

Acta Crystallographica Section C

**Crystal Structure
Communications**

ISSN 0108-2701

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Electronic paper

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Bis(2,6-diamino-3,5-dibromopyridinium) tetrabromocuprate(II)

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Received 9 August 2000

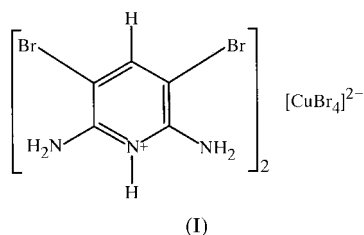
Accepted 4 September 2000

Data validation number: IUC0000243

The title compound, $(C_5H_6Br_2N_3)_2[CuBr_4]$, contains isolated substituted pyridinium cations and $[CuBr_4]^{2-}$ anions. The diaminodibromopyridinium ions are planar, while the Cu^{II} ions have a distorted compressed tetrahedral coordination with C_2 symmetry. The two independent *trans*-Br—Cu—Br angles are 128.9 (1) and 136.0 (1)°, with Cu—Br distances of 2.3939 (15) and 2.3790 (16) Å.

Comment

The catalytic halogenation of activated pyridine rings by copper(II) halides is a common phenomenon. The bromination step presumably involves reduction of Cu^{II} to Cu^I , with the subsequent re-oxidation to Cu^{II} by atmospheric oxygen. In our attempts to prepare various substituted pyridinium salts of copper(II) halides, we have frequently isolated the corresponding halogenated salts (Willett & West, 1987; Willett, 1988, 2000; Place & Willett, 1987; Willett & Halvorson, 1988). With 2,6-diaminopyridine, we have previously reported the



formation and isolation of the corresponding 3,5-dichloro derivative (Willett & West, 1987) as the $[CuCl_4]^{2-}$ salt. However, the compound crystallizes in a different space group.

In the title compound, (I), the cation is nearly planar. However, the Br5 atom lies 0.116 Å out of the plane of the pyridine ring. This is probably due to steric repulsion with the

adjacent NH_2 group. The $[CuBr_4]^{2-}$ anion has a slightly compressed tetrahedral geometry with a substantial (but not unusual) distortion from idealized D_{2d} symmetry (Place & Willett, 1988).

Experimental

2,6-Diaminopyridine (0.01 mol, 1.09 g) and $CuBr_2$ (0.005 mol, 1.12 g) were dissolved in dilute HBr (100 ml, *ca* 0.1 M) and the resultant solution was evaporated slowly at *ca* 323 K. The compound was obtained as small nearly opaque purple crystals after two days.

Crystal data

$(C_5H_6Br_2N_3)_2[CuBr_4]$
 $M_r = 919.08$
 Monoclinic, $C2/c$
 $a = 20.612$ (10) Å
 $b = 10.053$ (5) Å
 $c = 13.507$ (7) Å
 $\beta = 127.264$ (7)°
 $V = 2227.3$ (19) Å³
 $Z = 4$

$D_x = 2.741$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 5523 reflections
 $\theta = 2.38$ – 24.70 °
 $\mu = 15.340$ mm⁻¹
 $T = 293$ (2) K
 Plate, purple
 $0.380 \times 0.180 \times 0.025$ mm

Data collection

Bruker CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: empirical (*SADABS*; Bruker, 1998)
 $T_{min} = 0.045$, $T_{max} = 0.681$
 5523 measured reflections
 1849 independent reflections
 1274 reflections with $I > 2\sigma(I)$

$R_{int} = 0.056$
 $\theta_{max} = 24.70$ °
 $h = -16 \rightarrow 24$
 $k = -11 \rightarrow 11$
 $l = -15 \rightarrow 14$
 50 standard reflections
 frequency: beginning and end of data collection
 intensity decay: 0.01%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.129$
 $S = 1.019$
 1849 reflections
 138 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0744P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 1.31$ e Å⁻³
 $\Delta\rho_{min} = -0.96$ e Å⁻³

The H atoms were found on difference Fourier syntheses and the positional parameters and isotropic displacement parameters were refined. The X—H distances were restrained to a distance of 0.96 (5) Å. The largest residual electron-density peaks all lie within 1.06 Å of Br atoms.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *SHELXL97*.

References

- Bruker (1997). *SMART* (Version 4.045) and *SAINTE* (Version 4.035). Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (1998). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Place, H. & Willett, R. D. (1987). *Acta Cryst.* **C43**, 1497–1500.
 Place, H. & Willett, R. D. (1988). *Acta Cryst.* **C44**, 34–38.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Willett, R. D. (1988). *Acta Cryst.* **C44**, 450–453.
 Willett, R. D. (2000). *Inorg. Chem.* Submitted.
 Willett, R. D. & Halvorson, K. (1988). *Acta Cryst.* **C44**, 2068–2071.
 Willett, R. D. & West, D. X. (1987). *Acta Cryst.* **C43**, 2300–2303.