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# 1-Chloromethyl-1,4-diazoniabicyclo-[2.2.2]octane tetrachloridocuprate(II)

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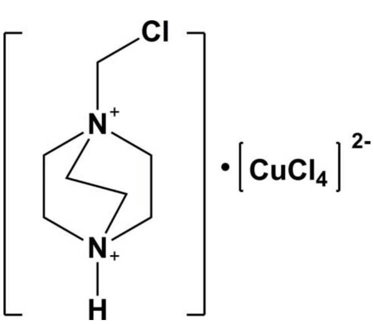
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.003 Å; $R$ factor = 0.022; $wR$ factor = 0.055; data-to-parameter ratio = 22.6.

In the crystal structure of the title compound, $(C_7H_{15}ClN_2)$-$[CuCl_4]$, a weak intermolecular N—H···Cl hydrogen bond is observed between the organic dication and the tetrahedral $[CuCl_4]^{2-}$ anion. The organic dication is distorted, as indicated by the N—C—C—N torsion angles, which range from 16.76 (4) to 19.54 (3)°.

## Related literature

For related 1,4-diazabicyclo[2.2.2]octane tetrachlorido-cuprate(II) and tetrachloridocobaltate(II) structures, and related references therein, see: Sun & Qu (2005); Qu & Sun (2005). For phase transitions of ferroelectric materials, see: Zhang *et al.* (2008); Ye *et al.* (2009).




## Experimental

### *Crystal data*

$(C_7H_{15}ClN_2)[CuCl_4]$
$M_r$ = 368.00
Orthorhombic, $P2_12_12_1$
$a$ = 9.878 (4) Å
$b$ = 11.167 (4) Å
$c$ = 12.201 (4) Å
$V$ = 1345.9 (8) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 2.59 mm$^{-1}$
$T$ = 293 K
0.30 × 0.25 × 0.20 mm

### *Data collection*

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min}$ = 0.465, $T_{max}$ = 0.596
6091 measured reflections
3072 independent reflections
2865 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.032

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.055
$S$ = 1.01
3072 reflections
136 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.39 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.36 e Å$^{-3}$
Absolute structure: Flack (1983), with 1298 Friedel pairs
Flack parameter: 0.006 (11)

**Table 1**
Selected bond lengths (Å).

| | | | |
|---|---|---|---|
| Cl2—Cu1 | 2.2537 (8) | Cl4—Cu1 | 2.2559 (9) |
| Cl3—Cu1 | 2.2539 (9) | Cl5—Cu1 | 2.2088 (11) |

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2$C$···Cl2 | 0.91 | 2.60 | 3.270 (2) | 131 |
| N2—H2$C$···Cl3 | 0.91 | 2.54 | 3.252 (2) | 136 |

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: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2354).

## References

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# supplementary materials

*Acta Cryst.* (2011). E**67**, m889 [ **doi:10.1107/S1600536811020782** ]

# 1-Chloromethyl-1,4-diazoniabicyclo[2.2.2]octane tetrachloridocuprate(II)

**T. Rong**

## Comment

The title compound (I), (Fig. 1), consists of protonated 1-(chloridomethyl)-1,4-diazabicyclo[2.2.2]octane-1,4-diium dications and $[CuCl_4]^{2-}$ anions. The organic dication is distorted, as indicated by the N—C—C—N torsion angles, which range from 16.76 (4) to 19.54 (3)°. In the structure of 1,4-dimethyl-1,4-diazonia[2.2.2]octane tetrachloridocuprate(II), of two independent dications one is almost undistorted with torsion angles between 0.6 (6) and 0.9 (5)°, whereas the other dication is distorted exhibiting torsion angles in the range of 5.5 (5) and 7.9 (5)° (Sun & Qu, 2005). In the isotypic cobalt(II) structure (Qu & Sun, 2005), two independent dications are slightly distorted with torsion angles range between 3.0 (4) and 8.7 (4)°. The $[CuCl_4]^{2-}$ anion in (I) possesses typical Cu—Cl bonds and its lengths range from 2.209 (1) to 2.2559 (9) Å (Table 1), while the Cl—Cu—Cl angles range from 95.98 (4) to 132.85 (3)°. The bifurcated N—H···(Cl,Cl) hydrogen bonds (Table 2) between the organic dications and the $[CuCl_4]^{2-}$ anions contribute to the stability of crystal packing (Fig. 2).

The study of ferroelectric materials has received much attention. Some materials have predominantly dielectric-ferroelectric performance.The title compound was studied as part of our work to obtain potential ferroelectric phase transition materials. Unluckily, the compound has no dielectric anomalies in the temperature range 93–453 K, suggesting that it might be only a paraelectric (Zhang *et al.*, 2008; Ye *et al.*, 2009).

## Experimental

1, 4-diazabicyclo [2.2.2]octane (5.6 g, 0.05 mol) was added in dichloromethane (20 ml) and the mixture was refluxed for 8 h. On standing for about 16 h at room temperature, the white precipitate of 1-(chloridomethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride was obtained.

The title compound was synthesized by adding a solution of 1-(chloridomethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium chloride (1.97 g, 10 mmol) in HCl (37%, 20 ml) to a solution of $CuCl_2$ (8 mmol) in 20 ml $H_2O$. After a few weeks, brown hygroscopic block crystals of the title compound were obtained on slow evaporation of the solvent.

## Refinement

Positional parameters of all H atoms bonded to C and N atoms were calculated geometrically and were allowed to ride on the C and N atoms to which they are bonded, with respective C—H and N—H distances of 0.97 Å and 0.91 Å and with $U_{iso}(H) = 1.2U_{eq}(C, N)$.

## Figures

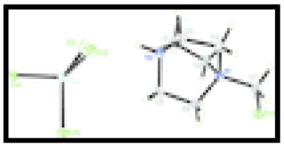

Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level.

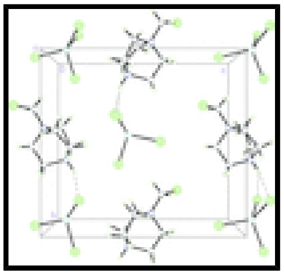

Fig. 2. A view of a packing section of the title compound, stacking along the *c* axis. Dashed lines indicate hydrogen bonds.

## 1-Chloromethyl-1,4-diazoniabicyclo[2.2.2]octane tetrachloridocuprate(II)

### *Crystal data*

| | |
|---|---|
| $(C_7H_{15}ClN_2)[CuCl_4]$ | $F(000) = 740$ |
| $M_r = 368.00$ | $D_x = 1.816$ Mg m$^{-3}$ |
| Orthorhombic, $P2_12_12_1$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Hall symbol: P 2ac 2ab | Cell parameters from 4288 reflections |
| $a = 9.878$ (4) Å | $\theta = 2.5–27.5°$ |
| $b = 11.167$ (4) Å | $\mu = 2.59$ mm$^{-1}$ |
| $c = 12.201$ (4) Å | $T = 293$ K |
| $V = 1345.9$ (8) Å$^3$ | Block, brown |
| $Z = 4$ | 0.30 × 0.25 × 0.20 mm |

### *Data collection*

| | |
|---|---|
| Rigaku Mercury2 diffractometer | 3072 independent reflections |
| Radiation source: fine-focus sealed tube | 2865 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.032$ |
| Detector resolution: 28.5714 pixels mm$^{-1}$ | $\theta_{max} = 27.5°$, $\theta_{min} = 2.5°$ |
| CCD profile fitting scans | $h = -12 \rightarrow 12$ |
| Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005) | $k = -14 \rightarrow 14$ |
| $T_{min} = 0.465$, $T_{max} = 0.596$ | $l = -15 \rightarrow 15$ |
| 6091 measured reflections | |

### *Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.022$ | H-atom parameters constrained |
| $wR(F^2) = 0.055$ | $w = 1/[\sigma^2(F_o^2) + (0.0267P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.01$ | $(\Delta/\sigma)_{max} = 0.001$ |
| 3072 reflections | $\Delta\rho_{max} = 0.39$ e Å$^{-3}$ |
| 136 parameters | $\Delta\rho_{min} = -0.36$ e Å$^{-3}$ |
| 0 restraints | Absolute structure: Flack (1983), with 1298 Friedel pairs |
| Primary atom site location: structure-invariant direct methods | Flack parameter: 0.006 (11) |

*Special details*

**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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.4179 (3) | 1.0325 (2) | 0.3874 (2) | 0.0310 (6) |
| H1A | 0.4300 | 0.9982 | 0.3150 | 0.037* |
| H1B | 0.3385 | 1.0836 | 0.3859 | 0.037* |
| C2 | 0.3989 (3) | 0.9330 (2) | 0.4717 (2) | 0.0267 (6) |
| H2A | 0.3256 | 0.9533 | 0.5212 | 0.032* |
| H2B | 0.3760 | 0.8586 | 0.4350 | 0.032* |
| C3 | 0.6657 (3) | 1.0334 (2) | 0.4017 (2) | 0.0303 (6) |
| H3A | 0.7419 | 1.0735 | 0.4359 | 0.036* |
| H3B | 0.6844 | 1.0253 | 0.3240 | 0.036* |
| C4 | 0.6448 (3) | 0.9099 (2) | 0.4533 (2) | 0.0286 (6) |
| H4A | 0.6235 | 0.8517 | 0.3968 | 0.034* |
| H4B | 0.7269 | 0.8845 | 0.4902 | 0.034* |
| C5 | 0.5303 (3) | 1.1391 (2) | 0.5373 (2) | 0.0288 (6) |
| H5A | 0.4426 | 1.1748 | 0.5519 | 0.035* |
| H5B | 0.5998 | 1.1973 | 0.5551 | 0.035* |
| C6 | 0.5486 (3) | 1.0273 (2) | 0.6064 (2) | 0.0282 (6) |
| H6A | 0.6388 | 1.0263 | 0.6380 | 0.034* |
| H6B | 0.4834 | 1.0269 | 0.6659 | 0.034* |
| C7 | 0.5329 (3) | 0.8043 (2) | 0.6006 (2) | 0.0336 (6) |
| H7A | 0.6137 | 0.8040 | 0.6457 | 0.040* |
| H7B | 0.5382 | 0.7367 | 0.5510 | 0.040* |
| Cl1 | 0.39073 (9) | 0.78795 (7) | 0.68465 (6) | 0.0493 (2) |
| N1 | 0.5285 (2) | 0.91796 (17) | 0.53523 (16) | 0.0212 (4) |
| N2 | 0.5402 (2) | 1.10429 (17) | 0.41845 (17) | 0.0255 (4) |
| H2C | 0.5438 | 1.1716 | 0.3765 | 0.031* |
| Cl2 | 0.36056 (6) | 1.33367 (5) | 0.33718 (6) | 0.03068 (15) |

| | | | | |
|---|---|---|---|---|
| Cl3 | 0.69739 (6) | 1.35292 (6) | 0.36324 (6) | 0.03568 (16) |
| Cl4 | 0.42453 (7) | 1.63249 (5) | 0.36275 (5) | 0.03390 (16) |
| Cl5 | 0.55993 (8) | 1.49699 (6) | 0.59012 (6) | 0.04221 (18) |
| Cu1 | 0.51283 (3) | 1.45593 (3) | 0.41718 (3) | 0.02648 (9) |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0292 (13) | 0.0314 (14) | 0.0325 (15) | −0.0047 (12) | −0.0084 (11) | 0.0029 (11) |
| C2 | 0.0233 (13) | 0.0228 (13) | 0.0339 (14) | −0.0040 (10) | −0.0025 (11) | −0.0032 (11) |
| C3 | 0.0237 (12) | 0.0379 (14) | 0.0294 (14) | 0.0008 (12) | 0.0058 (11) | 0.0033 (12) |
| C4 | 0.0255 (13) | 0.0314 (13) | 0.0289 (14) | 0.0070 (12) | 0.0048 (11) | 0.0014 (11) |
| C5 | 0.0342 (15) | 0.0215 (12) | 0.0305 (13) | −0.0036 (12) | 0.0031 (12) | −0.0053 (10) |
| C6 | 0.0338 (14) | 0.0260 (13) | 0.0248 (14) | −0.0091 (11) | 0.0016 (10) | −0.0047 (10) |
| C7 | 0.0426 (16) | 0.0270 (13) | 0.0312 (15) | −0.0047 (12) | −0.0017 (13) | 0.0070 (11) |
| Cl1 | 0.0659 (6) | 0.0429 (4) | 0.0392 (4) | −0.0177 (4) | 0.0166 (4) | 0.0024 (3) |
| N1 | 0.0226 (10) | 0.0194 (9) | 0.0217 (10) | −0.0025 (8) | −0.0004 (9) | −0.0012 (8) |
| N2 | 0.0260 (10) | 0.0214 (10) | 0.0292 (11) | −0.0023 (9) | −0.0003 (10) | 0.0027 (9) |
| Cl2 | 0.0259 (3) | 0.0249 (3) | 0.0412 (4) | −0.0006 (3) | −0.0059 (3) | −0.0022 (3) |
| Cl3 | 0.0241 (3) | 0.0314 (3) | 0.0516 (4) | 0.0000 (3) | −0.0010 (3) | −0.0042 (3) |
| Cl4 | 0.0505 (4) | 0.0211 (3) | 0.0302 (3) | 0.0052 (3) | −0.0030 (3) | −0.0007 (3) |
| Cl5 | 0.0568 (5) | 0.0438 (4) | 0.0260 (3) | 0.0048 (4) | −0.0066 (3) | −0.0006 (3) |
| Cu1 | 0.02908 (17) | 0.02223 (14) | 0.02814 (16) | 0.00119 (14) | −0.00354 (14) | −0.00133 (13) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| C1—N2 | 1.499 (3) | C5—C6 | 1.518 (3) |
| C1—C2 | 1.526 (3) | C5—H5A | 0.9700 |
| C1—H1A | 0.9700 | C5—H5B | 0.9700 |
| C1—H1B | 0.9700 | C6—N1 | 1.511 (3) |
| C2—N1 | 1.506 (3) | C6—H6A | 0.9700 |
| C2—H2A | 0.9700 | C6—H6B | 0.9700 |
| C2—H2B | 0.9700 | C7—N1 | 1.499 (3) |
| C3—N2 | 1.484 (3) | C7—Cl1 | 1.748 (3) |
| C3—C4 | 1.530 (3) | C7—H7A | 0.9700 |
| C3—H3A | 0.9700 | C7—H7B | 0.9700 |
| C3—H3B | 0.9700 | N2—H2C | 0.9100 |
| C4—N1 | 1.526 (3) | Cl2—Cu1 | 2.2537 (8) |
| C4—H4A | 0.9700 | Cl3—Cu1 | 2.2539 (9) |
| C4—H4B | 0.9700 | Cl4—Cu1 | 2.2559 (9) |
| C5—N2 | 1.504 (3) | Cl5—Cu1 | 2.2088 (11) |
| N2—C1—C2 | 108.56 (19) | N1—C6—C5 | 109.22 (19) |
| N2—C1—H1A | 110.0 | N1—C6—H6A | 109.8 |
| C2—C1—H1A | 110.0 | C5—C6—H6A | 109.8 |
| N2—C1—H1B | 110.0 | N1—C6—H6B | 109.8 |
| C2—C1—H1B | 110.0 | C5—C6—H6B | 109.8 |
| H1A—C1—H1B | 108.4 | H6A—C6—H6B | 108.3 |
| N1—C2—C1 | 108.86 (19) | N1—C7—Cl1 | 112.18 (19) |

| | | | |
|---|---|---|---|
| N1—C2—H2A | 109.9 | N1—C7—H7A | 109.2 |
| C1—C2—H2A | 109.9 | Cl1—C7—H7A | 109.2 |
| N1—C2—H2B | 109.9 | N1—C7—H7B | 109.2 |
| C1—C2—H2B | 109.9 | Cl1—C7—H7B | 109.2 |
| H2A—C2—H2B | 108.3 | H7A—C7—H7B | 107.9 |
| N2—C3—C4 | 108.13 (19) | C7—N1—C2 | 113.10 (19) |
| N2—C3—H3A | 110.1 | C7—N1—C6 | 111.95 (19) |
| C4—C3—H3A | 110.1 | C2—N1—C6 | 108.52 (19) |
| N2—C3—H3B | 110.1 | C7—N1—C4 | 106.10 (19) |
| C4—C3—H3B | 110.1 | C2—N1—C4 | 108.03 (19) |
| H3A—C3—H3B | 108.4 | C6—N1—C4 | 108.98 (18) |
| N1—C4—C3 | 108.55 (19) | C3—N2—C1 | 110.7 (2) |
| N1—C4—H4A | 110.0 | C3—N2—C5 | 109.0 (2) |
| C3—C4—H4A | 110.0 | C1—N2—C5 | 109.21 (19) |
| N1—C4—H4B | 110.0 | C3—N2—H2C | 109.3 |
| C3—C4—H4B | 110.0 | C1—N2—H2C | 109.3 |
| H4A—C4—H4B | 108.4 | C5—N2—H2C | 109.3 |
| N2—C5—C6 | 108.37 (19) | Cl5—Cu1—Cl2 | 132.85 (3) |
| N2—C5—H5A | 110.0 | Cl5—Cu1—Cl3 | 102.39 (3) |
| C6—C5—H5A | 110.0 | Cl2—Cu1—Cl3 | 95.98 (4) |
| N2—C5—H5B | 110.0 | Cl5—Cu1—Cl4 | 100.44 (3) |
| C6—C5—H5B | 110.0 | Cl2—Cu1—Cl4 | 98.27 (4) |
| H5A—C5—H5B | 108.4 | Cl3—Cu1—Cl4 | 132.29 (3) |

| | | | |
|---|---|---|---|
| N2—C1—C2—N1 | −16.8 (3) | C5—C6—N1—C4 | 68.1 (2) |
| N2—C3—C4—N1 | −19.5 (3) | C3—C4—N1—C7 | −167.6 (2) |
| N2—C5—C6—N1 | −16.8 (3) | C3—C4—N1—C2 | 70.9 (2) |
| Cl1—C7—N1—C2 | −52.6 (2) | C3—C4—N1—C6 | −46.9 (3) |
| Cl1—C7—N1—C6 | 70.4 (2) | C4—C3—N2—C1 | −47.8 (3) |
| Cl1—C7—N1—C4 | −170.83 (17) | C4—C3—N2—C5 | 72.3 (2) |
| C1—C2—N1—C7 | −166.0 (2) | C2—C1—N2—C3 | 69.9 (3) |
| C1—C2—N1—C6 | 69.1 (2) | C2—C1—N2—C5 | −50.1 (3) |
| C1—C2—N1—C4 | −48.9 (2) | C6—C5—N2—C3 | −51.1 (3) |
| C5—C6—N1—C7 | −174.9 (2) | C6—C5—N2—C1 | 70.0 (3) |
| C5—C6—N1—C2 | −49.3 (2) | | |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2C···Cl2 | 0.91 | 2.60 | 3.270 (2) | 131 |
| N2—H2C···Cl3 | 0.91 | 2.54 | 3.252 (2) | 136 |

Fig. 1

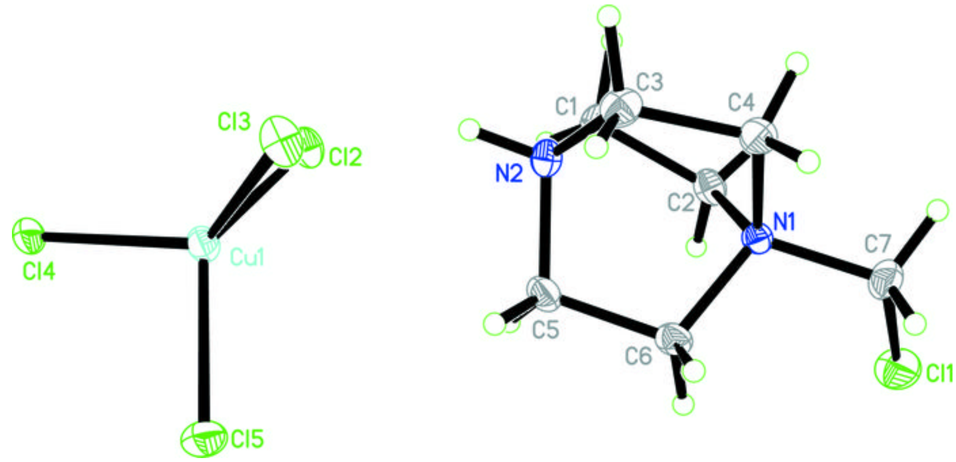

**Fig. 2**