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Nicotinium hydrogen sulfate

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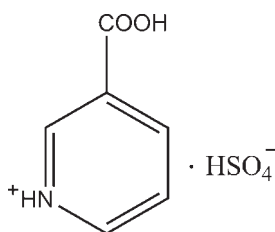
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.034; wR factor = 0.090; data-to-parameter ratio = 15.3.

The structure of title compound, $\text{C}_6\text{H}_6\text{NO}_2^+ \cdot \text{HSO}_4^-$, comprises discrete ions which are interconnected by $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds, leading to a neutral one-dimensional network along [001]. These hydrogen bonds appear to complement the Coulombic interaction and help to stabilize the structure further.

Related literature

For simple molecular–ionic crystals containing organic cations and acid radicals (1:1 molar ratio), see: Czupinski *et al.* (2002); Katrusiak & Szafranski (1999, 2006). For the structure of dinicotinium sulfate, see: Athimoolam & Rajaram (2005).



Experimental

Crystal data

 $\text{C}_6\text{H}_6\text{NO}_2^+ \cdot \text{HSO}_4^-$ $M_r = 221.19$

Monoclinic, $P2_1/c$
 $a = 8.2654$ (17) Å
 $b = 11.545$ (2) Å
 $c = 9.4669$ (19) Å
 $\beta = 109.43$ (3)°
 $V = 851.9$ (3) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.39$ mm⁻¹
 $T = 293$ K
 $0.25 \times 0.2 \times 0.2$ mm

Data collection

Rigaku SCXmini diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.91$, $T_{\max} = 0.93$

8643 measured reflections
1949 independent reflections
1788 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.090$
 $S = 1.14$
1949 reflections

127 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.21$ e Å⁻³
 $\Delta\rho_{\min} = -0.49$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O2}-\text{H2B} \cdots \text{O3}$	0.85	1.83	2.6697 (18)	169
$\text{O6}-\text{H1} \cdots \text{O5}^{\text{i}}$	0.89	1.73	2.6129 (17)	170
$\text{N1}-\text{H1B} \cdots \text{O4}^{\text{ii}}$	0.86	2.11	2.843 (2)	143

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

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*.

This work was supported by a start-up grant from Southeast University to Professor Ren-Gen Xiong.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2233).

References

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Czupinski, O., Bator, G., Ciunik, Z., Jakubas, R., Medycki, W. & Świergiel, J. (2002). *J. Phys. Condens. Matter*, **14**, 8497–8512.
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supporting information

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Nicotinium hydrogen sulfate

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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. (e.g. Czupiński *et al.*, 2002; Katrusiak & Szafranski, 1999; Katrusiak & Szafranski, 2006) the crystal structure of dinicotinium sulfate compound have been reported (Athimoolam *et al.*, 2005). In our laboratory, a compound containing protonated nicotinic acid and HSO₄⁻ anions has been synthesized, its crystal structure is reported herein.

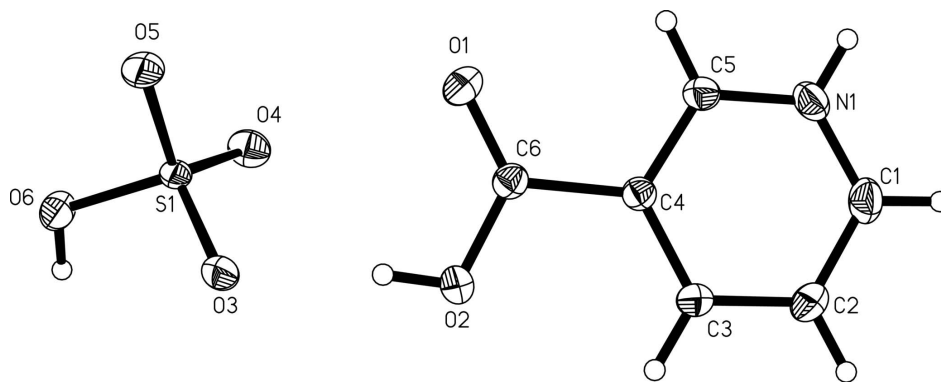
The asymmetric unit of the title compound, C₆H₆NO₂⁺.HSO₄⁻, (Fig. 1) consists of protonated nicotinic acid and HSO₄⁻ anions, the nicotinium cation is essentially planar. The protonation of the N site of the pyridine ring is demonstrated by the C—N bond distances and C—N—C bond angle. Usually, protonation on the aromatic ring leads to a slightly larger C—N—C bond angle (122.9 (2)°). Cations and anions are placed alternately and linked through intermolecular hydrogen bonds (Fig. 2 and Table 1). The structure of title compound C₆H₆NO₂⁺.HSO₄⁻, comprises discrete ions which are placed alternately and interconnected by N—H⋯O and O—H⋯O hydrogen bonds leading to a neutral one-dimensional network along [001] direction. These hydrogen bonds appear to complement the Coulombic interaction and help to stabilize the structure further.

S2. Experimental

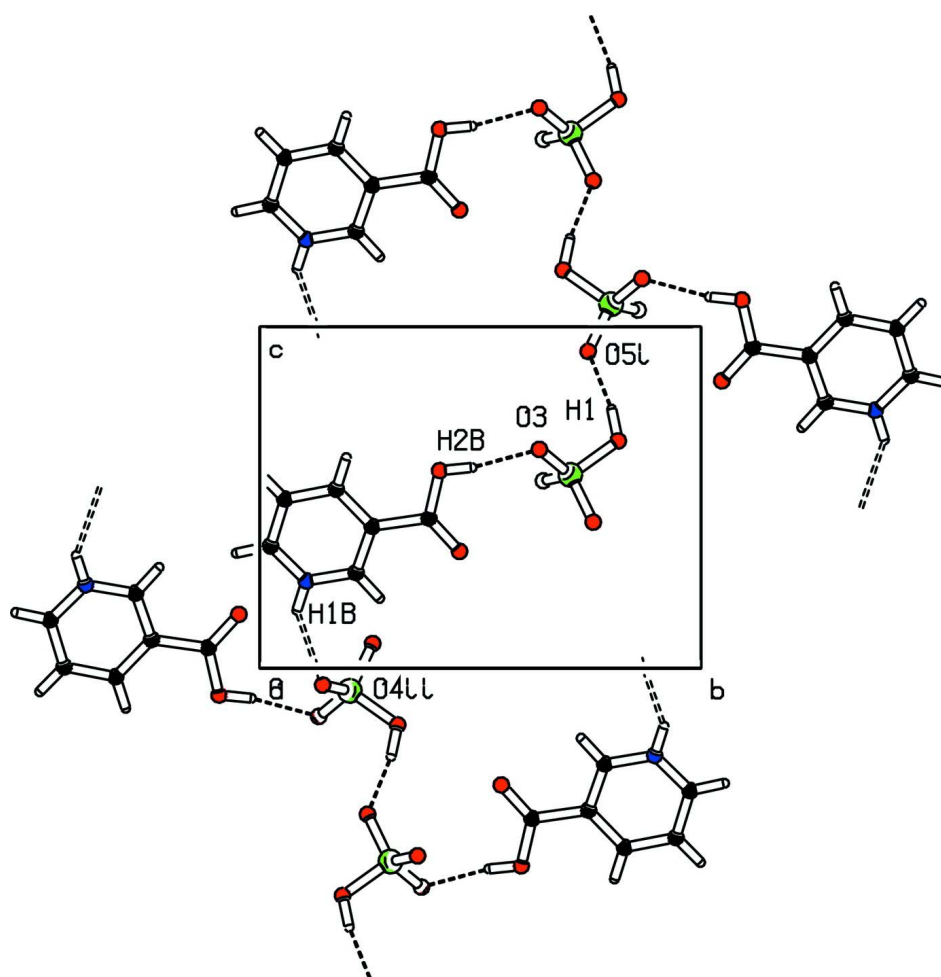
Nicotinic acid (10 mmol) and 10% aqueous H₂SO₄ in a molar ratio of 1:1 were mixed and dissolved in water by heating to 323 K forming a clear solution. The reaction mixture was cooled slowly to room temperature, crystals of the title compound were formed, collected and washed with dilute aqueous H₂SO₄.

S3. Refinement

All H atoms were placed in calculated positions, with C—H = 0.93 Å, O—H = 0.85 Å and N—H = 0.86 Å, and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ and $1.5U_{\text{eq}}(\text{O})$.

**Figure 1**

The asymmetric unit of the title compound with atom labels

**Figure 2**

The packing viewed along the *a* axis. Hydrogen bonds are drawn as dashed lines

Nicotinium hydrogen sulfate

Crystal data

C₆H₆NO₂⁺·HSO₄⁻ $M_r = 221.19$ Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

 $a = 8.2654 (17) \text{ \AA}$ $b = 11.545 (2) \text{ \AA}$ $c = 9.4669 (19) \text{ \AA}$ $\beta = 109.43 (3)^\circ$ $V = 851.9 (3) \text{ \AA}^3$ $Z = 4$ $F(000) = 456$ $D_x = 1.725 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1788 reflections

 $\theta = 3.2\text{--}27.5^\circ$ $\mu = 0.39 \text{ mm}^{-1}$ $T = 293 \text{ K}$

Block, colorless

 $0.25 \times 0.2 \times 0.2 \text{ mm}$

Data collection

Rigaku SCXmini

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 13.6612 pixels mm^{-1} ω scans

Absorption correction: multi-scan

(CrystalClear; Rigaku, 2005)

 $T_{\min} = 0.91, T_{\max} = 0.93$

8643 measured reflections

1949 independent reflections

1788 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.029$ $\theta_{\max} = 27.5^\circ, \theta_{\min} = 3.2^\circ$ $h = -10 \rightarrow 10$ $k = -14 \rightarrow 14$ $l = -12 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.090$ $S = 1.14$

1949 reflections

127 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

 $w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.3479P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.21 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.49 \text{ e \AA}^{-3}$

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.75328 (5)	0.70391 (3)	0.56623 (4)	0.02440 (13)
O1	0.71400 (17)	0.45258 (11)	0.34210 (15)	0.0396 (3)
O2	0.87198 (17)	0.40764 (11)	0.57869 (13)	0.0382 (3)
H2B	0.8839	0.4807	0.5877	0.057*

O3	0.90270 (15)	0.63375 (11)	0.64101 (13)	0.0340 (3)
O4	0.59511 (16)	0.64255 (12)	0.54911 (14)	0.0391 (3)
O5	0.75643 (18)	0.75578 (12)	0.42787 (13)	0.0395 (3)
O6	0.76089 (19)	0.81232 (11)	0.66597 (13)	0.0414 (4)
H1	0.7597	0.7975	0.7581	0.062*
N1	0.60598 (19)	0.10546 (14)	0.25572 (17)	0.0366 (4)
H1B	0.5361	0.0840	0.1701	0.044*
C4	0.75053 (19)	0.25493 (14)	0.41590 (17)	0.0259 (3)
C5	0.6393 (2)	0.21802 (15)	0.27984 (19)	0.0312 (4)
H5A	0.5877	0.2715	0.2050	0.037*
C3	0.8265 (2)	0.17308 (15)	0.52470 (19)	0.0334 (4)
H3A	0.9031	0.1960	0.6169	0.040*
C2	0.7879 (3)	0.05679 (16)	0.4957 (2)	0.0422 (4)
H2A	0.8372	0.0013	0.5685	0.051*
C6	0.7770 (2)	0.38299 (15)	0.43965 (18)	0.0282 (3)
C1	0.6761 (3)	0.02450 (16)	0.3583 (2)	0.0414 (4)
H1A	0.6494	-0.0532	0.3370	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0327 (2)	0.0247 (2)	0.01610 (19)	0.00166 (15)	0.00847 (15)	-0.00001 (13)
O1	0.0447 (7)	0.0301 (7)	0.0398 (7)	0.0039 (6)	0.0083 (6)	0.0078 (5)
O2	0.0476 (7)	0.0270 (6)	0.0332 (7)	-0.0027 (5)	0.0044 (5)	-0.0032 (5)
O3	0.0314 (6)	0.0327 (6)	0.0306 (6)	0.0016 (5)	0.0007 (5)	-0.0031 (5)
O4	0.0306 (6)	0.0493 (8)	0.0370 (7)	-0.0028 (6)	0.0104 (5)	0.0001 (6)
O5	0.0642 (9)	0.0384 (7)	0.0199 (6)	0.0022 (6)	0.0195 (6)	0.0021 (5)
O6	0.0776 (10)	0.0271 (6)	0.0241 (6)	0.0051 (6)	0.0230 (6)	-0.0019 (5)
N1	0.0338 (8)	0.0376 (8)	0.0334 (8)	-0.0030 (6)	0.0045 (6)	-0.0106 (6)
C4	0.0231 (7)	0.0274 (8)	0.0265 (8)	0.0008 (6)	0.0073 (6)	-0.0005 (6)
C5	0.0295 (8)	0.0336 (9)	0.0274 (8)	0.0029 (7)	0.0051 (6)	0.0002 (7)
C3	0.0338 (9)	0.0312 (9)	0.0291 (8)	0.0010 (7)	0.0025 (7)	0.0018 (7)
C2	0.0512 (11)	0.0281 (9)	0.0417 (11)	0.0031 (8)	0.0079 (8)	0.0069 (8)
C6	0.0251 (7)	0.0280 (8)	0.0309 (8)	0.0007 (6)	0.0086 (6)	0.0016 (6)
C1	0.0461 (11)	0.0268 (9)	0.0501 (11)	-0.0043 (8)	0.0145 (9)	-0.0059 (8)

Geometric parameters (Å, °)

S1—O4	1.4478 (13)	N1—H1B	0.8600
S1—O5	1.4483 (12)	C4—C5	1.377 (2)
S1—O3	1.4493 (13)	C4—C3	1.385 (2)
S1—O6	1.5565 (12)	C4—C6	1.500 (2)
O1—C6	1.204 (2)	C5—H5A	0.9300
O2—C6	1.320 (2)	C3—C2	1.386 (3)
O2—H2B	0.8501	C3—H3A	0.9300
O6—H1	0.8921	C2—C1	1.373 (3)
N1—C5	1.332 (2)	C2—H2A	0.9300
N1—C1	1.334 (2)	C1—H1A	0.9300

O4—S1—O5	112.85 (8)	N1—C5—H5A	120.1
O4—S1—O3	111.86 (8)	C4—C5—H5A	120.1
O5—S1—O3	113.83 (8)	C4—C3—C2	119.75 (16)
O4—S1—O6	108.30 (8)	C4—C3—H3A	120.1
O5—S1—O6	101.94 (7)	C2—C3—H3A	120.1
O3—S1—O6	107.28 (8)	C1—C2—C3	119.25 (17)
C6—O2—H2B	108.9	C1—C2—H2A	120.4
S1—O6—H1	115.3	C3—C2—H2A	120.4
C5—N1—C1	122.94 (16)	O1—C6—O2	125.66 (16)
C5—N1—H1B	118.5	O1—C6—C4	122.57 (15)
C1—N1—H1B	118.5	O2—C6—C4	111.75 (14)
C5—C4—C3	118.73 (16)	N1—C1—C2	119.48 (17)
C5—C4—C6	117.62 (15)	N1—C1—H1A	120.3
C3—C4—C6	123.61 (15)	C2—C1—H1A	120.3
N1—C5—C4	119.85 (16)		

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>
O2—H2B \cdots O3	0.85	1.83	2.6697 (18)	169
O6—H1 \cdots O5 ⁱ	0.89	1.73	2.6129 (17)	170
N1—H1B \cdots O4 ⁱⁱ	0.86	2.11	2.843 (2)	143

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