameric (3-amino-pyridinium)₄Cu₄Br₁₀ units, illustrated in Fig. 1. Bond distances and angles are given in Table 3. The tetrameric units contain two Cu^{II} atoms [labeled Cu(2)] and two Cu^I atoms [labeled Cu(1) and Cu(1')] for the two disordered sites]. The Cu^{II} atoms, located at the ends of the tetranuclear unit, are coordinated by three Br⁻ ions and two amino N atoms, yielding a square pyramidal geometry. The two N atoms are *trans* in the equatorial plane [Cu–N = 2.045 Å, average, and N(7)–Cu(2)–N(17) = 171.9 (4)°]. The two Br⁻ ions in the equatorial plane have distances Cu(2)–Br(4) = 2.501 (2) and Cu(2)–Br(5) = 2.425 Å [Br(4)–Cu(2)–Br(5) = 160.2 (1)°], the longer bond being associated with a Br atom bridging to a Cu^I ion. The axial Cu(2)–Br(2) distance is considerably longer at 2.716 (2) Å. These parameters may be compared with those for the square pyramidal coordination which occurs in the bibridged chains in (4-methyl-2-amino-

Table 1. *Crystallographic data-collection parameters and refinement details*

Crystal size (mm)	0.2 × 0.4 × 0.4
No. and 2 θ range (°) of reflections used for lattice constants	25, 20–27
Type of absorption correction	Laminar
Maximum transmission	0.564
Minimum transmission	0.339
Data-collection technique	ω scan
Scan range (°)	1
Scan speed (° min ⁻¹)	3.9 (min.) 29.0 (max.)
Check reflections monitored every 100 reflections	122, 124
Total reflections	3171
2 θ_{\max} (°)	50
Unique reflections	2949
R _{int} for equivalent reflections	0.0259
Observed reflections [$F \geq 3\sigma(F)$]	2368
<i>h, k, l</i>	0 < <i>h</i> < 10, –12 < <i>k</i> < 12, –15 < <i>l</i> < 15
<i>R</i>	0.0647 (3 σ), 0.0805 (all)
<i>wR</i>	0.0817 (3 σ), 0.0870 (all)
with $w = 1/[\sigma^2(F) + g(F)^2]$	$g = 0.00291$
Function minimized	$\sum w(F_o - F_c)^2$
Goodness of fit	1.110
$ \Delta/\sigma _{\max}$	0.120
Total parameters refined	202
Thermal parameters	Anisotropic on all non-H atoms
H atoms	Constrained to C–H and N–H = 0.96 Å, thermal parameters fixed at 1.2 Å ²
Largest peak on final difference map (e Å ⁻³)	1.66 near Br(5)
Most negative peak on final difference map (e Å ⁻³)	–1.23
Extinction corrections	Yes

Table 2. *Atomic coordinates (× 10⁴) and equivalent isotropic thermal parameters (Å² × 10³) for (3-aminopyridinium)₄Cu₄Br₁₀*

The equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized *U_{ij}* tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Br(1)	4849 (2)	2642 (1)	7195 (1)	37 (1)
Br(2)	7536 (2)	1441 (1)	872 (1)	37 (1)
Br(3)	2740 (2)	3822 (2)	4393 (1)	49 (1)
Cu(2)	5375 (2)	2343 (1)	2242 (1)	31 (1)
Br(4)	6405 (2)	1751 (1)	4042 (1)	39 (1)
Br(5)	3717 (2)	3174 (1)	933 (1)	49 (1)
Cu(1)	4989 (52)	3149 (52)	5312 (13)	69 (6)
Cu(1')	5383 (41)	3531 (27)	5404 (26)	56 (7)
N(7)	3849 (11)	232 (9)	1866 (8)	32 (3)
C(3)	2334 (13)	–108 (12)	2372 (9)	29 (4)
C(2)	963 (15)	238 (13)	1936 (11)	41 (5)
N(1)	–438 (12)	–51 (12)	2428 (10)	44 (4)
C(4)	–650 (16)	–673 (14)	3380 (12)	48 (5)
C(5)	669 (16)	–1010 (15)	3856 (11)	46 (5)
C(6)	2185 (14)	–678 (13)	3381 (10)	36 (4)
N(17)	6695 (11)	4482 (9)	2802 (8)	31 (3)
C(13)	8222 (13)	5038 (11)	2321 (10)	27 (4)
C(14)	8331 (15)	5820 (12)	1436 (10)	34 (4)
C(15)	9836 (16)	6351 (14)	985 (11)	43 (5)
C(16)	11217 (16)	6019 (15)	1385 (12)	51 (5)
N(11)	11064 (13)	5276 (14)	2263 (11)	57 (5)
C(12)	9683 (15)	4780 (13)	2742 (11)	40 (5)

*Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a stereoview of the unit-cell contents have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51247 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

pyridinium)CuBr₃ (Place, 1986) where Cu–Br_{eq} = 2.449 Å, Br_{eq}–Cu–Br_{eq} = 163.0°, and Cu–Br_{ax} = 2.616 Å.

Because of the disorder observed for the Cu^I ion, the description of its geometry is slightly more complicated. Both sides *A* and *B* are illustrated in Fig. 1. For site *A* (78% occupancy), the Cu^I ion has a trigonal coordination with Cu—Br distances ranging from 2.38 (2) to 2.44 (4) Å. A fourth Br⁻ ion is located at a distance of 2.96 (4) Å. For site *B*, the Cu^I atom is displaced 0.42 Å towards this Br⁻ ion, yielding a tetrahedral coordination at that site [Cu—Br distances range from 2.43 (3) to 2.60 (3) Å]. The bond distances in the trigonal site average 2.42 Å, 0.11 Å shorter than the average (2.53 Å) for the tetrahedral site. Again, the Br⁻ ions involved in bridging have considerably longer bond differences than the non-bridging Br⁻ ion, Br(1). The differences are 0.06 Å for the trigonal site and 0.13 Å for the tetrahedral site.

A single Cu—Br—Cu bridge links the Cu^{II} and Cu^I sites, with a bridging angle of 97.1 (8) (site *A*) or 98.3° (site *B*). The two Cu^I sites are bridged by two Br⁻ ions, Br(3) and its symmetry-related ion. If both trigonal sites are occupied in the tetranuclear species, then the bridges are asymmetrical [Cu—Br distances of 2.44 and 2.96 Å with a bridging angle of 86 (2)°]. If both *B* sites are occupied, then the distances are 2.60 and 2.56 Å with an angle of 80 (1)°. When one trigonal and one tetrahedral site are occupied (Fig. 1), one symmetric [Cu—Br = 2.44 and 2.56 Å, Cu—Br—Cu = 89 (1)°] and one asymmetric [Cu—Br = 2.66 and 2.96 Å, Cu—Br—Cu = 78 (1)°] bridge are formed.

Ignoring site *B* for the moment, the tetranuclear species can be visualized as two Cu^I/Cu^{II} binuclear units which are weakly interacting through the long Cu(1)···Br(3) linkages described above. In turn, the binuclear unit can be described as a Cu^{II} ion coordinated by two amino groups, two Br⁻ ions, on one monodentate CuBr₃²⁻ anion. The coordination of Cu^{II} by a cationic species is unusual, but not unknown.

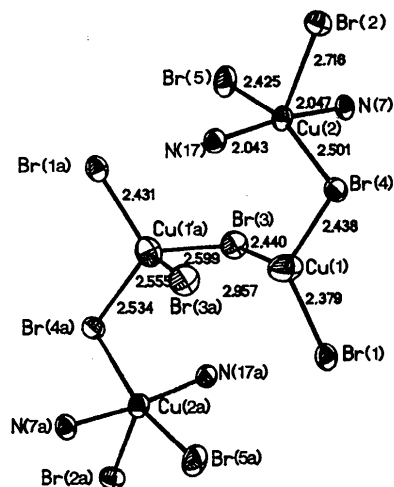


Fig. 1. Coordination core of the (3-aminopyridinium)₄Cu₄Br₁₀ tetranuclear unit. The symbol *a* denotes an atom related by a center of inversion.

Table 3. Bond lengths (Å) and angles (°) for (3-aminopyridinium)₄Cu₄Br₁₀

Br(1)—Cu(1)	2.379 (22)	N(7)—C(3)	1.399 (14)
Br(1)—Cu(1')	2.431 (32)	C(3)—C(12)	1.390 (18)
Br(2)—Cu(2)	2.716 (2)	C(3)—C(6)	1.392 (17)
Br(3)—Cu(1)	2.440 (46)	C(2)—N(1)	1.308 (16)
Br(3)—Cu(1')	2.599 (35)	N(1)—C(4)	1.355 (19)
Br(3)—Cu(1a)	2.957 (43)	C(4)—C(5)	1.367 (21)
Br(3)—Cu(1'a)	2.555 (24)	C(5)—C(6)	1.382 (18)
Cu(2)—Br(4)	2.501 (2)	N(17)—C(13)	1.416 (14)
Cu(2)—Br(5)	2.425 (2)	C(13)—C(14)	1.373 (17)
Cu(2)—N(7)	2.047 (8)	C(13)—C(12)	1.410 (18)
Cu(2)—N(17)	2.043 (8)	C(14)—C(15)	1.380 (18)
Br(4)—Cu(1)	2.438 (42)	C(15)—C(16)	1.375 (21)
Br(4)—Cu(1')	2.534 (31)	C(16)—N(11)	1.341 (21)
Cu(1)—Cu(1')	0.418 (47)	N(11)—C(12)	1.307 (17)
Cu(1)—Br(1)—Cu(1')	9.9 (11)	Br(4)—Cu(1)—Br(3a)	103.2 (13)
Cu(1)—Br(3)—Cu(1')	8.8 (11)	Cu(1')—Cu(1)—Br(3a)	14.7 (68)
Cu(1)—Br(3)—Cu(1a)	86.5 (16)	Br(1)—Cu(1')—Br(3)	112.9 (13)
Cu(1')—Br(3)—Cu(1a)	77.7 (10)	Br(1)—Cu(1')—Br(4)	111.1 (12)
Cu(1)—Br(3)—Cu(1'a)	88.8 (13)	Br(3)—Cu(1')—Br(4)	105.9 (10)
Cu(1')—Br(3)—Cu(1'a)	80.0 (11)	Br(1)—Cu(1')—Cu(1)	77.9 (52)
Cu(1a)—Br(3)—Cu(1'a)	2.4 (11)	Br(3)—Cu(1')—Cu(1)	63.2 (79)
Br(2)—Cu(2)—Br(4)	98.0 (1)	Br(4)—Cu(1')—Cu(1)	72.0 (70)
Br(2)—Cu(2)—Br(5)	101.8 (1)	Br(1)—Cu(1')—Br(3a)	113.4 (11)
Br(4)—Cu(2)—Br(5)	160.2 (1)	Br(3)—Cu(1')—Br(3a)	100.0 (11)
Br(2)—Cu(2)—N(7)	86.7 (3)	Br(4)—Cu(1')—Br(3a)	112.8 (12)
Br(4)—Cu(2)—N(7)	89.9 (3)	Cu(2a)—Cu(1')—Br(3a)	163.0 (78)
Br(5)—Cu(2)—N(7)	90.9 (3)	Cu(2)—N(7)—C(3)	117.8 (7)
Br(2)—Cu(2)—N(17)	101.0 (3)	N(7)—C(3)—C(2)	120.9 (11)
Br(4)—Cu(2)—N(17)	86.8 (3)	N(7)—C(3)—C(6)	121.4 (11)
Br(5)—Cu(2)—N(17)	89.7 (3)	C(2)—C(3)—C(6)	117.4 (11)
N(7)—Cu(2)—N(17)	171.9 (4)	C(3)—C(2)—N(1)	120.6 (12)
Cu(2)—Br(4)—Cu(1)	97.1 (8)	C(2)—N(1)—C(4)	123.4 (12)
Cu(2)—Br(4)—Cu(1')	98.3 (8)	N(1)—C(4)—C(5)	118.4 (12)
Cu(1)—Br(4)—Cu(1')	9.4 (11)	C(4)—C(5)—C(6)	119.9 (13)
Br(1)—Cu(1)—Br(3)	120.9 (17)	C(3)—C(6)—C(5)	120.0 (12)
Br(1)—Cu(1)—Br(4)	116.5 (21)	Cu(2)—N(17)—C(13)	117.4 (7)
Br(3)—Cu(1)—Br(4)	114.3 (7)	N(17)—C(13)—C(14)	121.9 (11)
Br(1)—Cu(1)—Cu(1')	92.2 (51)	N(17)—C(13)—C(12)	119.9 (11)
Br(3)—Cu(1)—Cu(1')	108.0 (85)	C(14)—C(13)—C(12)	118.1 (11)
Br(4)—Cu(1)—Cu(1')	98.7 (73)	C(13)—C(14)—C(15)	120.7 (12)
Br(1)—Cu(1)—Br(3a)	102.2 (9)	C(14)—C(15)—C(16)	119.4 (13)
Br(3)—Cu(1)—Br(3a)	93.5 (16)	C(15)—C(16)—N(11)	117.9 (12)
		C(16)—N(11)—C(12)	125.2 (13)
		C(13)—C(12)—N(11)	118.5 (13)

The symbol *a* denotes an atom related by a center of inversion.

Indeed, similar coordination occurs in (3-aminopyridinium)₂Cu₂Cl₆ and (3-aminopyridinium)₂Cu₂Br₆·H₂O (Blanchette & Willett, 1988).

The compound can be described as a Robin & Day (1967) type 2a mixed-valence compound. The Cu^{II} and Cu^I centers are clearly interacting [via the Br(5) bridge] in contrast to the (Bu₄N)₃Cu₃Cl₈ salt where well isolated Cu^I and Cu^{II} species exist. However, the coordination polyhedra are so different that the barrier to electron transfer will be sufficiently high to make the spectroscopic observation of an intervalence band very unlikely. The (Cu₂Cl₄)_n chain in (Et₄N)Cu₂Cl₄ (Willett, 1987) contains Cu^I and Cu^{II} sites, both of which have distorted tetrahedral sites, and the barrier is sufficiently low that the mixed-valence compound assumes an intense blue color, rather than the normal orange color of the tetrahedral CuCl₄²⁻ anion. Thus this 3-aminopyridinium system represents an intermediate between these two extremes.

The crystal structure gives direct evidence for the existence of the Cu^{I} species in the substituted pyridine/ CuBr_2/HBr system. Unfortunately, the isolated mixed-valence species did not contain a brominated pyridine-ring system. Hence, it is not possible to tie the existence of the Cu^{I} ion to the bromination process. Indeed, the Cu^{I} ion may be simply generated by an inorganic reaction involving the decomposition of CuBr_2 to CuBr and Br_2 . Nevertheless, the crystallization of organoammonium halocuprate(II) salts under anaerobic conditions appears to be a general method leading to the formation of mixed-valence copper halide systems.

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Structures of Ethylenediammonium Tetrabromocuprate(II) and Propylenediammonium Tetrabromocuprate(II)

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Abstract. $[\text{C}_2\text{H}_{10}\text{N}_2][\text{CuBr}_4]$, $M_r = 445.3$, monoclinic, $P2_1/a$, $a = 7.511$ (1), $b = 7.803$ (1), $c = 8.334$ (2) Å, $\beta = 92.12$ (2)°, $V = 488.1$ (1) Å³, $Z = 2$, $D_x = 3.02$ g cm⁻³, $F(000) = 410$, $\mu = 184.0$ cm⁻¹, numerical absorption correction, $T = 293$ K, 1417 unique reflections with $I > 3\sigma(I)$ refined to $R = 0.0504$ ($wR = 0.0392$). $[\text{C}_3\text{H}_{12}\text{N}_2][\text{CuBr}_4]$, $M_r = 459.3$, monoclinic, $P2_1/n$, $a = 8.086$ (2), $b = 7.566$ (2), $c = 17.622$ (5) Å, $\beta = 96.75$ (2)°, $V = 1071$ (1) Å³, $Z = 4$, $D_x = 2.85$ g cm⁻³, $F(000) = 852$, $\mu = 167.6$ cm⁻¹, empirical absorption correction assuming laminar crystal shape, $T = 293$ K, 864 unique reflections with $I > 3\sigma(I)$ refined to $R = 0.0359$ ($wR = 0.0473$). Both structures consist of antiferrodistortive perovskite layers with corner-shared Jahn–Teller elongated CuBr_6 octahedra with adjacent layers linked by the diammonium cations. The short Cu–Br distances average 2.440 Å while the longer semi-coordinate distances are 3.034 and 3.148 Å respectively for the two salts. The ethylenediammonium cation is in an all-*trans* conformation while the propylene analog has one *trans* and one *gauche* segment for a *tg* conformation. The layers are in a partially eclipsed conformation, leading to short interlayer Br...Br contacts of

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3.602 and 4.065 Å respectively. Correlations between the structural parameters and magnetic behavior are discussed.

Introduction. Compounds of the type $A_2\text{CuX}_4$, where A^+ = alkali metal ion or a monosubstituted ammonium ion and $X = \text{Cl}^-$ or Br^- , typically form antiferrodistortive versions of the two-dimensional layer perovskite family (Steadman & Willett, 1970; Barendregt & Schenk, 1970; Larsen, 1974; Willett, 1964). In these compounds, adjacent layers are staggered with respect to each other, e.g. Cu ions in one layer are aligned above (or below) the A^+ cations on adjacent layers. In this manner, essentially no superexchange coupling can occur between layers, and dipolar interactions essentially cancel, leading to the formation of nearly ideal two-dimensional magnetic systems (de Jongh & Miedema, 1974). With the replacement of two A^+ cations by a diammonium cation, $^+\text{H}_3\text{NC}_n\text{H}_{2n}\text{NH}_3^+$, adjacent layers are now eclipsed in the sense that the copper ions in adjacent layers lie nearly directly above each other (Phelps, Losee, Hatfield & Hodgson, 1976; Ferguson & Zaslow, 1971; Tichy, Benes, Hälgl & Arend, 1978). This allows for magnetic interactions to