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Redetermination of picolinic acid hydrochloride at 150 K

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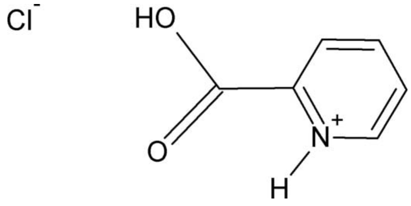
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.029; wR factor = 0.082; data-to-parameter ratio = 16.1.

The structure of the title compound, $C_6H_6NO_2^+\cdot Cl^-$, was previously determined at ambient temperature [Laurent (1965). *Acta Cryst.* **18**, 799–806]. This redetermination at 150 K is to a far higher precision. On cooling to 150 K, the unit cell contracts most in the π–π stacking direction, b, and rather less so in the directions involving the strongly hydrogen-bonded chains, a and c. The π–π stacking distance is $b/2$ (3.263 Å)All of the atoms lie on a mirror plane. There are two strong hydrogen bonds, O—H···Cl and N—H···Cl. Cations and anions form hydrogen-bonded, zigzag chains parallel to the a axis.

Related literature

Laurent (1965) previously determined the stucture of the title compound at ambient temperature with $R1$ = 0.147.



Experimental

Crystal data

$C_6H_6NO_2^+\cdot Cl^-$
M_r = 159.57
Orthorhombic, *Pnma*
a = 13.7876 (15) Å
b = 6.5268 (7) Å
c = 7.7517 (9) Å
V = 697.57 (13) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.48 mm^{-1}
T = 150 (2) K
0.54 × 0.33 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2007)
$T_{\min}$ = 0.782, $T_{\max}$ = 0.954
7281 measured reflections
1045 independent reflections
939 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.082
S = 1.13
1045 reflections
65 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.42 e Å^{-3}
$\Delta\rho_{\min}$ = −0.19 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl1$^{\rm i}$	0.82 (2)	2.34 (2)	3.1058 (14)	156 (2)
O1—H1*A*···Cl1	0.82 (3)	2.19 (3)	2.9982 (13)	167 (3)

Symmetry code: (i) $x+\frac{1}{2}, y, -z+\frac{3}{2}$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

We acknowledge the Loughborough University Development Fund for the provision of a studentship (NMSB).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2162).

References

Bruker (2000). *SHELXTL*. Version 6.10. Bruker AXS Inc., Madison, Wisconsin, USA.
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supplementary materials

Acta Cryst. (2007). E**63**, o4044 [**doi:10.1107/S1600536807044030**]

Redetermination of picolinic acid hydrochloride at 150 K

M. R. J. Elsegood, D. A. Hussain and **N. M. Sanchez-Ballester**

Comment

As part of our studies into complexes, co-crystals and solvates of pyridine and pyrazine (poly)carboxylates we inadvertently produced crystals of pyridine-2-carboxylic acid hydrochloride (I). Fig. 1. shows the asymmetric unit. The structure had been determined previously at ambient temperature with an *R* factor of 0.147 (Laurent, 1965). Comparison of the unit-cell parameters reveals that on cooling to 150 K, taking into account the different unit cell and space group settings, *a* contracts by 0.45%, *b* by 1.85% and *c* by 0.13% (see Figs. 2 & 3). We note that *b*/2 is the interlayer spacing with soft π-π stacking interactions only, while *a* and *c* incorporate the strong, less compressable, hydrogen bonds. The basic structure was discussed in datail in Laurent's paper. See tables for hydrogen bond geomery which has been determined here more precisely. Laurent notes an apparently very short C═O bond length of 1.17 Å, but the current study suggests a more normal value of 1.200 (2) Å.

Experimental

Picolinic acid (0.115 g; 0.934 mmol) in methanol/ethanol (10 ml, 1:1) was added dropwise to a solution of $Cu(PPh_3)_2(BH_4)$ (0.450 g; 0.746 mmol) in CH_2Cl_2 (10 ml). The solution was stirred for 15 min, then reduced in volume to give a yellow precipitate (0.468 g). Crystals were obtained by vapour diffusion from methanol/ethanol (1:1) with diethylether as precipitant. The source of the HCl is thought to have been the dichloromethane solvent in the initial reaction.

Refinement

Aromatic H atoms were placed in geometric positions (C—H distance = 0.95 Å) using a riding model. N*H* and O*H* hydrogen coordinates were freely refined. U_{iso} values were set to $1.2U_{eq}$ of the carrier atom for C*H* and N*H*, $1.5U_{eq}$ for O*H*.

Figures

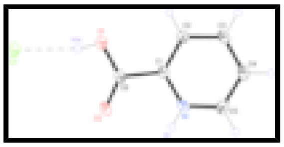

Fig. 1. View of **I**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

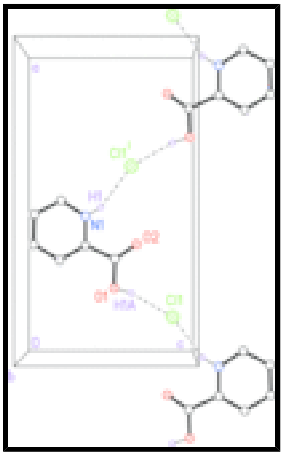

Fig. 2. Packing plot of **I** viewed parallel to *b*, showing the strong hydrogen bonds. Most hydrogen atoms have been removed for clarity. Symmetry code: (i) $x + 1/2, y, -z + 3/2$

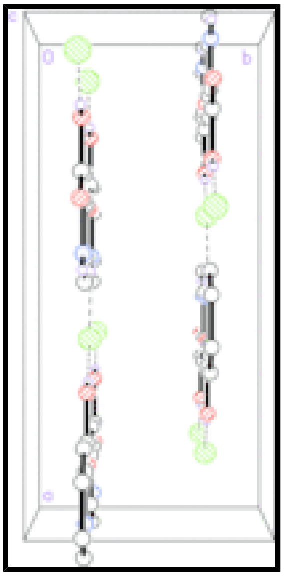

Fig. 3. Packing plot of **I** viewed parallel to *c*, showing the π-π stacked layer structure. Most hydrogen atoms have been removed for clarity.

picolinic acid hydrochloride

Crystal data

$C_6H_6NO_2^+ \cdot Cl^-$

$M_r = 159.57$

Orthorhombic, *Pnma*

Hall symbol: -P 2ac 2n

$a = 13.7876\ (15)$ Å

$b = 6.5268\ (7)$ Å

$c = 7.7517\ (9)$ Å

$V = 697.57\ (13)$ Å^3

$Z = 4$

$F_{000} = 328$

$D_x = 1.519$ Mg m^{-3}

Mo *K*α radiation
λ = 0.71073 Å

Cell parameters from 3266 reflections

θ = 3.0–30.4°

μ = 0.48 mm^{-1}

$T = 150\ (2)$ K

Plate, colourless

0.54 × 0.33 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer	1045 independent reflections
Radiation source: fine-focus sealed tube	939 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.024$
$T = 150(2)$ K	$\theta_{\text{max}} = 29.5°$
ω rotation with narrow frames scans	$\theta_{\text{min}} = 3.0°$
Absorption correction: multi-scan (SADABS; Sheldrick, 2007)	$h = -19 \rightarrow 18$
$T_{\text{min}} = 0.782$, $T_{\text{max}} = 0.954$	$k = -9 \rightarrow 9$
7281 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: geom except NH & OH coords freely refined
$R[F^2 > 2\sigma(F^2)] = 0.029$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.082$	$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2 + 0.234P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.13$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1045 reflections	$\Delta\rho_{\text{max}} = 0.42$ e Å^{-3}
65 parameters	$\Delta\rho_{\text{min}} = -0.19$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.12483 (3)	0.2500	0.87284 (5)	0.02637 (14)
C1	0.36168 (11)	0.2500	0.35614 (19)	0.0214 (3)
C2	0.31249 (12)	0.2500	0.20260 (19)	0.0245 (3)
H2	0.2436	0.2500	0.2010	0.029*

C3	0.36462 (12)	0.2500	0.0493 (2)	0.0270 (4)
H3	0.3315	0.2500	−0.0582	0.032*
C4	0.46489 (13)	0.2500	0.0538 (2)	0.0294 (4)
H4	0.5014	0.2500	−0.0502	0.035*
C5	0.51094 (12)	0.2500	0.2117 (2)	0.0292 (4)
H5	0.5798	0.2500	0.2173	0.035*
N1	0.45886 (11)	0.2500	0.35628 (17)	0.0233 (3)
H1	0.4884 (16)	0.2500	0.448 (3)	0.028*
C6	0.31613 (13)	0.2500	0.5312 (2)	0.0302 (4)
O1	0.22104 (9)	0.2500	0.52598 (16)	0.0299 (3)
H1A	0.204 (2)	0.2500	0.628 (3)	0.045*
O2	0.36553 (11)	0.2500	0.65865 (18)	0.0631 (7)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0215 (2)	0.0388 (2)	0.0188 (2)	0.000	0.00604 (13)	0.000
C1	0.0184 (7)	0.0329 (8)	0.0129 (6)	0.000	0.0009 (5)	0.000
C2	0.0178 (7)	0.0410 (9)	0.0147 (7)	0.000	−0.0002 (5)	0.000
C3	0.0252 (8)	0.0440 (10)	0.0118 (6)	0.000	−0.0018 (6)	0.000
C4	0.0254 (8)	0.0478 (11)	0.0150 (7)	0.000	0.0046 (6)	0.000
C5	0.0186 (7)	0.0475 (11)	0.0216 (8)	0.000	0.0023 (6)	0.000
N1	0.0186 (6)	0.0378 (8)	0.0135 (6)	0.000	−0.0029 (5)	0.000
C6	0.0229 (8)	0.0544 (11)	0.0134 (7)	0.000	0.0019 (6)	0.000
O1	0.0211 (6)	0.0534 (8)	0.0150 (5)	0.000	0.0035 (4)	0.000
O2	0.0252 (7)	0.152 (2)	0.0117 (6)	0.000	−0.0012 (5)	0.000

Geometric parameters (Å, °)

C1—N1	1.340 (2)	C4—H4	0.9500
C1—C2	1.370 (2)	C5—N1	1.331 (2)
C1—C6	1.495 (2)	C5—H5	0.9500
C2—C3	1.389 (2)	N1—H1	0.82 (2)
C2—H2	0.9500	C6—O2	1.200 (2)
C3—C4	1.383 (2)	C6—O1	1.312 (2)
C3—H3	0.9500	O1—H1A	0.82 (3)
C4—C5	1.379 (2)		
N1—C1—C2	119.72 (14)	C3—C4—H4	120.6
N1—C1—C6	114.79 (14)	N1—C5—C4	119.94 (16)
C2—C1—C6	125.48 (15)	N1—C5—H5	120.0
C1—C2—C3	119.16 (15)	C4—C5—H5	120.0
C1—C2—H2	120.4	C5—N1—C1	122.61 (14)
C3—C2—H2	120.4	C5—N1—H1	117.5 (16)
C4—C3—C2	119.72 (15)	C1—N1—H1	119.9 (16)
C4—C3—H3	120.1	O2—C6—O1	126.34 (16)
C2—C3—H3	120.1	O2—C6—C1	120.58 (16)
C5—C4—C3	118.85 (16)	O1—C6—C1	113.08 (14)
C5—C4—H4	120.6	C6—O1—H1A	105 (2)

N1—C1—C2—C3	0.0	C2—C1—N1—C5	0.0
C6—C1—C2—C3	180.0	C6—C1—N1—C5	180.0
C1—C2—C3—C4	0.0	N1—C1—C6—O2	0.0
C2—C3—C4—C5	0.0	C2—C1—C6—O2	180.0
C3—C4—C5—N1	0.0	N1—C1—C6—O1	180.0
C4—C5—N1—C1	0.0	C2—C1—C6—O1	0.0

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1^{i}	0.82 (2)	2.34 (2)	3.1058 (14)	156 (2)
O1—H1A···Cl1	0.82 (3)	2.19 (3)	2.9982 (13)	167 (3)

Symmetry codes: (i) *x*+1/2, *y*, −*z*+3/2.

Fig. 1

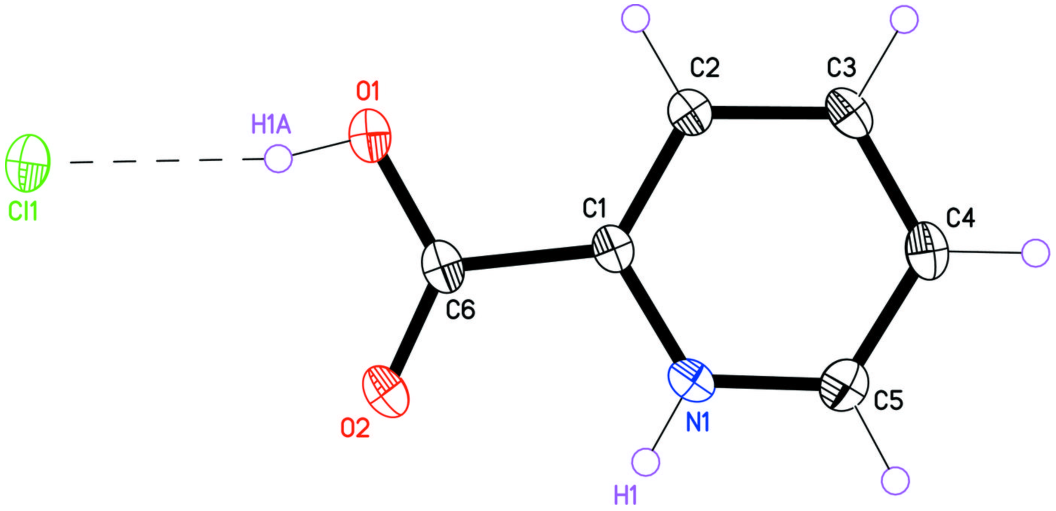

Fig. 2

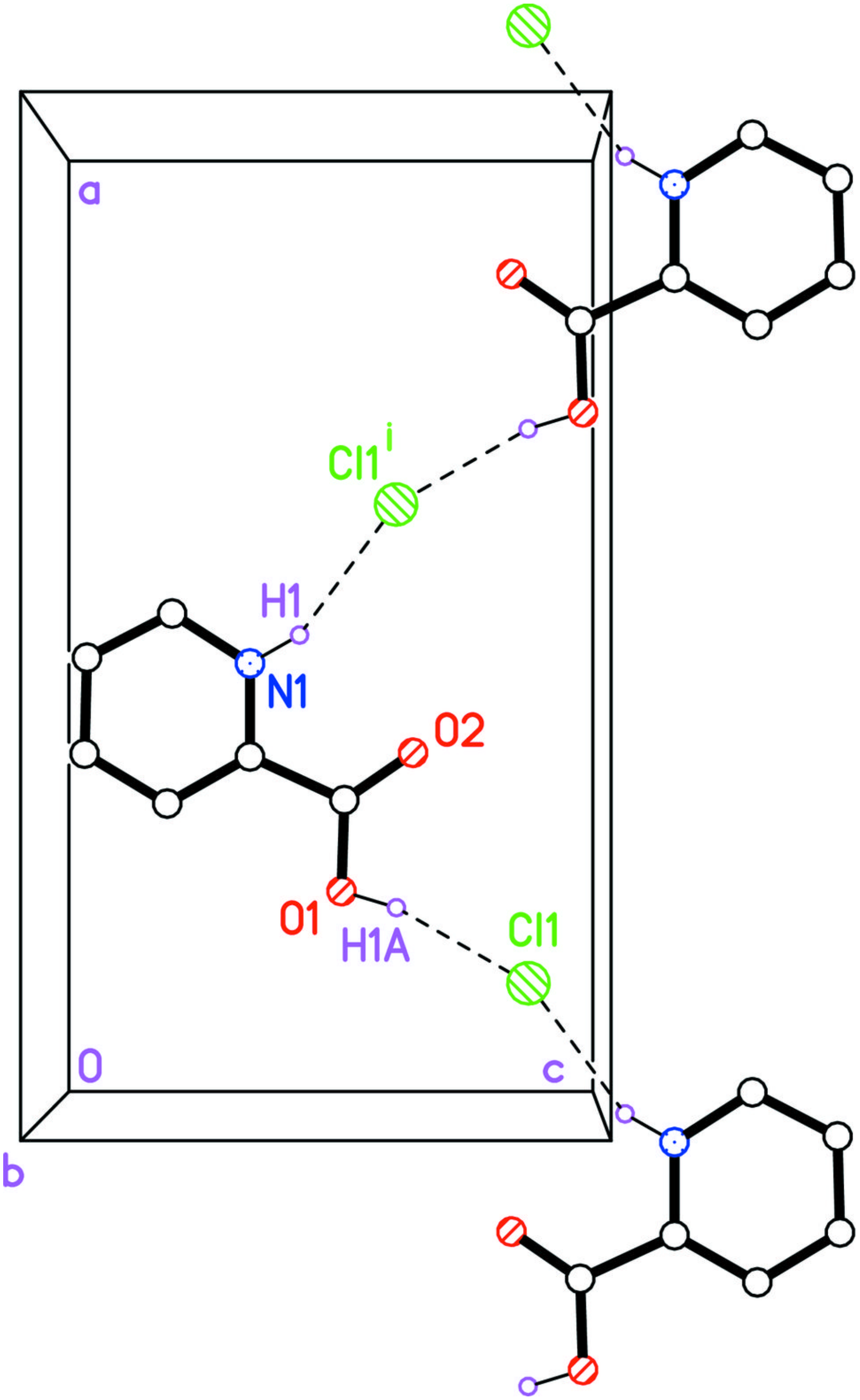

Fig. 3