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A copper(I) iodide chain with the 2-amino-4,6-dimethylpyridine cation

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In the title compound, (2-amino-4,6-dimethylpyridinium) diiodocuprate(I), $(C_7H_{11}N_2)[CuI_2]$, the planar 2-amino-4,6-dimethylpyridine species is protonated at the pyridine N atom. It interacts with the inorganic chains by extensive hydrogen bonding. The cation forms N—H···I hydrogen bonds from both its pyridine and amine N atoms. The copper(I) species is tetrahedrally bonded to four iodide ions (average Cu—I distance = 2.665 Å, with a standard uncertainty of 0.019 Å) and forms infinite edge-sharing chains. Atom-site symmetries: Cu (2); I, phenyl-C and N (*m*).

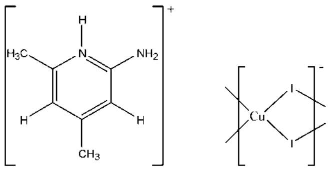
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.008 Å
R factor = 0.028
wR factor = 0.075
Data-to-parameter ratio = 19.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The use of pyridine derivates as templating agents for the self-assembly of organic–inorganic supramolecular materials has been widely studied (Matsumoto, 2003; Desiraju, 1995, 2001; Aakeröy *et al.*, 2000; Mitzi, 2001; Bond & Parsons, 2002). Recently, the structure of 4-dimethylaminopyridinium tribromocuprate(I) was reported; it contains discrete cations and anions (Haddad & Willett, 2001). Copper(I) bromide was also found to form chains with 2,6-diaminopyridinium as a cation (Liu *et al.*, 2001). Copper(II) bromide also forms chains in a complex with pyrazine (Fetzer *et al.*, 1989).



(I)

As part of studies on the lattice reduction of copper halides by organic amine cations to chains (Haddad *et al.*, 2003) and to sheets (Desiraju, 1995), we have prepared and characterized the title compound, (I). This proved to contain tetrahedral chains of stoichiometry $[CuI_2]^-$ separated by the organic 2-amino-4,6-dimethylpyridinium cations.

The cation in (I) is required to be planar since all atoms, except two H atoms of each methyl group related by reflection, lie on the *ac* mirror plane perpendicular to the *b* axis. (Fig. 1). The anionic chain consists of copper(I) bridged by two independent iodide ions. The Cu occupies a (0, y, 0) site with twofold symmetry, while I1 and I2 fall on mirror planes perpendicular to the b axis at y = 0.5 and y = 0, respectively. The coordination of copper(I) is distorted tetrahedral. The dihedral angle between the planes of the bridging moieties is 85.46 (3)° (Fig. 1).

Molecular orbital calculations (Avdeef & Fackler, 1978; Mehrotra & Hoffmann, 1978) show that there is no evidence for a metal–metal bond between two Cu atoms. This is due to

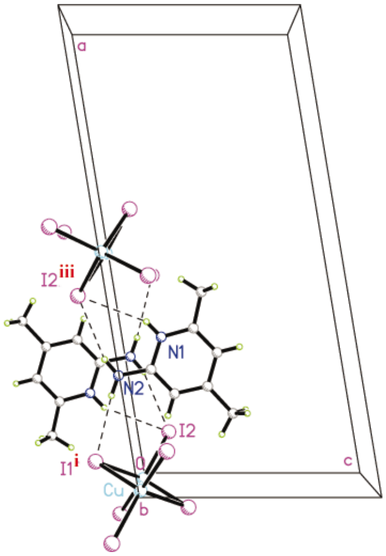


Figure 1
View down [010] of a fragment of (I). The symmetry codes are as in Table 2.

the bond distances and angles between Cu and I atoms (Table 1).

There are neither π–π stacking nor I$\cdots$I interactions of any significance in (I); the closest distance between iodine atoms in different chains is 9.643 (2) Å.

Cations are sandwiched between inorganic chains that run along the *b* axis (Fig. 2). The cations lie in the *ac* plane and form N—H$\cdots$I hydrogen bonds to the chains with similar geometrical parameters to those reported by Garden *et al.* (2002) and Freytag *et al.* (1999).

Experimental

0.5 mmol of CuI was added to 25 ml of 95% ethanol and the solution was heated gently for 10 min, The CuI did not dissolve well. 5 ml of concentrated HI was added, followed by 1 mmol of 2-amino-4,6-dimethylpyridine (99%). A yellow–brown solution formed and crystals developed upon slight cooling. They were collected then recystallized upon cooling from 95% hot ethanol. Large elongated transparent colorless plates developed. Two crops were collected on a frit but were not washed.

Crystal data

$(C_7H_{11}N_2)[CuI_2]$
$M_r = 440.52$
Monoclinic, $C2/m$
$a = 19.003$ (4) Å
$b = 6.7188$ (13) Å
$c = 9.2156$ (18) Å
$\beta = 99.37$ (3)°
$V = 1160.9$ (4) Å^3
$Z = 4$
$D_x = 2.509$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4476 reflections
$\theta = 2.2$–30.0°
$\mu = 7.16$ mm^{-1}
$T = 296$ (2) K
Plate, colorless
0.44 × 0.31 × 0.05 mm

Data collection

Bruker/Siemens SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min} = 0.070$, $T_{\max} = 0.697$
7083 measured reflections
1434 independent reflections
1316 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\max} = 27.5$°
$h = -24 \rightarrow 24$
$k = -8 \rightarrow 8$
$l = -11 \rightarrow 11$

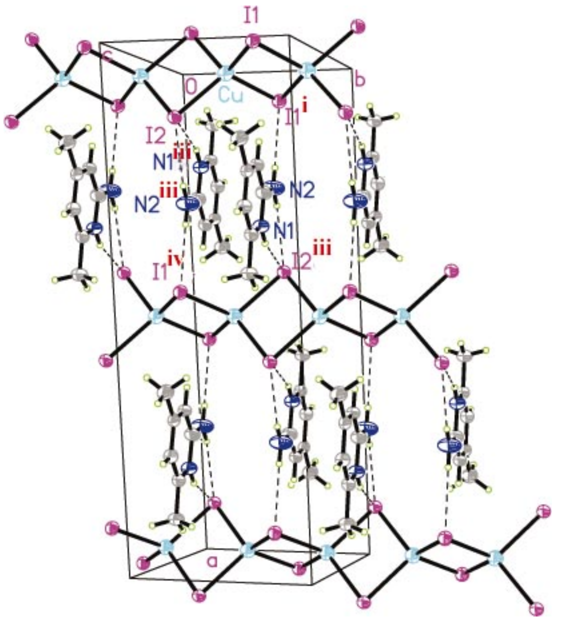


Figure 2
Packing diagram of (I), showing the extensive hydrogen bonding between the CuI_2^- chains and 2-amino-4,6-dimethylpyridine cations. [Symmetry codes: (i) $-x, 1-y, -z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (iv) $\frac{1}{2}+x, y-\frac{1}{2}, z$.] Displacement ellipsoids are drawn at the 30% probability level.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.075$
$S = 1.06$
1434 reflections
72 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 1.2949P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.08$ e Å^{-3}
$\Delta\rho_{\min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—I1	2.6482 (7)	Cu$\cdots$Cu$^{\rm i}$	3.2437 (17)
Cu—I2	2.6821 (8)	Cu$\cdots$Cu$^{\rm ii}$	3.4751 (17)
I1—Cu—I1$^{\rm i}$	104.47 (3)	I2$^{\rm ii}$—Cu—I2	99.24 (3)
I1—Cu—I2$^{\rm ii}$	116.387 (17)	Cu—I1—Cu$^{\rm i}$	75.53 (3)
I1—Cu—I2	110.431 (19)	Cu$^{\rm ii}$—I2—Cu	80.76 (3)

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $-x, -y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
N1—H1$\cdots$I2$^{\rm iii}$	0.86	2.96	3.753 (5)	155
N2—H2*B*$\cdots$I1$^{\rm i}$	0.86	2.74	3.599 (5)	174
N2—H2*A*$\cdots$I2$^{\rm iii}$	0.86	2.78	3.611 (6)	162

Symmetry codes: (i) $-x, 1-y, -z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$.

H atoms, other than methyl H atoms, were positioned geometrically and refined with a riding model, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$ of the carrier atom. Methyl atoms H6*A* and H7*A* were positioned with y = 0.5The other two H atoms in the asymmetric unit, H6*B* and H7*B*, were positioned to give ideal tetrahedral geometry for the methyl groups across the mirror plan. The largest residual electron-density peak lies 0.92 Å from the atom I1.

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Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1996); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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