C(1)	0.3795 (3)	−0.3151 (3)	0.8621 (2)	3.15 (6)
C(2)	0.2911 (3)	−0.4167 (3)	0.9369 (2)	3.83 (7)
C(3)	0.3795 (4)	−0.3694 (3)	1.0639 (2)	4.16 (7)
C(4)	0.5585 (4)	−0.2198 (4)	1.1235 (3)	4.83 (8)
C(5)	0.6465 (4)	−0.1231 (3)	1.0535 (3)	4.38 (7)
C(6)	0.5621 (3)	−0.1658 (3)	0.9213 (2)	3.22 (6)
C(7)	0.6409 (3)	−0.0712 (3)	0.8402 (3)	3.44 (6)
C(8)	0.5458 (3)	−0.1209 (3)	0.7147 (2)	3.28 (6)
C(9)	0.3644 (3)	−0.2733 (3)	0.6635 (2)	2.81 (5)
C(10)	0.2586 (3)	−0.3275 (3)	0.5265 (2)	2.99 (5)
C(11)	0.2310 (3)	−0.1989 (3)	0.4704 (3)	4.10 (7)
C(12)	0.1719 (3)	−0.4958 (3)	0.4451 (2)	3.09 (5)
C(13)	0.3110 (4)	−0.6496 (3)	0.5651 (3)	4.86 (7)
C(14)	0.0656 (4)	−0.8036 (4)	0.3523 (3)	5.06 (8)
H(2)	0.172 (3)	−0.519 (3)	0.893 (2)	4.4 (6)*
H(4)	0.608 (4)	−0.194 (3)	1.209 (2)	5.5 (7)*
H(5)	0.766 (4)	−0.026 (3)	1.096 (3)	6.4 (8)*
H(8)	0.591 (3)	−0.063 (3)	0.657 (2)	4.3 (6)*
H(11)	0.148 (3)	−0.251 (3)	0.377 (2)	5.5 (7)*
H(12)	0.093 (3)	−0.510 (3)	0.361 (2)	3.2 (5)*
H(13*a*)	0.336 (3)	−0.739 (3)	0.548 (2)	5.0 (6)*
H(13*b*)	0.253 (4)	−0.665 (4)	0.626 (3)	7.7 (9)*
H(13*c*)	0.432 (4)	−0.536 (4)	0.597 (3)	7.0 (8)*
H(14*a*)	−0.000 (5)	−0.782 (5)	0.281 (4)	11 (1)*
H(14*b*)	−0.020 (4)	−0.884 (4)	0.374 (3)	8.0 (9)*
H(14*c*)	0.127 (4)	−0.853 (4)	0.328 (3)	9 (1)*

* Atoms were refined isotropically.

Table 2. *Selected geometric parameters* (Å, °)

C(9)—C(10)	1.476 (3)	C(12)—N(2)	1.318 (3)
C(10)—C(11)	1.425 (4)	C(13)—N(2)	1.450 (4)
C(11)—O	1.220 (4)	C(14)—N(2)	1.458 (4)
C(10)—C(12)	1.380 (4)		
C(9)—C(10)—C(11)	118.5 (2)	C(10)—C(12)—N(2)	132.6 (2)
C(9)—C(10)—C(12)	126.7 (2)	C(12)—N(2)—C(13)	123.7 (2)
C(11)—C(10)—C(12)	114.7 (2)	C(12)—N(2)—C(14)	119.6 (3)
C(10)—C(11)—O	126.9 (3)	C(13)—N(2)—C(14)	116.7 (3)

The space group $P\bar{1}$ was assumed and confirmed by the successful refinement. The majority of the non-H atoms were obtained from the initial *E* map (*SIR*88; Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989) and the remainder were located in a $\Delta\rho$ map following initial full-matrix least-squares refinement (*MolEN*; Fair, 1990). All H atoms were located in a $\Delta\rho$ map following refinement of all non-H atoms with anisotropic displacement parameters and were refined with individual isotropic displacement parameters.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR*88 (Burla, Camalli, Cascarano, Giacovazzo, Polidori, Spagna & Viterbo, 1989). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: CR1173). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Carboxypyridinium Chloride Monohydrate

Graham Smith*

School of Chemistry, Queensland University of Technology, PO Box 2434, Brisbane 4001, Australia

Karl A. Byriel and Colin H. L. Kennard

Department of Chemistry, The University of Queensland, Brisbane 4072, Australia

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Abstract

The structure of the monohydrated polymorph of picolinic acid hydrochloride, $C_6H_6NO_2^+.Cl^-.H_2O$, has been determined and the role of the lattice water in the hydrogen bonding to the chloride ion considered. In the anhydrous complex of the same compound, an interaction between the chloride and the pyridinium proton is found [Cl···N 3.144 (2) Å]. In addition, the water of hydration forms bridging links between chloride ions [O—H···Cl 3.086 (2), 3.111 (2) Å] and with a carboxylic acid H atom [O···H—O 2.563 (3) Å]. An intramolecular hydrogen bond between the carboxyl O atom and the H atom of the pyridinium moiety is also found [O···H—N 2.669 (4) Å].

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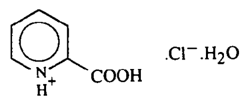
Comment

Picolinic acid (pyridine-2-carboxylic acid) is of considerable interest, particularly to coordination chemists, as it possesses a potentially uninegative bidentate (N,O) donor system with the ability to stabilize complexes through the formation of six-membered chelate rings about metal centres. In addition, the chelate complex formed is often neutral, enabling 'capture' of unstable oxidation states in metals, *e.g.* with tris(pyridine-2-carboxylato-*N*,*O*)manganese(III) monohydrate (Figgis, Raston, Sharma & White, 1978), and dibromo(pyridine-2-carboxylato-*N*,*O*)gold(III) (Dar *et al.*, 1992). Also, a number of simple structures involving common transition metals and often mixed-ligand systems appear both in earlier and current literature, *e.g.* bis(pyridine-2-carboxylato-*N*,*O*)copper(II) monohydrate (Faure, Loiseleur & Thomas-David, 1973) and (pyridine-2-carboxylato-*N*,*O*)ethylenediaminediacetato-N,N^1,O,O^1)cobalt(III) (Billing, Dobson, Pattrick & Carlton, 1991).

The structures of both picolinic acid (Takusagawa & Shimada, 1973) and its anhydrous hydrochloride (Laurent, 1965) have been determined. In an attempted preparation of an antimony(III) complex with picolinic acid, analogous to the trimethyl- and triphenylantimony(III) complexes with picolinic acid (Domagala, Huber & Preut, 1990), a white crystalline solid was isolated, which was subsequently identified as a hydrated polymorph of picolinic acid hydrochloride, (I). Since this compound had not previously been reported in the literature, its structure was determined and is reported here.



(I)

The planar 2-carboxypyridinium cation is conformationally similar to the anhydride (Laurent, 1965) [N(1)—C(2)—C(21)—O(22) −174.7 (3)°]. An intramolecular hydrogen bond is found between the pyridinium proton and the carboxylic O atom [N(1)—H(1)···O(23) 2.669 (4) Å: N—H···O 106 (3)°]. This proton also interacts with the chloride ion [N(1)—H(1)···Cl(1) 3.144 (2) Å; N—H···Cl 154 (3)°], similar to the anhydrous structure. However, unlike the anhydrous structure there is no carboxyl–chloride interaction. In addition, the lattice water participates in a bridging hydrogen-bonding network with both the chloride ion [O(100)—H(102)···Cl(1) 3.086 (2) Å: O—H···Cl 164 (3)°; O(100)—H(101)···Cl(1) 3.111 (2) Å: O—H···Cl 167 (3)°: $\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$], and the H atom of the carboxyl group [O(100)···H(22)—O(22) 2.563 (3) Å: O···H—O 172 (3)°: $1 + x, y, z$]. The atom-numbering scheme and the hydrogen-bonding associations are shown in Fig. 1.

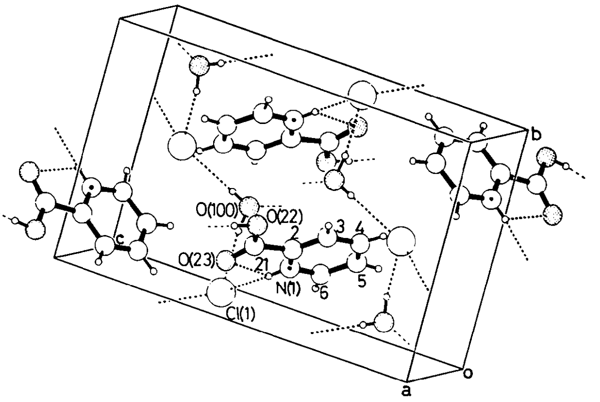


Fig. 1. Atom-numbering scheme and packing in the unit cell, showing hydrogen-bonding associations. Unless otherwise indicated, atoms are hydrogen.

Experimental

The title compound was isolated as a byproduct from the reaction mixture obtained after refluxing a 1:3 molar ratio of antimony(III) chloride and pyridine-2-carboxylic acid (picolinic acid) in water. Colourless prisms formed upon partial evaporation of the solution at room temperature.

Crystal data

$C_6H_6NO_2^+.Cl^-.H_2O$
$M_r = 177.6$
Monoclinic
$P2_1/n$
$a = 6.807$ (1) Å
$b = 8.5813$ (9) Å
$c = 13.994$ (4) Å
$\beta = 98.20$ (1)°
$V = 809.1$ (3) Å^3
$Z = 4$
$D_x = 1.458$ Mg m^{-3}
$D_m = 1.48$ Mg m^{-3}
D_m measured by flotation in $CHCl_3$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6$–14°
$\mu = 0.43$ mm^{-1}
$T = 298$ (2) K
Prismatic
0.30 × 0.13 × 0.10 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
$T_{min} = 0.98$, $T_{max} = 1.00$
2109 measured reflections
1951 independent reflections
1041 observed reflections [$I > 2.0\sigma(I)$]

$R_{int} = 0.029$
$\theta_{max} = 28°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 11$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 200 reflections intensity decay: ±1%

Refinement

Refinement on F^2
$R(F) = 0.039$
$wR(F^2) = 0.095$
$S = 1.01$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: none

1041 reflections
133 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.115P)^2 + 0.82P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cl(1)	0.2617 (1)	0.0006 (1)	0.6465 (1)	0.053 (1)
N(1)	0.3631 (3)	0.2008 (3)	0.4717 (2)	0.043 (1)
C(2)	0.5161 (4)	0.2907 (3)	0.4568 (2)	0.038 (1)
C(21)	0.6955 (4)	0.2773 (3)	0.5328 (2)	0.046 (1)
O(22)	0.8347 (3)	0.3757 (2)	0.5201 (2)	0.056 (1)
O(23)	0.6987 (3)	0.1826 (3)	0.5958 (2)	0.074 (1)
C(3)	0.5008 (5)	0.3839 (3)	0.3769 (2)	0.046 (1)
C(4)	0.3265 (5)	0.3803 (4)	0.3121 (2)	0.056 (1)
C(5)	0.1732 (5)	0.2860 (4)	0.3294 (2)	0.054 (1)
C(6)	0.1938 (4)	0.1955 (3)	0.4112 (2)	0.050 (1)
O(100)	0.1349 (3)	0.3455 (3)	0.6517 (2)	0.058 (1)

Table 2. *Selected geometric parameters* (Å, °)

N(1)—C(6)	1.330 (3)	C(21)—O(22)	1.300 (3)
N(1)—C(2)	1.335 (3)	C(3)—C(4)	1.388 (4)
C(2)—C(3)	1.366 (4)	C(4)—C(5)	1.369 (4)
C(2)—C(21)	1.505 (4)	C(5)—C(6)	1.373 (4)
C(21)—O(23)	1.197 (3)		
C(6)—N(1)—C(2)	123.0 (2)	O(22)—C(21)—C(2)	112.8 (2)
N(1)—C(2)—C(3)	119.7 (2)	C(2)—C(3)—C(4)	118.7 (3)
N(1)—C(2)—C(21)	114.7 (2)	C(5)—C(4)—C(3)	120.0 (3)
C(3)—C(2)—C(21)	125.6 (2)	C(4)—C(5)—C(6)	119.5 (3)
O(23)—C(21)—O(22)	127.2 (3)	N(1)—C(6)—C(5)	119.2 (3)
O(23)—C(21)—C(2)	120.0 (3)		

The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least squares (*SHELXL*93; Sheldrick, 1993) with anisotropic displacement parameters for all non-H atoms. H atoms were located by difference methods and included with both positional and displacement parameters refined. Other programs used were *Xtal*3.2 (Hall, Flack & Stewart, 1992) and *PLATON* (Spek, 1990).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AS1154). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3,4,5-Tetrafluoro-*N*-(4-fluorophenyl)-6-hydroxybenzamide: an Example of a Combined Inter- and Intramolecular O···H···O Bifurcated Hydrogen Bond

R. E. BANKS, R. A. DUBOISSON, R. G. PRITCHARD AND A. E. TIPPING

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England

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Abstract

Although the amide dimensions in the title molecule, $C_{13}H_6F_5NO_2$, show little difference from those of its unfluorinated analogue [Kashino, Matsushita, Iwamoto, Yamaguchi & Haisa (1986). *Acta Cryst.* C**42**, 457–462], the hydroxyl positions are reversed. Whereas in the former, the OH takes part in intra- [O···O 2.508 (3), H···O 1.69 (4) Å; O—H···O 153 (4)°] and intermolecular [O···O 3.029 (3), H···O 2.57 (4) Å; O—H···O 113 (3)°] bifurcated hydrogen bonding, in the latter structure the hydroxyl associates intramolecularly with the amide H atom as well as the amide O atom of a neighbouring molecule.

Comment

The structure determination reported here was carried out as part of a general investigation into the preparation of fluorine-containing arylnitrones and their use as 1,3-dipolar reagents (DuBoisson, 1986). From the reaction of *C*-(pentafluorophenyl)-*N*-(4-fluorophenyl)nitrone

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