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6-Aminonicotinic acid hydrochloride

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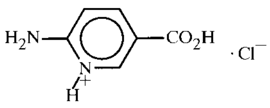
The title compound, 2-amino-5-carboxypyridinium chloride, $C_6H_7N_2O_2^+\cdot Cl^-$, was isolated from a 1 *M* HCl aqueous solution containing 2-amino-5-cyanopyridine. The structure is held together by extensive hydrogen bonding between the chloride ions and the carboxylic acid, amino and pyridinium H atoms. The molecules pack as sheets, with the sheets at a distance of 3.21 (3) Å from one another.

Comment

In our laboratories we are interested in the preparation and study of low-dimensional magnetic lattices which have the general formula A_2MX_4, where M is a 2+ transition metal ion, X = Cl or Br and A is a protonated organic base. Usually, these compounds pack in crystal lattices that create interesting low-dimensional magnetic lattices. The magnetic lattice arises from interactions between the MX_4^- ions. The nature of these interactions is controlled by the crystal lattice, which changes as the organic base is changed. Aromatic compounds containing substituents in the 5-position, such 2-amino-5-methylpyridine (Place & Willett, 1987) and 2-amino-5-chloropyridine (Albrecht, Landi *et al.*, 1997; Albrecht, Wynn *et al.*, 1999; Hammar *et al.*, 1997) have been shown to have very interesting magnetic properties. 2-Amino-5-cyanopyridine was synthesized according to the procedure of Gregory *et al.* (1947) in order to compare its suitability as a base with that of the previously mentioned derivatives. We have prepared metal complexes of 2-amino-5-cyanopyridine (J. Giantsidis & M. M. Turnbull, unpublished results) and were interested in what kind of interactions we might expect between the organic groups themselves. In the course of these studies, 6-aminonicotinic acid hydrochloride, (I), was crystallized from a solution of 2-amino-5-cyanopyridine in aqueous HCl and its structure is presented here.



(I)

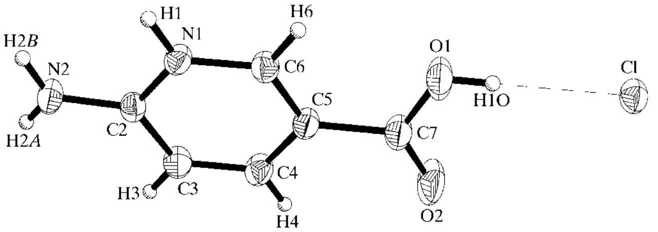


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as circles of an arbitrary radius.

A view of the molecule is shown in Fig. 1. The aromatic ring of (I) is planar, with a mean plane deviation of 0.0047 Å. The carboxyl and the amino groups are canted from that plane, likely as a result of hydrogen bonding in the lattice as in 2-aminonicotinic acid acid (Dobson & Gerkin, 1997).

The crystal lattice exists as nearly planar sheets of protonated 6-aminonicotinic acid molecules and chloride ions that run roughly parallel to the *b* face (see Fig. 2). The plane of the ring is canted 3.8 (2)° relative the *b* face. The ring axis, defined as the C2–C5 vector, is inclined at an angle of 16.4 (2)° relative to the *c* axis. The layers are close together [3.21 (3) Å], but are not linked by hydrogen bonding. However, within the sheets, hydrogen bonds form from the pyridinium proton to the chloride ion, and from one of the amino protons to the choride ion (Table 2). Also, there is a weak hydrogen bond from the other amino proton to the carbonyl oxygen. Even though the distance between N2 and O2 is the shortest, the angle is far from linear, resulting in a weaker interaction. An additional hydrogen bond forms from the carboxylic proton to the chloride ion.

Crystals of the 5-cyano compound are being prepared under anhydrous conditions and the use of 6-aminonicotinic acid for the preparation of low-dimensional magnetic lattices is underway.

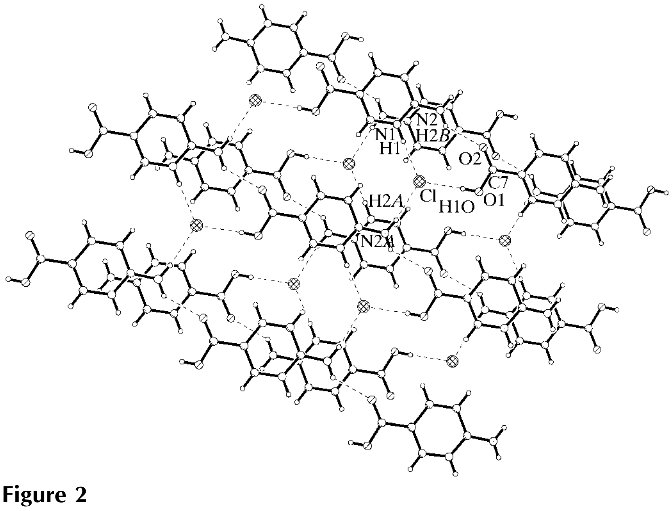


Figure 2
Packing diagram for (I) showing the hydrogen bonding and the relationship between successive sheets within the lattice.

Experimental

Crystals of (I) were grown by dissolving 2-amino-5-cyanopyridine in water (37 ml) and concentrated HCl (3 ml). Colourless rod-shaped crystals were collected after slow evaporation of the solvent. Infrared spectra showed, and X-ray data confirmed, that the cyano group had been hydrolyzed, resulting in the title compound. We were very surprised that under these mild conditions the cyano group hydrolyzed to the carboxylic acid. It is known that 6-aminonicotinic acid can be prepared by hydrolysis of 2-amino-5-cyanopyridine, but at elevated temperature and significantly higher HCl concentrations (Binz & Rath, 1928).

Crystal data

$C_6H_7N_2O_2^+\cdot Cl^-$
$M_r = 174.59$
Triclinic, $P\overline{1}$
$a = 6.844\ (2)$ Å
$b = 6.908\ (2)$ Å
$c = 9.061\ (3)$ Å
$\alpha = 101.398\ (4)^\circ$
$\beta = 90.799\ (4)^\circ$
$\gamma = 112.515\ (3)^\circ$
$V = 386.01\ (19)$ Å^3
$Z = 2$
$D_x = 1.502$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4366 reflections
$\theta = 2.3$–26.4°
$\mu = 0.443$ mm^{-1}
$T = 170\ (2)$ K
Prism, colourless
$0.80 \times 0.54 \times 0.37$ mm

Data collection

Siemens SMART CCD diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.532$, $T_{max} = 0.849$
4979 measured reflections
1566 independent reflections
1459 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 26.4^\circ$
$h = -8 \rightarrow 7$
$k = -8 \rightarrow 8$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.091$
$S = 1.135$
1566 reflections
112 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2 + 0.1511P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

H atoms on N and O were refined isotropically; those bonded to C were constrained.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.350 (2)	C4—C5	1.409 (3)
N1—C6	1.355 (2)	C5—C6	1.367 (2)
C2—N2	1.330 (2)	C5—C7	1.489 (2)
C2—C3	1.420 (2)	C7—O2	1.213 (2)
C3—C4	1.365 (2)	C7—O1	1.318 (2)
C2—N1—C6	122.97 (15)	C6—C5—C4	118.34 (16)
C2—N1—H1	118.4 (13)	C6—C5—C7	121.11 (16)
C6—N1—H1	118.6 (13)	C4—C5—C7	120.55 (16)
N2—C2—N1	119.18 (16)	N1—C6—C5	120.65 (16)
N2—C2—C3	123.12 (17)	O2—C7—O1	124.46 (17)
N1—C2—C3	117.70 (15)	O2—C7—C5	122.64 (17)
C4—C3—C2	119.91 (16)	O1—C7—C5	112.90 (15)
C3—C4—C5	120.43 (16)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$Cl^{i}	0.91 (2)	2.17 (2)	3.0766 (16)	177.1 (19)
N2—H2$A\cdots$Cl^{ii}	0.87 (3)	2.37 (3)	3.234 (2)	170 (2)
O1—H1O$\cdots$Cl	0.83 (3)	2.21 (3)	3.0381 (16)	177 (2)
N2—H2$B\cdots$O2^{i}	0.84 (2)	2.17 (2)	2.847 (2)	138 (2)

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1270). Services for accessing these data are described at the back of the journal.

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