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

Cong-hu Peng

Department of Chemical & Environmental Engineering, Anyang Institute of Technology, Anyang 455000, People's Republic of China
Correspondence e-mail: ayitpch@yahoo.com.cn

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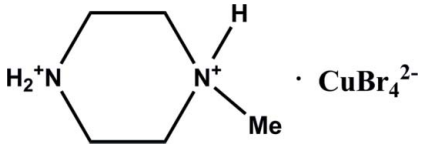
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.009 Å; R factor = 0.044; wR factor = 0.088; data-to-parameter ratio = 28.4.

The title compound, $(C_5H_{14}N_2)[CuBr_4]$, was synthesized by hydrothermal reaction of $CuBr_2$ with 1-methylpiperazine in an HBr/water solution. Both amine N atoms are protonated. The Cu—Br distances in the tetrahedral anion are in the range 2.3809 (11)–2.4131 (11) Å. In the crystal, moderately strong and weak intermolecular N—H···Br 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 chlorine analogue of the title compound, see: Peng (2011).



Experimental

Crystal data

$(C_5H_{14}N_2)[CuBr_4]$
M_r = 485.36
Orthorhombic, $P2_12_12_1$
a = 9.1933 (18) Å
b = 10.341 (2) Å
c = 14.255 (3) Å
V = 1355.2 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 13.37 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
14009 measured reflections
3092 independent reflections
2545 reflections with $I > 2\sigma(I)$
R_{int} = 0.079

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.088
S = 1.08
3092 reflections
109 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.92 e Å^{-3}
$\Delta\rho_{min}$ = −0.71 e Å^{-3}
Absolute structure: Flack (1983), 1312 Friedel pairs
Flack parameter: 0.05 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2*C*···Br3^{i}	0.90	2.50	3.339 (6)	154
N2—H2*D*···Br1^{ii}	0.90	2.68	3.354 (5)	133
N2—H2*D*···Br2^{ii}	0.90	2.76	3.457 (5)	135
N1—H1···Br4	0.90	2.55	3.345 (5)	148

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: VN2014).

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supporting information

Acta Cryst. (2011). E**67**, m967 [doi:10.1107/S1600536811024184]

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

Cong-hu Peng

S1. 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) tetrabromide copper(II).

The asymmetric unit is composed of one $CuBr_4^{2-}$ anion and one 1-methylpiperazine-1,4-diium cation (Fig.1). Both amine N atoms are protonated, indicating thus two positive charges on the cation that balance the two negative charges on the $CuBr_4^{2-}$ anion. 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···Br hydrogen bonds with the bond angles ranging from 132.7° to 154.3° and N···Br distances from 3.339 (6)Å to 3.457 (5)Å, respectively. Following the survey by Brammer *et al.* (2001) the N2—H2D···Br1 and N2—H2D···Br2 H-bonds should be considered to be clearly weaker than the N2—H2C···Br3 and N1—H1···Br4 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 chlorine analogue of the title compound is reported elsewhere in this issue (Peng, 2011).

S2. Experimental

A mixture of 1-methylpiperazine (0.4 mmol), $CuBr_2$ (0.4 mmol) and HBr/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.

S3. 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).

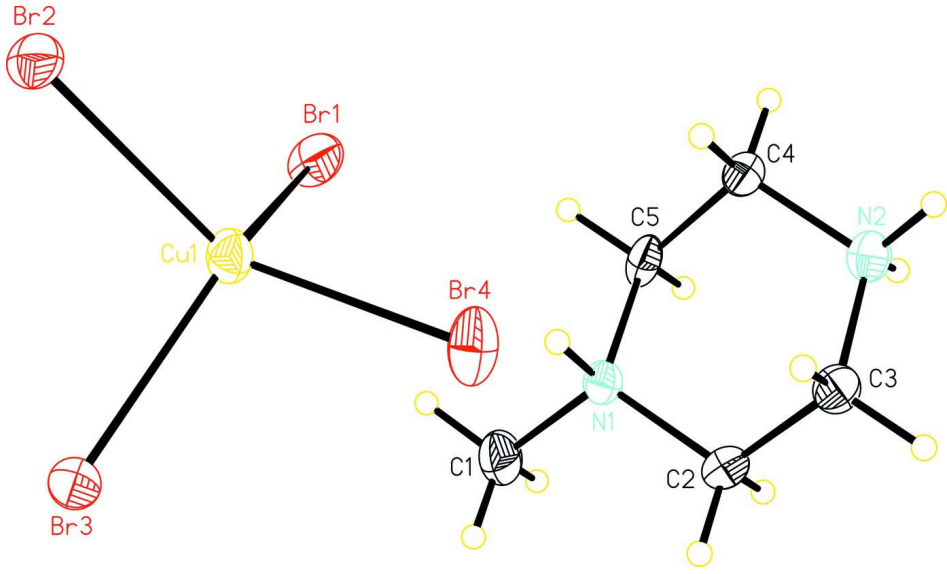

Figure 1

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

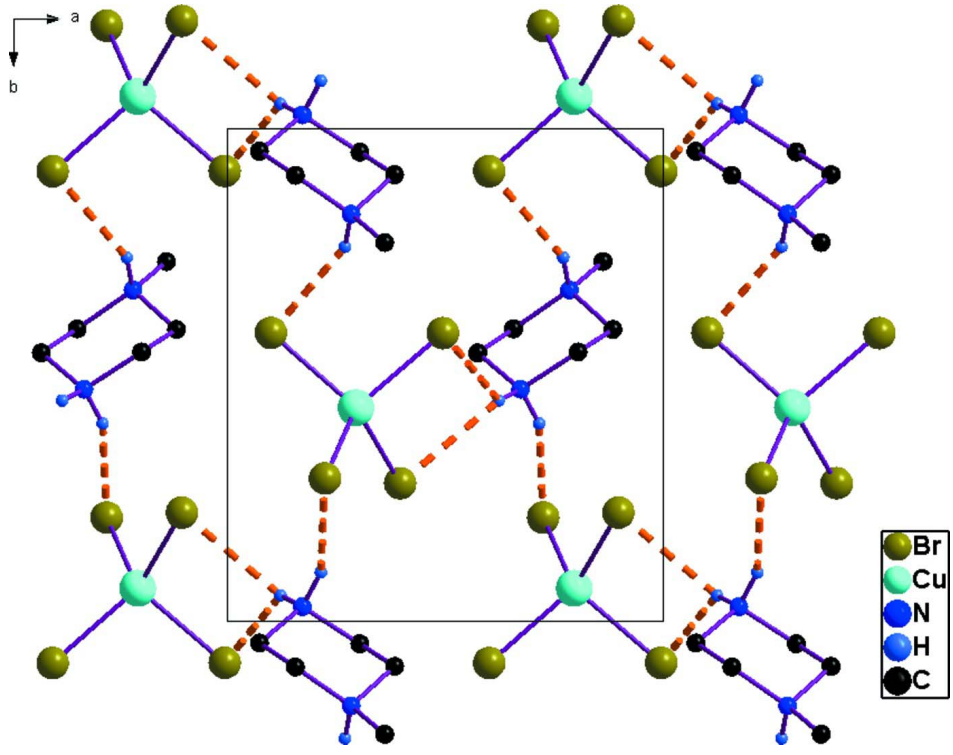

Figure 2

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

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

Crystal data

$(C_5H_{14}N_2)[CuBr_4]$
$M_r = 485.36$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 9.1933$ (18) Å
$b = 10.341$ (2) Å
$c = 14.255$ (3) Å
$V = 1355.2$ (5) Å^3
$Z = 4$
$F(000) = 908$
$D_x = 2.379$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3092 reflections
$\theta = 3.3$–$27.5°$
$\mu = 13.37$ 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 monochromator
Detector resolution: 13.6612 pixels mm^{-1}
profile data from φ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.89$, $T_{max} = 1.00$
14009 measured reflections
3092 independent reflections
2545 reflections with $I > 2\sigma(I)$
$R_{int} = 0.079$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.3°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 13$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.088$
$S = 1.08$
3092 reflections
109 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0277P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.92$ e Å^{-3}
$\Delta\rho_{min} = -0.71$ e Å^{-3}
Absolute structure: Flack (1983), 1312 Friedel pairs
Absolute structure parameter: 0.05 (2)

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 $F^2 > 2$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}
Br1	0.99472 (8)	0.08523 (7)	0.59527 (5)	0.0496 (2)
Br2	0.89670 (8)	−0.22010 (7)	0.49622 (5)	0.0430 (2)
Br3	0.72439 (8)	−0.21019 (7)	0.72661 (5)	0.04138 (19)

Cu1	0.79551 (9)	−0.06642 (7)	0.60209 (5)	0.0365 (2)
Br4	0.60073 (8)	0.08567 (7)	0.61127 (6)	0.0501 (2)
N2	0.6726 (5)	0.5289 (5)	0.5927 (4)	0.0367 (14)
H2C	0.7150	0.5985	0.6190	0.044*
H2D	0.6225	0.5519	0.5411	0.044*
N1	0.7844 (6)	0.3272 (4)	0.7129 (3)	0.0298 (12)
H1	0.7703	0.2609	0.6731	0.036*
C4	0.8043 (7)	0.4533 (7)	0.5656 (5)	0.0384 (16)
H4A	0.8684	0.5069	0.5281	0.046*
H4B	0.7756	0.3793	0.5281	0.046*
C5	0.8841 (7)	0.4074 (6)	0.6529 (5)	0.0364 (16)
H5A	0.9680	0.3564	0.6348	0.044*
H5B	0.9181	0.4815	0.6884	0.044*
C2	0.6566 (7)	0.4061 (7)	0.7413 (4)	0.0413 (17)
H2A	0.6892	0.4790	0.7786	0.050*
H2B	0.5922	0.3541	0.7798	0.050*
C3	0.5744 (7)	0.4550 (7)	0.6565 (5)	0.0397 (17)
H3A	0.5329	0.3824	0.6228	0.048*
H3B	0.4953	0.5104	0.6769	0.048*
C1	0.8613 (8)	0.2694 (7)	0.7956 (5)	0.050 (2)
H1A	0.7941	0.2181	0.8312	0.075*
H1B	0.8992	0.3374	0.8344	0.075*
H1C	0.9398	0.2159	0.7741	0.075*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0533 (5)	0.0344 (4)	0.0610 (5)	−0.0140 (4)	0.0190 (4)	−0.0117 (4)
Br2	0.0539 (4)	0.0333 (4)	0.0418 (4)	−0.0101 (4)	0.0066 (3)	−0.0080 (3)
Br3	0.0424 (4)	0.0365 (4)	0.0452 (4)	0.0005 (3)	0.0098 (3)	0.0034 (3)
Cu1	0.0389 (5)	0.0269 (4)	0.0436 (5)	−0.0011 (4)	0.0015 (4)	−0.0011 (4)
Br4	0.0374 (4)	0.0322 (4)	0.0805 (5)	0.0010 (3)	−0.0113 (4)	−0.0026 (4)
N2	0.033 (3)	0.035 (3)	0.041 (3)	0.002 (3)	−0.003 (3)	−0.001 (3)
N1	0.032 (3)	0.024 (3)	0.033 (3)	0.000 (2)	0.000 (2)	−0.002 (2)
C4	0.043 (4)	0.033 (4)	0.040 (4)	0.008 (3)	0.010 (3)	0.002 (3)
C5	0.026 (4)	0.027 (4)	0.057 (4)	0.006 (3)	0.003 (3)	−0.003 (3)
C2	0.038 (4)	0.046 (4)	0.040 (4)	0.009 (3)	0.011 (3)	0.003 (4)
C3	0.025 (4)	0.047 (4)	0.047 (4)	0.004 (3)	0.005 (3)	0.009 (4)
C1	0.053 (5)	0.048 (4)	0.049 (4)	0.015 (4)	−0.007 (3)	0.007 (4)

Geometric parameters (Å, º)

Br1—Cu1	2.4131 (11)	C4—H4A	0.9700
Br2—Cu1	2.3809 (11)	C4—H4B	0.9700
Br3—Cu1	2.4059 (10)	C5—H5A	0.9700
Cu1—Br4	2.3869 (11)	C5—H5B	0.9700
N2—C3	1.492 (8)	C2—C3	1.513 (9)
N2—C4	1.493 (7)	C2—H2A	0.9700

N2—H2C	0.9000	C2—H2B	0.9700
N2—H2D	0.9000	C3—H3A	0.9700
N1—C2	1.486 (8)	C3—H3B	0.9700
N1—C1	1.499 (8)	C1—H1A	0.9600
N1—C5	1.503 (8)	C1—H1B	0.9600
N1—H1	0.9000	C1—H1C	0.9600
C4—C5	1.520 (9)		

Br2—Cu1—Br4	140.15 (4)	N1—C5—C4	110.1 (5)
Br2—Cu1—Br3	99.28 (4)	N1—C5—H5A	109.6
Br4—Cu1—Br3	99.38 (4)	C4—C5—H5A	109.6
Br2—Cu1—Br1	96.41 (4)	N1—C5—H5B	109.6
Br4—Cu1—Br1	98.24 (4)	C4—C5—H5B	109.6
Br3—Cu1—Br1	129.61 (4)	H5A—C5—H5B	108.2
C3—N2—C4	112.3 (5)	N1—C2—C3	111.1 (5)
C3—N2—H2C	114.7	N1—C2—H2A	109.4
C4—N2—H2C	100.1	C3—C2—H2A	109.4
C3—N2—H2D	109.0	N1—C2—H2B	109.4
C4—N2—H2D	109.9	C3—C2—H2B	109.4
H2C—N2—H2D	110.6	H2A—C2—H2B	108.0
C2—N1—C1	112.2 (5)	N2—C3—C2	110.9 (5)
C2—N1—C5	109.5 (5)	N2—C3—H3A	109.5
C1—N1—C5	112.3 (5)	C2—C3—H3A	109.5
C2—N1—H1	118.5	N2—C3—H3B	109.5
C1—N1—H1	105.1	C2—C3—H3B	109.5
C5—N1—H1	98.6	H3A—C3—H3B	108.1
N2—C4—C5	110.1 (5)	N1—C1—H1A	109.5
N2—C4—H4A	109.7	N1—C1—H1B	109.5
C5—C4—H4A	109.7	H1A—C1—H1B	109.5
N2—C4—H4B	109.7	N1—C1—H1C	109.5
C5—C4—H4B	109.7	H1A—C1—H1C	109.5
H4A—C4—H4B	108.2	H1B—C1—H1C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*C*···Br3^{i}	0.90	2.50	3.339 (6)	154
N2—H2*D*···Br1^{ii}	0.90	2.68	3.354 (5)	133
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