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4-Cyanopyridinium hydrogen sulfate

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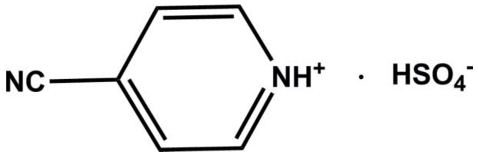
Key indicators: single-crystal X-ray study; *T* = 123 K; mean σ(C–C) = 0.002 Å; *R* factor = 0.034; *wR* factor = 0.092; data-to-parameter ratio = 15.7.

All non-H atoms of the cation of the title salt, $C_6H_5N_2^+\cdot HSO_4^-$, are essentially coplanar [r.m.s. deviation = 0.005 (1) Å] . In the crystal, N—H⋯O and O—H⋯O hydrogen bonds and weak C—H⋯O and C—H⋯N interactions link the molecules into a two-dimensional network parallel to the (001) plane. Weak π–π 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

$C_6H_5N_2^+\cdot HSO_4^-$
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) Å^3
Z = 8
Mo *K*α radiation
μ = 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_{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—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—H1⋯O4^{i}	0.89	1.87	2.7123 (16)	157
O2—H2⋯O1^{ii}	0.82	1.79	2.5859 (15)	165
C1—H1*A*⋯O1^{i}	0.93	2.50	3.2681 (19)	139
C2—H2*A*⋯O2^{iii}	0.93	2.43	3.3279 (19)	162
C4—H4*A*⋯O3	0.93	2.43	3.2189 (19)	143
C5—H5*A*⋯O3^{iv}	0.93	2.57	3.3192 (19)	138
C5—H5*A*⋯N2^{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*.

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

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supplementary materials

Acta Cryst. (2012). E**68**, o2176   [doi:10.1107/S1600536812027304]

4-Cyanopyridinium hydrogen sulfate

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Comment

Simple organic salts containing strong intrermolecular 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···O hydrogen bonds and weak C—H···O and C—H···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···Cg = 3.785 (1)Å, with Cg being the centriod of the pyridine ring).

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.

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 displcement parameers for these atoms were set to 1.2 (CH) times U_{eq} of the parent atom.

Computing details

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear* (Rigaku, 2005); data reduction: *CrystalClear* (Rigaku, 2005); 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* (Sheldrick, 2008).

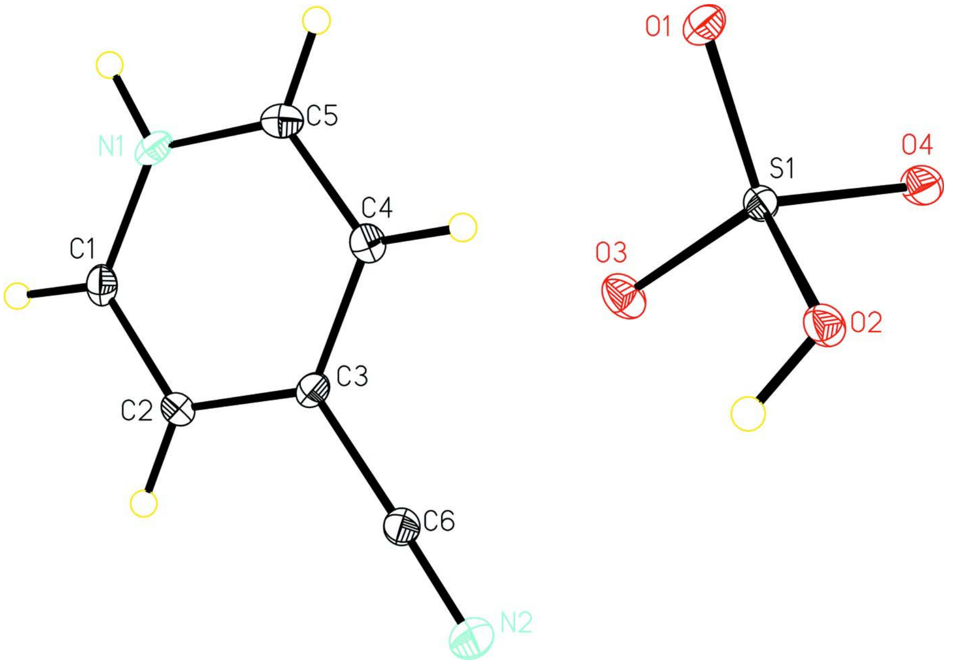

Figure 1

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.

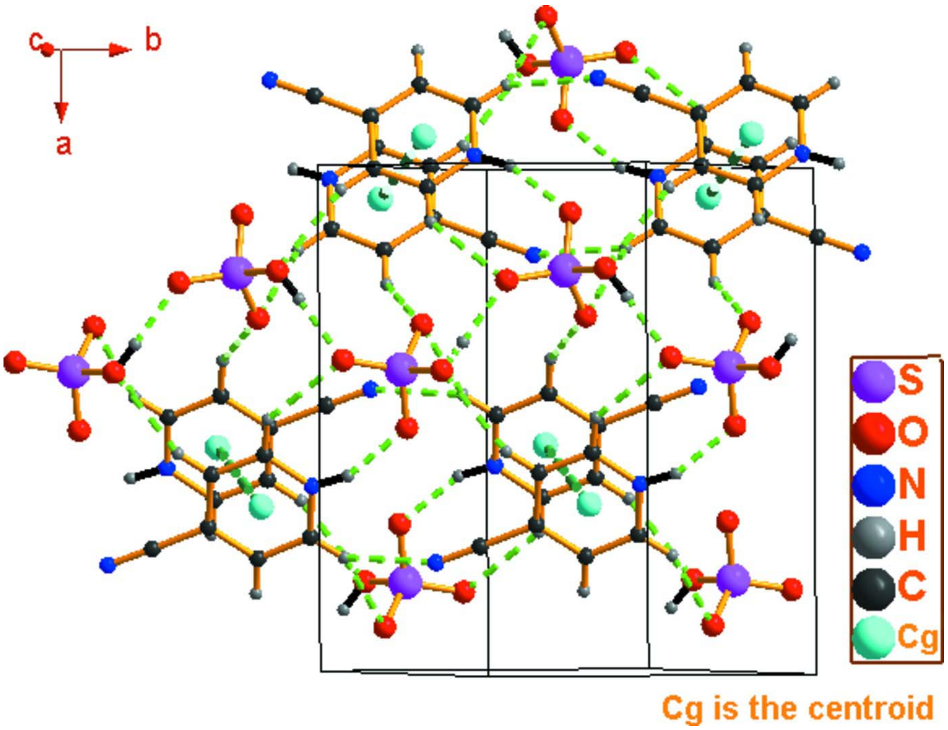

Figure 2

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

4-Cyanopyridinium hydrogen sulfate

Crystal data

$C_6H_5N_2^+\cdot HSO_4^-$	$F(000) = 832$
$M_r = 202.19$	$D_x = 1.652$ Mg m^{-3}
Orthorhombic, *Pbca*	Mo *Kα* radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2ab	Cell parameters from 1854 reflections
$a = 14.2959$ (12) Å	$\theta = 2.9$–27.5°
$b = 7.8817$ (8) Å	$\mu = 0.38$ mm^{-1}
$c = 14.4280$ (13) Å	$T = 123$ K
$V = 1625.7$ (3) Å^3	Block, colorless
$Z = 8$	0.10 × 0.05 × 0.05 mm

Data collection

Rigaku Mercury2 diffractometer	16314 measured reflections
Radiation source: fine-focus sealed tube	1854 independent reflections
Graphite monochromator	1795 reflections with $I > 2\sigma(I)$
Detector resolution: 13.6612 pixels mm^{-1}	$R_{\rm int} = 0.032$
CCD profile fitting scans	$\theta_{\rm max} = 27.5°$, $\theta_{\rm min} = 2.9°$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$h = -18 \rightarrow 18$
$T_{\rm min} = 0.910$, $T_{\rm max} = 1.000$	$k = -10 \rightarrow 10$
	$l = -18 \rightarrow 18$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained
$wR(F^2) = 0.092$	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.7898P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.19$	$(\Delta/\sigma)_{\rm max} < 0.001$
1854 reflections	$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
118 parameters	$\Delta\rho_{\rm min} = -0.40$ e Å^{-3}
2 restraints	
Primary atom site location: structure-invariant direct methods	

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 > 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*	$U_{\rm iso}$*/$U_{\rm eq}$
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 (Å^2)

	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, º)

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, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O4^{i}	0.89	1.87	2.7123 (16)	157
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C5—H5*A*···O3^{iv}	0.93	2.57	3.3192 (19)	138
C5—H5*A*···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) $x, y-1, z$.