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1,4-Diazoniabicyclo[2.2.2]octane tetrabromidocuprate(II) monohydrate

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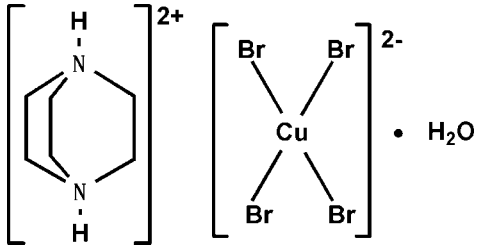
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.011 Å; R factor = 0.052; wR factor = 0.116; data-to-parameter ratio = 24.3.

In the title monohydrated salt, $(C_6H_{14}N_2)[CuBr_4]\cdot H_2O$, the copper(II) ion is coordinated by the four bromide ions in a flattened tetrahedral geometry. In the crystal, the cations, anions and water molecules interact *via* N—H···O, O—H···Br and N—H···Br hydrogen bonds, forming chains parallel to the *b* axis. The chains are further linked by O—H···Br hydrogen bonds into layers parallel to the *bc* plane.

Related literature

For related structures, see: Wei & Willett (1996, 2002); Brammer *et al.* (2002); Zhang *et al.* (2010).



Experimental

Crystal data

$(C_6H_{14}N_2)[CuBr_4]\cdot H_2O$
M_r = 515.39
Monoclinic, $P2_1/c$
a = 9.5171 (19) Å
b = 9.5341 (19) Å
c = 14.952 (3) Å
β = 93.93 (3)°
V = 1353.5 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 13.40 mm^{-1}
T = 298 K
0.20 × 0.20 × 0.20 mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.055, T_{max} = 0.086
13570 measured reflections
3111 independent reflections
2285 reflections with $I > 2\sigma(I)$
R_{int} = 0.124

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.116
S = 1.10
3111 reflections
128 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.22 e Å^{-3}
$\Delta\rho_{min}$ = −1.29 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2C···O1W	0.91	2.49	3.121 (8)	127
N2—H2C···O1W^{i}	0.91	1.98	2.788 (7)	147
O1W—H1WA···Br4^{ii}	0.85	2.75	3.456 (5)	141
O1W—H1WA···Br2^{ii}	0.85	2.86	3.461 (5)	129
O1W—H1WB···Br1^{iii}	0.85	2.55	3.319 (5)	152
N1—H1C···Br1	0.91	2.61	3.360 (5)	140
N1—H1C···Br4	0.91	2.92	3.546 (6)	127

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

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: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2552).

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1,4-Diazoniabicyclo[2.2.2]octane tetrabromidocuprate(II) monohydrate

Yi Zhang and Bo Wang

S1. Comment

Ferroelectric materials have attracted intensive interest not only due to their versatile technological applications in the field of electronics and optics, but also for their importance to the fundamental scientific research. Recently, monosalts of 1,4-diazabicyclo[2.2.2]octane (dabco) including dabco*HBF*$_4$, dabco*HClO*$_4$ and dabco*HReO*$_4$ have been reported to have excellent dielectric and ferroelectric properties (Wei & Willett, 1996, 2002; Brammer *et al.*, 2002). Our group has recently reported the compound $(dabcoH_2)_2Cl_3[CuCl_3(H_2O)_2].H_2O$ (Zhang *et al.*, 2010), which also shows good dielectric and ferroelectric properties. Herein we report the synthesis and crystal structure of the title compound, $(dabcoH_2)CuBr_4.H_2O$.

The asymmetric unit of the title compound contains one $(dabcoH_2)^{2+}$ cation, one $[CuBr_4]^{2-}$ anion and one water molecules (Fig 1). The copper(II) ion has a flattened tetrahedral coordination geometry provided by the four Br^- ions, with Cu—Br distances ranging from 2.3598 (12) to 2.4070 (12) Å. Generally, the Cu—Br bond lengths and Br—Cu—Br bond angles in a $[CuBr_4]^{2-}$ anion are not equal to one another but vary with the environment around the Br atoms. As atoms Br1, Br2 and Br4 are involved in hydrogen bonds, the Cu1—Br3 bond length is significantly shorter than the other Cu—Br bonds. The distortion from the ideal tetrahedral geometry is also indicated by the values of the Br—Cu—Br angles, which range from 96.75 (4) to 133.92 (5)°. The H1C and H2C protons of the 1,4-diazoniabicyclo(2.2.2)octane cation and the H1WA hydrogen atom of the water molecule are engaged in bifurcated N—H···Br, N—H···O and O—H···Br hydrogen bonds (Table 1), forming chains parallel to the *b* axis. The chains are further connected by O—H···Br hydrogen bonds into layers parallel to the (011) plane (Fig. 2).

S2. Experimental

To a concentrated HBr water solution (50 ml) 1,4-diazabicyclo[2.2.2]octane (10 mmol, 1.12 g) and of $CuBr_2.2H_2O$ (10 mmol, 2.60 g) were added with stirring. Brown single crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation of the solvent over a period of a week at room temperature. The dielectric constant of the compound as a function of temperature indicates that the permittivity is basically temperature-independent (ε= C/(T–T$_0$)), suggesting that the title compound is not ferroelectric or there may be no distinct phase transition occurring within the measured temperature range between 93 K and 362 K (m. p. 99 °C).

S3. Refinement

All H atoms were fixed geometrically and treated as riding, with C–H = 0.97 Å, N—H = 0.91 Å, O—H = 0.85 Å, and with U_{iso}(H) = 1.2 U_{eq}(C, N) or 1.2 U_{eq}(O).

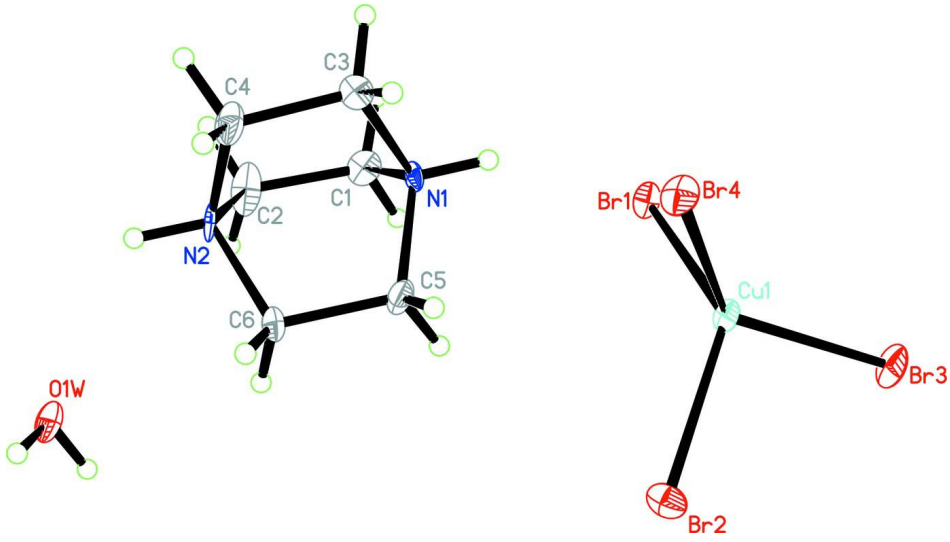

Figure 1

The molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

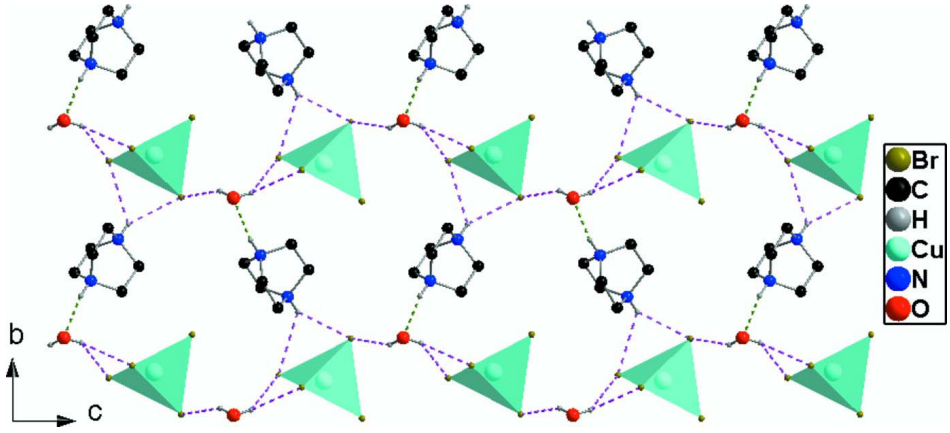

Figure 2

Packing diagram of the title compound viewed along the *a* axis. H atoms not involved in hydrogen bonding (dashed lines) are omitted.

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Crystal data

$(C_6H_{14}N_2)[CuBr_4]\cdot H_2O$
$M_r = 515.39$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 9.5171\ (19)$ Å
$b = 9.5341\ (19)$ Å
$c = 14.952\ (3)$ Å
$\beta = 93.93\ (3)°$
$V = 1353.5\ (5)$ Å^3
$Z = 4$
$F(000) = 972$
$D_x = 2.529$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2622 reflections
$\theta = 3.0–27.5°$
$\mu = 13.40$ mm^{-1}
$T = 298$ K
Polyhedron, brown
0.20 × 0.20 × 0.20 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} = 0.055, T_{max} = 0.086
13570 measured reflections
3111 independent reflections
2285 reflections with $I > 2\sigma(I)$
R_{int} = 0.124
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −12→12
k = −12→12
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.116
S = 1.10
3111 reflections
128 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
$w = 1/[\sigma^2(F_o^2) + (0.0225P)^2 + 2.0506P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.22 e Å^{-3}
$\Delta\rho_{min}$ = −1.29 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0204 (7)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.13288 (8)	1.07551 (7)	−0.32168 (5)	0.0252 (2)
Br2	0.47455 (8)	1.29945 (9)	−0.17676 (5)	0.0294 (3)
Br3	0.24026 (10)	1.44329 (8)	−0.35401 (5)	0.0343 (3)
Br4	0.12020 (9)	1.24314 (8)	−0.10831 (5)	0.0291 (2)
C1	0.2071 (9)	0.7578 (7)	−0.1967 (5)	0.0250 (18)
H1A	0.1136	0.7276	−0.2186	0.030*
H1B	0.2588	0.7837	−0.2479	0.030*
C2	0.2812 (10)	0.6413 (8)	−0.1464 (5)	0.039 (2)
H2A	0.2182	0.5619	−0.1423	0.046*
H2B	0.3620	0.6113	−0.1776	0.046*
C3	0.1196 (8)	0.8404 (8)	−0.0560 (5)	0.0221 (17)
H3A	0.0265	0.8058	−0.0751	0.027*
H3B	0.1094	0.9204	−0.0170	0.027*
C4	0.2029 (9)	0.7281 (8)	−0.0075 (6)	0.032 (2)

H4A	0.2322	0.7602	0.0524	0.039*
H4B	0.1444	0.6456	−0.0023	0.039*
C5	0.3414 (8)	0.9335 (7)	−0.1063 (5)	0.0265 (19)
H5A	0.3357	1.0120	−0.0654	0.032*
H5B	0.3896	0.9644	−0.1579	0.032*
C6	0.4211 (9)	0.8136 (8)	−0.0601 (6)	0.040 (2)
H6A	0.5019	0.7893	−0.0932	0.048*
H6B	0.4551	0.8418	−0.0001	0.048*
Cu1	0.24156 (9)	1.27018 (9)	−0.24116 (6)	0.0190 (3)
N1	0.1962 (6)	0.8822 (6)	−0.1354 (4)	0.0164 (13)
H1C	0.1478	0.9520	−0.1654	0.020*
N2	0.3277 (6)	0.6913 (6)	−0.0552 (4)	0.0204 (14)
H2C	0.3753	0.6211	−0.0251	0.024*
O1W	0.6324 (6)	0.5717 (5)	−0.0241 (3)	0.0316 (14)
H1WA	0.6670	0.5956	0.0276	0.047*
H1WB	0.6832	0.6044	−0.0638	0.047*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0381 (5)	0.0188 (4)	0.0181 (5)	−0.0005 (3)	−0.0012 (4)	−0.0011 (3)
Br2	0.0251 (4)	0.0452 (5)	0.0177 (5)	0.0018 (4)	0.0000 (3)	0.0023 (4)
Br3	0.0557 (6)	0.0281 (5)	0.0180 (5)	−0.0065 (4)	−0.0067 (4)	0.0144 (4)
Br4	0.0378 (5)	0.0327 (5)	0.0182 (5)	0.0007 (4)	0.0138 (4)	0.0031 (3)
C1	0.037 (5)	0.028 (4)	0.010 (4)	−0.003 (4)	0.002 (3)	−0.008 (3)
C2	0.077 (7)	0.025 (5)	0.015 (5)	0.015 (5)	0.009 (5)	−0.004 (4)
C3	0.027 (4)	0.029 (4)	0.010 (4)	0.003 (3)	0.003 (3)	−0.004 (3)
C4	0.046 (5)	0.029 (5)	0.024 (5)	0.009 (4)	0.012 (4)	0.010 (4)
C5	0.035 (4)	0.017 (4)	0.026 (5)	−0.007 (3)	−0.007 (4)	0.006 (3)
C6	0.029 (5)	0.035 (5)	0.054 (6)	−0.001 (4)	−0.011 (4)	0.029 (5)
Cu1	0.0288 (5)	0.0193 (5)	0.0087 (5)	−0.0016 (4)	0.0003 (4)	0.0041 (4)
N1	0.020 (3)	0.019 (3)	0.011 (3)	0.005 (3)	−0.002 (2)	0.007 (3)
N2	0.037 (4)	0.011 (3)	0.013 (3)	0.006 (3)	−0.002 (3)	0.008 (3)
O1W	0.045 (3)	0.027 (3)	0.023 (3)	0.000 (3)	0.008 (3)	0.010 (2)

Geometric parameters (Å, º)

Br1—Cu1	2.4070 (12)	C4—N2	1.469 (10)
Br2—Cu1	2.3726 (13)	C4—H4A	0.9700
Br3—Cu1	2.3598 (12)	C4—H4B	0.9700
Br4—Cu1	2.3792 (13)	C5—N1	1.502 (9)
C1—C2	1.492 (10)	C5—C6	1.512 (10)
C1—N1	1.507 (9)	C5—H5A	0.9700
C1—H1A	0.9700	C5—H5B	0.9700
C1—H1B	0.9700	C6—N2	1.471 (9)
C2—N2	1.483 (9)	C6—H6A	0.9700
C2—H2A	0.9700	C6—H6B	0.9700
C2—H2B	0.9700	N1—H1C	0.9100

C3—N1	1.489 (9)	N2—H2C	0.9100
C3—C4	1.490 (10)	O1W—H1WA	0.8501
C3—H3A	0.9700	O1W—H1WB	0.8500
C3—H3B	0.9700		
C2—C1—N1	109.2 (6)	C6—C5—H5B	110.1
C2—C1—H1A	109.8	H5A—C5—H5B	108.4
N1—C1—H1A	109.8	N2—C6—C5	109.6 (6)
C2—C1—H1B	109.8	N2—C6—H6A	109.7
N1—C1—H1B	109.8	C5—C6—H6A	109.7
H1A—C1—H1B	108.3	N2—C6—H6B	109.7
N2—C2—C1	109.0 (6)	C5—C6—H6B	109.7
N2—C2—H2A	109.9	H6A—C6—H6B	108.2
C1—C2—H2A	109.9	Br3—Cu1—Br2	99.61 (5)
N2—C2—H2B	109.9	Br3—Cu1—Br4	133.92 (5)
C1—C2—H2B	109.9	Br2—Cu1—Br4	99.64 (5)
H2A—C2—H2B	108.3	Br3—Cu1—Br1	101.57 (4)
N1—C3—C4	107.9 (6)	Br2—Cu1—Br1	130.64 (5)
N1—C3—H3A	110.1	Br4—Cu1—Br1	96.75 (4)
C4—C3—H3A	110.1	C3—N1—C5	110.3 (5)
N1—C3—H3B	110.1	C3—N1—C1	109.4 (5)
C4—C3—H3B	110.1	C5—N1—C1	109.4 (6)
H3A—C3—H3B	108.4	C3—N1—H1C	109.2
N2—C4—C3	110.9 (6)	C5—N1—H1C	109.2
N2—C4—H4A	109.5	C1—N1—H1C	109.2
C3—C4—H4A	109.5	C4—N2—C6	110.2 (6)
N2—C4—H4B	109.5	C4—N2—C2	108.8 (6)
C3—C4—H4B	109.5	C6—N2—C2	110.7 (6)
H4A—C4—H4B	108.1	C4—N2—H2C	109.0
N1—C5—C6	108.0 (6)	C6—N2—H2C	109.0
N1—C5—H5A	110.1	C2—N2—H2C	109.0
C6—C5—H5A	110.1	H1WA—O1W—H1WB	109.5
N1—C5—H5B	110.1		

Hydrogen-bond geometry (Å, º)

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