Data collection

AFC-6*R* diffractometer
$\omega/2\theta$ scans
  [speed 32° $\min^{-1}$, width (0.84 + 0.35tanθ)°]
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
  $T_{\min}$ = 0.98, $T_{\max}$ = 1.02
2984 measured reflections
2984 independent reflections
1250 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max}$ = 27.5°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 33$
$l = 0 \rightarrow 9$
3 standard reflections monitored every 400 reflections intensity variation: −3.57%

Refinement

Refinement on F
R = 0.043
wR = 0.047
S = 1.86
1250 reflections
119 parameters
H-atom positions calculated, U(H) based on $U_{\rm eq}$ of C atom to which H is bonded
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max}$ = 0.041
$\Delta\rho_{\max}$ = 1.04 e Å^{-3}
$\Delta\rho_{\min}$ = −1.42 e Å^{-3}
Extinction correction: Zachariasen (1967), type II, Gaussian, isotropic
Extinction coefficient: 0.44425
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Hg	0.48087 (5)	0.03983 (2)	0.25613 (9)	0.0370
S(1)	0.4764 (3)	−0.0462 (1)	0.2230 (6)	0.0379
S(2)	0.2686 (4)	−0.0188 (1)	0.4617 (5)	0.0397
O(1)	0.3234 (9)	−0.1053 (3)	0.325 (1)	0.0337
C(1)	0.345 (1)	−0.0575 (4)	0.342 (2)	0.0219
C(2)	0.228 (1)	−0.1270 (5)	0.430 (2)	0.0447
C(3)	0.233 (2)	−0.1805 (5)	0.397 (2)	0.0562
C(11)	0.493 (1)	0.1155 (5)	0.270 (2)	0.0343
C(12)	0.574 (2)	0.1396 (5)	0.150 (2)	0.0385
C(13)	0.581 (2)	0.1893 (6)	0.154 (2)	0.0512
C(14)	0.512 (2)	0.2153 (5)	0.278 (2)	0.0584
C(15)	0.436 (2)	0.1923 (5)	0.394 (2)	0.0523
C(16)	0.428 (2)	0.1424 (5)	0.391 (2)	0.0386

Table 2. *Selected geometric parameters* (Å, °)

Hg—S(1)	2.342 (3)	C(11)—C(12)	1.41 (2)
Hg—C(11)	2.06 (1)	C(11)—C(16)	1.34 (2)
S(1)—C(1)	1.73 (1)	C(12)—C(13)	1.35 (2)
S(2)—C(1)	1.60 (1)	C(13)—C(14)	1.37 (2)
O(1)—C(1)	1.32 (1)	C(14)—C(15)	1.34 (2)
O(1)—C(2)	1.43 (2)	C(15)—C(16)	1.35 (2)
C(2)—C(3)	1.47 (2)		
S(1)—Hg—C(11)	176.1 (4)	Hg—C(11)—C(16)	122 (1)
Hg—S(1)—C(1)	98.4 (4)	C(12)—C(11)—C(16)	119 (1)
C(1)—O(1)—C(2)	119 (1)	C(11)—C(12)—C(13)	119 (1)
S(1)—C(1)—S(2)	126.8 (8)	C(12)—C(13)—C(14)	119 (1)
S(1)—C(1)—O(1)	106.3 (9)	C(13)—C(14)—C(15)	121 (1)
S(2)—C(1)—O(1)	126 (1)	C(14)—C(15)—C(16)	119 (1)
O(1)—C(2)—C(3)	106 (1)	C(11)—C(16)—C(15)	121 (1)
Hg—C(11)—C(12)	118 (1)		

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Software used to prepare material for publication: *TEXSAN FINISH*.

The Australian Research Council is thanked for the support of the crystallographic facility.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1099). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(4-aminopyridinium) Hexabromodicuprate(II) Diaquatetrabromodicopper(II)

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Abstract

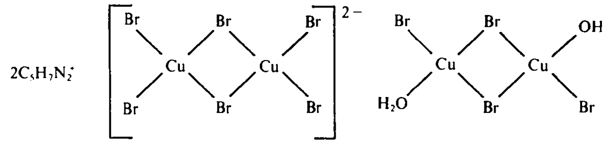
The structure of $(C_5H_7N_2)_2[Cu_2Br_6].[Cu_2Br_4(H_2O)_2]$ consists of stacks of alternating $Cu_2Br_6^{2-}$ anions and neutral $Cu_2Br_4(H_2O)_2$ molecules with the cations separating the stacks. The two chemically distinct species within the stack are both centrosymmetric quasi-planar bibridged dimers. The water molecules in the neutral dimers are located in *trans* positions.

Cu—Br distances within the two dimers are essentially identical with Cu—Br(terminal) = 2.401 (average) and Cu—Br(bridging) = 2.443 Å (average). The bridging Cu—Br—Cu angle is substantially smaller in the neutral dimer [92.3 (1) *versus* 95.6 (1)°]. The dimers are linked by longer semi-coordinate Cu···Br bonds [range 2.940 (2)–3.200 (2) Å] to form stacks (represented by an envelope diagram).

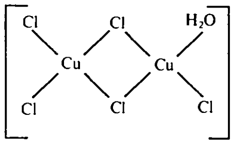
Comment

Because of interest in the magnetic behavior of mixed CuX_2/ligand systems (Grigereit, Drumheller, Scott, Pon & Willett, 1992), an attempt was made to prepare the bromide analog of 4-animopyridinium [$Cu_2Cl_5(H_2O)$] hydrate (Bond & Willett, 1987). 20 mmol of $CuBr_2$ in H_2O, 2.5 mmol of 4-aminopyridine in 50/50 ethanol/water and 60 mmol of HBr solution were heated and stirred. Upon cooling, purple needle-like crystals separated out.

This compound, (I), contains the first reported instance of a $Cu_2X_4(H_2O)_2$ species, although a trimeric $Cu_3Cl_6(H_2O)_2$ species has been reported (Swank & Willett, 1974). Several other stacked $Cu_2X_4L_2$ systems are known, including $Cu_2Cl_4(CH_3CN)_2$ (Willett & Rundle, 1964) and $Cu_2Br_4(py)_2$ (Swank & Willett, 1980). Chloride salts with the same stoichiometry as the title compound (Bond & Willett, 1987, 1989) contain a single non-centrosymmetric dimeric monoanion (II).

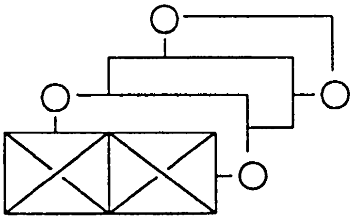


(I)



(II)

The stacking pattern of the title compound (see below) is similar to that of $KCuCl_3$ (Geiser, Willett, Lindbeck & Emerson, 1986) except for the complication of the alternation of species.



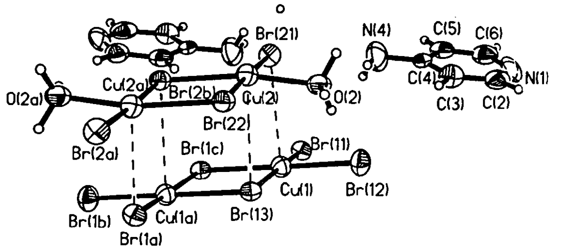


Fig. 1. Illustration of the unit-cell contents.

Experimental

Crystal data

$2(C_5H_7N_2)[Cu_2Br_6]$.-
$[Cu_2Br_4(H_2O)_2]$
M_r = 1279.4
Triclinic
$P\bar{1}$
a = 7.904 (2) Å
b = 9.460 (2) Å
c = 10.261 (2) Å
α = 101.2 (2)°
β = 92.74 (2)°
γ = 110.22 (2)°
V = 700.6 (2) Å^3

Z = 1
D_x = 3.03 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 20–30°
μ = 17.27 mm^{-1}
T = 295 K
Rod-like
0.33 × 0.18 × 0.16 mm
Purple

Data collection

Syntex $P2_1$ upgraded to Nicolet $R3$ diffractometer
ω scans
Absorption correction: empirical
T_{min} = 0.131, T_{max} = 0.821
1836 measured reflections
1517 independent reflections

1479 observed reflections [$|F| > 3\sigma(F)$]
R_{int} = 0.0286
θ_{max} = 22.5°
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 9$
$l = 0 \rightarrow 11$
2 standard reflections monitored every 96 reflections
intensity variation: none

Refinement

Refinement on F
R = 0.0604 (0.0718, all data)
wR = 0.0730 (0.0746, all data)
S = 1.43
1479 reflections
137 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0013F^2]$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = −1.6 e Å^{-3}
$\Delta\rho_{min}$ = 1.8 e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 8 (11) × 10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu(1)	0.6257 (2)	0.1164 (2)	0.3910 (2)	0.035 (1)
Cu(2)	0.1197 (2)	0.0937 (2)	0.3818 (2)	0.035 (1)
Br(11)	0.7912 (2)	0.0597 (2)	0.2122 (2)	0.036 (1)

Br(12)	0.7001 (2)	0.3827 (2)	0.3767 (2)	0.045 (1)
Br(13)	0.4696 (2)	0.1535 (2)	0.5853 (1)	0.033 (1)
Br(21)	0.2618 (2)	0.0296 (2)	0.1892 (1)	0.039 (1)
Br(22)	−0.0116 (2)	0.1683 (2)	0.5840 (1)	0.033 (1)
O(2)	0.2457 (12)	0.3153 (10)	0.3789 (9)	0.039 (4)
N(1)	0.9101 (19)	0.6804 (16)	−0.0680 (17)	0.061 (7)
C(2)	0.821 (2)	0.6818 (19)	0.0382 (18)	0.057 (8)
C(3)	0.715 (2)	0.5454 (17)	0.0682 (15)	0.046 (7)
C(4)	0.6997 (18)	0.4050 (15)	−0.0182 (14)	0.037 (6)
C(5)	0.7955 (19)	0.4134 (18)	−0.1304 (14)	0.044 (7)
C(6)	0.898 (2)	0.550 (2)	−0.1517 (16)	0.053 (8)
N(4)	0.5978 (18)	0.2642 (14)	0.0045 (15)	0.063 (7)

Table 2. *Selected geometric parameters* (Å, °)

Centrosymmetrically related atoms within the same dimer are denoted by (*a*) and atoms in an adjacent dimer are denoted by (*b*).

Cu(1)—Br(11)	2.386 (2)	Cu(1)—Br(21*b*)	3.221 (2)
Cu(1)—Br(12)	2.417 (2)	Cu(1)—Br(22*b*)	3.240 (3)
Cu(1)—Br(13)	2.426 (2)	N(1)—C(2)	1.33 (3)
Cu(1)—Br(13*a*)	2.465 (2)	N(1)—C(6)	1.33 (2)
Cu(2)—Br(21)	2.399 (2)	C(2)—C(3)	1.38 (2)
Cu(2)—Br(22)	2.454 (2)	C(3)—C(4)	1.41 (2)
Cu(2)—O(2)	1.992 (9)	C(4)—C(5)	1.41 (2)
Cu(2)—Br(22*a*)	2.428 (2)	C(4)—N(4)	1.368 (18)
Cu(2)—Br(11*b*)	2.940 (2)	C(5)—C(6)	1.33 (2)
Cu(2)—Br(13*b*)	3.200 (2)		
Br(11)—Cu(1)—Br(12)	94.0 (1)	O(2)—Cu(2)—Br(22*a*)	169.6 (3)
Br(11)—Cu(1)—Br(13)	173.1 (1)	Cu(1)—Br(13)—Cu(1*a*)	95.6 (1)
Br(12)—Cu(1)—Br(13)	91.6 (1)	Cu(2)—Br(22)—Cu(2*b*)	92.3 (1)
Br(11)—Cu(1)—Br(13*a*)	90.1 (1)	C(2)—N(1)—C(6)	122.4 (15)
Br(12)—Cu(1)—Br(13*a*)	175.6 (1)	N(1)—C(2)—C(3)	120.4 (15)
Br(13)—Cu(1)—Br(13*a*)	84.4 (1)	C(2)—C(3)—C(4)	118.6 (15)
Br(21)—Cu(2)—Br(22)	177.3 (1)	C(3)—C(4)—C(5)	117.5 (13)
Br(21)—Cu(2)—O(2)	87.6 (3)	C(3)—C(4)—N(4)	122.4 (14)
Br(22)—Cu(2)—O(2)	90.6 (3)	C(5)—C(4)—N(4)	120.1 (13)
Br(21)—Cu(2)—Br(22*a*)	93.7 (1)	C(4)—C(5)—C(6)	120.6 (15)
Br(22)—Cu(2)—Br(22*a*)	87.7 (1)	N(1)—C(6)—C(5)	120.5 (16)

The structure solution was obtained *via* the direct-methods routine *SOLV* in the *SHELXTL* crystallographic program package (Sheldrick, 1985); refinement also used *SHELXTL*. A difference synthesis based on the Cu and Br positions thus obtained yielded the C-, N- and O-atom positions. H atoms were constrained to ideal positions (C—H and N—H = 0.96 Å) and assigned isotropic displacement parameters 1.2 times larger than those of the associated atoms. Because of the rather large residual electron density in the region of the heavy atoms (up to 2.6 e Å^{-3}), the accuracy of the absorption corrections seemed questionable. The data were further corrected utilizing a ΔF refinement with the program *XABS* (Sheldrick, 1990). This resulted in a reduction of R from 0.075 to 0.060, and a reduction of the residual electron density to ±1.8 e Å^{-3}.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and structure determination details, as well as a packing diagram have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71385 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1014]

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Di-μ-chlorobis[chloro(4,7-diphenyl-1,10-phenanthroline)copper(II)]

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Abstract

The crystal structure of $[\{CuCl(C_{24}H_{16}N_2)\}_2(\mu\text{-}Cl)_2]$ contains dimers formed by pairs of $[CuCl_2(4,7\text{-diphenyl-}1,10\text{-phenanthroline-}N,N)]$ units related by an inversion centre.