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# (±)-2-Methylpiperazin-1-ium perchlorate

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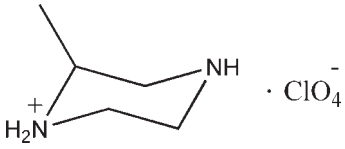
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.005 Å; $R$ factor = 0.075; $wR$ factor = 0.224; data-to-parameter ratio = 18.9.

In the title compound, $C_5H_{13}N_2^+\cdot ClO_4^-$, the monoprotonated piperazine ring adopts a chair conformation. In the crystal structure, cations and anions are linked by intermolecular N—H···O and N—H···N hydrogen bonds into layers parallel to $(\bar{1}01)$.

## Related literature

For the properties of simple molecular–ionic crystals, see: Czupiński *et al.* (2002); Katrusiak & Szafrański (1999, 2006).




## Experimental

### Crystal data

$C_5H_{13}N_2^+\cdot ClO_4^-$
$M_r$ = 200.62
Monoclinic, $P2_1/n$
$a$ = 6.8977 (5) Å
$b$ = 8.1292 (6) Å
$c$ = 16.2201 (11) Å
$\beta$ = 98.614 (3)°
$V$ = 899.25 (11) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.41 mm$^{-1}$
$T$ = 293 K
0.30 × 0.25 × 0.20 mm

### Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min}$ = 0.80, $T_{max}$ = 0.90
8953 measured reflections
2055 independent reflections
1541 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.040

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.075
$wR(F^2)$ = 0.224
$S$ = 1.05
2055 reflections
109 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.86 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.56 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1*C*···O1 | 0.90 | 2.38 | 3.258 (6) | 166 |
| N1—H1*C*···O3 | 0.90 | 2.54 | 3.250 (5) | 136 |
| N2—H2*D*···O2$^{i}$ | 0.90 | 2.43 | 2.998 (7) | 121 |
| N2—H2*C*···N1$^{ii}$ | 0.90 | 1.99 | 2.883 (4) | 169 |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2472).

## References

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Katrusiak, A. & Szafrański, M. (2006). *J. Am. Chem. Soc.* **128**, 15775-15785.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
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# supporting information

*Acta Cryst.* (2010). E**66**, o2114 [https://doi.org/10.1107/S160053681002862X]

## (±)-2-Methylpiperazin-1-ium perchlorate

**Cong-Hu Peng**

### S1. Comment

Recently, much attention has been devoted to simple molecular–ionic crystals containing organic cations and acid radicals in 1:1 molar ratio due to the tunability of their special structural features and their interesting physical properties (Czupiński *et al.*, 2002; Katrusiak & Szafrański, 1999; Katrusiak & Szafrański, 2006). As a contribution in this field, the crystal structure of title salt is reported here.

The asymmetric unit of the title compound (Fig.1) consists of a monoprotonated 2-methylpiperazinium cation and a $ClO_4^-$anions. The piperazine ring adopts a chair conformation. In the crystal structure, cations and anions are linked by intermolecular N—H···O and N—H···N hydrogen bonds (Table 1) into layers parallel to the ($\bar{1}$ 0 1) plane (Fig.2).

### S2. Experimental

(±)-2-Methylpiperazine (20 mmol) and 10% aqueous $HClO_4$ solution in a molar ratio of 1:1 were mixed and dissolved in 25 ml water. The mixture was heated to 343 K to form a clear solution. On slow cooling of the reaction mixture to room temperature, block crystals of the title compound were formed.

### S3. Refinement

All H atoms were placed in calculated positions, with C—H = 0.96–0.98Å and N—H = 0.90 Å, and refined using a riding model, with $U_{iso}$(H) = 1.2$U_{eq}$(C, N) or 1.5 $U_{eq}$(C) for methyl H atoms.

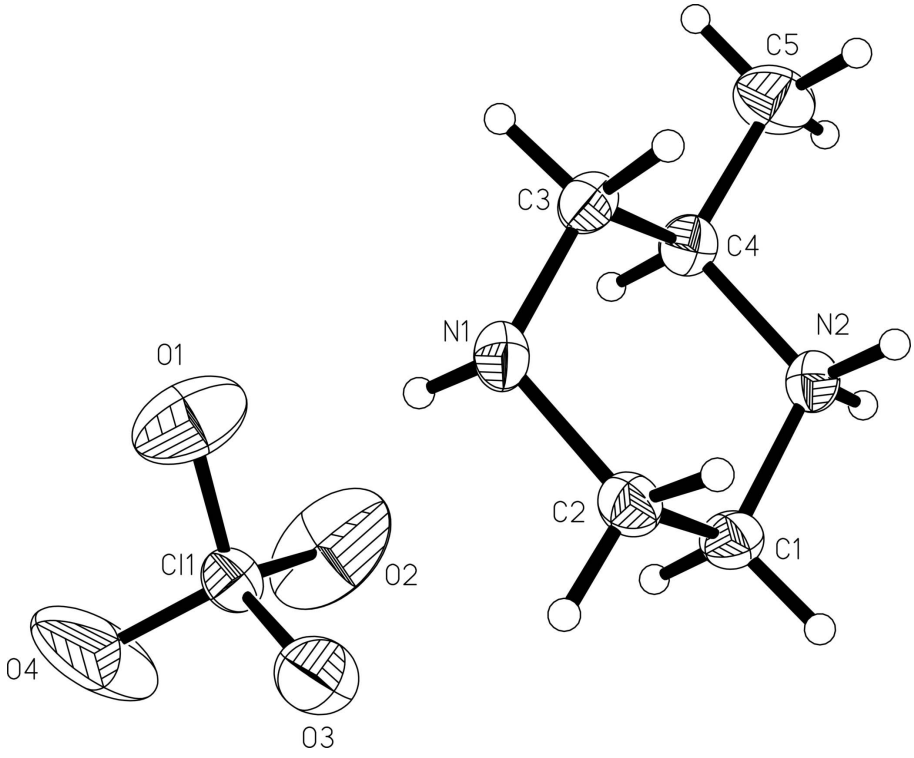


**Figure 1**

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

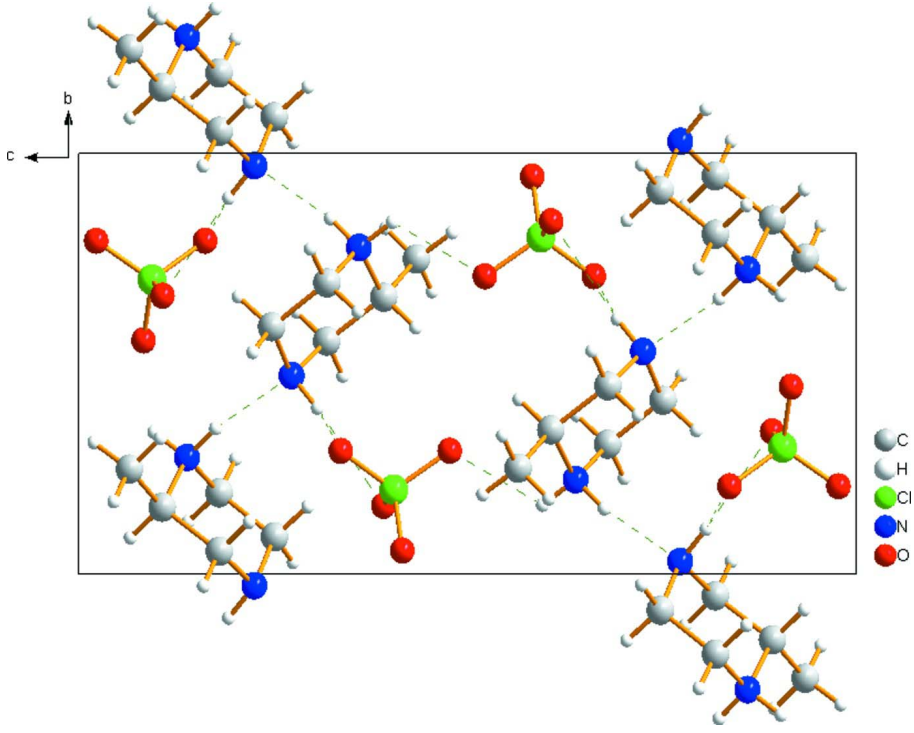

**Figure 2**

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

## (±)-2-Methylpiperazin-1-ium perchlorate

*Crystal data*

$C_5H_{13}N_2^+·ClO_4^-$
$M_r$ = 200.62
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
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$c$ = 16.2201 (11) Å
$\beta$ = 98.614 (3)°
$V$ = 899.25 (11) Å$^3$
$Z$ = 4
$F(000)$ = 424
$D_x$ = 1.482 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71075 Å
Cell parameters from 1541 reflections
$\theta$ = 3.1–27.5°
$\mu$ = 0.41 mm$^{-1}$
$T$ = 293 K
Block, colourless
0.30 × 0.25 × 0.20 mm

*Data collection*

Rigaku SCXmini diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.6612 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min}$ = 0.80, $T_{max}$ = 0.90
8953 measured reflections
2055 independent reflections
1541 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.040
$\theta_{max}$ = 27.5°, $\theta_{min}$ = 3.1°
$h$ = −8→8
$k$ = −10→10
$l$ = −21→20

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.075
$wR(F^2)$ = 0.224
$S$ = 1.05
2055 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
$w = 1/[\sigma^2(F_o^2) + (0.1123P)^2 + 1.4914P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.86 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.56 e Å$^{-3}$

*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$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.4992 (5) | 0.6921 (5) | 0.6807 (2) | 0.0414 (8) |

| | | | | |
|---|---|---|---|---|
| H1B | 0.5975 | 0.7730 | 0.7019 | 0.050* |
| H1A | 0.5525 | 0.6233 | 0.6407 | 0.050* |
| C2 | 0.4487 (5) | 0.5875 (5) | 0.7518 (2) | 0.0406 (8) |
| H2A | 0.5644 | 0.5267 | 0.7759 | 0.049* |
| H2B | 0.4118 | 0.6591 | 0.7947 | 0.049* |
| C3 | 0.1170 (5) | 0.5531 (5) | 0.6809 (2) | 0.0389 (8) |
| H3A | 0.0599 | 0.6227 | 0.7194 | 0.047* |
| H3B | 0.0205 | 0.4703 | 0.6603 | 0.047* |
| C4 | 0.1591 (5) | 0.6579 (5) | 0.6075 (2) | 0.0384 (8) |
| H4A | 0.2062 | 0.5856 | 0.5664 | 0.046* |
| C5 | −0.0190 (7) | 0.7490 (7) | 0.5654 (3) | 0.0646 (13) |
| H5A | 0.0152 | 0.8117 | 0.5196 | 0.097* |
| H5B | −0.0656 | 0.8218 | 0.6048 | 0.097* |
| H5C | −0.1201 | 0.6716 | 0.5452 | 0.097* |
| Cl1 | 0.56264 (14) | 0.19954 (12) | 0.59443 (6) | 0.0442 (4) |
| N1 | 0.2890 (5) | 0.4712 (4) | 0.7261 (2) | 0.0392 (7) |
| H1C | 0.3305 | 0.3941 | 0.6929 | 0.047* |
| N2 | 0.3194 (4) | 0.7764 (3) | 0.63945 (18) | 0.0352 (7) |
| H2D | 0.3494 | 0.8369 | 0.5966 | 0.042* |
| H2C | 0.2761 | 0.8453 | 0.6761 | 0.042* |
| O1 | 0.3667 (7) | 0.1613 (7) | 0.6079 (3) | 0.1041 (16) |
| O2 | 0.5363 (11) | 0.2923 (9) | 0.5226 (3) | 0.154 (3) |
| O3 | 0.6614 (5) | 0.2921 (5) | 0.6628 (2) | 0.0759 (11) |
| O4 | 0.6557 (9) | 0.0550 (9) | 0.5835 (6) | 0.215 (5) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0355 (18) | 0.044 (2) | 0.046 (2) | −0.0020 (15) | 0.0098 (15) | 0.0026 (16) |
| C2 | 0.0404 (19) | 0.0397 (19) | 0.0410 (19) | 0.0043 (15) | 0.0037 (15) | 0.0042 (15) |
| C3 | 0.0395 (19) | 0.0380 (18) | 0.0401 (18) | −0.0068 (15) | 0.0095 (15) | −0.0047 (15) |
| C4 | 0.043 (2) | 0.0402 (19) | 0.0315 (17) | −0.0016 (15) | 0.0028 (14) | −0.0028 (14) |
| C5 | 0.054 (3) | 0.079 (3) | 0.056 (3) | 0.010 (2) | −0.007 (2) | 0.004 (2) |
| Cl1 | 0.0500 (6) | 0.0457 (6) | 0.0378 (5) | 0.0080 (4) | 0.0094 (4) | −0.0044 (4) |
| N1 | 0.0481 (18) | 0.0298 (14) | 0.0415 (16) | 0.0004 (13) | 0.0130 (13) | 0.0016 (12) |
| N2 | 0.0422 (16) | 0.0319 (15) | 0.0329 (15) | −0.0012 (12) | 0.0103 (12) | 0.0013 (12) |
| O1 | 0.089 (3) | 0.149 (4) | 0.080 (3) | −0.040 (3) | 0.034 (2) | −0.028 (3) |
| O2 | 0.196 (7) | 0.199 (7) | 0.067 (3) | −0.086 (5) | 0.017 (3) | 0.048 (4) |
| O3 | 0.072 (2) | 0.076 (2) | 0.074 (2) | 0.0078 (18) | −0.0083 (19) | −0.0251 (19) |
| O4 | 0.132 (5) | 0.151 (5) | 0.318 (11) | 0.089 (4) | −0.105 (6) | −0.155 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—N2 | 1.485 (5) | C4—C5 | 1.507 (6) |
| C1—C2 | 1.514 (5) | C4—H4A | 0.9800 |
| C1—H1B | 0.9700 | C5—H5A | 0.9600 |
| C1—H1A | 0.9700 | C5—H5B | 0.9600 |
| C2—N1 | 1.465 (5) | C5—H5C | 0.9600 |

| | | | |
|---|---|---|---|
| C2—H2A | 0.9700 | Cl1—O4 | 1.363 (5) |
| C2—H2B | 0.9700 | Cl1—O2 | 1.377 (5) |
| C3—N1 | 1.459 (5) | Cl1—O3 | 1.426 (4) |
| C3—C4 | 1.526 (5) | Cl1—O1 | 1.436 (4) |
| C3—H3A | 0.9700 | N1—H1C | 0.8998 |
| C3—H3B | 0.9700 | N2—H2D | 0.9000 |
| C4—N2 | 1.500 (5) | N2—H2C | 0.9000 |

| | | | |
|---|---|---|---|
| N2—C1—C2 | 109.3 (3) | C3—C4—H4A | 108.5 |
| N2—C1—H1B | 109.8 | C4—C5—H5A | 109.5 |
| C2—C1—H1B | 109.8 | C4—C5—H5B | 109.5 |
| N2—C1—H1A | 109.8 | H5A—C5—H5B | 109.5 |
| C2—C1—H1A | 109.8 | C4—C5—H5C | 109.5 |
| H1B—C1—H1A | 108.3 | H5A—C5—H5C | 109.5 |
| N1—C2—C1 | 113.3 (3) | H5B—C5—H5C | 109.5 |
| N1—C2—H2A | 108.9 | O4—Cl1—O2 | 111.5 (6) |
| C1—C2—H2A | 108.9 | O4—Cl1—O3 | 112.1 (3) |
| N1—C2—H2B | 108.9 | O2—Cl1—O3 | 110.9 (3) |
| C1—C2—H2B | 108.9 | O4—Cl1—O1 | 107.8 (5) |
| H2A—C2—H2B | 107.7 | O2—Cl1—O1 | 103.9 (4) |
| N1—C3—C4 | 114.3 (3) | O3—Cl1—O1 | 110.3 (2) |
| N1—C3—H3A | 108.7 | C3—N1—C2 | 111.6 (3) |
| C4—C3—H3A | 108.7 | C3—N1—H1C | 109.0 |
| N1—C3—H3B | 108.7 | C2—N1—H1C | 109.1 |
| C4—C3—H3B | 108.7 | C1—N2—C4 | 112.5 (3) |
| H3A—C3—H3B | 107.6 | C1—N2—H2D | 109.1 |
| N2—C4—C5 | 110.5 (3) | C4—N2—H2D | 109.1 |
| N2—C4—C3 | 107.8 (3) | C1—N2—H2C | 109.1 |
| C5—C4—C3 | 113.0 (4) | C4—N2—H2C | 109.1 |
| N2—C4—H4A | 108.5 | H2D—N2—H2C | 107.8 |
| C5—C4—H4A | 108.5 | | |

| | | | |
|---|---|---|---|
| N2—C1—C2—N1 | 54.6 (4) | C1—C2—N1—C3 | −52.3 (4) |
| N1—C3—C4—N2 | −54.1 (4) | C2—C1—N2—C4 | −57.7 (4) |
| N1—C3—C4—C5 | −176.4 (3) | C5—C4—N2—C1 | −179.4 (3) |
| C4—C3—N1—C2 | 52.7 (4) | C3—C4—N2—C1 | 56.8 (4) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*C*···O1 | 0.90 | 2.38 | 3.258 (6) | 166 |
| N1—H1*C*···O3 | 0.90 | 2.54 | 3.250 (5) | 136 |
| N2—H2*D*···O2$^{i}$ | 0.90 | 2.43 | 2.998 (7) | 121 |
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Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+1/2, *y*+1/2, −*z*+3/2.