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4-Cyanopyridinium hydrogen sulfate

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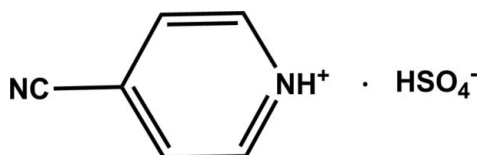
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Key indicators: single-crystal X-ray study; $T = 123$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.034; wR factor = 0.092; data-to-parameter ratio = 15.7.

All non-H atoms of the cation of the title salt, $\text{C}_6\text{H}_5\text{N}_2^+\cdot\text{HSO}_4^-$, are essentially coplanar [r.m.s. deviation = 0.005 (1) Å]. In the crystal, $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds and weak $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{N}$ interactions link the molecules into a two-dimensional network parallel to the (001) plane. Weak $\pi-\pi$ stacking interactions between the pyridine rings of neighbouring molecules further stabilize the structure [centroid-centroid distance = 3.785 (1) Å].

Related literature

For materials which display ferroelectric–paraelectric phase transitions, see: Chen *et al.* (2001); Huang *et al.* (1999); Zhang *et al.* (2001); For the structures and properties of related compounds, see: Wang *et al.* (2002); Xue *et al.* (2002); Ye *et al.* (2008).



Experimental

Crystal data

 $\text{C}_6\text{H}_5\text{N}_2^+\cdot\text{HSO}_4^-$ $M_r = 202.19$ Orthorhombic, $Pbca$ $a = 14.2959$ (12) Å $b = 7.8817$ (8) Å $c = 14.4280$ (13) Å $V = 1625.7$ (3) Å³ $Z = 8$ Mo $K\alpha$ radiation $\mu = 0.38$ mm⁻¹ $T = 123$ K

0.10 × 0.05 × 0.05 mm

Data collection

Rigaku Mercury2 diffractometer

Absorption correction: multi-scan

(CrystalClear; Rigaku, 2005)

 $T_{\min} = 0.910$, $T_{\max} = 1.000$

16314 measured reflections

1854 independent reflections

1795 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.032$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.092$ $S = 1.19$

1854 reflections

118 parameters

2 restraints

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.33$ e Å⁻³ $\Delta\rho_{\min} = -0.40$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1}\cdots\text{O4}^{\text{i}}$	0.89	1.87	2.7123 (16)	157
$\text{O2}-\text{H2}\cdots\text{O1}^{\text{ii}}$	0.82	1.79	2.5859 (15)	165
$\text{C1}-\text{H1A}\cdots\text{O1}^{\text{i}}$	0.93	2.50	3.2681 (19)	139
$\text{C2}-\text{H2A}\cdots\text{O2}^{\text{iii}}$	0.93	2.43	3.3279 (19)	162
$\text{C4}-\text{H4A}\cdots\text{O3}$	0.93	2.43	3.2189 (19)	143
$\text{C5}-\text{H5A}\cdots\text{O3}^{\text{iv}}$	0.93	2.57	3.3192 (19)	138
$\text{C5}-\text{H5A}\cdots\text{N2}^{\text{v}}$	0.93	2.53	3.211 (2)	130

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

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: *SHELXTL*.

This work was supported by a start-up grant from Southeast University, China.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: JJ2139).

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supporting information

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4-Cyanopyridinium hydrogen sulfate

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S1. Comment

Simple organic salts containing strong intramolecular H-bonds have attracted attention as materials which display ferroelectric-paraelectric phase transitions (Chen *et al.*, 2001; Huang, *et al.* 1999; Zhang, *et al.* 2001). In an effort to obtain phase transition crystals of organic salts, various organic molecules have been studied with a series of new crystal materials (Wang *et al.*, 2002; Xue, *et al.* 2002; Ye *et al.*, 2008). Herewith, we present the synthesis and crystal structure of the title compound, $C_6H_5N_2^+.HSO_4^-(I)$.

The asymmetric unit of (I) is comprised of one 4-cyanopyridinium cation and one HSO_4^- anion (Fig. 1). All non-H atoms of the cation are essentially coplanar [r.m.s. deviation = 0.005 (1)Å]. Bond lengths and angles in each of these units are in normal ranges.

In the crystal, N—H \cdots O hydrogen bonds and weak C—H \cdots O and C—H \cdots N intermolecular interactions bring the organic molecules into a 2D network (Table 1, Fig. 2). In addition, weak π – π stacking interactions between the pyridine rings of neighbouring organic molecules further stabilize the structure ($Cg\cdots Cg = 3.785$ (1)Å, with Cg being the centroid of the pyridine ring).

S2. Experimental

Isonicotinonitrile (10 mmol) and H_2SO_4 (1.0 mL, 10mmol/L) and ethanol (50 mL) were added into a 100mL flask. The mixture was stirred at 60°C for 2 h. The precipitate was then filtrated. Colourless crystals suitable for X-ray diffraction were obtained by slow evaporation of the solution.

S3. Refinement

H1, and H2 were refined freely. In the last stages of the refinement these atoms were restrained with $N1-H1 = 0.89$ (2)Å and $O2-H2 = 0.82$ (2)Å with $U_{iso}(H) = 1.2U_{eq}(N)$ and $U_{iso}(H)=1.5U_{eq}(O)$. All the remaining H atoms attached to C atoms were placed in calculated positions and then refined using the riding model with C—H lengths of 0.93 Å (CH). The isotropic displacement parameters for these atoms were set to 1.2 (CH) times U_{eq} of the parent atom.

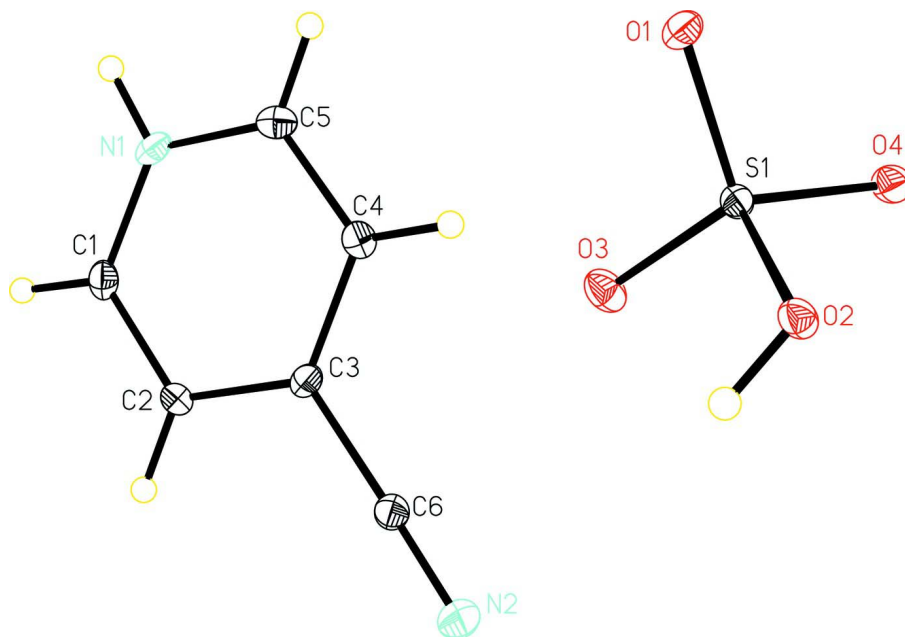


Figure 1

Molecular structure of the title compound showing the atom labeling scheme and 50% probability displacement ellipsoids for one cation-anion unit and bimolecular unit in the asymmetric unit.

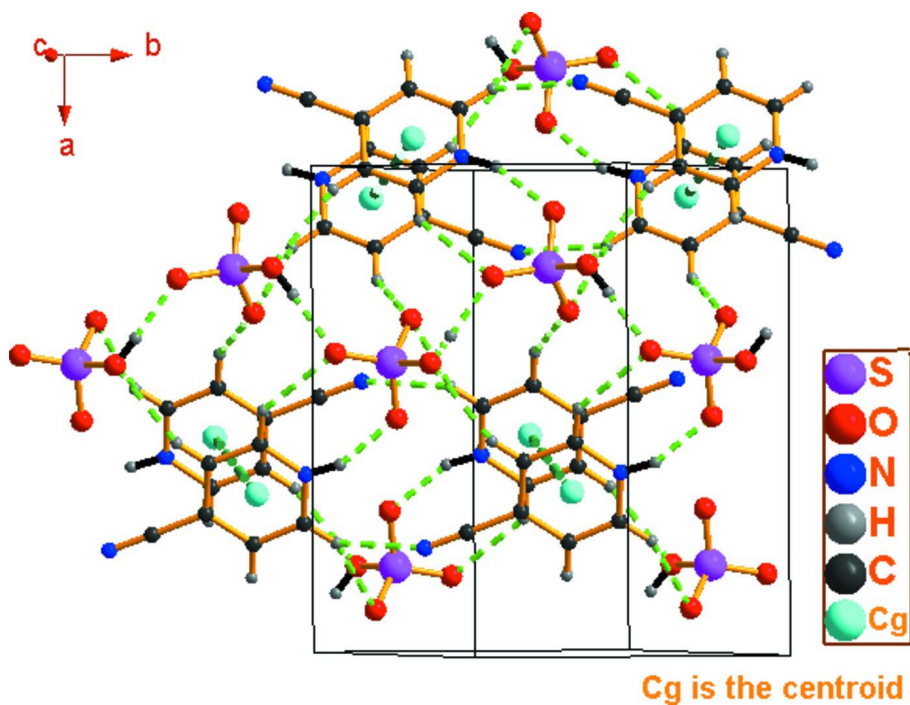


Figure 2

Crystal packing of the title compound viewed along the *c* axis showing N—H \cdots O and O—H \cdots O hydrogen bonds (dotted lines), weak C—H \cdots O, C—H \cdots N intermolecular interactions (dotted lines) and weak π — π stacking interactions (dashed lines).

4-Cyanopyridinium hydrogen sulfate

Crystal data

 $C_6H_5N_2^+ \cdot HSO_4^-$ $M_r = 202.19$ Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

 $a = 14.2959$ (12) Å $b = 7.8817$ (8) Å $c = 14.4280$ (13) Å $V = 1625.7$ (3) Å³ $Z = 8$ $F(000) = 832$ $D_x = 1.652$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1854 reflections

 $\theta = 2.9$ – 27.5° $\mu = 0.38$ mm⁻¹ $T = 123$ K

Block, colorless

 $0.10 \times 0.05 \times 0.05$ mm

Data collection

Rigaku Mercury2

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 13.6612 pixels mm⁻¹

CCD profile fitting scans

Absorption correction: multi-scan

(CrystalClear; Rigaku, 2005) $T_{\min} = 0.910$, $T_{\max} = 1.000$

16314 measured reflections

1854 independent reflections

1795 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.032$ $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.9^\circ$ $h = -18 \rightarrow 18$ $k = -10 \rightarrow 10$ $l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.034$ $wR(F^2) = 0.092$ $S = 1.19$

1854 reflections

118 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-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.7898P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.33$ e Å⁻³ $\Delta\rho_{\min} = -0.40$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\sigma(F^2)$ 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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.17080 (2)	0.57874 (4)	0.66263 (2)	0.01293 (13)
O1	0.18628 (8)	0.43049 (13)	0.72165 (8)	0.0186 (2)
N1	0.48319 (9)	0.22311 (16)	0.39112 (9)	0.0182 (3)
H1	0.4995	0.1142	0.3932	0.022*

C1	0.53425 (11)	0.3477 (2)	0.35266 (11)	0.0198 (3)
H1A	0.5907	0.3226	0.3236	0.024*
O2	0.16838 (7)	0.73568 (14)	0.72925 (7)	0.0165 (2)
H2	0.2140	0.7945	0.7167	0.025*
N2	0.35791 (11)	0.85408 (19)	0.40783 (12)	0.0317 (4)
C2	0.50280 (11)	0.5123 (2)	0.35638 (11)	0.0182 (3)
H2A	0.5370	0.6000	0.3297	0.022*
O3	0.24390 (8)	0.60728 (15)	0.59562 (7)	0.0200 (3)
C3	0.41822 (10)	0.54447 (18)	0.40125 (10)	0.0154 (3)
O4	0.07646 (8)	0.57536 (13)	0.62351 (8)	0.0190 (3)
C4	0.36712 (11)	0.41442 (19)	0.44145 (10)	0.0173 (3)
H4A	0.3113	0.4365	0.4724	0.021*
C5	0.40147 (11)	0.2508 (2)	0.43428 (10)	0.0182 (3)
H5A	0.3681	0.1605	0.4593	0.022*
C6	0.38364 (11)	0.7175 (2)	0.40508 (12)	0.0204 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0118 (2)	0.0120 (2)	0.0150 (2)	-0.00042 (11)	0.00102 (12)	-0.00076 (12)
O1	0.0191 (5)	0.0144 (5)	0.0223 (6)	0.0046 (4)	0.0025 (4)	0.0028 (4)
N1	0.0220 (6)	0.0129 (6)	0.0196 (6)	0.0040 (5)	-0.0051 (5)	-0.0009 (5)
C1	0.0139 (7)	0.0225 (8)	0.0230 (7)	0.0022 (6)	-0.0007 (5)	-0.0026 (6)
O2	0.0151 (5)	0.0146 (5)	0.0198 (6)	-0.0026 (4)	0.0034 (4)	-0.0042 (4)
N2	0.0259 (7)	0.0183 (8)	0.0511 (10)	0.0021 (6)	0.0009 (7)	-0.0049 (7)
C2	0.0149 (7)	0.0166 (7)	0.0231 (7)	-0.0024 (5)	-0.0004 (6)	0.0013 (6)
O3	0.0189 (5)	0.0220 (6)	0.0192 (5)	-0.0039 (4)	0.0059 (4)	-0.0035 (4)
C3	0.0164 (7)	0.0134 (7)	0.0164 (7)	0.0019 (5)	-0.0045 (5)	-0.0025 (5)
O4	0.0157 (5)	0.0164 (5)	0.0249 (6)	-0.0028 (4)	-0.0049 (4)	0.0013 (4)
C4	0.0164 (7)	0.0189 (8)	0.0166 (7)	-0.0007 (5)	0.0005 (5)	-0.0028 (5)
C5	0.0242 (8)	0.0163 (7)	0.0142 (7)	-0.0026 (6)	-0.0017 (6)	0.0003 (6)
C6	0.0168 (7)	0.0163 (8)	0.0281 (8)	-0.0005 (6)	-0.0022 (6)	-0.0034 (6)

Geometric parameters (Å, °)

S1—O3	1.4414 (11)	O2—H2	0.8198
S1—O4	1.4622 (11)	N2—C6	1.138 (2)
S1—O1	1.4626 (11)	C2—C3	1.395 (2)
S1—O2	1.5669 (11)	C2—H2A	0.9300
N1—C5	1.342 (2)	C3—C4	1.386 (2)
N1—C1	1.343 (2)	C3—C6	1.452 (2)
N1—H1	0.8902	C4—C5	1.384 (2)
C1—C2	1.375 (2)	C4—H4A	0.9300
C1—H1A	0.9300	C5—H5A	0.9300
O3—S1—O4	114.37 (7)	C1—C2—C3	118.23 (14)
O3—S1—O1	113.92 (7)	C1—C2—H2A	120.9
O4—S1—O1	110.48 (6)	C3—C2—H2A	120.9

O3—S1—O2	107.71 (6)	C4—C3—C2	121.13 (14)
O4—S1—O2	103.34 (6)	C4—C3—C6	119.96 (14)
O1—S1—O2	106.07 (6)	C2—C3—C6	118.91 (14)
C5—N1—C1	123.08 (13)	C5—C4—C3	118.09 (14)
C5—N1—H1	111.7	C5—C4—H4A	121.0
C1—N1—H1	125.2	C3—C4—H4A	121.0
N1—C1—C2	119.75 (14)	N1—C5—C4	119.71 (14)
N1—C1—H1A	120.1	N1—C5—H5A	120.1
C2—C1—H1A	120.1	C4—C5—H5A	120.1
S1—O2—H2	107.1	N2—C6—C3	178.92 (18)

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>
N1—H1 \cdots O4 ⁱ	0.89	1.87	2.7123 (16)	157
O2—H2 \cdots O1 ⁱⁱ	0.82	1.79	2.5859 (15)	165
C1—H1A \cdots O1 ⁱ	0.93	2.50	3.2681 (19)	139
C2—H2A \cdots O2 ⁱⁱⁱ	0.93	2.43	3.3279 (19)	162
C4—H4A \cdots O3	0.93	2.43	3.2189 (19)	143
C5—H5A \cdots O3 ^{iv}	0.93	2.57	3.3192 (19)	138
C5—H5A \cdots N2 ^v	0.93	2.53	3.211 (2)	130

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