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3-Carboxypyridinium hydrogen oxalate

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In the title compound, $C_6H_6NO_2^+\cdot C_2HO_4^-$, the cations and anions are situated on a mirror plane. The crystal structure involves two-dimensional lamellar sheets formed by cations and anions linked through N—H···O and O—H···O hydrogen bonds. These sheets are separated by a distance of 3.024 (1) Å.

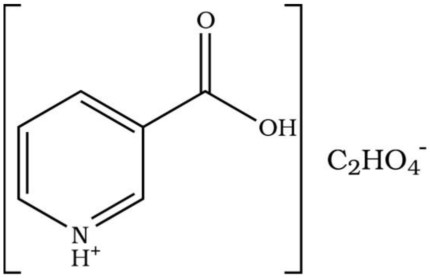
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.108
Data-to-parameter ratio = 10.4

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

Comment

Nicotinic acid (pyridine-3-carboxylic 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. A nicotinic acid complex, *viz*. 5-methylpyrazine-2-carboxylic acid 4-oxide, is a commonly used drug for hypercholesterolemia (Lorenzen *et al.*, 2001). Many of its pharmacological properties are detailed in our previous publications (Athimoolam *et al.*, 2005; Athimoolam & Rajaram, 2005*a*,*b*). A series of ionic crystals of nicotinic acid–inorganic/organic complexes were grown in our laboratory to study the characteristic features of nicotinic acid, surveyed from the Cambridge Structure Database (Version 5.27; Allen, 2002), *viz*., the twisting of the carboxyl group and hydrogen-bonding extension through the N and O sites of the vitamin. In a continuation of this work, we report here the crystal structure of the title compound, (I).



(I)

The crystal structure of (I) is built of 3-carboxypyridinium cations and hydrogen oxalate anions (Fig. 1). The compound crystallizes in the space group $P2_1/m$. All atoms are situated on a mirror plane (Wyckoff position *e*). The protonation of the N site of the pyridine ring is demonstrated by the C—N bond distances and C—N—C bond angle. Usually, protonation on the aromatic ring leads to a displacement of the specific protonated atomic site (N atom) from the aromatic plane and a slightly larger C—N—C bond angle (>120°). This is observed in the present structure (Table 1). Another characteristic feature, twisting of the carboxyl group from the pyridine plane, is not observed in the present structure due to the mirror plane symmetry.

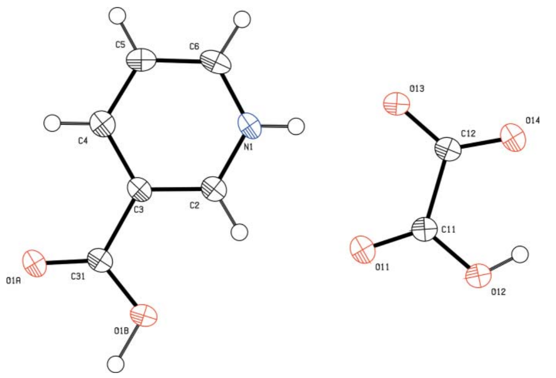


Figure 1
The molecular structure of the title compound, (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

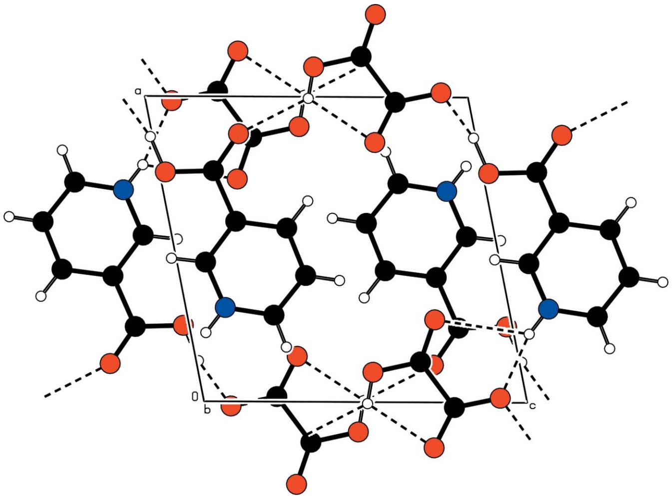


Figure 2
Packing diagram of (I), viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

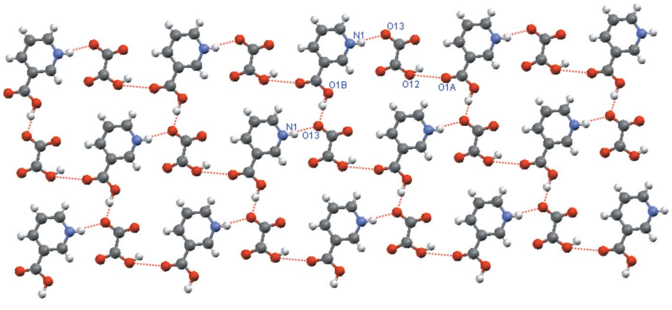


Figure 3
The sheet-like structure of cations and anions generated by hydrogen bonds (shown as dashed lines).

Cations and anions are placed alternately and linked through intermolecular hydrogen bonds (Fig. 2 and Table 2). The N—H···O and oxalate O—H···O bonds form a chain running along the diagonal of the *ac*-plane with graph-set motif $C_2^2(11)$. These one-dimensional chains are cross-linked through carboxypyridinium O—H···O bonds, forming two-dimensional sheets of the cations and anions (Fig. 3). This sheet-like structure parallel to the *ac*-plane leads to a strong X-ray intensity for the (020) plane. These lamellar sheets are separated by an interlayer distance of 3.024 (1) Å. There are no hydrogen-bonding interactions between these layers.

Experimental

The title compound, (I), was crystallized by slow evaporation of a aqueous mixture of nicotinic acid and oxalic acid in a 1:1 stoichiometric ratio.

Crystal data

$C_6H_6NO_2^+ \cdot C_2HO_4^-$
$M_r = 213.15$
Monoclinic, $P2_1/m$
$a = 8.438$ (6) Å
$b = 6.048$ (2) Å
$c = 8.774$ (5) Å
$\beta = 101.29$ (3)°
$V = 439.1$ (4) Å^3
$Z = 2$
$D_x = 1.612$ Mg m^{-3}
$D_m = 1.59(2)$ Mg m^{-3}
D_m measured by flotation using a mixture of xylene and bromoform
Mo $K\alpha$ radiation
$\mu = 0.14$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.23 × 0.21 × 0.14 mm

Data collection

Enraf–Nonius MACH3 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.960$, $T_{\max} = 0.978$
1304 measured reflections
1046 independent reflections
865 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 27.0°$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.108$
$S = 1.08$
1046 reflections
101 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 0.0801P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Extinction correction: *SHELXTL/PC*
Extinction coefficient: 0.029 (8)

Table 1
Selected geometric parameters (Å, °).

N1—C6	1.339 (2)	C11—O11	1.206 (2)
N1—C2	1.344 (2)	C11—O12	1.317 (2)
C31—O1*A*	1.214 (2)	C12—O14	1.223 (2)
C31—O1*B*	1.304 (2)	C12—O13	1.268 (2)
C6—N1—C2	122.30 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O13	0.98 (3)	1.79 (3)	2.748 (2)	163 (3)
O1*B*—H1*B*···O13$^{\rm i}$	1.03 (4)	1.53 (4)	2.5438 (18)	168 (3)
O12—H12···O1*A*$^{\rm ii}$	0.87 (3)	2.12 (3)	2.7280 (18)	126 (2)
O12—H12···O14	0.87 (3)	2.16 (3)	2.6376 (19)	114 (2)

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

The H atoms on N1, O1*B* and O12 were located in a difference fourier map and refined isotropically. All other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom).

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: *Mercury* (Macrae *et al.*, 2006) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL/PC*.

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