

Dinicotinium sulfate

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Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.008$ Å
 R factor = 0.062
 wR factor = 0.205
Data-to-parameter ratio = 11.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the title complex, $2\text{C}_6\text{H}_6\text{NO}_2^+\cdot\text{SO}_4^{2-}$, the carboxyl groups of the two nicotinium cations (*A* and *B*) are twisted from the pyridinium ring, with dihedral angles of 9.1 (5) and 7.0 (9)°, respectively. Packing involves classical $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. Cations *A* are interlinked through an O atom of the sulfate anion, forming an infinite chain running along the *b* axis and leading to cationic layers separated by a distance of 3.106 (4) Å. Cations *B* form an inversion-related closed hydrogen-bonded loop.

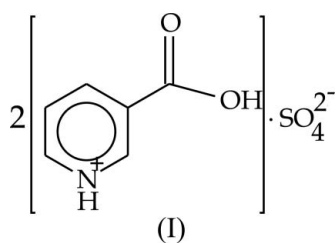
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Comment

Hypercholesterolemia is a relevant risk factor with regard to the development of atherosclerotic diseases. Nicotinic acid, a B vitamin, also known as niacin, is a lipid-lowering agent widely used to treat hypertriglyceridemia by the inhibition of lipolysis in adipose tissue. The nicotinic acid complex 5-methylpyrazine-2-carboxylic acid 4-oxide is a commonly used drug for hypercholesterolemia (Lorenzen *et al.*, 2001). Coordination complexes of nicotinic acid with metals such as Sn possess antitumour activity greater than the well known *cis*-platin or doxorubicin (Gielen *et al.*, 1992). Also, the enzyme nicotinic acid mononucleotide adenylyltransferase is essential for the synthesis of nicotinamide adenine dinucleotide in all living cells and is a potential target for antibiotics (Kim *et al.*, 2004). Because of their pharmacological importance, nicotinic acid and related compounds are the object of extensive study. The crystal structures of nicotinic acid (Wright & King, 1953; Kutoglu & Scheringer, 1983), dinicotinic acid (Takusagawa *et al.*, 1973), isonicotinic acid (Takusagawa & Shimada, 1976), isonicotinic acid hydrazide (Bhat *et al.*, 1974), nicotinium tetrachlorocuprate(II) (Choi *et al.*, 2002), 2-aminonicotinic acid (Dobson & Gerkin, 1997), 6-aminonicotinic acid hydrochloride (Giantsidis & Turnbull, 2000), nicotinic acid chloride hydrochloride (Nättinen & Rissanen, 2003), 3,5-dinitrobenzoic acid nicotinic acid (Zhu & Zheng, 2004), 2-(methylsulfanyl)nicotinic acid (Basavoju *et al.*, 2005), nicotinamide (Wright & King, 1954), 1-methylnicotinamide iodide, chloride and picrate (Freeman & Bugg, 1974), and dinicotinamidium squarate (Bulut *et al.*, 2003) have been reported previously. The crystal structure of nicotinic acid complexed with the protein leghaemoglobin (Ellis *et al.*, 1997) and the haem-nicotinate interaction in leghaemoglobin (Patel *et al.*, 2000) were also studied. As part of our investigations of nicotinic acid complexes with inorganic acids, nicotinic acid was treated with sulfuric acid, and the crystal structure of the resulting salt is reported here.



The title compound, (I), contains two nicotinium cations (*A* and *B*) and a sulfate anion in the asymmetric unit (Fig. 1). The protons from the sulfuric acid are transferred to the nicotinic acid, forming two nicotinium cations. The least-squares plane through cation *A* makes an angle of 50.8 (1)° with that for cation *B*. Cations *A* and *B* are stacked close to the $z = 0$ and $z = \frac{1}{2}$ planes, respectively. The C–N–C bond angle and the C–N bond distances in both cations confirm protonation on the N atom of the aromatic rings. The pyridinium rings are essentially planar, with a maximum deviation of 0.007 (3) Å for N11 in cation *A* and 0.018 (4) Å for C23 in cation *B*. As found in other nicotinic acid–inorganic acid complexes, the carboxyl group is twisted from the pyridinium ring plane, with dihedral angles of 9.1 (5) and 7.0 (9)° for cations *A* and *B*, respectively. Protonation of the O atoms of the carboxyl groups is unambiguously confirmed from the C–O bond distances and C–C–O bond angles. Deviation of the carbonyl atom O1A [0.191 (9) Å] from the pyridinium plane is slightly greater than that of O1B [0.157 (9) Å] in cation *A*. This is reversed in cation *B*, with O2B [0.235 (9) Å] deviating further from the ring

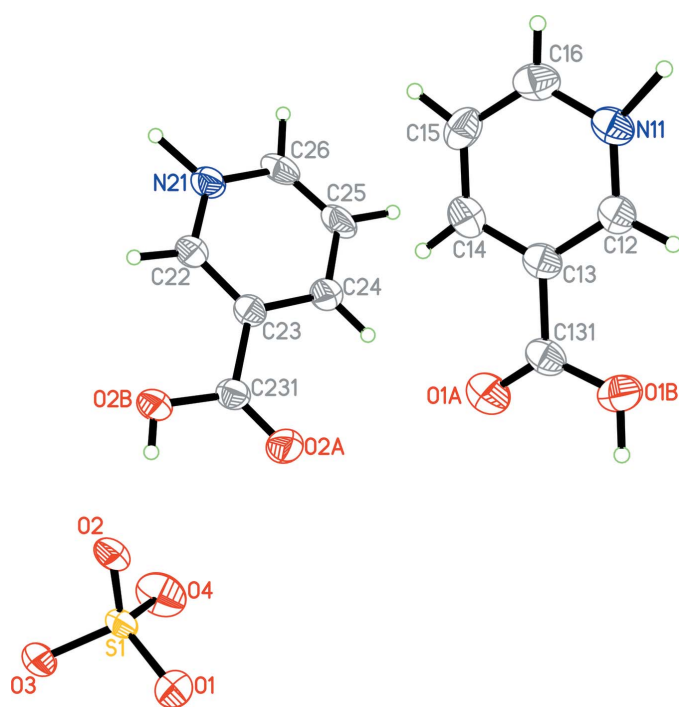


Figure 1
The asymmetric unit of the title compound, showing the atom-numbering scheme and 50% probability displacement ellipsoids.

plane than O2A [0.149 (9) Å], as found in 2-aminonicotinic acid (Dobson & Gerkin, 1997) (Table 1). The SO_4^{2-} anion shows nearly tetrahedral symmetry. The crystal is stabilized by extensive hydrogen bonding through three O atoms of the sulfate anions (Fig. 2). The *B* cations are interlinked through N–H···O and O–H···O hydrogen bonds to the anions, forming an inversion-related closed hydrogen-bonded loop (Fig. 3). In residue *A*, the cations form infinite chains running along the *b* axis by connecting to adjacent cations through the

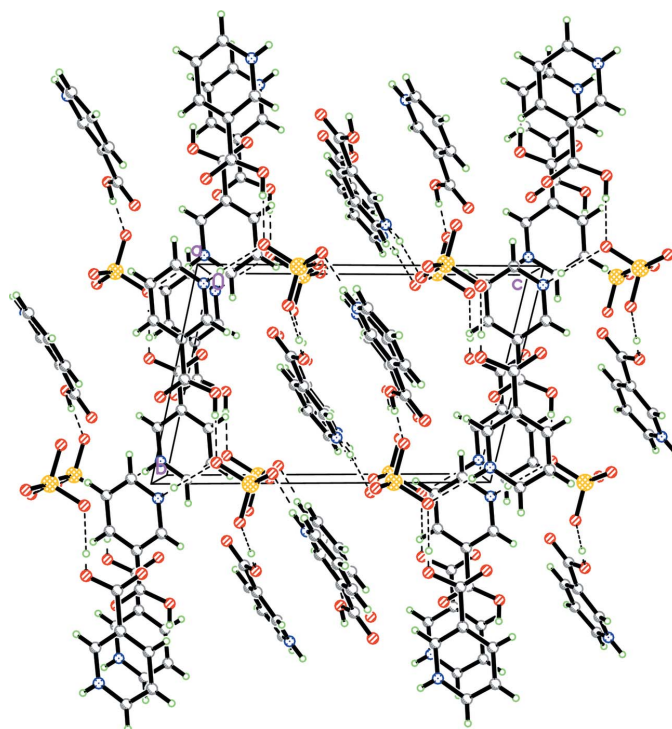


Figure 2
The packing of the molecule, viewed down the *b* axis, with hydrogen bonds drawn as dashed lines.

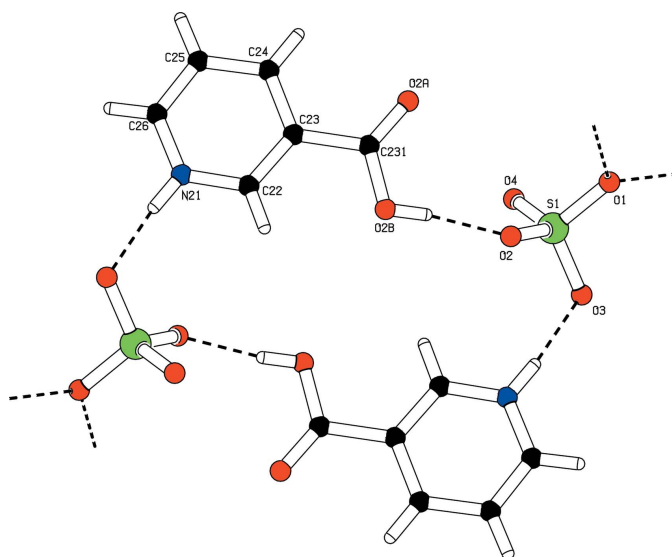


Figure 3
The inversion-related closed hydrogen-bonded loop formed by cation *B*. Hydrogen bonds are drawn as dashed lines.

O1 atom of the sulfate anion, *viz.* N11—H11···O1···H1B—O1B(*x*, *y* + 1, *z*), leading to cationic layers separated by 3.106 (4) Å but not linked by any hydrogen bonding (Fig. 4 and Table 2).

Experimental

The title compound was crystallized from a solution of a mixture of nicotinic acid and sulfuric acid in a 2:1 stoichiometric ratio. Slow evaporation of the mixture at room temperature produced colourless block-like crystals, one of which was cut and used to collect the intensity data.

Crystal data

2C₅H₆NO₂⁺·SO₄²⁻
M_r = 344.30
 Triclinic, *P* $\bar{1}$
a = 6.9663 (7) Å
b = 8.3306 (14) Å
c = 12.5098 (12) Å
 α = 101.253 (11)°
 β = 95.746 (8)°
 γ = 102.685 (11)°
V = 686.85 (15) Å³
Z = 2
D_x = 1.665 Mg m⁻³

D_m = 1.654 (8) Mg m⁻³
D_m measured by flotation using a mixture of CCl₄ and CHBr₃
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 10.0–14.3°
 μ = 0.28 mm⁻¹
T = 293 (2) K
 Block, colourless
 0.25 × 0.22 × 0.19 mm

Data collection

Nonius MACH3 four-circle diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.898, *T_{max}* = 0.947
 3062 measured reflections
 2414 independent reflections
 1650 reflections with *I* > 2σ(*I*)

R_{int} = 0.020
 θ_{\max} = 25.0°
h = -1 → 8
k = -9 → 9
l = -14 → 14
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.062
wR (*F*²) = 0.205
S = 1.13
 2409 reflections
 211 parameters
 H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0826*P*)² + 2.2093*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/*σ*)_{max} < 0.001
 Δ*ρ*_{max} = 0.53 e Å⁻³
 Δ*ρ*_{min} = -0.59 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N11—C12	1.331 (7)	N21—C22	1.338 (7)
N11—C16	1.342 (7)	N21—C26	1.345 (7)
C131—O1A	1.204 (7)	C231—O2A	1.193 (6)
C131—O1B	1.311 (7)	C231—O2B	1.318 (6)
C12—N11—C16	122.9 (5)	C22—N21—C26	121.9 (5)
O1A—C131—O1B	124.9 (5)	O2A—C231—O2B	125.0 (5)
C14—C13—C131—O1A	9.6 (8)	C24—C23—C231—O2A	2.3 (8)
C14—C13—C131—O1B	-171.9 (5)	C24—C23—C231—O2B	-175.1 (5)

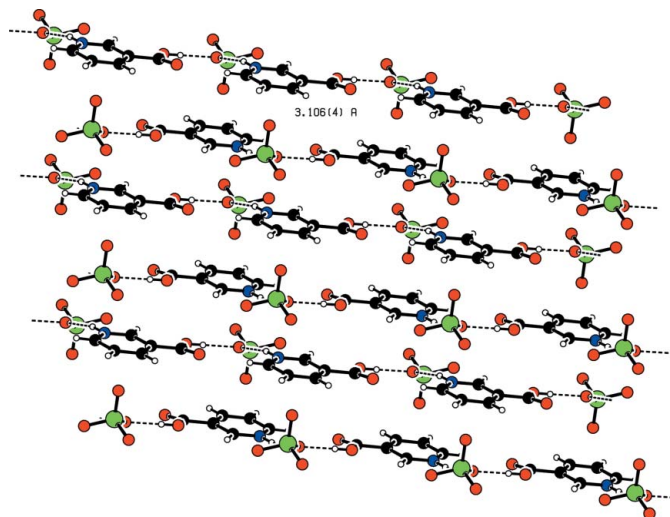


Figure 4

Cationic layers separated by a distance of 3.106 (4) Å, with hydrogen bonds drawn as dashed lines.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N11—H11···O1 ⁱ	0.86	1.91	2.755 (6)	165
O1B—H1B···O1 ⁱⁱ	0.82	1.76	2.582 (6)	178
O2B—H2B···O2	0.82	1.72	2.528 (5)	168
N21—H21···O3 ⁱⁱⁱ	0.86	1.80	2.641 (6)	167

Symmetry codes: (i) -*x* + 1, -*y* + 1, -*z*; (ii) -*x* + 1, -*y*, -*z*; (iii) -*x* + 2, -*y* + 1, -*z* + 1.

Five strong reflections were omitted from the final refinement as they showed *I_o* << *I_c*. This may be due to primary extinction. All H atoms were placed in geometrically calculated positions, with C—H = 0.93 Å, N—H = 0.86 Å and O—H = 0.82 Å, and allowed to ride on their carrier atoms, with *U_{iso}*(H) = 1.2*U_{eq}*(C) and 1.5*U_{eq}*(N,O).

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* and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL/PC*.

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