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3-Carboxypyridinium ammonium sulfate sulfamic acid solvate

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Key indicators

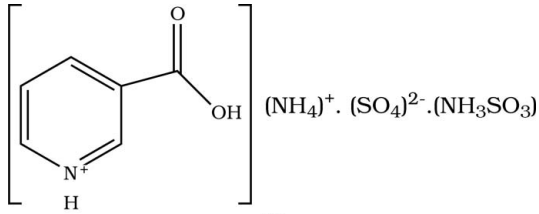
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.046
wR factor = 0.137
Data-to-parameter ratio = 11.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the title compound, $C_6H_6NO_2^+\cdot NH_4^+\cdot SO_4^{2-}\cdot NH_3SO_3$, 3-carboxypyridinium ions form N—H···O hydrogen-bonded chains along the b axis. Ammonium and sulfate ions and sulfamic acid molecules form a two-dimensional network of hydrogen bonds parallel to (001). This leads to the formation of alternate hydrophilic and hydrophobic layers.

Comment

Nicotinic acid (pyridine-3-carboxylic acid) is a B vitamin known as niacin, and has a variety of pharmacological properties as detailed in our previous publications (Athimoolam & Rajaram, 2005*a*,*b*). As vitamin B is one of the important biological compounds in many fields such as the pharmaceutical industry, it is very useful to study ionic crystals of the vitamin in an inorganic environment. In this paper, we report the crystal structure of the title compound, (I).



(I)

The asymmetric unit of (I) consists of a 3-carboxypyridinium and an ammonium cation, a sulfate anion and a sulfamic acid molecule (Fig. 1). The carboxyl group (C31/O1*A*/O1*B*) is twisted with respect to the pyridine ring (N1/C2–C6) by a dihedral angle of 5.1 (3)°. As shown in Fig. 2, the sulfate anions, ammonium cations and the sulfamic acid molecules are arranged at nearly $z = \frac{1}{2}$ and are connected through hydrogen bonds (Table 2), forming a two-dimensional sheet parallel to (001). This leads to alternate hydrophilic and hydrophobic layers in the crystal structure. The nicotinium cations form N—H···O hydrogen-bonded chains [$C(6)$ motif] running along the b axis (Fig. 3).

Experimental

The title compound, (I), was crystallized from an aqueous (25 ml water) mixture of nicotinic acid and sulfamic acid in the stochiometric ratio of 1:2. The chemical reaction has resulted in the dissociation of sulfamic acid into ammonia (NH_3) and sulfuric acid by hydrolysis. The product, obtained within a period of one week, was purified by multiple recrystallization from doubly distilled water. Colourless crystals of (I) suitable for X-ray analysis were grown by slow evaporation of an aqueous solution at room temperature.

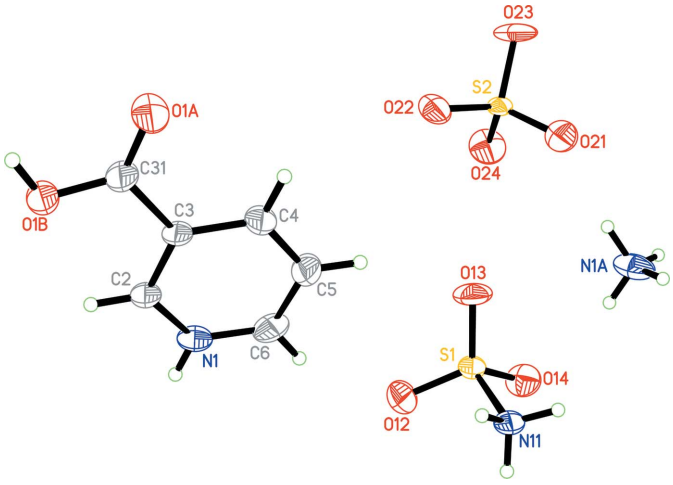


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids.

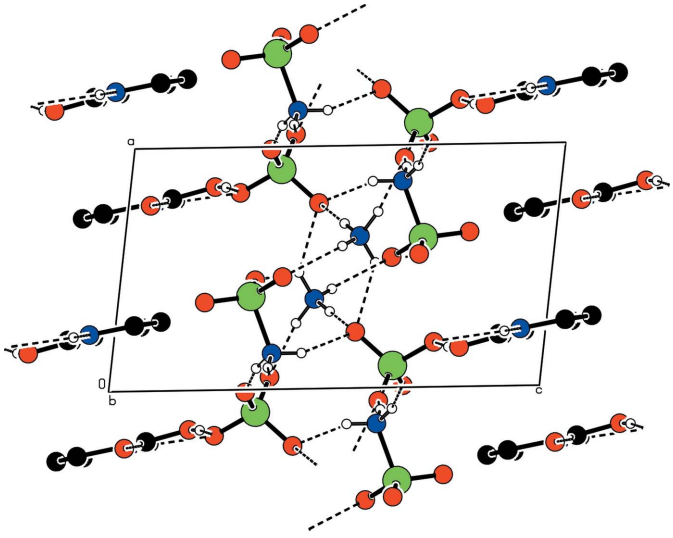


Figure 2
Packing diagram of (I), viewed down the *b* axis. H atoms have been omitted unless they are involved in hydrogen bonds (dashed lines).

Crystal data

$C_6H_6NO_2^+\cdot NH_4^+\cdot SO_4^{2-}\cdot NH_3SO_3$
M_r = 335.31
Triclinic, $P\overline{1}$
a = 7.1301 (4) Å
b = 7.4212 (3) Å
c = 12.5334 (6) Å
α = 89.291 (9)°
β = 82.863 (11)°
γ = 84.845 (10)°
V = 655.39 (6) Å^3
Z = 2
D_x = 1.699 Mg m^{-3}
D_m = 1.68 Mg m^{-3}
D_m measured by flotation in a mixture of xylene and bromoform
Mo $K\alpha$ radiation
μ = 0.46 mm^{-1}
T = 293 (2) K
Prism, colourless
0.21 × 0.19 × 0.17 mm

Data collection

MACH3-Nonius diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.908, T_{max} = 0.999
(expected range = 0.841–0.925)
2905 measured reflections
2300 independent reflections
2068 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 25.0°
3 standard reflections
frequency: 60 min
intensity decay: none

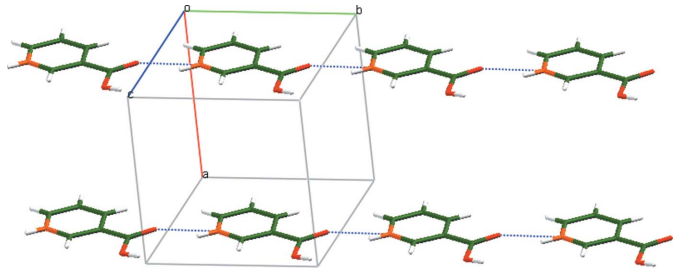


Figure 3
Chains of nicotinium cations in (I). Dotted lines indicate hydrogen bonds.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.137
S = 1.09
2300 reflections
199 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0802P)^2 + 0.8693P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.73 e Å^{-3}
$\Delta\rho_{min}$ = −0.64 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C6	1.333 (4)	C31—O1*B*	1.298 (4)
N1—C2	1.335 (4)	S1—N11	1.767 (3)
C31—O1*A*	1.209 (4)		
C6—N1—C2	123.5 (3)		
C2—C3—C31—O1*A*	−174.2 (4)	C4—C3—C31—O1*B*	−176.0 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*B*—H1*B*···O22^{i}	0.82	1.74	2.546 (3)	167
N1—H1···O1*A*^{ii}	0.86	2.10	2.748 (3)	131
N1—H1···O22^{iii}	0.86	2.17	2.889 (4)	141
N1*A*—H1*A*···O23^{iv}	0.94 (5)	1.91 (5)	2.831 (4)	168 (4)
N1*A*—H2*A*···O21^{v}	0.98 (6)	2.11 (6)	2.864 (4)	132 (4)
N1*A*—H3*A*···O14	0.84 (7)	2.19 (7)	2.999 (4)	160 (6)
N1*A*—H4*A*···O21	0.89 (6)	2.01 (6)	2.889 (4)	172 (5)
N11—H11*A*···O24^{vi}	0.89	1.96	2.798 (3)	156
N11—H11*B*···O21^{v}	0.89	1.94	2.773 (4)	155
N11—H11*C*···O23^{vii}	0.89	1.96	2.803 (3)	158
C6—H6···O1*A*^{ii}	0.93	2.42	2.905 (4)	113

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

H atoms of the ammonium cation were located in difference maps and refined isotropically. All other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93, O—H = 0.82 and N—H = 0.86 or 0.89 Å, and with U_{iso}(H) = 1.5U_{eq}(N,O) or 1.2U_{eq}(C,N) for the pyridinium group.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms &

Wocadlo, 1995); program(s) used to solve structure: *SHELXTL/PC* (Bruker, 2000); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*, *MERCURY* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL/PC*.

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References

Athimoolam, S. & Rajaram, R. K. (2005*a*). *Acta Cryst.* E**61**, o2674–o2676.
Athimoolam, S. & Rajaram, R. K. (2005*b*). *Acta Cryst.* E**61**, o2764–o2767.
Bruker (2000). *SHELXTL/PC*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg. Germany.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.