Nicotinium dihydrogenphosphate

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Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.030
wR factor = 0.084
Data-to-parameter ratio = 9.7

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

In the title complex, $C_6H_6NO_2^+ \cdot H_2PO_4^-$, the nicotinium cations are sandwiched between layers of dihydrogenphosphate anions. The structure is held together by extensive hydrogen bonding between the O and N atoms of nicotinium cations and the O atoms of the phosphate anions, and between the O atoms of the phosphate anions themselves. The nicotinium cations are packed in layers, with an interlayer distance of 3.116 (5) Å.

Comment

Nicotinic acid, a B vitamin also known as niacin, and its associated complexes have a variety of pharmacological properties. Principal among these is the lowering of serum cholesterol levels (Brutts & Lundholm, 1971). Niacin forms coordination complexes with Sn which have been found to have better antitumour activity than the well known *cis*-platin or doxorubicin (Gielen *et al.*, 1992). In addition, 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). The crystal structures of nicotinic acid (Wright & King, 1953; Kutoglu & Scheringer, 1983), isonicotinic acid (Takusagawa & Shimada, 1976), isonicotinic acid hydrazide (Bhat *et al.*, 1974), 6-aminonicotinic acid hydrochloride (Giantsidis & Turnbull, 2000), 2-(methylsulfanyl)nicotinic acid (Basavoju *et al.*, 2005), nicotinamide (Wright & King, 1954), 1-methyl nicotinamide 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 has also been studied (Ellis *et al.*, 1997). The structure of the title compound, (I), is reported in the present investigation as part of a programme of work on pharmaceutical compounds.

(I)
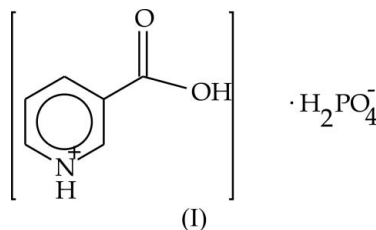
The title compound (I), also known as 3-carboxypyridinium dihydrogenphosphate, has a nicotinium cation and a dihydrogenphosphate anion in the asymmetric unit of the monoclinic unit cell. One of the H atoms in the inorganic acid is transferred to the N atom of the nicotinic acid. This protonation is well confirmed by the C—N bond distances and C—N—C bond angle. The pyridinium ring is planar, with a mean
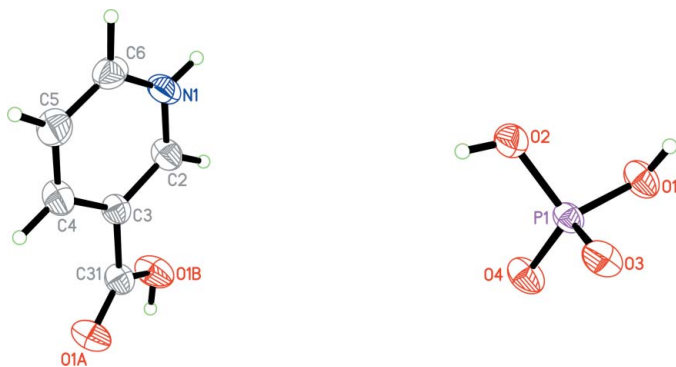
Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme and 50% probability displacement ellipsoids.
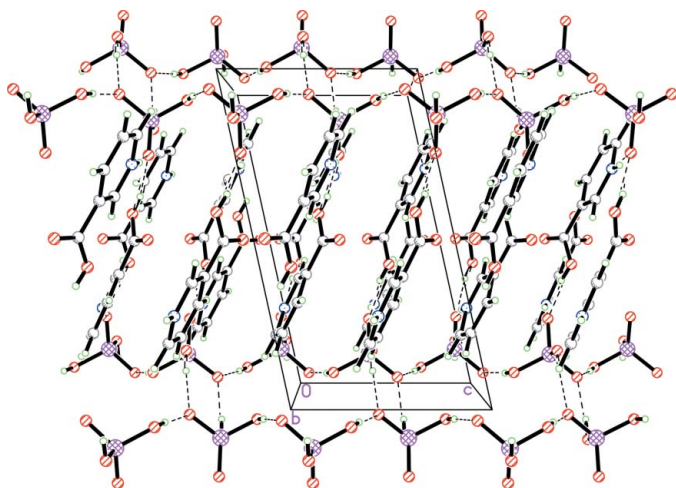
Figure 2
A packing diagram for (I), viewed down the *b* axis. Hydrogen bonds are drawn as dashed lines.

deviation of 0.0039 Å. The planar carboxyl group is twisted from the pyridinium plane, with a dihedral angle of 21.7 (2)°. The deviation from the pyridinium plane is slightly higher for atom O1*B* [0.427 (3) Å] than for atom O1*A* [0.401 (3) Å], probably as a result of hydrogen bonding, as in 2-aminonicotinic acid (Dobson & Gerkin, 1997). The C—O bond distances and C—C—O bond angles confirm that the H atom is connected to atom O1*B* (Table 1).

The P—O distances in the phosphate anions are as expected, with average single- and double-bonded P—O distances of 1.55 and 1.49 Å, respectively (Blessing, 1986). The lengthening of the P–O double bonds is due to the formation of strong O—H···O hydrogen bonds. The tetrahedral geometry of the dihydrogenphosphate anion has also suffered due to the hydrogen-bonding interactions. All four phosphate O atoms are involved in hydrogen bonding, with two as donors and two as acceptors. The doubly-bonded O atoms of the anion act as acceptors in hydrogen bonds to both O and N donor atoms (Table 2). Two dihydrogenphosphate anions are linked by inversion-related O1—H1P···O3 hydrogen bonds, while a glide-related hydrogen-bonded chain of O2P—H2P···O3 bonds runs along the *c* axis, generating double chains along c. The cations are linked to these anion chains by

O1—H1*B*···O4 hydrogen bonds and the classical hydrogen-bonding network is completed by N1—H1···O4 interactions. These serve to pack the nicotinium cations into layers separated by 3.116 (5) Å but not linked by any hydrogen bonding (Fig. 2).

Experimental

Crystal data

$C_6H_6NO_2{}^+ \cdot H_2PO_4{}^-$	D_m measured by flotation in a
$M_r = 221.10$	mixture of $CHBr_3$ and CCl_4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.158$ (5) Å	Cell parameters from 25
$b = 10.593$ (4) Å	reflections
$c = 7.001$ (3) Å	$\theta = 9.7–14.3°$
$\beta = 102.35$ (3)°	$\mu = 0.32$ mm^{-1}
$V = 880.8$ (6) Å^3	$T = 293$ (2) K
$Z = 4$	Block, colourless
$D_x = 1.667$ Mg m^{-3}	$0.20 \times 0.17 \times 0.14$ mm
$D_m = 1.652$ Mg m^{-3}	

Data collection

Nonius MACH3 four-circle	$R_{int} = 0.047$
diffractometer	$\theta_{max} = 25.0°$
$\omega/2\theta$ scans	$h = -14 \rightarrow 14$
Absorption correction: ψ scan	$k = -12 \rightarrow 1$
(North *et al.*, 1968)	$l = 0 \rightarrow 8$
$T_{min} = 0.847$, $T_{max} = 1.000$	3 standard reflections
1880 measured reflections	frequency: 60 min
1545 independent reflections	intensity decay: none
1317 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0512P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$+ 0.2334P]$
$wR(F^2) = 0.084$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
1545 reflections	$\Delta\rho_{max} = 0.25$ e Å^{-3}
160 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
All H-atom parameters refined	Extinction correction: *SHELXTL/ PC*
	Extinction coefficient: 0.131 (7)

Table 1
Selected geometric parameters (Å, °).

N1—C6	1.334 (3)	P1—O4	1.5026 (13)
N1—C2	1.340 (3)	P1—O3	1.5135 (14)
C31—O1*A*	1.204 (2)	P1—O2	1.5603 (16)
C31—O1*B*	1.317 (2)	P1—O1	1.5640 (14)
C6—N1—C2	122.37 (18)	O1*B*—C31—C3	113.40 (16)
O1*A*—C31—C3	121.89 (17)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O4^i	0.83 (3)	1.92 (3)	2.746 (2)	171 (2)
O1*B*—H1*B*···O4^{ii}	0.81 (3)	1.78 (3)	2.586 (2)	169 (3)
O1—H1P···O3^{iii}	0.83 (3)	1.78 (3)	2.613 (2)	175 (3)
O2—H2P···O3^{iv}	0.84 (4)	1.73 (4)	2.561 (2)	173 (3)

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

All H atoms were located and refined isotropically.

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*; software used to prepare material for publication: *SHELXTL/PC*.

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