metal-organic compounds

(2R)-2-Methylpiperazinediium tetrachloridocuprate(II)

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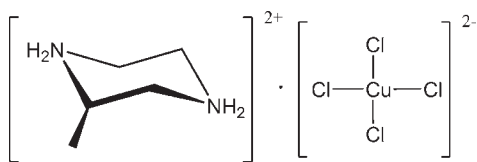Correspondence e-mail: clz1977@sina.com

In the title compound, $(C_5H_{14}N_2)[CuCl_4]$, the copper(II) ion has a slightly tetrahedrally distorted square-planar coordination geometry and the diprotonated piperazine ring adopts a chair conformation. In the crystal structure, cations and anions are linked by intermolecular N—H⋯Cl hydrogen bonds, forming a three-dimensional network.

Related literature

For the ferroelectric and non-linear optical properties of chiral organic ligands, see: Fu *et al.* (2007); Qu *et al.* (2003). For transition metal complexes of 2-methylpiperazine, see: Ye *et al.* (2009). For puckering parameters, see: Cremer & Pople (1975).

Experimental

Crystal data

$(C_5H_{14}N_2)[CuCl_4]$	V = 1144.1 (4) Å³
M_r = 307.53	Z = 4
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
a = 6.0169 (12) Å	μ = 2.80 mm⁻¹
b = 12.985 (3) Å	T = 293 K
c = 14.644 (3) Å	0.30 × 0.25 × 0.22 mm

Data collection

Rigaku SCXmini diffractometer	11992 measured reflections
Absorption correction: multi-scan	2627 independent reflections
(*CrystalClear*; Rigaku, 2005)	2469 reflections with $I > 2\sigma(I)$
T_{min} = 0.87, T_{max} = 0.90	R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.025	H-atom parameters constrained
$wR(F^2)$ = 0.060	$\Delta\rho_{max}$ = 0.30 e Å⁻³
S = 1.10	$\Delta\rho_{min}$ = −0.53 e Å⁻³
2627 reflections	Absolute structure: Flack (1983),
111 parameters	1091 Friedel pairs
1 restraint	Flack parameter: 0.00 (3)

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯Cl1[i]	0.90	2.36	3.149 (6)	147
N1—H1B⋯Cl1[ii]	0.90	2.31	3.182 (6)	163
N2—H2A⋯Cl4[iii]	0.90	2.33	3.218 (6)	168
N2—H2B⋯Cl4[iv]	0.90	2.39	3.192 (6)	148

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{5}{2}, -z$; (ii) $x - \frac{1}{2}, -y + \frac{5}{2}, -z$; (iii) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.

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: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2412).

References

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Fu, D.-W., Song, Y.-M., Wang, G.-X., Ye, Q., Xiong, R.-G., Akutagawa, T., Nakamura, T., Chan, P. W. H. & Huang, S. D. (2007). *J. Am. Chem. Soc.* **129**, 5346–5347.
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supporting information

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S1. Comment

The existence of a chiral centre in an organic ligand is very important for the construction noncentrosymmetric or chiral coordination polymers that exhibit desirable physical properties such as ferroelectricity (Fu *et al.*, 2007) and nonlinear optical second harmonic generation (Qu *et al.*, 2003). Chiral (*R*)-2-methylpiperazine has a chiral centre which have shown tremendous scope in the synthesis of transition metal complexes (Ye *et al.*, 2009). The construction of new members of this family of ligands is an important direction in the development of modern coordination chemistry. We report here the crystal structure of the title compound
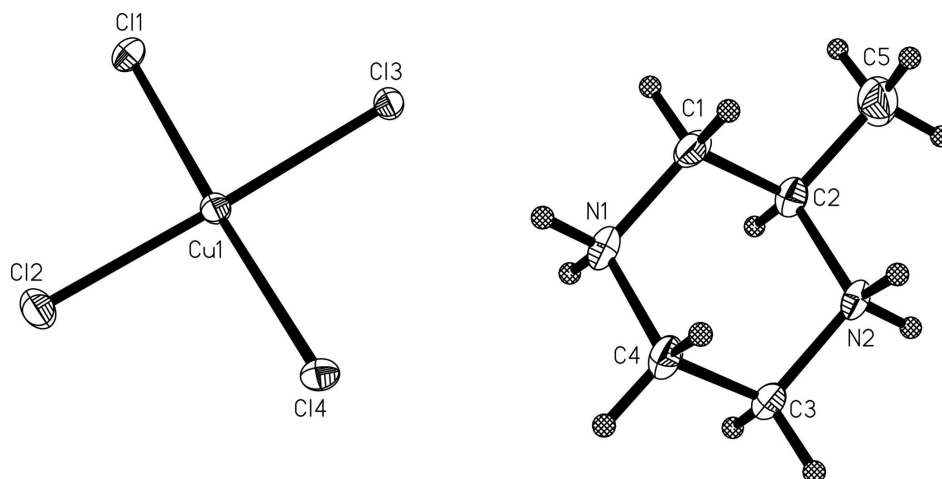
   The asymmetric unit of the title compound consists of a diprotonated (*R*)-2-methylpiperazine cation and a tetrachloro-cuprate anion (Fig. 1). The copper(II) metal centre is in a slightly tetrahedrally distorted square-planar coordination geometry (maximum displacement 0.0252 (18) Å for atom Cl1). The 6-membered piperazine ring adopts a chair conformation, with puckering parameters (Cremer & Pople, 1975) $Q = 0.570$ (6) Å, $\theta = 178.6$ (6)° and $\varphi = -127.3$ (3)°. The crystal structure is stabilized by inter-ion N—H···Cl hydrogen interactions (Table 1) forming a three-dimensional network (Fig. 2).

S2. Experimental

A mixture of (*R*)-2-methylpiperazine (1 mmol, 0.1 g), $CuCl_2$ (1 mmol, 0.136 g) and 10% aqueous HCl (6 ml) were mixed and dissolved in 30 ml water by heating to 353 K (10 minute) forming a clear solution. The reaction mixture was then cooled slowly to room temperature. Single crystals of the title compound suitable for X-ray analysis were formed after 12 days on slow evaporation of the solvent.
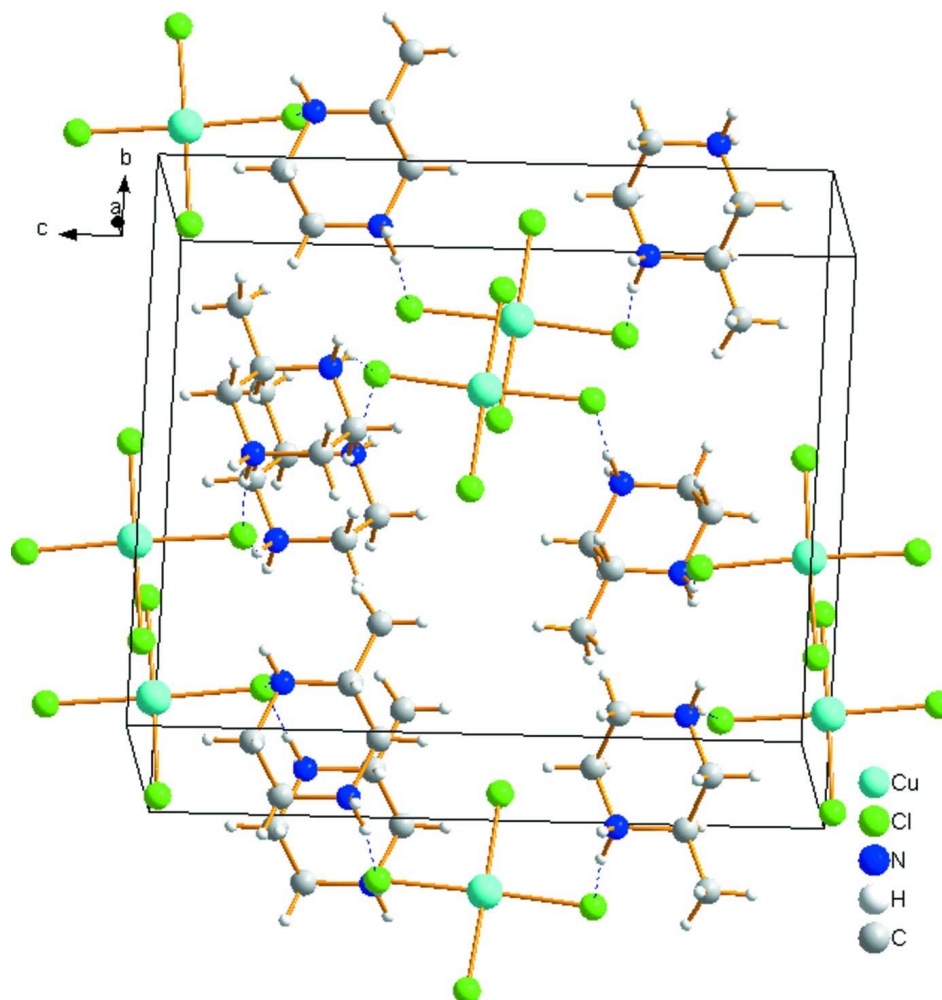
S3. Refinement

All H atoms were placed in calculated positions with C—H = 0.93-0.98 Å, N—H = 0.90 Å, and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C, N)$ or $1.5 U_{eq}(C)$ for methyl H atoms.

Figure 1

The asymmetric unit of the title compound with atom labels. Displacement ellipsoids were drawn at the 30% probability level.

Figure 2

Packing diagram viewed approximately along the *a* axis. Hydrogen bonds are drawn as dashed lines.

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Crystal data

(C₅H₁₄N₂)[CuCl₄]

$(C_5H_{14}N_2)[CuCl_4]$
$M_r = 307.53$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 6.0169 (12)$ Å
$b = 12.985 (3)$ Å
$c = 14.644 (3)$ Å
$V = 1144.1 (4)$ Å³
$Z = 4$

$F(000) = 620$
$D_x = 1.785$ Mg m⁻³
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2469 reflections
$\theta = 3.1$–27.5°
$\mu = 2.80$ mm⁻¹
$T = 293$ K
Block, yellow
$0.30 \times 0.25 \times 0.22$ mm

Data collection

Rigaku SCXmini
    diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.6612 pixels mm⁻¹
ω scans
Absorption correction: multi-scan
    (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.87$, $T_{max} = 0.90$

11992 measured reflections
2627 independent reflections
2469 reflections with $I > 2\sigma(I)$
$R_{int} = 0.051$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -7 \rightarrow 7$
$k = -16 \rightarrow 16$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.060$
$S = 1.10$
2627 reflections
111 parameters
1 restraint
Primary atom site location: structure-invariant
    direct methods
Secondary atom site location: difference Fourier
    map

Hydrogen site location: inferred from
    neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2 + 0.0175P]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.30$ e Å⁻³
$\Delta\rho_{min} = -0.53$ e Å⁻³
Extinction correction: *SHELXL97* (Sheldrick,
    2008), Fc*=kFc[1+0.001xFc²λ³/sin(2θ)]⁻¹ᐟ⁴
Extinction coefficient: 0.193 (9)
Absolute structure: Flack (1983), 1091 Friedel
    pairs
Absolute structure parameter: 0.00 (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.

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 $F^2 > \sigma(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.82482 (13)	1.34903 (5)	0.01022 (5)	0.0237 (3)
Cl4	0.8203 (3)	1.32659 (11)	0.17172 (9)	0.0251 (4)
Cl3	0.8247 (3)	1.17476 (11)	−0.00811 (9)	0.0256 (4)
Cl2	0.8317 (3)	1.52141 (11)	0.02454 (12)	0.0365 (4)
Cl1	0.8196 (3)	1.36387 (11)	−0.14937 (10)	0.0250 (4)
N1	0.8224 (9)	1.0679 (4)	0.1788 (3)	0.0289 (11)
H1A	0.9338	1.1063	0.1559	0.035*
H1B	0.6932	1.0976	0.1626	0.035*
N2	0.6773 (9)	0.8919 (4)	0.2799 (3)	0.0263 (11)
H2A	0.8089	0.8638	0.2951	0.032*
H2B	0.5692	0.8523	0.3038	0.032*
C5	0.6696 (17)	0.7855 (5)	0.1398 (5)	0.055 (2)
H5C	0.5702	0.7410	0.1725	0.083*
H5B	0.8190	0.7603	0.1458	0.083*
H5A	0.6288	0.7867	0.0764	0.083*
C2	0.6553 (12)	0.8933 (5)	0.1786 (4)	0.0300 (14)
H2C	0.5097	0.9221	0.1630	0.036*
C4	0.8395 (11)	1.0661 (5)	0.2797 (4)	0.0309 (14)
H4B	0.8227	1.1354	0.3035	0.037*
H4A	0.9850	1.0408	0.2975	0.037*
C3	0.6623 (12)	0.9975 (5)	0.3195 (4)	0.0304 (13)
H3B	0.6801	0.9939	0.3853	0.036*
H3A	0.5170	1.0264	0.3067	0.036*
C1	0.8335 (12)	0.9624 (5)	0.1390 (4)	0.0323 (14)
H1D	0.9786	0.9329	0.1512	0.039*
H1C	0.8150	0.9666	0.0733	0.039*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0339 (4)	0.0198 (4)	0.0174 (4)	−0.0001 (3)	−0.0003 (3)	0.0000 (3)
Cl4	0.0236 (7)	0.0309 (8)	0.0209 (7)	−0.0006 (7)	−0.0001 (7)	−0.0035 (6)
Cl3	0.0392 (8)	0.0197 (7)	0.0178 (7)	−0.0004 (7)	0.0001 (7)	0.0001 (5)
Cl2	0.0540 (10)	0.0222 (8)	0.0333 (9)	−0.0006 (8)	−0.0017 (10)	−0.0016 (6)
Cl1	0.0238 (7)	0.0308 (8)	0.0205 (7)	−0.0010 (7)	−0.0001 (7)	0.0047 (6)
N1	0.025 (2)	0.034 (3)	0.028 (3)	−0.004 (3)	0.000 (3)	0.013 (2)
N2	0.026 (2)	0.028 (3)	0.024 (3)	−0.004 (3)	0.002 (3)	0.011 (2)
C5	0.090 (6)	0.035 (4)	0.041 (5)	−0.005 (5)	−0.005 (6)	0.000 (3)
C2	0.033 (3)	0.031 (3)	0.026 (3)	−0.001 (3)	−0.003 (3)	0.007 (3)
C4	0.037 (3)	0.031 (3)	0.025 (3)	−0.004 (3)	−0.003 (3)	0.009 (3)
C3	0.037 (3)	0.032 (3)	0.023 (3)	0.001 (3)	0.005 (3)	0.006 (3)
C1	0.037 (3)	0.039 (4)	0.022 (3)	0.000 (3)	0.005 (3)	0.007 (3)

Geometric parameters (Å, °)

Cu1—Cl2	2.2485 (16)	C5—H5C	0.9600
Cu1—Cl3	2.2788 (16)	C5—H5B	0.9600
Cu1—Cl1	2.3451 (15)	C5—H5A	0.9600
Cu1—Cl4	2.3831 (15)	C2—C1	1.514 (9)
N1—C4	1.482 (8)	C2—H2C	0.9800
N1—C1	1.490 (8)	C4—C3	1.506 (9)
N1—H1A	0.9000	C4—H4B	0.9700
N1—H1B	0.9000	C4—H4A	0.9700
N2—C2	1.489 (8)	C3—H3B	0.9700
N2—C3	1.492 (7)	C3—H3A	0.9700
N2—H2A	0.9000	C1—H1D	0.9700
N2—H2B	0.9000	C1—H1C	0.9700
C5—C2	1.513 (9)		
Cl2—Cu1—Cl3	178.25 (7)	N2—C2—C5	111.0 (5)
Cl2—Cu1—Cl1	90.66 (6)	N2—C2—C1	109.0 (5)
Cl3—Cu1—Cl1	87.95 (5)	C5—C2—C1	111.4 (6)
Cl2—Cu1—Cl4	91.68 (6)	N2—C2—H2C	108.5
Cl3—Cu1—Cl4	89.74 (5)	C5—C2—H2C	108.5
Cl1—Cu1—Cl4	177.28 (6)	C1—C2—H2C	108.5
C4—N1—C1	111.9 (4)	N1—C4—C3	110.3 (6)
C4—N1—H1A	109.2	N1—C4—H4B	109.6
C1—N1—H1A	109.2	C3—C4—H4B	109.6
C4—N1—H1B	109.2	N1—C4—H4A	109.6
C1—N1—H1B	109.2	C3—C4—H4A	109.6
H1A—N1—H1B	107.9	H4B—C4—H4A	108.1
C2—N2—C3	111.8 (4)	N2—C3—C4	110.5 (5)
C2—N2—H2A	109.3	N2—C3—H3B	109.6
C3—N2—H2A	109.3	C4—C3—H3B	109.6
C2—N2—H2B	109.3	N2—C3—H3A	109.6
C3—N2—H2B	109.3	C4—C3—H3A	109.6
H2A—N2—H2B	107.9	H3B—C3—H3A	108.1
C2—C5—H5C	109.5	N1—C1—C2	111.3 (5)
C2—C5—H5B	109.5	N1—C1—H1D	109.4
H5C—C5—H5B	109.5	C2—C1—H1D	109.4
C2—C5—H5A	109.5	N1—C1—H1C	109.4
H5C—C5—H5A	109.5	C2—C1—H1C	109.4
H5B—C5—H5A	109.5	H1D—C1—H1C	108.0
C3—N2—C2—C5	−179.7 (7)	N1—C4—C3—N2	56.1 (7)
C3—N2—C2—C1	57.3 (7)	C4—N1—C1—C2	56.4 (7)
C1—N1—C4—C3	−55.8 (7)	N2—C2—C1—N1	−56.0 (7)
C2—N2—C3—C4	−58.1 (7)	C5—C2—C1—N1	−178.8 (6)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl1[i]	0.90	2.36	3.149 (6)	147
N1—H1B···Cl1[ii]	0.90	2.31	3.182 (6)	163
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Symmetry codes: (i) x+1/2, −y+5/2, −z; (ii) x−1/2, −y+5/2, −z; (iii) −x+2, y−1/2, −z+1/2; (iv) −x+1, y−1/2, −z+1/2.