1,1'-Dimethyl-4,4'-bipyridinium bis(tetrafluoridoborate)

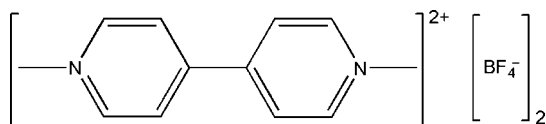## Fan Yang,[a] Jian-Cheng Deng,[a]* Zhi-Gang Li[b] and Jing-Wei Xu[b]‡

[a]The College of Chemistry, Xiangtan University, Hunan 411105, People's Republic of China, and [b]National Analytical Research Center of Electrochemistry and Spectroscopy, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

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In the title compound, $C_{12}H_{14}N_2{}^{2+} \cdot 2BF_4{}^-$, the cation has a centre of symmetry at the mid-point of the central C—C bond. π–π interactions, with a shortest atom-to-atom distance of 3.757 (4) Å, extend the crystal structure into a one-dimensional supramolecular chain.

Related literature

For related literature, see: Dou *et al.* (2007).

Experimental

Crystal data

$C_{12}H_{14}N_2{}^{2+} \cdot 2BF_4{}^-$	V = 762.9 (5) Å^3
M_r = 359.87	Z = 2
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 5.824 (2) Å	μ = 0.16 mm^{-1}
b = 8.849 (3) Å	T = 293 (2) K
c = 14.855 (6) Å	$0.26 \times 0.12 \times 0.07$ mm
β = 94.825 (5)°	

Data collection

Bruker APEX CCD area-detector diffractometer	3923 measured reflections
Absorption correction: multi-scan (*SAINT-Plus*; Bruker, 2003)	1508 independent reflections
	843 reflections with $I > 2\sigma(I)$
T_{min} = 0.960, T_{max} = 0.988	R_{int} = 0.029

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.082	110 parameters
$wR(F^2)$ = 0.249	H-atom parameters constrained
S = 1.02	$\Delta\rho_{max}$ = 0.35 e Å^{-3}
1508 reflections	$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

References

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Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

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supplementary materials

1,1'-Dimethyl-4,4'-bipyridinium bis(tetrafluoridoborate)

F. Yang, J.-C. Deng, Z.-G. Li and J.-W. Xu

Comment

Dou *et al.* have reported a structure, synthesized by *in situ* reaction under hydrothermal conditions, in which pyridine nitrogen atoms are covalently bonded to methyl groups and the counterion are ClO_4^- anions (Dou *et al.*, 2007). Here we report the structure of the title compound, which is essentially isomorphous with the perchlorate compound.

The title compound, shown in Fig. 1, consists of 1,1'-dimethyl-4,4'-bipyridinium cations and tetrafluoroborate anions. There is a centre of symmetry at the mid-point of the C—C bond linking the two pyridine rings. The two pyridine rings are exactly parallel by symmetry, and essentially coplanar.

In the crystal structure, there are π···π interactions between pyridine rings at (x, y, z) and $(1 - x, 1 - y, -z)$, with the shortest atom-to-atom distance of 3.757 (4) Å, which leads to a one-dimensional supramolecular chain running in the c-direction. (Fig. 2).

Experimental

Compound (I) was solvothermally prepared from a reaction mixture of $Cu(BF_4)_2$ (0.2 mmol), 4,4'-bipyridine (0.1 mmol), methanol (3 ml) and distilled water (8 ml) in a molar ratio of 2:1:740:4444; the pH value was adjusted to 4.6 with trimethyl-amine and acetic acid. The mixture was stirred for 20 min at room temperature and then sealed in a Teflon-lined stainless steel autoclave with a 23 ml capacity at 423 K for 72 h. After cooling to room temperature, colourless block-shaped crystals were obtained; these were washed with deionized water, filtered, and dried in air (yield 54% based on Cu).

Refinement

H atoms were placed geometrically and included in the refinement with fixed individual displacement parameters [U_{iso}(H) = $1.2U_{eq}$(C,N)], using a riding model, with C—H distances of 0.93 Å for sp^2 C and 0.96 Å for methyl C.
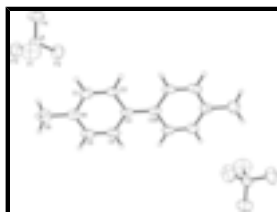
Figures

Fig. 1. A view of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (A) −x, 1 − y, −z].
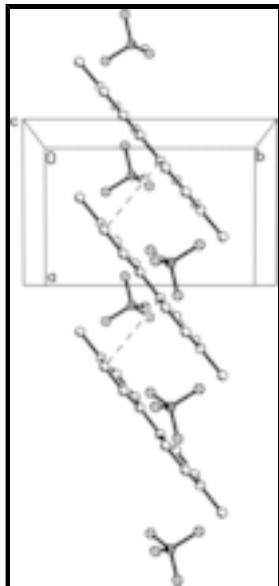
Fig. 2. Perspective view along the *c* axis of the packing of the title compound. For the sake of clarity, H atoms have been omitted. Dashed lines indicated π···π interactions.

1,1'-Dimethyl-4,4'-bipyridinium bis(tetrafluoroborate)

Crystal data

$C_{12}H_{14}N_2{}^{2+}·2BF_4{}^-$	$F_{000} = 364$
$M_r = 359.87$	$D_x = 1.567$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 852 reflections
$a = 5.824$ (2) Å	$\theta = 2.7–21.8º$
$b = 8.849$ (3) Å	$\mu = 0.16$ mm^{-1}
$c = 14.855$ (6) Å	$T = 293$ (2) K
$\beta = 94.825$ (5)º	Block, white
$V = 762.9$ (5) Å^3	$0.26 \times 0.12 \times 0.07$ mm
$Z = 2$	

Data collection

Bruker APEX CCD area-detector diffractometer	1508 independent reflections
Radiation source: fine-focus sealed tube	843 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.029$
$T = 293(2)$ K	$\theta_{max} = 26.1º$
φ and ω scans	$\theta_{min} = 2.7º$
Absorption correction: multi-scan (SAINT-Plus; Bruker, 2003)	$h = -7 \rightarrow 7$
$T_{min} = 0.960$, $T_{max} = 0.988$	$k = -7 \rightarrow 10$
3923 measured reflections	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.082$	H-atom parameters constrained
$wR(F^2) = 0.249$	$w = 1/[\sigma^2(F_o^2) + (0.1212P)^2 + 0.6686P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.027$
1508 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
110 parameters	$\Delta\rho_{min} = -0.23$ 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 $F^2 > 2sigma(F^2)$ 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*	$U_{iso}*/U_{eq}$
N1	0.4587 (6)	0.7384 (4)	0.0761 (2)	0.0562 (10)
C1	0.3344 (8)	0.6666 (6)	0.1356 (3)	0.0630 (13)
H1	0.3694	0.6820	0.1972	0.076*
C2	0.1604 (8)	0.5727 (6)	0.1078 (3)	0.0595 (12)
H2	0.0809	0.5225	0.1505	0.071*
C3	0.0967 (7)	0.5493 (4)	0.0157 (2)	0.0467 (10)
C4	0.2275 (9)	0.6266 (5)	−0.0436 (3)	0.0638 (13)
H4	0.1937	0.6151	−0.1056	0.077*
C5	0.4030 (9)	0.7182 (6)	−0.0129 (3)	0.0667 (13)
H5	0.4872	0.7684	−0.0542	0.080*
C6	0.6523 (9)	0.8417 (6)	0.1092 (4)	0.0796 (15)
H6A	0.5918	0.9252	0.1411	0.119*
H6B	0.7278	0.8789	0.0587	0.119*
H6C	0.7609	0.7871	0.1491	0.119*
B	0.8454 (9)	0.5924 (6)	0.3254 (3)	0.0587 (14)
F1	0.7199 (7)	0.7234 (4)	0.3254 (3)	0.1178 (14)
F2	0.7561 (6)	0.5028 (4)	0.2566 (2)	0.0984 (12)
F3	1.0703 (5)	0.6258 (4)	0.3118 (2)	0.0984 (12)

F4	0.8324 (6)	0.5244 (5)	0.4071 (2)	0.1099 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.059 (2)	0.059 (2)	0.052 (2)	0.0147 (18)	0.0171 (17)	0.0058 (17)
C1	0.064 (3)	0.085 (3)	0.042 (2)	0.005 (3)	0.017 (2)	0.002 (2)
C2	0.067 (3)	0.077 (3)	0.037 (2)	0.003 (2)	0.022 (2)	0.012 (2)
C3	0.060 (2)	0.048 (2)	0.034 (2)	0.0214 (18)	0.0180 (17)	0.0048 (16)
C4	0.087 (3)	0.073 (3)	0.034 (2)	0.003 (3)	0.017 (2)	0.007 (2)
C5	0.090 (3)	0.070 (3)	0.044 (2)	0.005 (3)	0.026 (2)	0.010 (2)
C6	0.072 (3)	0.088 (4)	0.080 (4)	0.001 (3)	0.012 (3)	−0.002 (3)
B	0.063 (3)	0.068 (3)	0.048 (3)	−0.008 (3)	0.020 (2)	−0.007 (3)
F1	0.145 (3)	0.103 (3)	0.110 (3)	0.041 (2)	0.038 (2)	−0.007 (2)
F2	0.106 (2)	0.116 (3)	0.075 (2)	−0.028 (2)	0.0209 (17)	−0.0357 (18)
F3	0.076 (2)	0.145 (3)	0.078 (2)	−0.030 (2)	0.0309 (16)	−0.0211 (19)
F4	0.122 (3)	0.153 (3)	0.0570 (18)	−0.022 (2)	0.0204 (17)	0.0248 (19)

Geometric parameters (Å, °)

N1—C5	1.347 (6)	C4—H4	0.9300
N1—C1	1.348 (5)	C5—H5	0.9300
N1—C6	1.502 (6)	C6—H6A	0.9600
C1—C2	1.348 (7)	C6—H6B	0.9600
C1—H1	0.9300	C6—H6C	0.9600
C2—C3	1.402 (5)	B—F4	1.361 (6)
C2—H2	0.9300	B—F2	1.362 (6)
C3—C4	1.392 (6)	B—F1	1.371 (6)
C3—C3^i	1.470 (9)	B—F3	1.374 (6)
C4—C5	1.353 (7)		
C5—N1—C1	118.9 (4)	N1—C5—C4	121.5 (4)
C5—N1—C6	121.0 (4)	N1—C5—H5	119.2
C1—N1—C6	120.2 (4)	C4—C5—H5	119.2
C2—C1—N1	121.4 (4)	N1—C6—H6A	109.5
C2—C1—H1	119.3	N1—C6—H6B	109.5
N1—C1—H1	119.3	H6A—C6—H6B	109.5
C1—C2—C3	121.4 (4)	N1—C6—H6C	109.5
C1—C2—H2	119.3	H6A—C6—H6C	109.5
C3—C2—H2	119.3	H6B—C6—H6C	109.5
C4—C3—C2	115.5 (4)	F4—B—F2	111.4 (4)
C4—C3—C3^i	122.5 (4)	F4—B—F1	107.7 (4)
C2—C3—C3^i	122.0 (4)	F2—B—F1	108.8 (4)
C5—C4—C3	121.3 (4)	F4—B—F3	110.6 (4)
C5—C4—H4	119.4	F2—B—F3	108.9 (4)
C3—C4—H4	119.4	F1—B—F3	109.4 (5)

Symmetry codes: (i) −x, −y+1, −z.

Fig. 1

Fig. 2