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1,1′-(Hexane-1,6-diyl)dipyridinium bis(hexafluorophosphate)

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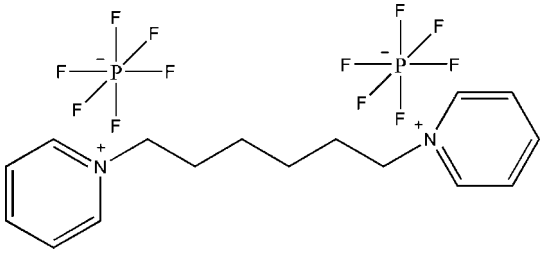
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.007 Å; disorder in solvent or counterion; R factor = 0.065; wR factor = 0.166; data-to-parameter ratio = 10.1.

The asymmetric unit of the title compound, $C_{16}H_{22}N_2^{2+}\cdot 2PF_6^-$, contains one half-molecule and a hexafluorophosphate anion. In the crystal structure, intermolecular C—H···F hydrogen bonds link the molecules. The F atoms in the hexafluorophosphate anion are disordered over two positions and were refined with occupancies of 0.43 (2) and 0.57 (2).

Related literature

For general background, see: Jared *et al.* (2005). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_{16}H_{22}N_2^{2+}\cdot 2PF_6^-$
M_r = 532.30 (3)
Triclinic, $P\overline{1}$
a = 7.9140 (16) Å
b = 9.2930 (18) Å
c = 9.4870 (19) Å
α = 65.13 (3)°
β = 65.46 (3)°
γ = 74.37 (3)°
V = 572.0 (3) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.29 mm^{-1}
T = 298 (2) K
0.30 × 0.30 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.917, T_{max} = 0.944
2172 measured reflections
2014 independent reflections
1499 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.166
S = 1.00
2014 reflections
200 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···F4′^{i}	0.93	2.48	3.333 (17)	153
C2—H2A···F2′^{ii}	0.93	2.53	3.267 (18)	137
C3—H3A···F3′^{ii}	0.93	2.47	3.257 (15)	142
C4—H4A···F1′^{iii}	0.93	2.52	3.287 (14)	140

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); 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*.

The authors thank Professor Hua-qin Wang of the Analysis Centre, Nanjing University, for carrying out the X-ray crystallographic analysis.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2581).

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supplementary materials

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1,1'-(Hexane-1,6-diyl)dipyridinium bis(hexafluorophosphate)

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Comment

The title compound is a dicationic ionic liquid, which has high thermal stability. Applications of the dicationic ionic liquid are found in biochemistry as well as many areas of chemistry (Jared *et al.*, 2005). We report herein the crystal structure of the title compound.

The asymmetric unit of the title compound (Fig. 1) contains one-half molecule and a hexafluorophosphate molecule, where the bond lengths (Allen *et al.*, 1987) and angles are within normal ranges.

In the crystal structure, intermolecular C-H···F hydrogen bonds (Table 1) link the molecules (Fig. 2), in which they may be effective in the stabilization of the structure.

Experimental

For the preparation of the title compound, 1,6-dibromide hexane (12.2 g, 0.05 mol) was added to acetonitrile solution (50 ml) of dehydrate pyridine (7.91 g, 0.10 mol) at 353 K. After stirring for 24 h, the mixture was cooled to room temperature and filtered. The solid was washed with ethyl acetate and dried. Then, the solid (2.01 g, 5 mmol) was dissolved in distilled water (50 ml) and potassium hexafluorophosphate (1.84 g, 10 mmol) was added. After stirring at room temperature for 3 h, the colorless solid formed was collected by filtration, washed with distilled water (50 ml) and dried. The product was purified by repeated crystallization. Crystals suitable for X-ray analysis were obtained by slow evaporation of acetone (yield; 3.08 g, 80%, m.p. 513 K).

Refinement

The F1, F2, F3, F4, F5 and F6 atoms in hexafluorophosphate were disordered over two positions. During the refinement process the disordered atoms were refined with occupancies of 0.43 (2) for F1, F2, F3, F4, F5 , F6 and 0.57 (2) for F1', F2', F3', F4', F5', F6', respectively. H atoms were positioned geometrically, with C-H = 0.93 and 0.97 Å for aromatic and methylene H, respectively, and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

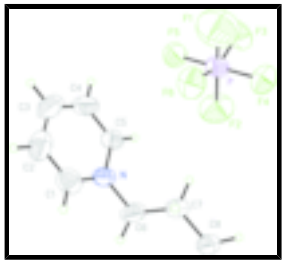

Fig. 1. The asymmetric unit of the title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

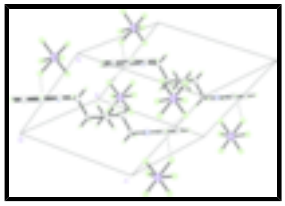

Fig. 2. A partial packing diagram of the title compound. Hydrogen bonds are shown as dashed lines.

1,1'-(Hexane-1,6-diyl)dipyridinium bis(hexafluorophosphate)

Crystal data

$C_{16}H_{22}N_2^{2+}\cdot 2P_1F_6^-$	$Z = 1$
$M_r = 532.30$ (3)	$F_{000} = 270$
Triclinic, $P\overline{1}$	$D_x = 1.545$ Mg m^{-3}
Hall symbol: -P 1	Melting point: 513 K
$a = 7.9140$ (16) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 9.2930$ (18) Å	Cell parameters from 25 reflections
$c = 9.4870$ (19) Å	$\theta = 10$–12^o
$\alpha = 65.13$ (3)°	$\mu = 0.29$ mm^{-1}
$\beta = 65.46$ (3)°	$T = 298$ (2) K
$\gamma = 74.37$ (3)°	Block, colorless
$V = 572.0$ (3) Å^3	0.30 × 0.30 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.047$
Radiation source: fine-focus sealed tube	$\theta_{max} = 25.1^o$
Monochromator: graphite	$\theta_{min} = 2.4^o$
$T = 298$(2) K	$h = -8\rightarrow 9$
$\omega/2\theta$ scans	$k = -9\rightarrow 10$
Absorption correction: ψ scan (North *et al.*, 1968)	$l = 0\rightarrow 11$
$T_{min} = 0.917$, $T_{max} = 0.944$	3 standard reflections
2172 measured reflections	every 120 min
2014 independent reflections	intensity decay: none
1499 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.065$	H-atom parameters constrained
$wR(F^2) = 0.166$	$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 0.95P]$ where $P = (F_o^2 + 2F_c^2)/3$

S = 1.01	$(\Delta/\sigma)_{max} < 0.001$
2014 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
200 parameters	$\Delta\rho_{min} = -0.38$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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}	Occ. (<1)
P	0.16995 (14)	0.79005 (13)	0.78487 (13)	0.0539 (4)	
N	0.6355 (4)	0.7536 (4)	0.2462 (4)	0.0472 (8)	
F1	−0.006 (3)	0.696 (3)	0.842 (2)	0.156 (6)	0.43 (2)
F2	0.369 (2)	0.8457 (19)	0.721 (2)	0.104 (5)	0.43 (2)
F3	0.034 (2)	0.8894 (16)	0.8982 (15)	0.091 (4)	0.43 (2)
F4	0.215 (2)	0.645 (2)	0.939 (2)	0.076 (4)	0.43 (2)
F5	0.126 (2)	0.936 (2)	0.635 (2)	0.078 (4)	0.43 (2)
F6	0.223 (3)	0.677 (3)	0.684 (2)	0.076 (4)	0.43 (2)
F1'	−0.0338 (9)	0.7809 (16)	0.8155 (14)	0.118 (4)	0.57 (2)
F2'	0.375 (2)	0.785 (2)	0.775 (2)	0.144 (5)	0.57 (2)
F3'	0.127 (2)	0.9036 (12)	0.8910 (13)	0.098 (3)	0.57 (2)
F4'	0.150 (2)	0.6338 (18)	0.9501 (17)	0.090 (4)	0.57 (2)
F5'	0.195 (2)	0.9495 (17)	0.6211 (17)	0.094 (4)	0.57 (2)
F6'	0.2820 (19)	0.6854 (19)	0.6687 (18)	0.082 (4)	0.57 (2)
C1	0.6255 (6)	0.6893 (5)	0.1468 (5)	0.0607 (11)	
H1A	0.7227	0.6159	0.1113	0.073*	
C2	0.4732 (7)	0.7312 (6)	0.0972 (6)	0.0735 (13)	
H2A	0.4661	0.6866	0.0288	0.088*	
C3	0.3292 (6)	0.8420 (6)	0.1517 (6)	0.0751 (14)	
H3A	0.2260	0.8736	0.1179	0.090*	
C4	0.3402 (6)	0.9030 (6)	0.2537 (6)	0.0721 (13)	
H4A	0.2428	0.9751	0.2913	0.087*	
C5	0.4934 (5)	0.8603 (5)	0.3029 (5)	0.0543 (10)	
H5A	0.5003	0.9029	0.3730	0.065*	
C6	0.7977 (5)	0.7070 (5)	0.3014 (5)	0.0580 (10)	
H6A	0.8387	0.8022	0.2896	0.070*	
H6B	0.8998	0.6558	0.2307	0.070*	

C7	0.7536 (5)	0.5942 (5)	0.4801 (5)	0.0563 (10)
H7A	0.7184	0.4969	0.4908	0.068*
H7B	0.6475	0.6434	0.5502	0.068*
C8	0.9189 (5)	0.5519 (5)	0.5406 (5)	0.0602 (11)
H8A	0.9628	0.6498	0.5183	0.072*
H8B	0.8761	0.4963	0.6595	0.072*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P	0.0470 (6)	0.0550 (6)	0.0538 (6)	0.0051 (4)	−0.0114 (5)	−0.0263 (5)
N	0.0332 (15)	0.0466 (17)	0.0475 (17)	−0.0002 (13)	−0.0093 (13)	−0.0107 (14)
F1	0.136 (9)	0.160 (11)	0.165 (9)	−0.050 (8)	−0.033 (7)	−0.049 (8)
F2	0.082 (6)	0.104 (7)	0.133 (9)	−0.045 (5)	−0.035 (6)	−0.030 (6)
F3	0.101 (8)	0.077 (5)	0.074 (5)	0.016 (5)	−0.007 (5)	−0.048 (4)
F4	0.085 (8)	0.067 (5)	0.077 (7)	−0.003 (6)	−0.043 (6)	−0.016 (4)
F5	0.070 (6)	0.080 (7)	0.059 (5)	0.015 (5)	−0.024 (5)	−0.015 (4)
F6	0.097 (9)	0.078 (5)	0.083 (8)	−0.014 (6)	−0.038 (7)	−0.046 (5)
F1'	0.041 (3)	0.113 (7)	0.173 (7)	−0.002 (3)	−0.039 (3)	−0.027 (5)
F2'	0.118 (6)	0.180 (10)	0.147 (8)	−0.033 (7)	−0.069 (6)	−0.036 (7)
F3'	0.126 (7)	0.088 (4)	0.086 (4)	0.000 (5)	−0.021 (5)	−0.058 (3)
F4'	0.090 (7)	0.068 (4)	0.074 (4)	0.010 (5)	−0.009 (5)	−0.022 (3)
F5'	0.124 (8)	0.077 (4)	0.069 (4)	−0.014 (6)	−0.023 (6)	−0.023 (3)
F6'	0.074 (6)	0.078 (5)	0.075 (4)	0.002 (4)	0.003 (4)	−0.043 (3)
C1	0.064 (3)	0.052 (2)	0.057 (2)	0.0000 (19)	−0.015 (2)	−0.022 (2)
C2	0.084 (3)	0.086 (3)	0.066 (3)	−0.017 (3)	−0.040 (3)	−0.023 (3)
C3	0.051 (3)	0.095 (4)	0.066 (3)	−0.015 (2)	−0.031 (2)	−0.002 (3)
C4	0.042 (2)	0.083 (3)	0.066 (3)	0.014 (2)	−0.014 (2)	−0.021 (2)
C5	0.050 (2)	0.056 (2)	0.053 (2)	0.0118 (18)	−0.0171 (18)	−0.0268 (19)
C6	0.0340 (19)	0.066 (3)	0.066 (3)	−0.0019 (17)	−0.0187 (18)	−0.017 (2)
C7	0.0339 (19)	0.074 (3)	0.057 (2)	0.0055 (18)	−0.0156 (17)	−0.027 (2)
C8	0.044 (2)	0.082 (3)	0.060 (2)	0.009 (2)	−0.0230 (19)	−0.035 (2)

Geometric parameters (Å, °)

P—F1'	1.535 (7)	C3—C4	1.350 (7)
P—F6	1.567 (19)	C3—H3A	0.9300
P—F2'	1.575 (15)	C4—C5	1.379 (6)
P—F3	1.582 (11)	C4—H4A	0.9300
P—F2	1.583 (14)	C5—N	1.372 (5)
P—F5	1.588 (16)	C5—H5A	0.9300
P—F6'	1.604 (14)	N—C6	1.476 (5)
P—F4'	1.611 (14)	C6—C7	1.518 (6)
P—F4	1.612 (18)	C6—H6A	0.9700
P—F5'	1.617 (14)	C6—H6B	0.9700
P—F1	1.619 (15)	C7—C8	1.534 (5)
P—F3'	1.631 (9)	C7—H7A	0.9700
C1—N	1.347 (5)	C7—H7B	0.9700

C1—C2	1.375 (6)	C8—C8^{i}	1.518 (7)
C1—H1A	0.9300	C8—H8A	0.9700
C2—C3	1.397 (7)	C8—H8B	0.9700
C2—H2A	0.9300		
F1'—P—F6	85.7 (10)	F4—P—F1	83.6 (8)
F1'—P—F2'	173.4 (6)	F5'—P—F1	116.5 (8)
F6—P—F2'	95.7 (10)	F1'—P—F3'	97.5 (6)
F1'—P—F3	70.4 (7)	F6—P—F3'	176.5 (11)
F6—P—F3	156.1 (13)	F2'—P—F3'	80.9 (7)
F2'—P—F3	107.8 (9)	F2—P—F3'	78.8 (9)
F1'—P—F2	164.7 (6)	F5—P—F3'	92.5 (8)
F6—P—F2	98.4 (9)	F6'—P—F3'	160.7 (10)
F3—P—F2	105.1 (10)	F4'—P—F3'	90.4 (7)
F1'—P—F5	76.2 (6)	F4—P—F3'	86.1 (8)
F6—P—F5	89.5 (10)	F5'—P—F3'	88.0 (6)
F2'—P—F5	110.2 (6)	F1—P—F3'	112.6 (7)
F3—P—F5	86.5 (8)	N—C1—C2	120.6 (4)
F2—P—F5	89.1 (7)	N—C1—H1A	119.7
F1'—P—F6'	101.7 (9)	C2—C1—H1A	119.7
F2'—P—F6'	80.1 (9)	C1—C2—C3	118.7 (4)
F3—P—F6'	172.1 (12)	C1—C2—H2A	120.7
F2—P—F6'	82.4 (8)	C3—C2—H2A	120.7
F5—P—F6'	91.2 (9)	C4—C3—C2	119.8 (4)
F1'—P—F4'	86.0 (5)	C4—C3—H3A	120.1
F6—P—F4'	88.5 (9)	C2—C3—H3A	120.1
F2'—P—F4'	87.5 (6)	C3—C4—C5	121.1 (4)
F3—P—F4'	88.2 (7)	C3—C4—H4A	119.4
F2—P—F4'	108.7 (6)	C5—C4—H4A	119.4
F5—P—F4'	162.2 (6)	N—C5—C4	118.6 (4)
F6'—P—F4'	91.8 (7)	N—C5—H5A	120.7
F1'—P—F4	104.3 (6)	C4—C5—H5A	120.7
F6—P—F4	91.8 (10)	C1—N—C5	121.2 (3)
F2'—P—F4	69.2 (7)	C1—N—C6	120.7 (3)
F3—P—F4	92.5 (9)	C5—N—C6	118.1 (3)
F2—P—F4	90.3 (7)	N—C6—C7	112.5 (3)
F5—P—F4	178.6 (11)	N—C6—H6A	109.1
F6'—P—F4	90.0 (9)	C7—C6—H6A	109.1
F1'—P—F5'	95.7 (6)	N—C6—H6B	109.1
F6—P—F5'	93.0 (9)	C7—C6—H6B	109.1
F2'—P—F5'	90.7 (6)	H6A—C6—H6B	107.8
F3—P—F5'	91.0 (7)	C6—C7—C8	112.7 (3)
F2—P—F5'	69.5 (6)	C6—C7—H7A	109.0
F6'—P—F5'	89.2 (8)	C8—C7—H7A	109.0
F4'—P—F5'	177.8 (7)	C6—C7—H7B	109.0
F4—P—F5'	159.8 (6)	C8—C7—H7B	109.0
F6—P—F1	69.9 (12)	H7A—C7—H7B	107.8
F2'—P—F1	149.1 (8)	C8^{i}—C8—C7	113.4 (4)
F3—P—F1	87.2 (7)	C8^{i}—C8—H8A	108.9

F2—P—F1	166.6 (10)	C7—C8—H8A	108.9
F5—P—F1	97.2 (9)	C8^{i}—C8—H8B	108.9
F6'—P—F1	85.7 (11)	C7—C8—H8B	108.9
F4'—P—F1	65.6 (7)	H8A—C8—H8B	107.7

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1A···F4'^{ii}	0.93	2.48	3.333 (17)	153
C2—H2A···F2'^{iii}	0.93	2.53	3.267 (18)	137
C3—H3A···F3'^{iii}	0.93	2.47	3.257 (15)	142
C4—H4A···F1'^{iv}	0.93	2.52	3.287 (14)	140

Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*+1; (iii) *x*, *y*, *z*−1; (iv) −*x*, −*y*+2, −*z*+1.

Fig. 1

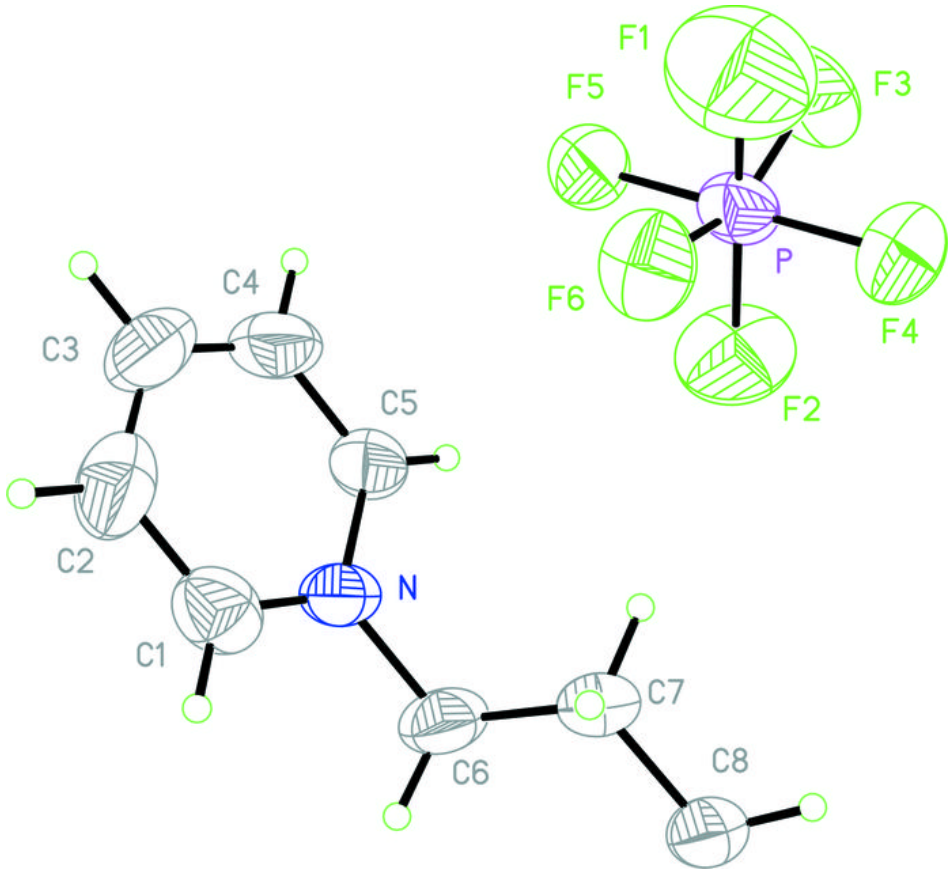

Fig. 2