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3,5-Dicarboxypyridinium fluoride

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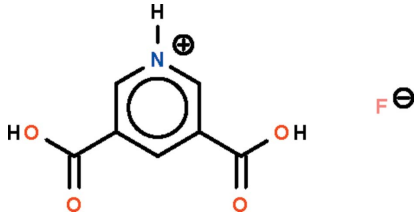
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.034; wR factor = 0.105; data-to-parameter ratio = 13.2.

The cation of the title salt, $C_7H_6NO_4^+\cdot F^-$, lies on a twofold rotation axis that passes through the N and 4-C atoms of the pyridine ring; the carboxylic acid substituent features unambiguous carbon–oxygen single and double bonds. The fluoride ion is a hydrogen-bond acceptor to two hydroxy and one amino groups, these O—H···F and N—H···F hydrogen bonds leading to the formation of a layer structure parallel to the *ab* plane. The F atom lies on a position of *2* site symmetry.

Related literature

For the crystal structure of pyridine-3,5-dicarboxylic acid, see: Cowan *et al.* (2005); Takusagawa *et al.* (1973).



Experimental

Crystal data

$C_7H_6NO_4^+\cdot F^-$
M_r = 187.13
Monoclinic, $C2/c$
a = 11.3959 (14) Å
b = 11.4503 (14) Å
c = 6.1601 (7) Å
β = 104.197 (2)°
V = 779.26 (16) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.15 mm^{-1}
T = 293 K
0.40 × 0.35 × 0.25 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.686, T_{max} = 0.746
2354 measured reflections
883 independent reflections
750 reflections with $I > 2\sigma(I)$
R_{int} = 0.012

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.105
S = 1.11
883 reflections
67 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···F1	0.86 (1)	1.60 (1)	2.458 (1)	176 (2)
N1—H2···F1^{i}	0.88 (1)	1.68 (1)	2.563 (2)	180

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

We thank Huizhou University and the University of Malaya for supporting this study.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2360).

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supporting information

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3,5-Dicarboxypyridinium fluoride

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S1. Comment

The organic salt was the crystalline product obtained in a hydrothermal reaction involving molybdic acid, hydrogen fluoride and pyridine-3,5-dicarboxylic acid; the reaction merely involved the protonation of the carboxylic acid by hydrogen fluoride. The parent carboxylic acid itself displays short O–H···O hydrogen bonds (Cowan *et al.*, 2005; Takusagawa *et al.*, 1973). The hydrogen fluoride salt, $C_7H_6NO_4^+$ F^- (Scheme I, Fig. 1), lies on a twofold rotation axis that passes through the pyridine ring; the carboxylic acid substituent features unambiguous carbon-oxygen single- and double-bonds [1.306 (1), 1.207 (1) Å]. The fluoride ion is hydrogen bond acceptor to two hydroxy and one amino groups, these O–H···F and N–H···F hydrogen bonds leading to the formation of a layer structure parallel to the *a*–*b* plane (Fig. 2).

S2. Experimental

To a solution of molybdic acid, H_2MoO_4 (1 mmol) in water (10 ml) was added 3,5-pyridinedicarboxylic acid (5 mmol). The mixture was placed in a 23 ml, Teflon-lined, stainless steel Parr bomb. Several drops of hydrofluoric acid were added. The bomb was heated at 373 for 3 days. It was then cooled to room temperature at 5 K per hour. Yellow block-shaped crystals were obtained in about 50% yield.

S3. Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.93 Å) and were included in the refinement in the riding model approximation, with *U*(H) set to 1.2*U*(C).

The amino and hydroxy H-atoms were located in a difference Fourier map, and were refined with a distance restraint of N–H 0.88±0.01 and O–H 0.84±0.01 Å; their temperature factors were freely refined.

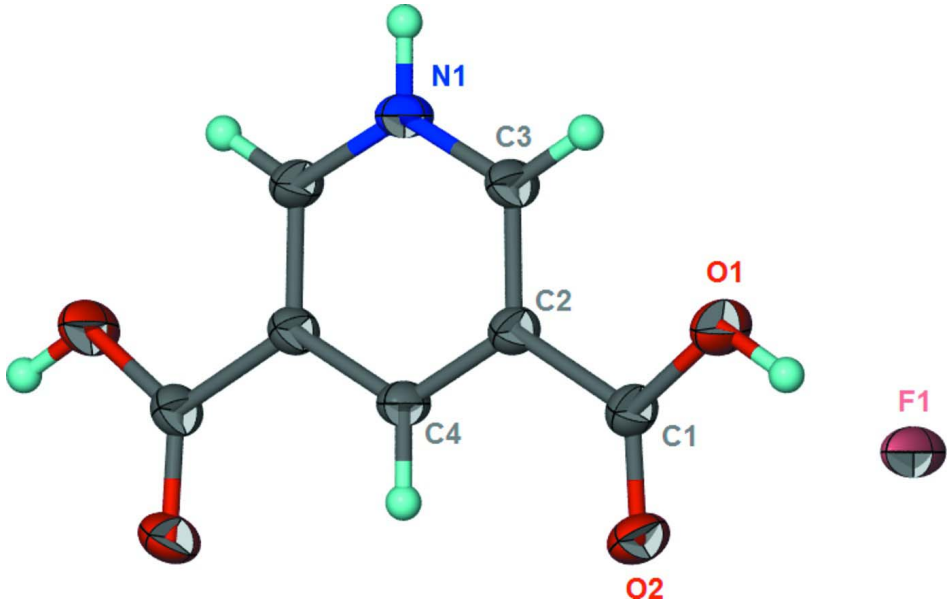

Figure 1

Thermal ellipsoid plot (Barbour, 2001) of $C_7H_6NO_4^+$ F^- at the 50% probability level; hydrogen atoms are drawn as spheres of arbitrary radius. The unlabeled atoms are related to the labeled ones by –*x*, *y*, 3/2 - *z*.

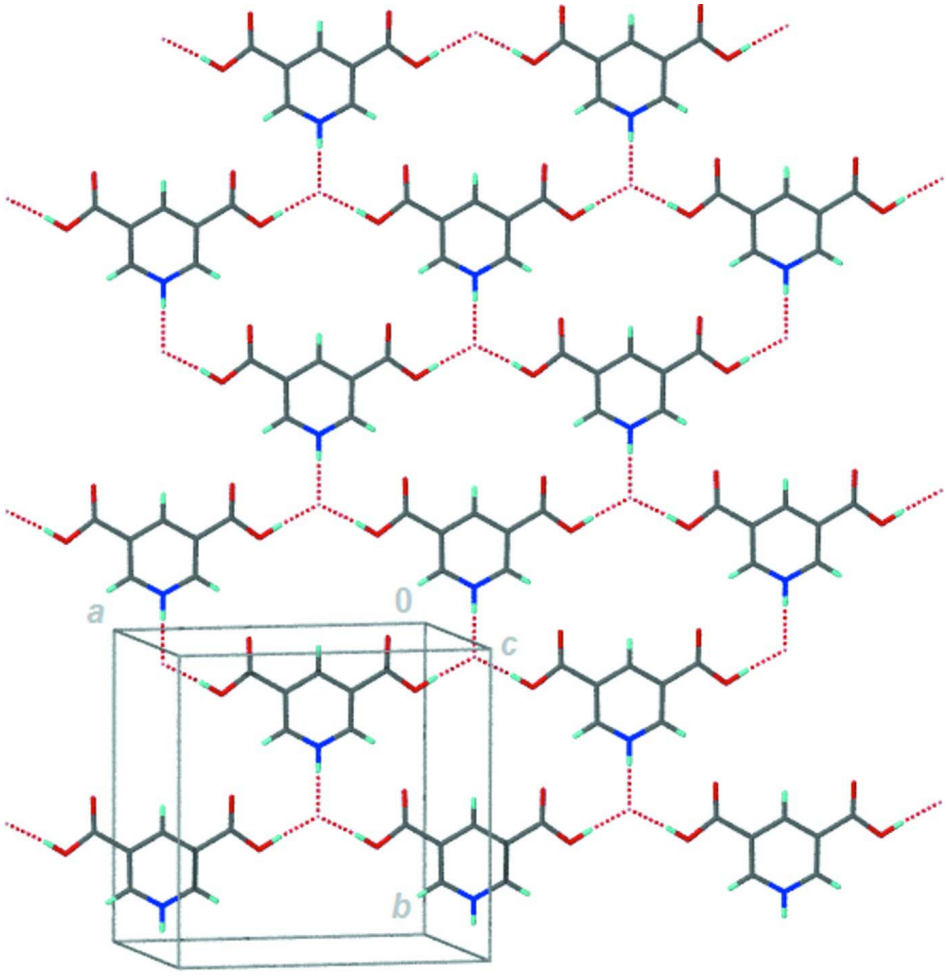

Figure 2

Layer structure.

3,5-Dicarboxypyridinium fluoride

Crystal data

$C_7H_6NO_4^+\cdot F^-$
$M_r = 187.13$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 11.3959\ (14)$ Å
$b = 11.4503\ (14)$ Å
$c = 6.1601\ (7)$ Å
$\beta = 104.197\ (2)°$
$V = 779.26\ (16)$ Å^3
$Z = 4$
$F(000) = 384$
$D_x = 1.595$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1129 reflections
$\theta = 2.6–28.4°$
$\mu = 0.15$ mm^{-1}
$T = 293$ K
Block, yellow
0.40 × 0.35 × 0.25 mm

Data collection

Bruker SMART APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.686$, $T_{max} = 0.746$
2354 measured reflections
883 independent reflections

750 reflections with $I > 2\sigma(I)$
$R_{int} = 0.012$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.6°$
$h = -10 \rightarrow 14$
$k = -13 \rightarrow 14$
$l = -8 \rightarrow 5$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.105$
$S = 1.11$
883 reflections
67 parameters
2 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
$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 0.1524P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
F1	0.5000	0.54662 (9)	0.7500	0.0536 (4)
O1	0.30965 (8)	0.64863 (8)	0.74566 (19)	0.0454 (3)
H1	0.3745 (12)	0.6097 (17)	0.747 (3)	0.069 (6)*
O2	0.21589 (9)	0.47552 (8)	0.71733 (17)	0.0428 (3)
H2	0.0000	0.8997 (9)	0.7500	0.050 (6)*
N1	0.0000	0.82283 (12)	0.7500	0.0346 (4)
C1	0.21620 (10)	0.58059 (11)	0.7326 (2)	0.0321 (3)
C2	0.10381 (10)	0.64621 (10)	0.73953 (19)	0.0294 (3)
C3	0.10135 (10)	0.76662 (11)	0.7394 (2)	0.0328 (3)
H3	0.1701	0.8087	0.7320	0.039*
C4	0.0000	0.58621 (14)	0.7500	0.0294 (4)
H4	0.0000	0.5050	0.7500	0.035*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
F1	0.0272 (6)	0.0273 (6)	0.1130 (11)	0.000	0.0301 (6)	0.000
O1	0.0245 (5)	0.0335 (5)	0.0811 (7)	0.0017 (4)	0.0183 (5)	−0.0042 (5)
O2	0.0370 (6)	0.0281 (5)	0.0663 (7)	0.0059 (4)	0.0184 (5)	−0.0033 (4)
N1	0.0268 (7)	0.0209 (7)	0.0570 (9)	0.000	0.0121 (6)	0.000
C1	0.0265 (6)	0.0299 (6)	0.0409 (7)	0.0029 (5)	0.0102 (5)	−0.0008 (5)
C2	0.0249 (6)	0.0254 (6)	0.0385 (6)	0.0012 (4)	0.0087 (5)	−0.0012 (4)
C3	0.0239 (6)	0.0260 (6)	0.0495 (7)	−0.0025 (4)	0.0108 (5)	−0.0004 (5)
C4	0.0272 (8)	0.0218 (7)	0.0394 (9)	0.000	0.0085 (6)	0.000

Geometric parameters (Å, º)

O1—C1	1.306 (1)	C1—C2	1.495 (2)
O1—H1	0.86 (1)	C2—C3	1.379 (2)
O2—C1	1.207 (2)	C2—C4	1.383 (1)

N1—C3^{i}	1.338 (1)	C3—H3	0.9300
N1—C3	1.338 (1)	C4—C2^{i}	1.383 (1)
N1—H2	0.88 (1)	C4—H4	0.9300
C1—O1—H1	112.1 (14)	C3—C2—C1	121.33 (11)
C3^{i}—N1—C3	122.48 (15)	C4—C2—C1	120.03 (11)
C3^{i}—N1—H2	118.76 (7)	N1—C3—C2	119.92 (11)
C3—N1—H2	118.76 (7)	N1—C3—H3	120.0
O2—C1—O1	125.90 (11)	C2—C3—H3	120.0
O2—C1—C2	121.15 (11)	C2—C4—C2^{i}	120.44 (15)
O1—C1—C2	112.95 (11)	C2—C4—H4	119.8
C3—C2—C4	118.62 (11)	C2^{i}—C4—H4	119.8
O2—C1—C2—C3	−174.90 (12)	C4—C2—C3—N1	0.20 (16)
O1—C1—C2—C3	5.39 (16)	C1—C2—C3—N1	−178.73 (9)
O2—C1—C2—C4	6.18 (17)	C3—C2—C4—C2^{i}	−0.10 (8)
O1—C1—C2—C4	−173.53 (9)	C1—C2—C4—C2^{i}	178.85 (11)
C3^{i}—N1—C3—C2	−0.10 (8)		

Symmetry code: (i) $-x, y, -z+3/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···F1	0.86 (1)	1.60 (1)	2.458 (1)	176 (2)
N1—H2···F1^{ii}	0.88 (1)	1.68 (1)	2.563 (2)	180

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