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Bis(1-methylpiperazine-1,4-diium) tetrachloridocuprate(II)

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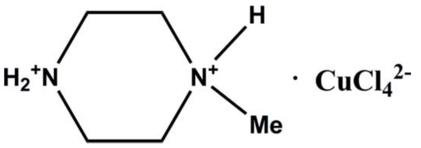
Key indicators: single-crystal X-ray study; *T* = 298 K; mean σ(C–C) = 0.004 Å; *R* factor = 0.025; *wR* factor = 0.059; data-to-parameter ratio = 25.3.

The title compound, $(C_5H_{14}N_2)[CuCl_4]$, was synthesized by hydrothermal reaction of $CuCl_2$ with 1-methylpiperazine in an HCl/water solution. Both amine N atoms are protonated. The piperazine ring adopts a chair conformation. The Cu—Cl distances in the tetrahedral anion are in the range 2.2360 (7)–2.2732 (7) Å. In the crystal, moderately strong and weak intermolecular N—H⋯Cl hydrogen bonds link the anion and cation units into an infinite two-dimensional network parallel to the *ab* plane.

Related literature

For related amino coordination compounds, see: Fu *et al.* (2009); Aminabhavi *et al.* (1986); Dai & Fu (2008*a*,*b*). For halogen atoms as hydrogen-bond acceptors, see: Brammer *et al.* (2001). For the bromide analogue of the title compound, see: Peng (2011).



Experimental

Crystal data

$(C_5H_{14}N_2)[CuCl_4]$
M_r = 307.52
Orthorhombic, $P2_12_12_1$
a = 8.9717 (18) Å
b = 9.945 (2) Å
c = 13.753 (3) Å
V = 1227.1 (4) Å^3
Z = 4
Mo *Kα* radiation
μ = 2.61 mm^{-1}
T = 298 K
0.20 × 0.05 × 0.05 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.89, T_{max} = 1.00
12813 measured reflections
2808 independent reflections
2616 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025
$wR(F^2)$ = 0.059
S = 1.11
2808 reflections
111 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Absolute structure: Flack (1983), 1185 Friedel pairs
Flack parameter: 0.010 (11)

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N2—H2*A*⋯Cl3^{i}	0.90	2.31	3.179 (2)	162
N2—H2*B*⋯Cl2^{ii}	0.90	2.52	3.185 (2)	132
N2—H2*B*⋯Cl1^{ii}	0.90	2.65	3.306 (2)	130
N1—H1⋯Cl4	0.90	2.31	3.1895 (19)	164

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: VN2015).

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supplementary materials

Acta Cryst. (2011). E**67**, m979 [**doi:10.1107/S1600536811024354**]

Bis(1-methylpiperazine-1,4-diium) tetrachloridocuprate(II)

C. Peng

Comment

Amino derivatives of piperazine have found a wide range of applications in material science, due to their magnetic, fluorescent and dielectric properties. There has also been an increased interest in the preparation of amino coordination compounds (Aminabhavi *et al.* 1986; Dai & Fu 2008*a*; Dai & Fu 2008*b*; Fu, *et al.* 2009). We report here the crystal structure of the title compound, *Bis*-(1-methylpiperazine-1,4-diium) tetrachloride copper(II).

The asymmetric unit is composed of one $CuCl_4^{2-}$ anion, and one 1-methylpiperazine-1,4-diium cation (Fig.1). Both amine N atoms are protonated, thus indicating two positive charges on the 1-methylpiperazine-1,4-diium cation that balance the two negative charges on the $CuCl_4^{2-}$ anion. The Cu-Cl distances are in the range from 2.2360 (7) to 2.2732 (7) Å, shorter than its bromide analogue in this issue (Peng, 2011). The piperazine ring adopts a chair conformation. The geometric parameters of the title compound are in the normal range.

In the crystal structure, all H atoms of the amine groups are involved in intermolecular N—H···Cl hydrogen bonds with the bond angles ranging from 130.4° to 164.0° and N···Cl distances from 3.179 (2)Å to 3.306 (2)Å, respectively. Following the survey by Brammer *et al.* (2001), the N2—H2B···Cl1 and N2—H2B···Cl2 H-bonds should be considered to be clearly weaker than the N2—H2A···Cl3 and N1—H1···Cl4 interactions (Table 1). The hydrogen bonds link the cations and anions into an infinite two-dimensional network parallel to the *ab*-plane (Fig.2). The bromide analogue of the title compound is reported elsewhere in this issue (Peng, 2011).

Experimental

A mixture of 1-methylpiperazine (0.4 mmol), $CuCl_2$ (0.4 mmol) and HCl/distilled water (10ml,1:4) sealed in a teflon-lined stainless steel vessel, was maintained at 100 °C. Blue block-shaped crystals suitable for X-ray analysis were obtained after 3 days.

Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding on the parent atoms with C-H = 0.97 Å (methylene) and C-H = 0.96 Å (methyl) with $U_{iso}(H) = 1.2U_{eq}$ (methylene) and $U_{iso}(H) = 1.5U_{eq}$ (methyl). The positional parameters of the H atoms (N1, N2) were initially refined freely, subsequently restrained using a distance of 0.90 Å and in the final refinements treated in riding motion on their parent nitrogen atoms with $U_{iso}(H)=1.2U_{eq}(N)$.

Figures

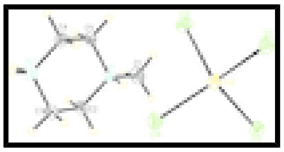

Fig. 1. Molecular view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

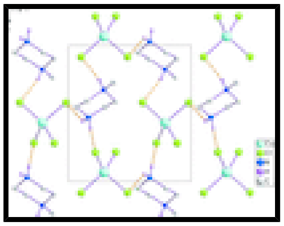

Fig. 2. The crystal packing of the title compound viewed along the *c* axis showing the two-dimensional hydrogen bond network (dashed line). Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

Bis(1-methylpiperazine-1,4-diium) tetrachloridocuprate(II)

Crystal data

$(C_5H_{14}N_2)[CuCl_4]$

$M_r = 307.52$

Orthorhombic, $P2_12_12_1$

Hall symbol: P 2ac 2ab

$a = 8.9717$ (18) Å

$b = 9.945$ (2) Å

$c = 13.753$ (3) Å

$V = 1227.1$ (4) Å^3

$Z = 4$

$F(000) = 620$

$D_x = 1.665$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2808 reflections

$\theta = 3.1$–27.5°

$\mu = 2.61$ mm^{-1}

$T = 298$ K

Block, blue

0.20 × 0.05 × 0.05 mm

Data collection

Rigaku Mercury2
diffractometer

Radiation source: fine-focus sealed tube

graphite

Detector resolution: 13.6612 pixels mm^{-1}

profile data from φ scans

Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)

$T_{min} = 0.89$, $T_{max} = 1.00$

12813 measured reflections

2808 independent reflections

2616 reflections with $I > 2\sigma(I)$

$R_{int} = 0.036$

$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$

$h = -11 \rightarrow 11$

$k = -12 \rightarrow 12$

$l = -17 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

Hydrogen site location: inferred from neighbouring
sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.022P)^2 + 0.1621P]$

	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.059$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.11$	$\Delta\rho_{max} = 0.35$ e Å^{-3}
2808 reflections	$\Delta\rho_{min} = -0.30$ e Å^{-3}
111 parameters	Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints	Extinction coefficient: 0.0271 (9)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1185 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.010 (11)

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.78864 (3)	0.56811 (3)	0.60180 (2)	0.03632 (10)
Cl2	0.98061 (8)	0.41919 (7)	0.59536 (5)	0.05205 (19)
Cl3	0.71852 (8)	0.71379 (6)	0.71940 (5)	0.04349 (16)
N2	0.6621 (2)	−0.0291 (2)	0.58707 (15)	0.0377 (5)
H2A	0.6784	−0.1116	0.6118	0.045*
H2B	0.6166	−0.0538	0.5316	0.045*
Cl4	0.60364 (7)	0.41742 (6)	0.61497 (6)	0.04956 (18)
N1	0.7864 (2)	0.17565 (17)	0.70981 (13)	0.0304 (4)
H1	0.7517	0.2466	0.6761	0.037*
Cl1	0.88660 (8)	0.71628 (6)	0.49755 (5)	0.04457 (17)
C4	0.7962 (3)	0.0489 (2)	0.55755 (18)	0.0401 (5)
H4A	0.7658	0.1277	0.5211	0.048*
H4B	0.8585	−0.0060	0.5158	0.048*
C5	0.8834 (3)	0.0914 (2)	0.64550 (18)	0.0361 (5)
H5A	0.9174	0.0126	0.6808	0.043*
H5B	0.9702	0.1426	0.6256	0.043*
C1	0.8693 (3)	0.2304 (3)	0.79610 (19)	0.0491 (7)
H1A	0.8080	0.2948	0.8292	0.074*
H1B	0.9594	0.2731	0.7746	0.074*
H1C	0.8935	0.1581	0.8396	0.074*
C2	0.6547 (3)	0.0954 (3)	0.74224 (18)	0.0383 (6)
H2C	0.5919	0.1502	0.7838	0.046*

H2D	0.6882	0.0184	0.7796	0.046*
C3	0.5663 (3)	0.0481 (3)	0.65572 (18)	0.0397 (6)
H3A	0.4848	−0.0083	0.6776	0.048*
H3B	0.5241	0.1252	0.6224	0.048*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.03892 (17)	0.02711 (15)	0.04294 (17)	0.00232 (13)	0.00213 (13)	0.00148 (13)
Cl2	0.0549 (4)	0.0356 (3)	0.0656 (4)	0.0155 (3)	0.0214 (3)	0.0148 (4)
Cl3	0.0472 (3)	0.0367 (3)	0.0466 (3)	−0.0003 (3)	0.0106 (3)	−0.0032 (3)
N2	0.0397 (11)	0.0306 (10)	0.0428 (12)	−0.0029 (8)	−0.0008 (9)	−0.0038 (9)
Cl4	0.0380 (3)	0.0328 (3)	0.0779 (5)	−0.0016 (3)	−0.0067 (3)	0.0037 (3)
N1	0.0304 (9)	0.0270 (9)	0.0340 (10)	0.0017 (8)	−0.0019 (9)	−0.0003 (8)
Cl1	0.0558 (4)	0.0348 (3)	0.0431 (3)	0.0093 (3)	0.0080 (3)	0.0093 (3)
C4	0.0483 (14)	0.0315 (12)	0.0403 (13)	−0.0010 (12)	0.0147 (11)	−0.0016 (11)
C5	0.0288 (12)	0.0280 (12)	0.0516 (14)	0.0007 (10)	0.0079 (10)	0.0019 (11)
C1	0.0456 (15)	0.0592 (17)	0.0424 (14)	−0.0092 (13)	−0.0093 (12)	−0.0046 (13)
C2	0.0324 (13)	0.0435 (14)	0.0391 (13)	−0.0042 (10)	0.0070 (10)	−0.0004 (11)
C3	0.0316 (12)	0.0422 (14)	0.0454 (14)	−0.0038 (11)	−0.0004 (10)	−0.0057 (13)

Geometric parameters (Å, °)

Cu1—Cl1	2.2360 (7)	C4—H4A	0.9700
Cu1—Cl4	2.2435 (8)	C4—H4B	0.9700
Cu1—Cl3	2.2606 (7)	C5—H5A	0.9700
Cu1—Cl2	2.2732 (7)	C5—H5B	0.9700
N2—C4	1.488 (3)	C1—H1A	0.9600
N2—C3	1.490 (3)	C1—H1B	0.9600
N2—H2A	0.9001	C1—H1C	0.9600
N2—H2B	0.8999	C2—C3	1.505 (3)
N1—C2	1.494 (3)	C2—H2C	0.9700
N1—C5	1.497 (3)	C2—H2D	0.9700
N1—C1	1.502 (3)	C3—H3A	0.9700
N1—H1	0.8998	C3—H3B	0.9700
C4—C5	1.502 (4)		

Cl1—Cu1—Cl4	141.52 (3)	N1—C5—C4	109.30 (19)
Cl1—Cu1—Cl3	98.38 (3)	N1—C5—H5A	109.8
Cl4—Cu1—Cl3	99.47 (3)	C4—C5—H5A	109.8
Cl1—Cu1—Cl2	96.12 (3)	N1—C5—H5B	109.8
Cl4—Cu1—Cl2	97.38 (3)	C4—C5—H5B	109.8
Cl3—Cu1—Cl2	131.02 (3)	H5A—C5—H5B	108.3
C4—N2—C3	111.74 (19)	N1—C1—H1A	109.5
C4—N2—H2A	116.6	N1—C1—H1B	109.5
C3—N2—H2A	108.9	H1A—C1—H1B	109.5
C4—N2—H2B	106.1	N1—C1—H1C	109.5
C3—N2—H2B	114.6	H1A—C1—H1C	109.5
H2A—N2—H2B	98.4	H1B—C1—H1C	109.5

C2—N1—C5	109.69 (17)	N1—C2—C3	110.34 (19)
C2—N1—C1	110.44 (19)	N1—C2—H2C	109.6
C5—N1—C1	112.44 (19)	C3—C2—H2C	109.6
C2—N1—H1	107.4	N1—C2—H2D	109.6
C5—N1—H1	109.6	C3—C2—H2D	109.6
C1—N1—H1	107.1	H2C—C2—H2D	108.1
N2—C4—C5	110.40 (19)	N2—C3—C2	110.97 (19)
N2—C4—H4A	109.6	N2—C3—H3A	109.4
C5—C4—H4A	109.6	C2—C3—H3A	109.4
N2—C4—H4B	109.6	N2—C3—H3B	109.4
C5—C4—H4B	109.6	C2—C3—H3B	109.4
H4A—C4—H4B	108.1	H3A—C3—H3B	108.0

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···Cl3^{i}	0.90	2.31	3.179 (2)	162
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Symmetry codes: (i) *x*, *y*−1, *z*; (ii) *x*−1/2, −*y*+1/2, −*z*+1.

Fig. 1

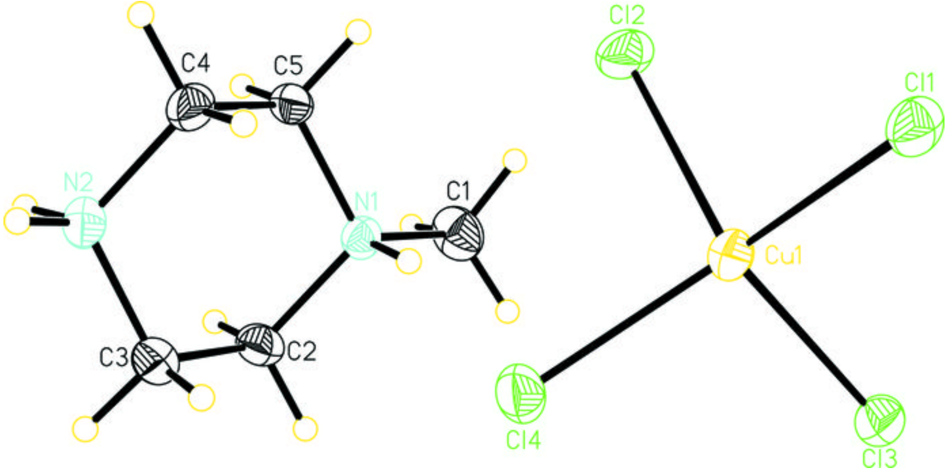

Fig. 2