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Bis(3-methylpyridinium) tetrachlorido-cuprate(II)

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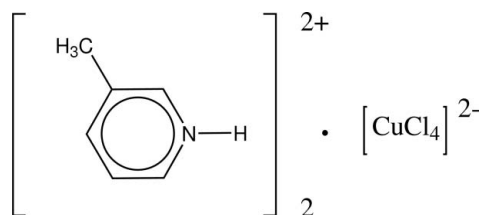
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Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.024; wR factor = 0.062; data-to-parameter ratio = 21.4.

The title compound, $(\text{C}_6\text{H}_8\text{N})_2[\text{CuCl}_4]$, is composed of two 3-methylpyridinium cation and one tetrachloridocuprate(II) anion. The geometry around the copper(II) ion is that of a distorted tetrahedron. In the crystal structure, the anions and cations are linked by three different $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds. In addition, the crystal structure exhibits aromatic $\pi-\pi$ interactions between the pyridinium rings of two discrete units [centroid-centroid distance = 3.704 (2) Å].

Related literature

For general background on the influence of crystal-packing forces on the geometry of the tetrahalogenidocuprate(II) species, see: Schneider *et al.* (2007); Parent *et al.* (2007); Haddad *et al.* (2006); Marzotto *et al.* (2001); Choi *et al.* (2002); Awwadi *et al.* (2007). For the electronic spectrum in DMF solution, see Lee *et al.* (2002). For related literature, see: Lee *et al.* (2008).



Experimental

Crystal data

$(\text{C}_6\text{H}_8\text{N})_2[\text{CuCl}_4]$
 $M_r = 393.61$
Monoclinic, $P2_1/n$
 $a = 9.0438$ (3) Å

$b = 13.0530$ (4) Å
 $c = 13.7391$ (5) Å
 $\beta = 103.541$ (2)°
 $V = 1576.80$ (9) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 2.05$ mm⁻¹

$T = 123$ K
 $0.25 \times 0.24 \times 0.23$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2002)
 $T_{\min} = 0.603$, $T_{\max} = 0.62$
16009 measured reflections
3899 independent reflections
3429 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.062$
 $S = 1.04$
3899 reflections
182 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.36$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.35$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{Cl1}$	0.80 (2)	2.44 (2)	3.136 (2)	146 (2)
$\text{N2}-\text{H2}\cdots\text{Cl1}$	0.81 (2)	2.66 (2)	3.270 (2)	134 (2)
$\text{N2}-\text{H2}\cdots\text{Cl2}$	0.81 (2)	2.50 (2)	3.196 (2)	145 (2)

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997) and DIAMOND (Brandenburg, 1998); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LX2094).

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supporting information

Acta Cryst. (2009). E65, m384 [doi:10.1107/S1600536809007818]

Bis(3-methylpyridinium) tetrachloridocuprate(II)

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S1. Comment

The four-coordinated tetrahalocuprate (II) ions, $[\text{CuCl}_4]^{2-}$ possess a variety of geometries from square planar to near tetrahedral symmetry, and the geometry of tetrahalocuprate (II) species is influenced by the crystal-packing forces resulted from the size and shape of counter cations (Schneider *et al.*, 2007; Parent *et al.*, 2007), hydrogen bonding to cations (Haddad *et al.*, 2006; Marzotto *et al.*, 2001; Choi *et al.*, 2002), and halide-halide interactions in solid (Awwadi *et al.*, 2007). Herein, we report the crystal structure of the title compound, bis(3-methylpyridinium)tetrachloridocuprate(II) (Fig. 1).

The $[\text{CuCl}_4]^{2-}$ anion in the title compound is distorted to be approximately D_{2d} , somewhat distorted from tetrahedral as a result of hydrogen bonding interactions with two 3-methylpyridinium cations. The range of Cl—Cu—Cl angles is $99.28(2)$ – $137.32(2)^\circ$, which is far away from tetrahedral geometry. The Cl1 atom of $[\text{CuCl}_4]^{2-}$ anion forms a three-center hydrogen bond with two protonated pyridinium N atoms (Fig. 2 & Table 1). On the other hand, the Cl2 atom forms a common two-center hydrogen bond with nicotinium cations. As shown in Fig. 2, there are weak π – π interactions between pyridinium rings of two discrete units. The $\text{Cg1}\cdots\text{Cg2}^i$ distance is $3.704(2)$ Å (Cg1 and Cg2 are the centroids of the C1–C5/N1 pyridinium ring and the C7–C11/N2 pyridinium ring, respectively; symmetry code as in Fig.2 & Table 1).

S2. Experimental

A total 1 mmol (0.093 g) of 3-methylpyridine and 1 mmol (0.170 g) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were dissolved in 10 mL of ethanol acidified with 5 mL of concentrated HCl. The mixture solution was heated and refluxed for 1 hr. The single crystals were obtained by slow evaporation in ethanol solution for 7 days. Elemental analysis was performed at the Korean Basic Science Center. Anal. (%) calculated for $\text{C}_{12}\text{H}_{16}\text{Cl}_4\text{CuN}_2$: C, 36.62; H, 4.10; N, 7.12; found: C, 37.23; H, 4.33; N, 7.17. Spectroscopic analysis: The electronic spectrum in DMF solution: ν_1 ; 874 nm ($\epsilon = 20\text{M}^{-1}\text{cm}^{-1}$), ν_2 ; 1038 (71), ν_3 ; 1326 (62). The peak was analyzed into three peaks based on the distorted tetrahedral structure around copper(II) metal ion (Lee *et al.*, 2002). These bands are tentatively assigned to $d_{x^2-y^2}(^2B_2) \rightarrow d_{xz}, d_{yz}(^2E)$, $d_{x^2-y^2} \rightarrow d_{xy}(^2B_1)$, $d_{x^2-y^2} \rightarrow d_z(^2A_1)$, respectively.

S3. Refinement

The H1 and H8 atoms were located in a difference map and refined freely. Other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 - 0.96 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic and $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

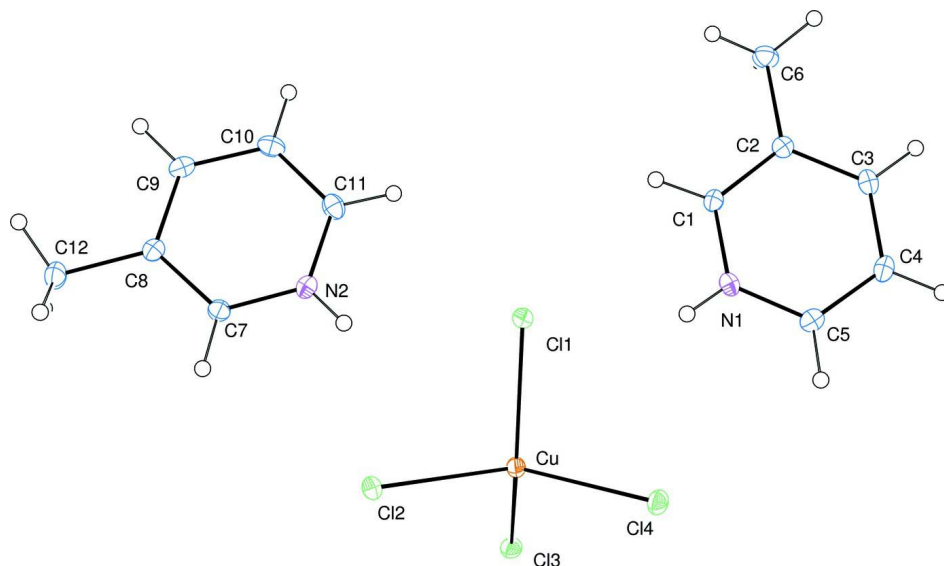


Figure 1

The molecular structure of the title compound, showing displacement ellipsoids drawn at the 30% probability level.

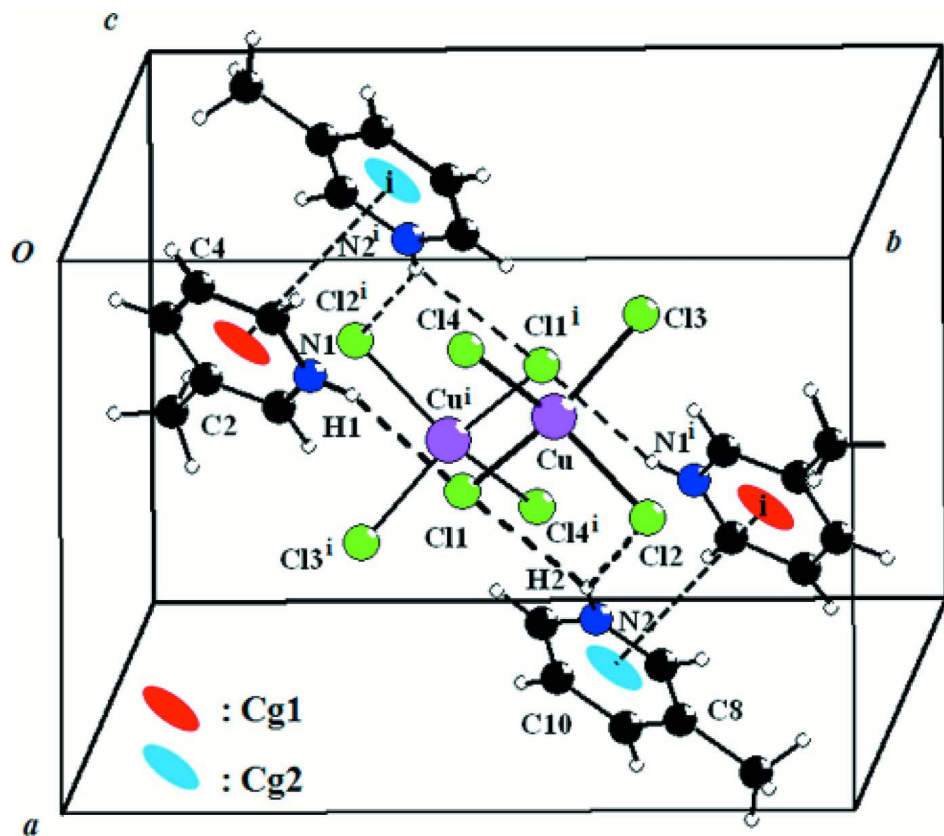


Figure 2

N—H...Cl and π — π interactions (dotted lines) in the title compound. Cg denotes the ring centroid. [Symmetry code: (i) - $x+1, -y+1, -z+1$]

Bis(3-methylpyridinium) tetrachloridocuprate(II)*Crystal data*

(C₆H₈N)₂[CuCl₄]
M_r = 393.61
 Monoclinic, *P*2₁/*n*
 Hall symbol: -*P* 2₁*y*
a = 9.0438 (3) Å
b = 13.0530 (4) Å
c = 13.7391 (5) Å
 β = 103.541 (2)°
V = 1576.80 (9) Å³
Z = 4

F(000) = 796
D_x = 1.658 Mg m⁻³
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 7316 reflections
 θ = 2.8–28.3°
 μ = 2.05 mm⁻¹
T = 123 K
 Block, orange
 0.25 × 0.24 × 0.23 mm

Data collection

Bruker SMART CCD area-detector
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2002)
T_{min} = 0.603, *T_{max}* = 0.62
 16009 measured reflections

3899 independent reflections
 3429 reflections with *I* > 2σ(*I*)
R_{int} = 0.036
 θ_{\max} = 28.3°, θ_{\min} = 2.2°
h = -11→12
k = -17→17
l = -17→18

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.024
wR(*F*²) = 0.062
S = 1.04
 3899 reflections
 182 parameters
 0 restraints

H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0228P)^2 + 0.7012P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.36 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e \AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{iso}</i> */ <i>U_{eq}</i>
Cu	0.55797 (2)	0.545725 (15)	0.703075 (14)	0.01588 (6)
Cl1	0.65531 (4)	0.43858 (3)	0.60513 (3)	0.02068 (9)
Cl2	0.75323 (4)	0.65743 (3)	0.73115 (3)	0.02099 (9)
Cl3	0.36357 (4)	0.65699 (3)	0.68081 (3)	0.01929 (9)
Cl4	0.46771 (5)	0.42349 (3)	0.78922 (3)	0.02114 (9)
N1	0.44305 (15)	0.24760 (11)	0.59904 (10)	0.0181 (3)
H1	0.486 (2)	0.2980 (17)	0.6238 (15)	0.031 (6)*
C1	0.46256 (17)	0.21958 (12)	0.50880 (11)	0.0172 (3)
H1A	0.5226	0.2594	0.4771	0.021*
C2	0.39398 (17)	0.13197 (12)	0.46271 (11)	0.0175 (3)
C3	0.30426 (18)	0.07611 (13)	0.51325 (12)	0.0207 (3)

H3	0.2563	0.0168	0.4843	0.025*
C4	0.28506 (18)	0.10739 (13)	0.60617 (12)	0.0214 (3)
H4	0.2243	0.0698	0.6392	0.026*
C5	0.35733 (18)	0.19485 (13)	0.64851 (12)	0.0198 (3)
H5	0.3467	0.217	0.7108	0.024*
C6	0.4135 (2)	0.10069 (14)	0.36131 (12)	0.0244 (4)
H6A	0.3316	0.1282	0.3106	0.037*
H6B	0.413	0.0273	0.3567	0.037*
H6C	0.5086	0.1266	0.3519	0.037*
N2	0.85716 (15)	0.61542 (11)	0.52789 (10)	0.0188 (3)
H2	0.820 (3)	0.5984 (19)	0.5735 (17)	0.044 (7)*
C7	0.94635 (17)	0.69916 (13)	0.54089 (11)	0.0182 (3)
H7	0.9581	0.7377	0.5992	0.022*
C8	1.02028 (17)	0.72809 (12)	0.46826 (11)	0.0178 (3)
C9	0.99762 (18)	0.66842 (13)	0.38198 (12)	0.0197 (3)
H9	1.0457	0.6861	0.3315	0.024*
C10	0.90430 (19)	0.58299 (13)	0.37064 (12)	0.0223 (3)
H10	0.8895	0.5436	0.3128	0.027*
C11	0.83398 (19)	0.55690 (13)	0.44509 (12)	0.0214 (3)
H11	0.7712	0.4997	0.4386	0.026*
C12	1.1178 (2)	0.82208 (13)	0.48099 (13)	0.0253 (4)
H12A	1.0547	0.8815	0.4636	0.038*
H12B	1.1875	0.8177	0.4381	0.038*
H12C	1.1738	0.8273	0.5494	0.038*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.01598 (11)	0.01411 (10)	0.01823 (11)	-0.00095 (7)	0.00540 (8)	-0.00009 (7)
C11	0.0225 (2)	0.01704 (18)	0.0254 (2)	-0.00297 (15)	0.01148 (16)	-0.00423 (14)
C12	0.02040 (19)	0.02015 (19)	0.02291 (19)	-0.00627 (15)	0.00604 (15)	-0.00435 (15)
C13	0.02013 (19)	0.01763 (18)	0.02150 (19)	0.00232 (14)	0.00768 (15)	0.00053 (14)
C14	0.0242 (2)	0.01839 (19)	0.02248 (19)	-0.00029 (15)	0.00882 (15)	0.00461 (14)
N1	0.0172 (6)	0.0156 (7)	0.0202 (7)	-0.0019 (5)	0.0016 (5)	-0.0005 (5)
C1	0.0163 (7)	0.0172 (7)	0.0186 (7)	0.0000 (6)	0.0048 (6)	0.0028 (6)
C2	0.0168 (7)	0.0177 (7)	0.0174 (7)	0.0020 (6)	0.0028 (6)	0.0017 (6)
C3	0.0197 (8)	0.0171 (8)	0.0243 (8)	-0.0027 (6)	0.0029 (6)	0.0012 (6)
C4	0.0189 (8)	0.0215 (8)	0.0245 (8)	-0.0009 (6)	0.0066 (6)	0.0061 (7)
C5	0.0184 (7)	0.0233 (8)	0.0177 (7)	0.0030 (6)	0.0042 (6)	0.0025 (6)
C6	0.0300 (9)	0.0238 (9)	0.0192 (8)	0.0011 (7)	0.0053 (7)	-0.0024 (7)
N2	0.0180 (7)	0.0204 (7)	0.0185 (7)	-0.0002 (5)	0.0056 (5)	0.0027 (5)
C7	0.0186 (8)	0.0183 (8)	0.0173 (7)	0.0003 (6)	0.0034 (6)	-0.0004 (6)
C8	0.0157 (7)	0.0185 (8)	0.0191 (7)	0.0030 (6)	0.0039 (6)	0.0029 (6)
C9	0.0206 (8)	0.0228 (8)	0.0162 (7)	0.0069 (6)	0.0056 (6)	0.0042 (6)
C10	0.0254 (8)	0.0225 (8)	0.0172 (7)	0.0039 (7)	0.0015 (6)	-0.0035 (6)
C11	0.0196 (8)	0.0186 (8)	0.0238 (8)	-0.0006 (6)	0.0005 (6)	0.0001 (6)
C12	0.0263 (9)	0.0237 (9)	0.0272 (9)	-0.0058 (7)	0.0089 (7)	0.0020 (7)

Geometric parameters (Å, °)

Cu—C13	2.2455 (4)	C6—H6B	0.96
Cu—C14	2.2506 (4)	C6—H6C	0.96
Cu—C12	2.2526 (4)	N2—C7	1.345 (2)
Cu—C11	2.2576 (4)	N2—C11	1.345 (2)
N1—C5	1.336 (2)	N2—H2	0.81 (2)
N1—C1	1.343 (2)	C7—C8	1.378 (2)
N1—H1	0.80 (2)	C7—H7	0.93
C1—C2	1.382 (2)	C8—C9	1.393 (2)
C1—H1A	0.93	C8—C12	1.497 (2)
C2—C3	1.391 (2)	C9—C10	1.385 (2)
C2—C6	1.501 (2)	C9—H9	0.93
C3—C4	1.389 (2)	C10—C11	1.368 (2)
C3—H3	0.93	C10—H10	0.93
C4—C5	1.375 (2)	C11—H11	0.93
C4—H4	0.93	C12—H12A	0.96
C5—H5	0.93	C12—H12B	0.96
C6—H6A	0.96	C12—H12C	0.96
C13—Cu—C14	99.283 (16)	C2—C6—H6C	109.5
C13—Cu—C12	99.327 (17)	H6A—C6—H6C	109.5
C14—Cu—C12	137.322 (16)	H6B—C6—H6C	109.5
C13—Cu—C11	136.189 (16)	C7—N2—C11	122.92 (15)
C14—Cu—C11	96.568 (17)	C7—N2—H2	117.7 (17)
C12—Cu—C11	95.946 (16)	C11—N2—H2	119.3 (17)
C5—N1—C1	123.14 (15)	N2—C7—C8	120.27 (15)
C5—N1—H1	119.2 (15)	N2—C7—H7	119.9
C1—N1—H1	117.7 (15)	C8—C7—H7	119.9
N1—C1—C2	120.43 (15)	C7—C8—C9	117.62 (15)
N1—C1—H1A	119.8	C7—C8—C12	120.84 (15)
C2—C1—H1A	119.8	C9—C8—C12	121.53 (15)
C1—C2—C3	117.17 (15)	C10—C9—C8	120.68 (15)
C1—C2—C6	120.83 (15)	C10—C9—H9	119.7
C3—C2—C6	121.98 (15)	C8—C9—H9	119.7
C4—C3—C2	121.16 (15)	C11—C10—C9	119.60 (15)
C4—C3—H3	119.4	C11—C10—H10	120.2
C2—C3—H3	119.4	C9—C10—H10	120.2
C5—C4—C3	118.91 (16)	N2—C11—C10	118.90 (16)
C5—C4—H4	120.5	N2—C11—H11	120.5
C3—C4—H4	120.5	C10—C11—H11	120.5
N1—C5—C4	119.19 (16)	C8—C12—H12A	109.5
N1—C5—H5	120.4	C8—C12—H12B	109.5
C4—C5—H5	120.4	H12A—C12—H12B	109.5
C2—C6—H6A	109.5	C8—C12—H12C	109.5
C2—C6—H6B	109.5	H12A—C12—H12C	109.5
H6A—C6—H6B	109.5	H12B—C12—H12C	109.5

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1...C11	0.80 (2)	2.44 (2)	3.136 (2)	146 (2)
N2—H2...C11	0.81 (2)	2.66 (2)	3.270 (2)	134 (2)
N2—H2...C12	0.81 (2)	2.50 (2)	3.196 (2)	145 (2)