

S. Athimoolam and R. K. Rajaram*

Department of Physics, Madurai Kamaraj University, Madurai 625 021, India

Correspondence e-mail:
rkrspmku@yahoo.co.in**Key indicators**Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(C-C) = 0.004$ Å
 R factor = 0.043
 wR factor = 0.127
Data-to-parameter ratio = 9.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.**Bis(nicotinic acid) hydrogen perchlorate**

The title compound, $2C_6H_5NO_2 \cdot H^+ \cdot ClO_4^-$, consists of [(nicotinic acid) $_2H$] $^+$ cations and ClO_4^- anions. Two nicotinic acid zwitterions are linked by a strong symmetric $O-H \cdots O$ hydrogen bond, with the H atom on an inversion center and an $O \cdots O$ distance of 2.464 (4) Å, forming a cation. The nicotinic acid cation forms hydrogen bonds to adjacent cations, giving two-dimensional layers. The Cl atom of the perchlorate anion lies on a twofold axis.

Received 11 July 2005

Accepted 18 July 2005

Online 23 July 2005

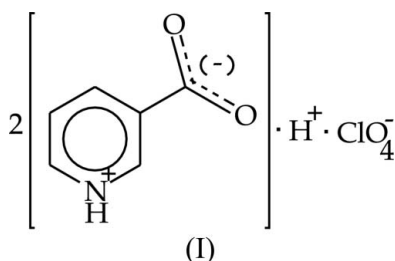
Comment

In organic complexes with inorganic acids, when the number of H atoms liberated from the inorganic acid is less than the number of organic molecules, the H atom may be shared by the two molecules, leading to the formation of a hydrogen-bonded cation, as found in [(nicotinic acid) $_2H$] $^+$ iodide (Goher *et al.*, 2003), bis(β -alanine) hydrogen nitrate (Sridhar *et al.*, 2001) and bis(L-proline) hydrogen nitrate (Pandiarajan *et al.*, 2002). Nicotinic acid (vitamin B) and its complexes have a variety of pharmacological properties, such as lowering of serum cholesterol levels (Brutts & Lundholm, 1971). Metal coordination complexes of nicotinic acid possess antitumor activity (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 (Taku-sagawa & 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), 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. 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) has also been studied. To study the hydrogen-bonding pattern in pharmacologically important nicotinic acid complexes, nicotinic acid was treated with different inorganic acids and the structure of a complex with perchloric acid is reported in the present investigation.

The asymmetric unit of the title compound, (I), contains a nicotinic acid residue, half of an H atom on an inversion center and half of a perchlorate anion with twofold rotation site symmetry. The pyridinium ring is planar, with an r.m.s. deviation of 0.008 Å. The planar carboxyl group is twisted

from the pyridinium plane by an angle of $10.6(4)^\circ$. Carboxyl atom O1B [0.301(5) Å] lies farther from this plane than atom O1A [0.098(5) Å], as a result of the strong symmetric O—H···O hydrogen bond between the nicotinic acid molecules. Similar twisting is observed in the nicotinic acid complex with orthophosphoric acid (Athimoolam *et al.*, 2005) and in 2-aminonicotinic acid (Dobson & Gerkin, 1997). In the cation, the N atoms are protonated because of the migration of the carboxyl H atom to form a zwitterion. Protonation of the N atom is confirmed by the C—N bond distances and the C—N—C bond angle (Table 1).



The perchlorate anions show nearly tetrahedral symmetry and are sandwiched between bilayers of nicotinic acid residues. The two zwitterions in the cation are linked by an O1B—H1B···O1Bⁱ hydrogen bond (Table 2). Each cation is further engaged in N—H···O hydrogen bonds with adjacent cations (Table 2). Thus a chain results and is extended along the *c* axis of the unit cell. Linking of the zwitterions by the symmetric O—H···O hydrogen bond links two nicotinic acid chains and leads to a double layer or two-dimensional network running in the *bc* plane (Fig. 2). Each approximately planar cation $\{[(\text{nicotinic acid})_2\text{H}]^+\}$ is inclined at an angle of $38.13(4)^\circ$ to the adjacent cation to which it is hydrogen bonded.

Experimental

The title compound was crystallized from a nicotinic acid and perchloric acid mixture in the stoichiometric ratio of 2:1 at room temperature by the technique of slow evaporation. Caution: Although no problems were encountered in this work, perchlorate compounds are potentially explosive. They should be prepared in small amounts and handled with care.

Crystal data

$2\text{C}_6\text{H}_5\text{NO}_2\cdot\text{H}^+\cdot\text{ClO}_4^-$
 $M_r = 346.68$
 Monoclinic, $C2/c$
 $a = 11.824(3) \text{ \AA}$
 $b = 9.6214(11) \text{ \AA}$
 $c = 13.669(2) \text{ \AA}$
 $\beta = 111.990(18)^\circ$
 $V = 1441.9(4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.597 \text{ Mg m}^{-3}$
 $D_m = 1.583 \text{ Mg m}^{-3}$

D_m measured by flotation in a mixture of xylene and bromoform
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 9.7\text{--}14.2^\circ$
 $\mu = 0.31 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Block, colorless
 $0.19 \times 0.15 \times 0.12 \text{ mm}$

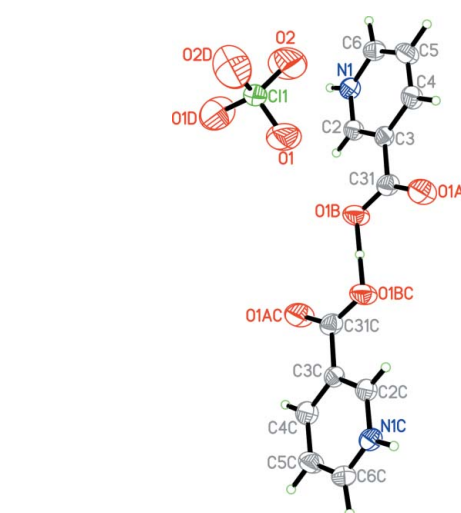


Figure 1

The molecular structure of the title compound, showing the atom-numbering scheme and with 50% probability displacement ellipsoids. Atoms labeled with the suffixes *C* and *D* are generated by the symmetry operations $(\frac{1}{2} - x, -\frac{1}{2} - y, 2 - z)$ and $(-x, y, \frac{3}{2} - z)$, respectively.

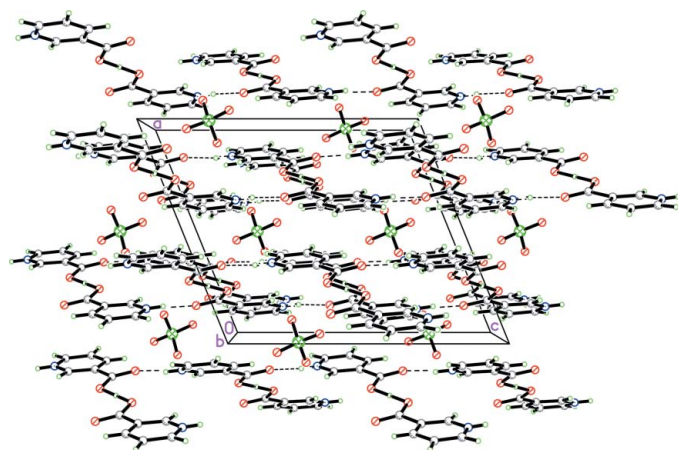


Figure 2

Packing diagram for (I), viewed down the *b* axis (Bruker, 2000). Dashed lines indicate hydrogen bonds.

Data collection

Nonius MACH3 four-circle diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.970$, $T_{\max} = 0.999$
 1490 measured reflections
 1261 independent reflections
 1030 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = 0 \rightarrow 14$
 $k = -1 \rightarrow 11$
 $l = -16 \rightarrow 15$
 3 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.127$
 $S = 1.06$
 1261 reflections
 127 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2 + 2.6398P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.45 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0039 (11)

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.328 (3)	N1—C6	1.341 (4)
C2—N1—C6	123.0 (2)		
C4—C3—C31—O1A	−11.3 (4)	C2—C3—C31—O1B	−9.8 (4)

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>
O1B—H1B···O1B ⁱ	1.23	1.23	2.464 (4)	180
N1—H1···O1A ⁱⁱ	0.87 (3)	1.80 (3)	2.652 (3)	168 (3)

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

All the H atoms were located and refined isotropically [C—H = 0.90 (3)–0.99 (4) Å].

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*.

The authors thank the Department of Science and Technology, Government of India, for establishing a single-crystal diffractometer facility at the School of Physics, Madurai Kamaraj University, Madurai, through the FIST program.

References

- Athimoolam, S., Anitha, K. & Rajaram, R. K. (2005). *Acta Cryst.* **E61**, o2553–o2555.
- Basavoju, S., Reddy, C. M. & Desiraju, G. R. (2005). *Acta Cryst.* **E61**, o822–o823.
- Bhat, T. N., Singh, T. P. & Vijayan, M. (1974). *Acta Cryst.* **B30**, 2921–2922.
- Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Brutts, R. & Lundholm, L. (1971). *J. Atheroscler. Res.* pp 14–19.
- Bulut, A., Yesilel, O. Z., Dege, N., Icbudak, H., Olmaz, H. & Bujukgungor, O. (2003). *Acta Cryst.* **C59**, o727–o729.
- Choi, S. N., Lee, Y. M., Lee, H. W., Kangb, S. K. & Kim, Y. I. (2002). *Acta Cryst.* **E58**, m583–m585.
- Dobson, A. J. & Gerkin, R. E. (1997). *Acta Cryst.* **C53**, 1427–1429.
- Ellis, P. J., Appleby, C. A., Guss, J. M., Hunter, W. N., Ollis, D. L. & Freeman, H. C. (1997). *Acta Cryst.* **D53**, 302–310.
- Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
- Freeman, G. R. & Bugg, C. E. (1974). *Acta Cryst.* **B30**, 431–443.
- Giantsidis, J. & Turnbull, M. M. (2000). *Acta Cryst.* **C56**, 334–335.
- Gielen, M., Khloufi, A. E., Biesemans, M. & Willem, R. (1992). *Polyhedron*, **11**, 1861–1868.
- Goher, M. A. S., Mautner, F. A., Mak, T. C. W. & Abu-Youssef, M. A. M. (2003). *Monatsh. Chem.* **134**, 1519–1527.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Kim, H. L., Yoon, H. J., Ha, J. Y., Lee, B. I., Lee, H. H., Mikami, B. & Suh, W. S. (2004). *Acta Cryst.* **D60**, 948–949.
- Kutoglu, A. & Scheringer, C. (1983). *Acta Cryst.* **C39**, 232–234.
- Nättinen, K. I. & Rissanen, K. (2003). *CrystEngComm*, **5**, 326–330.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Pandiarajan, S., Sridhar, B. & Rajaram, R. K. (2002). *Acta Cryst.* **E58**, o862–o864.
- Patel, N., Jones, D. K. & Raven, E. L. (2000). *Eur. J. Biochem.* **267**, 2581–2587.
- Sridhar, B., Srinivasan, N. & Rajaram, R. K. (2001). *Acta Cryst.* **E57**, o1004–o1006.
- Takusagawa, F. & Shimada, A. (1976). *Acta Cryst.* **B32**, 1925–1927.
- Wright, W. B. & King, G. S. D. (1953). *Acta Cryst.* **6**, 305–310.
- Wright, W. B. & King, G. S. D. (1954). *Acta Cryst.* **7**, 283–288.