

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

1,4-Dimethylpiperazine-1,4-dium bis(hexafluorophosphate) dihydrate

Su-Wen Sun

College of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, People's Republic of China
Correspondence e-mail: sunsuwen_5127@163.com

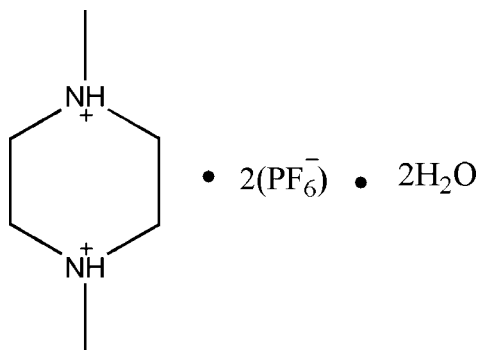
Received 29 March 2012; accepted 18 April 2012

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.068; wR factor = 0.163; data-to-parameter ratio = 15.2.

In the title hydrated molecular salt, $\text{C}_6\text{H}_{16}\text{N}_2^+ \cdot 2\text{PF}_6^- \cdot 2\text{H}_2\text{O}$, the complete 1,4-dimethylpiperazine-1,4-dium dication is generated by crystallographic inversion symmetry and both C—N bonds are in equatorial orientations. In the crystal, the components are linked by O—H...F and N—H...O hydrogen bonds but there are no direct links between cations and anions.

Related literature

For background to molecular ferroelectrics, see: Fu *et al.* (2009); Ye *et al.* (2006).



Experimental

Crystal data

 $\text{C}_6\text{H}_{16}\text{N}_2^+ \cdot 2\text{PF}_6^- \cdot 2\text{H}_2\text{O}$ $M_r = 442.18$

Monoclinic, $P2_1/n$
 $a = 8.1382$ (16) Å
 $b = 6.3666$ (13) Å
 $c = 15.758$ (3) Å
 $\beta = 99.55$ (3)°
 $V = 805.1$ (3) Å³

$Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.40$ mm⁻¹
 $T = 293$ K
 $0.30 \times 0.30 \times 0.20$ mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.489$, $T_{\max} = 1.000$

8084 measured reflections
1849 independent reflections
1093 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.079$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.163$
 $S = 1.06$
1849 reflections
122 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.37$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.36$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1}\cdots\text{F6}^{\text{i}}$	0.85 (1)	2.18 (2)	3.008 (5)	167 (5)
$\text{O1}-\text{H2}\cdots\text{F3}^{\text{ii}}$	0.84 (1)	2.42 (4)	2.923 (5)	119 (4)
$\text{N1}-\text{H3}\cdots\text{O1}^{\text{iii}}$	0.88 (4)	1.98 (4)	2.814 (4)	159 (4)

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

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*.

The author is grateful to the starter fund of Southeast University for financial support to buy the X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6717).

References

- Fu, D.-W., Ge, J.-Z., Dai, J., Ye, H.-Y. & Qu, Z.-R. (2009). *Inorg. Chem. Commun.* **12**, 994–997.
Rigaku (2005). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Ye, Q., Song, Y.-M., Wang, G.-X., Chen, K. & Fu, D.-W. (2006). *J. Am. Chem. Soc.* **128**, 6554–6555.

supporting information

Acta Cryst. (2012). E68, o1514 [doi:10.1107/S1600536812017229]

1,4-Dimethylpiperazine-1,4-dium bis(hexafluorophosphate) dihydrate

Su-Wen Sun

S1. Comment

Dielectric constant measurements of compounds as a function of temperature is the basic methods to find the materials which possess potential ferroelectric phase changes (Fu *et al.*,2009;Ye *et al.*,2006).The dielectric constant of the title compound has been measured, but showed no dielectric disuniformity in the range 120–385 K (mp. 393–402 K)

The asymmetric unit of the title compound is shown in Fig. 1. crystallized in the monoclinic P2(1)/n space group, The crystal packing Fig. 2 features O—H···F and N—H···O hydrogen bonds(O1—H1··· F6, O1—H2···F3, N1—H3···O1) between the C₆H₁₆N₂⁺ cations and PF₆⁻ anions and H₂O (see; Table 1).

S2. Experimental

1,4-Dimethyl-piperazine (0.57 g) and an excess of hexafluorophosphoric acid (0.95 g) were dissolved in methanol without any precipitation under stirring at the ambient temperature. Colourless blocks of the title compound were obtained by slow evaporation at room temperature over two days.

S3. Refinement

H atoms were placed in calculated positions (N—H = 0.89 Å; C—H = 0.96 Å and 0.97 Å for Csp³ atoms), assigned fixed U_{iso} values [1.5U_{eq}(Csp³,N)] and allowed to ride.The H1 and H2 on the O1 were restrained with O—H =0.85 Å yielding O1—H1 = 0.8448 Å and O1 —H2 = 0.8440 Å, with U_{iso}(H) = 1.2 U_{iso}(O)

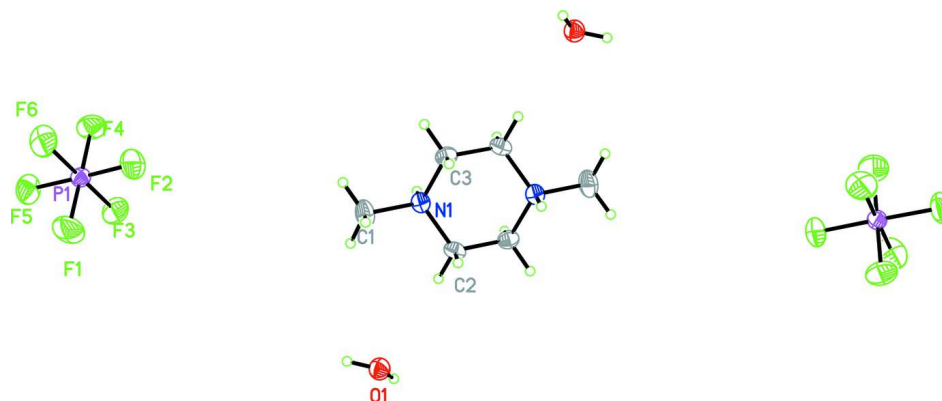


Figure 1

T The molecular structure of the title compound, showing the atomic numbering scheme with 30% probability displacement ellipsoids.

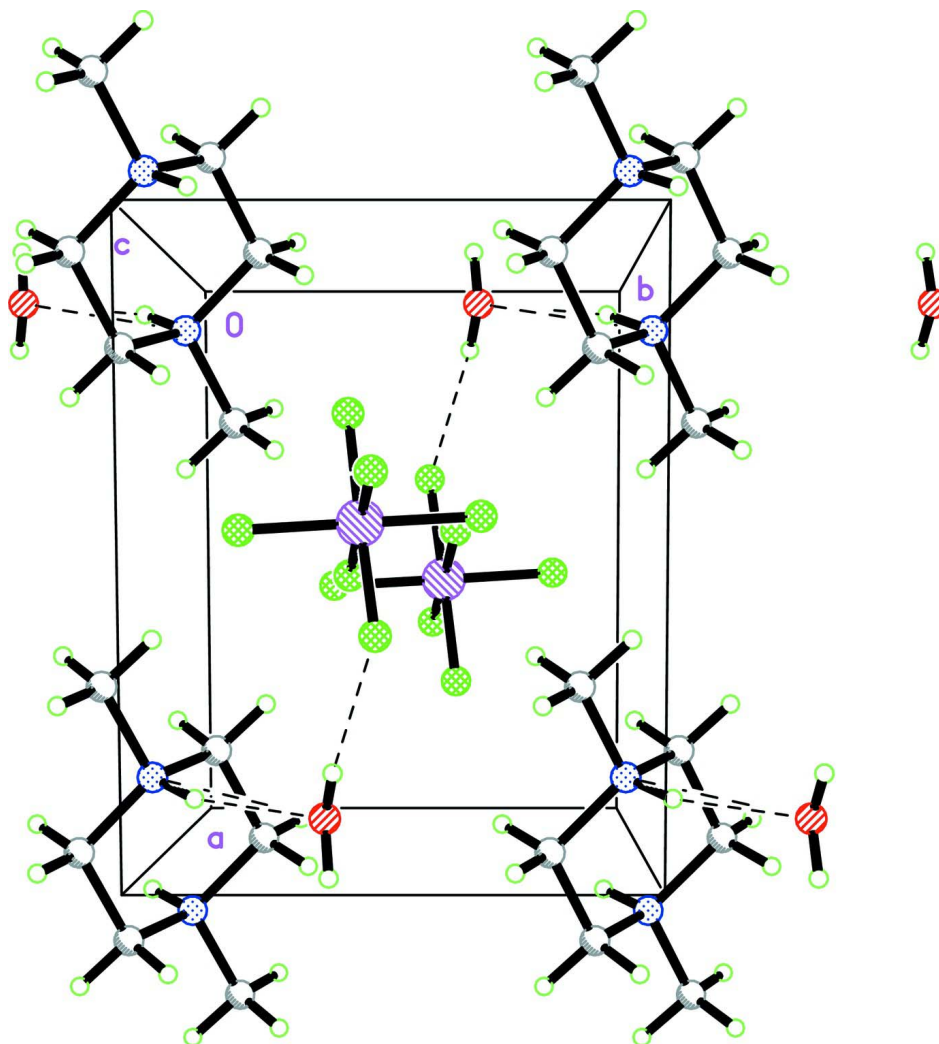


Figure 2

A view of the packing of the title compound, stacking along the *b* axis. Dashed lines indicate hydrogen bonds.

1,4-Dimethylpiperazine-1,4-dium bis(hexafluorophosphate) dihydrate

Crystal data

$C_6H_{16}N_2^+ \cdot 2PF_6^- \cdot 2H_2O$

$M_r = 442.18$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 8.1382\ (16)\ \text{\AA}$

$b = 6.3666\ (13)\ \text{\AA}$

$c = 15.758\ (3)\ \text{\AA}$

$\beta = 99.55\ (3)^\circ$

$V = 805.1\ (3)\ \text{\AA}^3$

$Z = 2$

$F(000) = 448$

$D_x = 1.824\ \text{Mg m}^{-3}$

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

$\theta = 3.0\text{--}27.5^\circ$

$\mu = 0.40\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colorless

$0.30 \times 0.30 \times 0.20\ \text{mm}$

Data collection

Rigaku Mercury CCD
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω scans
Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.489$, $T_{\max} = 1.000$

8084 measured reflections
1849 independent reflections
1093 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.079$
 $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.0^\circ$
 $h = -10 \rightarrow 10$
 $k = -8 \rightarrow 8$
 $l = -20 \rightarrow 20$

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.163$
 $S = 1.06$
1849 reflections
122 parameters
3 restraints
Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map
Hydrogen site location: inferred from
neighbouring sites
H atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 0.8793P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
P1	0.95245 (13)	0.08087 (17)	0.17417 (6)	0.0411 (3)
F2	0.8739 (4)	0.0534 (5)	0.25799 (19)	0.0871 (10)
F5	1.0375 (4)	0.1087 (5)	0.09153 (17)	0.0832 (10)
F3	0.7745 (3)	0.1086 (5)	0.1178 (2)	0.0921 (11)
F4	0.9416 (4)	-0.1629 (4)	0.1595 (2)	0.0809 (9)
F6	1.1318 (4)	0.0484 (6)	0.22919 (18)	0.0884 (11)
F1	0.9643 (5)	0.3248 (5)	0.1878 (2)	0.1043 (13)
N1	0.1232 (4)	0.0309 (5)	0.4452 (2)	0.0373 (8)
C3	0.1606 (5)	-0.0920 (6)	0.5267 (2)	0.0430 (10)
H3A	0.2412	-0.2008	0.5206	0.052*
H3B	0.2089	0.0001	0.5733	0.052*
C2	-0.0059 (5)	0.1900 (6)	0.4520 (2)	0.0418 (10)
H2A	-0.0324	0.2650	0.3979	0.050*
H2B	0.0370	0.2908	0.4963	0.050*
C1	0.2776 (5)	0.1300 (7)	0.4226 (3)	0.0585 (13)

H1A	0.2493	0.2095	0.3704	0.088*
H1B	0.3561	0.0223	0.4144	0.088*
H1C	0.3262	0.2215	0.4683	0.088*
O1	0.0661 (4)	0.6583 (5)	0.34880 (19)	0.0503 (8)
H1	0.144 (4)	0.639 (9)	0.320 (3)	0.09 (2)*
H2	-0.027 (3)	0.648 (9)	0.317 (3)	0.11 (2)*
H3	0.092 (5)	-0.064 (7)	0.406 (3)	0.050 (12)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0418 (6)	0.0436 (6)	0.0374 (6)	0.0029 (5)	0.0049 (4)	0.0021 (5)
F2	0.106 (3)	0.100 (2)	0.0671 (19)	0.0070 (19)	0.0484 (18)	0.0093 (17)
F5	0.081 (2)	0.123 (3)	0.0512 (17)	0.0102 (18)	0.0271 (15)	0.0156 (16)
F3	0.0463 (17)	0.120 (3)	0.102 (2)	0.0144 (17)	-0.0091 (16)	0.036 (2)
F4	0.091 (2)	0.0488 (17)	0.100 (2)	0.0019 (15)	0.0079 (18)	-0.0138 (15)
F6	0.0546 (18)	0.129 (3)	0.0720 (19)	-0.0122 (17)	-0.0164 (15)	0.0205 (19)
F1	0.141 (3)	0.0461 (19)	0.135 (3)	-0.0075 (18)	0.052 (3)	-0.0085 (18)
N1	0.0398 (19)	0.0371 (19)	0.0347 (18)	-0.0072 (14)	0.0053 (14)	-0.0064 (15)
C3	0.042 (2)	0.043 (2)	0.042 (2)	0.0057 (18)	-0.0009 (17)	0.0016 (18)
C2	0.055 (3)	0.034 (2)	0.036 (2)	0.0004 (18)	0.0031 (18)	0.0050 (17)
C1	0.054 (3)	0.065 (3)	0.060 (3)	-0.023 (2)	0.021 (2)	-0.009 (2)
O1	0.052 (2)	0.0492 (19)	0.0513 (18)	-0.0009 (15)	0.0137 (17)	-0.0023 (14)

Geometric parameters (Å, °)

P1—F2	1.569 (3)	C3—H3A	0.9700
P1—F4	1.570 (3)	C3—H3B	0.9700
P1—F1	1.569 (3)	C2—C3 ⁱ	1.492 (6)
P1—F3	1.578 (3)	C2—H2A	0.9700
P1—F5	1.583 (3)	C2—H2B	0.9700
P1—F6	1.583 (3)	C1—H1A	0.9600
N1—C2	1.476 (5)	C1—H1B	0.9600
N1—C3	1.491 (5)	C1—H1C	0.9600
N1—C1	1.501 (5)	O1—H1	0.845 (10)
N1—H3	0.88 (4)	O1—H2	0.844 (10)
C3—C2 ⁱ	1.492 (6)		
F2—P1—F4	89.64 (18)	C1—N1—H3	106 (3)
F2—P1—F1	91.11 (18)	C2 ⁱ —C3—N1	110.7 (3)
F4—P1—F1	179.25 (19)	C2 ⁱ —C3—H3A	109.5
F2—P1—F3	91.30 (19)	N1—C3—H3A	109.5
F4—P1—F3	90.21 (18)	C2 ⁱ —C3—H3B	109.5
F1—P1—F3	89.8 (2)	N1—C3—H3B	109.5
F2—P1—F5	178.11 (18)	H3A—C3—H3B	108.1
F4—P1—F5	90.61 (18)	N1—C2—C3 ⁱ	111.5 (3)
F1—P1—F5	88.65 (19)	N1—C2—H2A	109.3
F3—P1—F5	90.57 (17)	C3 ⁱ —C2—H2A	109.3

F2—P1—F6	89.52 (18)	N1—C2—H2B	109.3
F4—P1—F6	88.61 (18)	C3 ⁱ —C2—H2B	109.3
F1—P1—F6	91.4 (2)	H2A—C2—H2B	108.0
F3—P1—F6	178.6 (2)	N1—C1—H1A	109.5
F5—P1—F6	88.61 (17)	N1—C1—H1B	109.5
C2—N1—C3	110.1 (3)	H1A—C1—H1B	109.5
C2—N1—C1	111.3 (3)	N1—C1—H1C	109.5
C3—N1—C1	111.5 (3)	H1A—C1—H1C	109.5
C2—N1—H3	113 (3)	H1B—C1—H1C	109.5
C3—N1—H3	104 (3)	H1—O1—H2	110 (2)

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H1...F6 ⁱⁱ	0.85 (1)	2.18 (2)	3.008 (5)	167 (5)
O1—H2...F3 ⁱⁱⁱ	0.84 (1)	2.42 (4)	2.923 (5)	119 (4)
N1—H3...O1 ^{iv}	0.88 (4)	1.98 (4)	2.814 (4)	159 (4)

Symmetry codes: (ii) $-x+3/2, y+1/2, -z+1/2$; (iii) $-x+1/2, y+1/2, -z+1/2$; (iv) $x, y-1, z$.