

Structure of Catalytically Related Species Involving Copper(II) Halides. V. $C_5H_6BrN_2O^+.Br^-$ and $2C_5H_6BrN_2O^+.Cu_2Br_6^{2-}.2H_2O$

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Abstract. $C_5H_6BrN_2O^+.Br^-$, $M_r=270.0$, triclinic, $P\bar{1}$, $a=6.301(2)$, $b=7.037(2)$, $c=8.881(2)$ Å, $\alpha=81.47(2)$, $\beta=86.21(2)$, $\gamma=86.16(2)^\circ$, $V=387.9(2)$ Å³. $Z=2$, $D_x=2.31$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda=0.71069$ Å, $\mu=102.8$ cm⁻¹, $F(000)=256$, $T=293$ K, 1385 unique reflections, of which 1164 had $F \geq 3\sigma(F)$, refined to a final value of $R=0.0346$ for the 3σ data set ($wR=0.0440$). The 2-amino-4-bromohydroxypyridinium bromide structure consists of the trisubstituted pyridinium cation and the halide anion. Hydrogen bonding of the hydroxyl, pyridinium, and one amino proton to the bromide ion stabilize the lattice. The bromo substitution of the 4-position of the pyridinium ring occurred during preparation of the copper(II) salt described below [$C-Br=1.877(6)$ Å]. $2C_5H_6BrN_2O^+.Cu_2Br_6^{2-}.2H_2O$, $M_r=1022.66$, triclinic, $P\bar{1}$, $a=4.100(1)$, $b=11.362(2)$, $c=13.221(3)$ Å, $\alpha=75.49$, $\beta=86.43$, $\gamma=82.71(2)^\circ$, $V=591.2(2)$ Å³, $Z=1$, $D_x=2.87$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda=0.71069$ Å, $\mu=152.30$ cm⁻¹, $F(000)=474$, $T=293$ K, 1545 unique reflections, of which 1337 had $F \geq 3\sigma(F)$, refined to a final value of $R=0.0433$ for the 3σ data set ($wR=0.0543$). The structure of this compound, bis(2-amino-4-bromo-3-hydroxypyridinium)hexabromodicuprate(II) dihydrate, consists of the trisubstituted pyridinium cations, planar bi-bridged $Cu_2Br_6^{2-}$ dimers, and water molecules. $Cu-Br$ bond distances within the centrosymmetric dimer average 2.398(8) (terminal) and 2.458(8) Å (bridging), and the $Cu-Br-Cu$ bridging angle is 97.1(1)°. The dimers aggregate through the formation of semi-coordinate $Cu-Br$ bonds to form stacks parallel to the a axis. The pyridinium cations were brominated in the 4-position during the preparation of the compound [$C-Br=1.898(9)$ Å]. These cations also stack parallel to the a axis.

Introduction. The synthesis of $ACuX_3$ salts, where A is a substituted pyridinium cation and $X=Cl^-$ or Br^- , has produced a wide range of magnetically interesting materials. These have included pseudo-planar bi-bridged $Cu_3X_8^{2-}$ trimers (Grigereit, Ramakrishna, Place, Willett, Pellacani, Manfredini, Menabue, Bonamartini-Corradi & Battaglia, 1987) and $Cu_4Cl_{10}^{2-}$ tetramers (Halvorson, Grigereit & Willett, 1987) as well as

infinite bi-bridged chains of basal shared square-pyramidal CuX_3^{2-} species (Geiser, Gaura, Willett & West, 1986; Place, 1986). During the course of the structural investigations of these materials, it was observed that halogenation of the pyridine rings frequently occurred, especially when $X=Br^-$ (Grigereit *et al.*, 1987; Place & Willett, 1987; Place, 1986; Willett & West, 1987). This presumably occurs catalytically *via* a copper(I) species with subsequent reoxidation of the metal by molecular oxygen. In this paper, we present the structural results on an additional compound in this series in which a dimeric $Cu_2Br_6^{2-}$ anion is found and for which bromination of the pyridine ring is again observed. The structure of the simple brominated pyridinium salt is also reported.

Experimental. The compounds were prepared by the reaction of stoichiometric amounts of 2-amino-3-hydroxypyridine and $CuBr_2$ in an excess of dilute aqueous HBr solution. The solution was heated to remove excess solvent. In addition to the nearly opaque pleochroic brownish-violet crystals of the copper(II) bromide salt which separated out upon slow evaporation of the remaining solution, a few colorless crystals also appeared which proved to be $C_5H_6Br_2N_2O$.

A well formed parallelepiped ($0.34 \times 0.34 \times 0.15$ mm) was selected from among the colorless $C_5H_6Br_2N_2O$ crystals present in the sample. Triclinic lattice constants from 25 high-angle reflections ($36 \leq 2\theta \leq 43^\circ$) accurately centered on a Syntex $P2_1$ diffractometer, upgraded to Nicolet $P3F$ specifications, with Mo $K\alpha$ radiation and a graphite monochromator (Campana, Shepherd & Litchman, 1980). 1483 reflections measured, $2\theta \leq 50^\circ$, $-7 \leq h \leq 7$, $-8 \leq k \leq 8$, $0 \leq l \leq 10$. Agreement between equivalent reflections, $R_{int}=0.023$. Numerical absorption corrections (min. transmission = 0.041, max. transmission = 0.266). 2 standards measured every 94 reflections; variations within counting statistics. Scan speed for the ω -scan data collection ranged from 3.91 to 29.3° min⁻¹; scan width = 1.0°; 1483 unique reflections, 1164 with $F \geq 3\sigma(F)$. The structure was solved from the Patterson function, which yielded the two Br-atom positions. The C, N and O atoms were found on the first difference Fourier map based on phases calculated from

the Br-atom positions. H atoms were located on subsequent difference maps. Refinement on F for non-H-atom positions and anisotropic thermal parameters proceeded smoothly. Ring H atoms were constrained to $C-H$ and $N-H = 0.96 \text{ \AA}$, but positional parameters for the amino and hydroxyl H atoms were allowed to vary independently. Isotropic thermal parameters were fixed at approximately 1.2 times the equivalent isotropic thermal parameters of the corresponding heavier atom. $R = 0.0346$, $wR = 0.0440$ for observed data (0.0436 and 0.0452 respectively for all data). $w = [\sigma^2(F) + g|F|^2]^{-1}$, $g = 0.00048$. Goodness of fit = 1.421. Mean $|\Delta/\sigma| = 0.021$, max. $|\Delta/\sigma| = 0.088$. 100 parameters. No extinction corrections. Max. residual on final difference map, $0.5 e \text{ \AA}^{-3}$ near Br(1), min. residual $-0.9 e \text{ \AA}^{-3}$. All calculations performed on a Data General Eclipse S140 computer (SHELXTL; Sheldrick, 1984, 1986). Atomic scattering factors of SHELXTL used. Non-H-atom positional parameters given in Table 1 with bond distances and angles in Table 2 and Fig. 1.

A small platelet (approximately $0.20 \times 0.25 \times 0.10 \text{ mm}$) was selected from the opaque $C_{10}H_{16}Br_8Cu_2N_4O_4$ crystals for crystallographic examination. Triclinic lattice constants from 25 high-angle reflections ($35 \leq 2\theta \leq 43^\circ$) accurately centered on a Syntex $P2_1$ diffractometer, upgraded to Nicolet $P3F$ specifications. 1809 reflections measured, $2\theta \leq 45^\circ$, $0 \leq h \leq 4$, $-12 \leq k \leq 12$, $-14 \leq l \leq 14$. 1545 unique reflections, 1337 with $F \leq 3\sigma(F)$. $R_{int} = 0.0164$. 2 standards monitored every 96 reflections ($11\bar{2}$ and $1\bar{1}4$) varied $\pm 2\%$ during data collection. ω scan, 0.85° scan width. Scan speed varied from 3.91 to $29.30^\circ \text{ min}^{-1}$. Empirical ψ -scan absorption corrections assuming ellipsoidally shaped crystal. Max. transmission = 0.955, min. transmission = 0.247.

The Patterson function revealed five major peaks which could be interpreted in terms of a planar $Cu_2Br_6^{2-}$ dimer. Their distances from the origin were, in order of decreasing peak height with vector assignment in parentheses: 3.49 ($Cu-Cu$, $Br-Br \times 4$), 2.41 ($Cu-Br \times 4$), 2.40 ($Cu-Br \times 4$), 3.41 ($Br-Br \times 3$) and 4.81 \AA ($Br-Br \times 2$). A difference synthesis based on this information yielded another major peak, remote from the $Cu_2Br_6^{2-}$ anion, which was assumed to be another Br atom. Another cycle of parameter refinement on F and difference synthesis yielded all remaining non-H atoms, including the water O atom. $R = 0.043$, $wR = 0.054$ for observed data. $g = 0.00088$. Goodness of fit = 1.343. Mean $|\Delta/\sigma| = 0.11$. Max. $|\Delta/\sigma| = 0.158$. 138 parameters. Ring H atoms constrained to calculated positions ($C-H$, $N-H = 0.96 \text{ \AA}$). Hydroxyl H atom constrained loosely to $O-H = 0.96 \text{ \AA}$. Water $O-H$ distances constrained to be equal, with $H-O-H = 109.5^\circ$. H-atom thermal parameters fixed approximately 20% larger than the corresponding heavy atom (U for water H atoms fixed

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for $C_5H_6Br_2N_2O$

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

	x	y	z	U_{eq}
Br(1')	1238 (1)	1947 (1)	2945 (1)	36 (1)
Br(4)	2353 (1)	6810 (1)	52 (1)	46 (1)
N(1)	6618 (7)	8093 (7)	3709 (6)	34 (2)
C(2)	4677 (8)	7437 (8)	4182 (7)	30 (2)
C(3)	3390 (8)	6940 (8)	3058 (6)	28 (2)
C(4)	4125 (8)	7245 (8)	1569 (7)	33 (2)
C(5)	6143 (9)	7943 (9)	1141 (7)	37 (2)
C(6)	7337 (9)	8346 (9)	2244 (7)	38 (2)
N(2)	4029 (8)	7249 (8)	5633 (6)	41 (2)
O(3)	1478 (6)	6294 (6)	3610 (5)	37 (1)

Table 2. Bond lengths (\AA), bond angles ($^\circ$) and hydrogen-bonding distances (\AA) for $C_5H_6Br_2N_2O$

Br(4)-C(4)	1.877 (6)	C(3)-O(3)	1.352 (6)
N(1)-C(2)	1.355 (7)	C(4)-C(5)	1.403 (8)
N(1)-C(6)	1.339 (8)	C(5)-C(6)	1.347 (9)
C(2)-C(3)	1.423 (8)	N(2)-H(2B)	0.95 (5)
C(2)-N(2)	1.316 (8)	N(2)-H(2A)	0.94 (5)
C(3)-C(4)	1.363 (8)	O(3)-H(3)	0.95 (4)
C(2)-N(1)-C(6)	123.2 (5)	Br(4)-C(4)-C(5)	119.3 (4)
N(1)-C(2)-C(3)	117.6 (5)	C(3)-C(4)-C(5)	121.5 (6)
N(1)-C(2)-N(2)	120.8 (5)	C(4)-C(5)-C(6)	118.1 (5)
C(3)-C(2)-N(2)	121.6 (5)	N(1)-C(6)-C(5)	121.0 (5)
C(2)-C(3)-C(4)	118.4 (5)	C(2)-N(2)-H(2B)	116 (4)
C(2)-C(3)-O(3)	114.4 (5)	C(2)-N(2)-H(2A)	124 (3)
C(4)-C(3)-O(3)	127.0 (5)	H(2B)-N(2)-H(2A)	120 (5)
Br(4)-C(4)-C(3)	119.2 (4)	C(3)-O(3)-H(3)	111 (4)
O(3)...Br(1')	3.215 (5)	H(3)...Br(1')	2.28 (5)
N(1)...Br(1')	3.340 (6)	H(1)...Br(1')	2.45 (5)
N(2)...Br(1')	3.427 (6)	H(2A)...Br(1')	2.67 (5)
N(2)...Br(1')	3.512 (6)	H(2B)...Br(1')	2.83 (5)

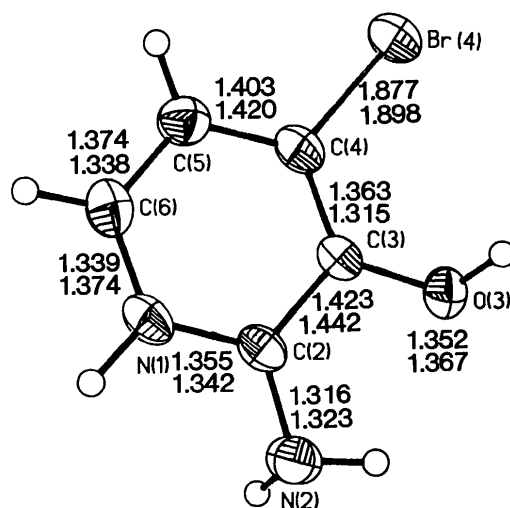


Fig. 1. Illustration of the $C_5H_6NOBr^+$ cation in $C_{10}H_{16}Br_8Cu_2N_4O_4$. The upper set of distances is for $C_5H_6Br_2N_2O$ and the lower set for $C_{10}H_{16}Br_8Cu_2N_4O_4$. The thermal ellipsoids, in this and subsequent illustrations, are drawn at the 50% probability level.

at 0.06 Å²). Largest residuals on final difference map 0.9 e Å⁻³ near Br(1), -0.9 e Å⁻³. Non-H-atom positional parameters are given in Table 3 with bond distances and angles in Table 4 and Figs. 1 and 2.*

Discussion. The pyridinium cations in the two structures, Fig. 1, are essentially identical, with all differences less than 3σ. Catalytically, the significance in

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44500 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Atomic coordinates (×10⁴) and equivalent isotropic thermal parameters (Å² × 10³) for C₁₀H₁₆Br₈-Cu₂N₄O₄

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</i> _{eq}
Cu	2176 (3)	-1505 (1)	620 (1)	30 (1)
Br(1)	5687 (3)	-2173 (1)	2080 (1)	41 (1)
Br(2)	-1402 (3)	-597 (1)	-861 (1)	28 (1)
Br(3)	3145 (3)	-3410 (1)	107 (1)	31 (1)
Br(4)	1999 (3)	-3313 (1)	4569 (1)	42 (1)
N(1)	-1748 (21)	-3724 (8)	7968 (6)	39 (3)
C(2)	-2938 (24)	-2714 (9)	7264 (7)	27 (3)
N(2)	-5179 (23)	-1880 (8)	7516 (6)	40 (3)
C(3)	-1700 (25)	-2581 (9)	6201 (7)	29 (4)
O(3)	-2989 (18)	-1498 (6)	5567 (5)	39 (3)
C(4)	399 (25)	-3456 (8)	5968 (7)	26 (3)
C(5)	1609 (27)	-4513 (9)	6735 (7)	38 (4)
C(6)	537 (26)	-4616 (9)	7727 (8)	36 (4)
<i>W</i>	-1314 (30)	-445 (8)	3544 (8)	76 (4)

Table 4. Bond lengths (Å), bond angles (°) and hydrogen-bonding distances (Å) for C₁₀H₁₆Br₈-Cu₂N₄O₄

Cu—Br(1)	2.390 (2)	Cu—Br(2a)	2.451 (1)
Cu—Br(3)	2.405 (2)	Cu—Br(2a)	2.466 (2)
Br(2)—Cu _a	2.466 (2)	Br(4)—C(4)	1.898 (9)
N(1)—C(2)	1.342 (11)	N(1)—C(6)	1.374 (14)
C(2)—N(2)	1.323 (13)	C(2)—C(3)	1.422 (13)
C(3)—O(3)	1.367 (10)	C(3)—C(4)	1.315 (14)
O(3)—H(3)	0.960 (63)	C(4)—C(5)	1.420 (12)
C(5)—C(6)	1.338 (14)		
Br(1)—Cu—Br(2)	173.9 (1)	Br(1)—Cu—Br(3)	94.6 (1)
Br(2)—Cu—Br(3)	91.3 (1)	Br(1)—Cu—Br(2a)	91.0 (1)
Br(2)—Cu—Br(2a)	82.9 (1)	Br(3)—Cu—Br(2a)	171.1 (1)
Cu—Br(2)—Cu _a	97.1 (1)	C(2)—N(1)—C(6)	123.8 (8)
N(1)—C(2)—N(2)	122.4 (8)	N(1)—C(2)—C(3)	116.8 (9)
N(2)—C(2)—C(3)	120.8 (8)	C(2)—C(3)—O(3)	111.4 (8)
C(2)—C(3)—C(4)	119.3 (8)	O(3)—C(3)—C(4)	129.3 (8)
C(3)—O(3)—H(3)	104.8 (57)	Br(4)—C(4)—C(3)	119.9 (6)
Br(4)—C(4)—C(5)	117.7 (7)	C(3)—C(4)—C(5)	122.3 (88)
C(4)—C(5)—C(6)	118.3 (9)	N(1)—C(6)—C(5)	119.5 (8)
<i>W</i> ...Br(1)	3.453	H(<i>WA</i>)...Br(1)	2.54 (1)
<i>W</i> ...N(2)	2.906	H(<i>WB</i>)...N(2)	1.99 (1)
O(3)... <i>W</i>	2.727	H(3)... <i>W</i>	1.90 (1)
N(1)...Br(3)	3.477	H(1)...Br(3)	2.60 (1)
N(2)...Br(2)	3.419	H(2A)...Br(2)	2.53 (1)
N(2)...Br(2)	3.631	H(2B)...Br(2)	3.27 (1)
N(2)...Br(3)	3.501	H(2B)...Br(3)	3.22 (1)

both structures is the bromination of the pyridine ring in the 4-position. The exogenous C—N and C—O bonds show considerable shortening over normal single-bond lengths, at 1.32 (1) and 1.36 (1) Å, respectively. This causes a lengthening of the C(2)—C(3) bond [1.43 (1) Å] and, surprisingly, of the C(4)—C(5) bond [1.41 (1) Å]. The interior angles at N(1) and C(2) are substantially larger and smaller (respectively) than 120° while the O—C(3)—C(4) angles at 128° (average) reflect the steric crowding of the larger Br atom.

The copper(II) structure consists of planar Cu₂Br₆²⁻ ions, substituted pyridinium cations and water molecules, held together by hydrogen-bonding interactions. Within the dimer, Fig. 2, the copper(II) ion has a nearly square-planar coordination geometry, with bridging distances [2.458 (8) Å] elongated with respect to the terminal distances [2.398 (8) Å] as anticipated. The terminal Br(1)—Cu—Br(3) angle is substantially greater

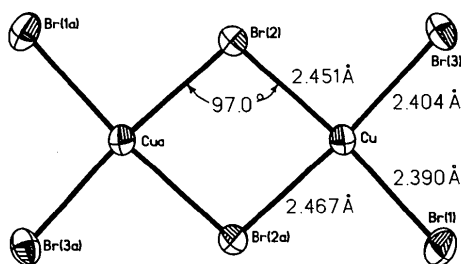


Fig. 2. Illustration of the Cu₂Br₆²⁻ dimer in C₁₀H₁₆Br₈Cu₂N₄O₄. The symbol *a* denotes an atom related by a center of inversion.

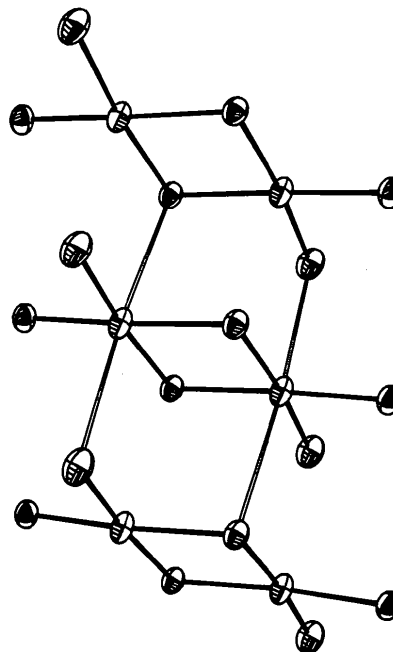


Fig. 3. Illustration of the stacking of Cu₂Br₆²⁻ ions in C₁₀H₁₆Br₈Cu₂N₄O₄.

than 90° [$94.6(1)^\circ$] while the interior Br(2)—Cu—Br(2a) angle is much smaller than 90° [$82.9(1)^\circ$]. The *trans* Br—Cu—Br angles are $173.9(9)$ and $171.1(1)^\circ$.

The anions and cations form stacks parallel to the short crystallographic (*a*) axis; the anions are shown in Fig. 3. The dimer stacks are characterized by the formation of semicoordinate Cu—Br bonds of $3.243(2)$ and $3.296(2)$ Å and are analogous to those in KCuCl_3 and NH_4CuCl_3 (Willett, Rundle, Dwiggens & Kruh, 1963), and is denoted a $2(\frac{1}{2}, \frac{1}{2})$ stack in the notation recently introduced for the stacking of $\text{Cu}_n\text{X}_{2n+2}^{2-}$ oligomers (Geiser, Willett, Lindbeck & Emerson, 1986).

Extensive hydrogen bonding gives rigidity to the lattices (Tables 2 and 4). In the copper(II) salt, the water molecule, *W*, forms donor hydrogen bonds to Br(1) and the amino N(2) atom of the pyridinium ion. It also accepts a hydrogen bond from the hydroxyl group. The pyridinium N(1) atom hydrogen bonds to Br(3), and the amino N(2) atom forms a normal hydrogen bond to Br(2) and a bifurcated hydrogen bond to Br(2) and Br(3). In the simple bromide salt, the hydroxyl proton forms a relatively short hydrogen bond to the lattice Br(1') ion while the pyridinium and amino

protons form longer bonds. Proton H(2B) actually appears to form a bifurcated hydrogen bond involving the Br(1') ion and lone pair on the adjacent O atom in the same cation.

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Structures of Four Complexes of Copper with *N*-Methylimidazole and Chloro Ligands

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Abstract. (1): Tetrakis(*N*-methylimidazole-*N'*)-copper(II) trichlorocuprate(I) hydrate, $[\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_4][\text{CuCl}_3] \cdot \text{H}_2\text{O}$, $M_r = 579.9$, triclinic, *P*1, $a = 8.244(1)$, $b = 9.440(1)$, $c = 15.992(2)$ Å, $\alpha = 96.00(1)$, $\beta = 99.04(1)$, $\gamma = 100.92(1)^\circ$, $V = 1195.2$ Å³, $Z = 2$, $D_x = 1.611$ Mg m⁻³, $F(000) = 590$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.15$ mm⁻¹, $T = 291$ K, $R = 0.044$ for 3607 reflections with $F > 4\sigma(F)$. (2): Hexachlorotetrakis(*N*-methylimidazole-*N'*)oxotetra-copper(II), $[\text{Cu}_4\text{OCl}_6(\text{C}_4\text{H}_6\text{N}_2)_4]$, $M_r = 811.3$ (ignoring acetonitrile solvent), orthorhombic, *Pbca*, $a = 18.946(1)$, $b = 19.043(1)$, $c = 33.256(2)$ Å, $V = 11998$ Å³, $Z = 16$, $D_x = 1.796$ Mg m⁻³, $F(000) = 6432$, $\mu(\text{Mo } K\alpha) = 3.37$ mm⁻¹, $T = 291$ K, $R = 0.068$ for 4794 reflections. (3): Hexachlorotetrakis(*N*-methyl-

imidazole-*N'*)oxotetracopper(II) chlorotetrakis(*N*-methylimidazole-*N'*)copper(II) chloride, $[\text{Cu}_4\text{OCl}_6(\text{C}_4\text{H}_6\text{N}_2)_4][\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_4\text{Cl}]\text{Cl}$, $M_r = 1274.2$, orthorhombic, *Pca*2₁, $a = 14.637(1)$, $b = 13.233(1)$, $c = 26.490(2)$ Å, $V = 5130.9$ Å³, $Z = 4$, $D_x = 1.649$ Mg m⁻³, $F(000) = 2564$, $\mu(\text{Mo } K\alpha) = 2.51$ mm⁻¹, $T = 291$ K, $R = 0.052$ for 6999 reflections. (4): Diaquatetrakis(*N*-methylimidazole-*N'*)copper(II) chloride hydrate, $[\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)_4(\text{H}_2\text{O})_2] \cdot \text{Cl}_2 \cdot \text{H}_2\text{O}$, $M_r = 516.9$, triclinic, *P*1, $a = 9.198(1)$, $b = 9.338(1)$, $c = 15.520(2)$ Å, $\alpha = 99.41(1)$, $\beta = 105.59(1)$, $\gamma = 103.36(1)^\circ$, $V = 1212.5$ Å³, $Z = 2$, $D_x = 1.416$ Mg m⁻³, $F(000) = 538$, $\mu(\text{Mo } K\alpha) = 1.16$ mm⁻¹, $T = 291$ K, $R = 0.036$ for 2959 reflections. The square-planar coordinated $[\text{Cu}(\text{Meim})_4]^{2+}$