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Piperazine-1,4-dium bis(perchlorate) dihydrate

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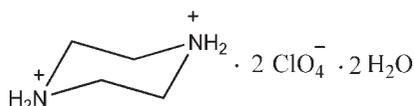
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.045; wR factor = 0.109; data-to-parameter ratio = 17.6.

The asymmetric unit of the title compound, $\text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot 2\text{ClO}_4^- \cdot 2\text{H}_2\text{O}$, contains half of a piperazinedium cation, one perchlorate anion and one water molecule. The diprotonated piperazine ring, which is completed by crystallographic inversion symmetry, adopts a chair conformation. In the crystal structure, the cations and anions are linked by intermolecular $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds into a three-dimensional network.

Related literature

For background to simple molecular-ionic crystals containing organic cations and acid radicals (1:1 molar ratio), see: Katrusiak & Szafranski (1999, 2006).



Experimental

Crystal data

$\text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot 2\text{ClO}_4^- \cdot 2\text{H}_2\text{O}$
 $M_r = 323.09$
Monoclinic, $P2_1/c$

$a = 7.2588$ (15) Å
 $b = 6.5089$ (13) Å
 $c = 14.543$ (4) Å

$\beta = 113.56$ (3)°
 $V = 629.8$ (3) Å³
 $Z = 2$
Mo $K\alpha$ radiation

$\mu = 0.56$ mm⁻¹
 $T = 293$ K
 $0.28 \times 0.26 \times 0.20$ mm

Data collection

Rigaku Mercury 2 diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku/MSC, 2005)
 $T_{\min} = 0.856$, $T_{\max} = 0.896$

6362 measured reflections
1458 independent reflections
1130 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.060$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.109$
 $S = 1.07$
1458 reflections

83 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.28$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.25$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N1}-\text{H1B} \cdots \text{O5}^{\text{i}}$	0.90	2.00	2.875 (3)	165
$\text{N1}-\text{H1A} \cdots \text{O5}^{\text{ii}}$	0.90	2.14	2.883 (3)	140
$\text{N1}-\text{H1A} \cdots \text{O3}^{\text{iii}}$	0.90	2.49	3.060 (3)	122
$\text{N1}-\text{H1A} \cdots \text{O2}^{\text{iv}}$	0.90	2.56	3.040 (3)	114
$\text{O5}-\text{H5WB} \cdots \text{O3}^{\text{v}}$	0.77	2.26	2.999 (3)	161
$\text{O5}-\text{H5WA} \cdots \text{O1}$	0.82	2.59	3.192 (3)	131
$\text{O5}-\text{H5WA} \cdots \text{O4}$	0.82	2.26	3.040 (3)	159

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

Data collection: *CrystalClear* (Rigaku/MSC, 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*.

This work was supported by a start-up grant from Anyang Institute of Technology.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2304).

References

Katrusiak, A. & Szafranski, M. (1999). *Phys. Rev. Lett.* **82**, 576–579.
Katrusiak, A. & Szafranski, M. (2006). *J. Am. Chem. Soc.* **128**, 15775–15785.
Rigaku/MS (2005). *CrystalClear*. Rigaku/MS, The Woodlands, Texas, USA
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supporting information

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Piperazine-1,4-dium bis(perchlorate) dihydrate

Cong-hu Peng

S1. Comment

Recently, much attention has been devoted to simple molecular–ionic crystals containing organic cations and acid radicals (1:1 molar ratio) due to the tunability of their special structural features and their interesting physical properties (Katrusiak & Szafranski, 1999; Katrusiak & Szafranski, 2006). In our laboratory, the title compound has been synthesized and its crystal structure is reported herein.

The asymmetric unit of the title compound consists of a half piperazine cation, one chlorate anion and one water molecule (Fig. 1). The diprotonated piperazine ring adopts a chair conformation. In the crystal structure, cations and anions are linked by intermolecular N—H⋯O and O—H⋯O hydrogen bonds into a three-dimensional network (Tab. 1 & Fig. 2).

S2. Experimental

Piperazine (1.7 g, 20 mmol) and 10% aqueous HClO₄ (25 ml) in a molar ratio of 1:1 were mixed and dissolved in 30 ml water by heating to 353 K forming a clear solution. The reaction mixture was cooled slowly to room temperature, block crystals of the title compound were formed after fifteen days.

S3. Refinement

The H atoms of piperzinium ion were placed in calculated positions, with C—H = 0.97 and N—H = 0.90 Å, and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C/N})$. The hydrogen atoms of the water molecule were located from a difference fourier map and were fixed at those positions with $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$.

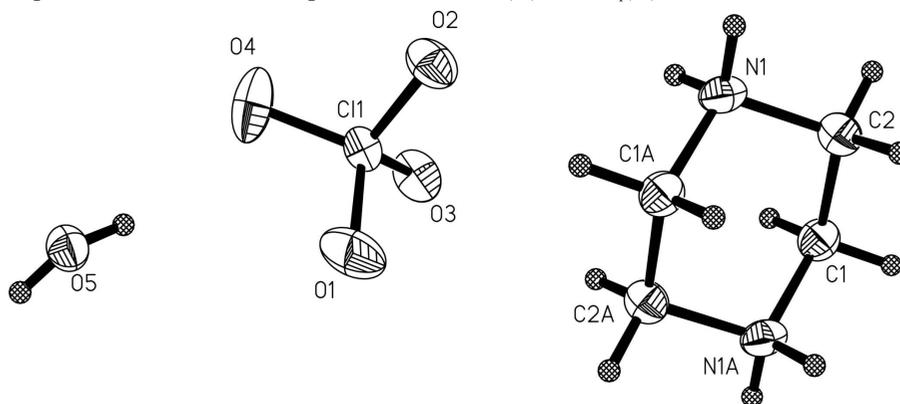


Figure 1

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

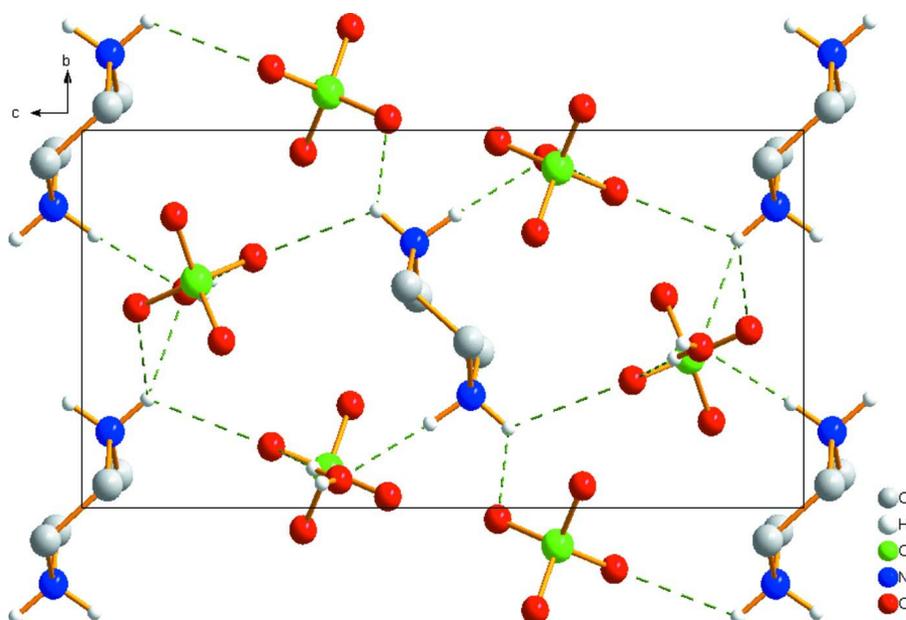


Figure 2

The unit cell packing of the title compound viewed along the a -axis; hydrogen bonds are drawn as dashed lines.

Piperazine-1,4-dium bis(perchlorate) dihydrate

Crystal data

$C_4H_{12}N_2^{2+} \cdot 2ClO_4^- \cdot 2H_2O$

$M_r = 323.09$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 7.2588 (15) \text{ \AA}$

$b = 6.5089 (13) \text{ \AA}$

$c = 14.543 (4) \text{ \AA}$

$\beta = 113.56 (3)^\circ$

$V = 629.8 (3) \text{ \AA}^3$

$Z = 2$

$F(000) = 336$

$D_x = 1.704 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1130 reflections

$\theta = 3.1\text{--}27.5^\circ$

$\mu = 0.56 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Block, colorless

$0.28 \times 0.26 \times 0.20 \text{ mm}$

Data collection

Rigaku Mercury 2
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: $13.6612 \text{ pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan

(*CrystalClear*; Rigaku/MSC, 2005)

$T_{\min} = 0.856$, $T_{\max} = 0.896$

6362 measured reflections

1458 independent reflections

1130 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.060$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.1^\circ$

$h = -9 \rightarrow 9$

$k = -8 \rightarrow 8$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.109$

$S = 1.07$

1458 reflections

83 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

$$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 0.361P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.044 (4)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.3021 (4)	1.0866 (4)	0.94987 (19)	0.0411 (6)
H1C	0.2516	1.0117	0.8870	0.049*
H1D	0.1989	1.1821	0.9491	0.049*
C2	0.3493 (4)	0.9393 (4)	1.03562 (19)	0.0426 (6)
H2B	0.3904	1.0149	1.0981	0.051*
H2A	0.2303	0.8603	1.0272	0.051*
C11	0.78737 (8)	0.59992 (10)	0.84112 (4)	0.0390 (2)
N1	0.5133 (3)	0.7985 (3)	1.03919 (15)	0.0401 (5)
H1B	0.4715	0.7234	0.9825	0.048*
H1A	0.5420	0.7115	1.0912	0.048*
O1	0.9198 (3)	0.7709 (4)	0.87194 (18)	0.0765 (7)
O2	0.7472 (3)	0.5298 (3)	0.92385 (14)	0.0561 (6)
O3	0.6016 (3)	0.6622 (3)	0.76257 (13)	0.0562 (6)
O4	0.8781 (4)	0.4421 (4)	0.80648 (18)	0.0853 (8)
O5	1.3089 (2)	0.5745 (3)	0.85594 (12)	0.0421 (5)
H5WB	1.3600	0.6040	0.8207	0.063*
H5WA	1.1857	0.5653	0.8324	0.063*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0416 (14)	0.0393 (14)	0.0403 (14)	0.0025 (11)	0.0140 (11)	0.0007 (11)
C2	0.0444 (14)	0.0446 (15)	0.0407 (14)	-0.0009 (12)	0.0189 (12)	0.0031 (11)
C11	0.0336 (3)	0.0498 (4)	0.0351 (3)	-0.0020 (3)	0.0152 (2)	-0.0022 (3)
N1	0.0538 (13)	0.0292 (10)	0.0348 (11)	-0.0025 (9)	0.0149 (9)	0.0020 (9)
O1	0.0532 (13)	0.0832 (17)	0.0868 (16)	-0.0303 (12)	0.0214 (12)	0.0037 (13)
O2	0.0542 (11)	0.0726 (14)	0.0442 (11)	-0.0003 (10)	0.0226 (9)	0.0140 (10)
O3	0.0415 (10)	0.0814 (15)	0.0391 (10)	0.0024 (10)	0.0091 (9)	0.0105 (10)
O4	0.0803 (16)	0.102 (2)	0.0775 (17)	0.0328 (15)	0.0362 (14)	-0.0225 (14)

O5 0.0373 (9) 0.0469 (11) 0.0433 (10) 0.0015 (8) 0.0174 (8) 0.0026 (8)

Geometric parameters (Å, °)

C1—N1 ⁱ	1.487 (3)	C11—O1	1.421 (2)
C1—C2	1.500 (3)	C11—O2	1.4218 (19)
C1—H1C	0.97	C11—O3	1.4339 (19)
C1—H1D	0.97	N1—C1 ⁱ	1.487 (3)
C2—N1	1.487 (3)	N1—H1B	0.90
C2—H2B	0.97	N1—H1A	0.90
C2—H2A	0.97	O5—H5WB	0.77
C11—O4	1.417 (2)	O5—H5WA	0.82
N1 ⁱ —C1—C2	109.6 (2)	O4—C11—O2	110.46 (15)
N1 ⁱ —C1—H1C	109.7	O1—C11—O2	109.05 (14)
C2—C1—H1C	109.7	O4—C11—O3	110.15 (14)
N1 ⁱ —C1—H1D	109.7	O1—C11—O3	109.38 (14)
C2—C1—H1D	109.7	O2—C11—O3	108.62 (12)
H1C—C1—H1D	108.2	C2—N1—C1 ⁱ	111.62 (19)
N1—C2—C1	109.7 (2)	C2—N1—H1B	109.3
N1—C2—H2B	109.7	C1 ⁱ —N1—H1B	109.3
C1—C2—H2B	109.7	C2—N1—H1A	109.3
N1—C2—H2A	109.7	C1 ⁱ —N1—H1A	109.3
C1—C2—H2A	109.7	H1B—N1—H1A	108.0
H2B—C2—H2A	108.2	H5WB—O5—H5WA	118.5
O4—C11—O1	109.16 (16)		

Symmetry code: (i) $-x+1, -y+2, -z+2$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1B \cdots O5 ⁱⁱ	0.90	2.00	2.875 (3)	165
N1—H1A \cdots O5 ⁱⁱⁱ	0.90	2.14	2.883 (3)	140
N1—H1A \cdots O3 ^{iv}	0.90	2.49	3.060 (3)	122
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