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The crystal structure of 5-nitropicolinic acid monohydrate, $C_6H_6N_2O_5$

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Abstract

$C_6H_6N_2O_5$, monoclinic, $C2/c$ (no. 15), $a = 13.1766(11)$ Å, $b = 5.1019(4)$ Å, $c = 22.602(2)$ Å, $\beta = 91.081(3)^\circ$, $V = 1519.2(2)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0334$, $wR_{ref}(F^2) = 0.0961$, $T = 150(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All of materials are used as received. 1.68 g 5-Nitropicolinic acid (1 mmol), was added to 15 mL THF solution and stirred for 30 min without heating, then the solution was filtered and evaporated in air under room temperature. 3 days later, colorless crystals were harvested, yield 80.3% (based on 5-nitropicolinic acid).

Experimental details

The structure was solved by direct methods with the SHELXS program. All H-atoms were positioned with idealized

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	$0.25 \times 0.15 \times 0.10$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.15 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.2° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9766, 1366, 0.036
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1107
$N(\text{param})_{\text{refined}}$:	122
Programs:	Bruker [1], SHELX [2], Olex2 [3, 4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.55169(12)	0.4268(3)	0.43019(7)	0.0310(4)
C2	0.46086(11)	0.5367(3)	0.39724(7)	0.0304(4)
C3	0.47436(12)	0.7411(3)	0.35774(7)	0.0342(4)
H3	0.54017(12)	0.8096(3)	0.35098(7)	0.0411(5)*
C4	0.39033(12)	0.8436(3)	0.32835(7)	0.0343(4)
H4	0.39624(12)	0.9851(3)	0.30133(7)	0.0411(5)*
C5	0.29770(11)	0.7315(3)	0.33993(7)	0.0312(4)
C6	0.28908(12)	0.5256(3)	0.37959(7)	0.0316(4)
H6	0.22418(12)	0.4517(3)	0.38645(7)	0.0379(4)*
N1	0.37030(10)	0.4295(3)	0.40830(6)	0.0319(3)
N2	0.20582(10)	0.8320(3)	0.31020(6)	0.0327(3)
O1	0.52946(8)	0.2305(2)	0.46469(5)	0.0401(3)
H1	0.58291(19)	0.172(3)	0.4806(7)	0.0601(5)*
O2	0.63621(8)	0.5163(2)	0.42386(5)	0.0362(3)
O3	0.20945(9)	1.0516(2)	0.28846(5)	0.0412(3)
O4	0.12992(8)	0.6920(2)	0.30901(5)	0.0393(3)
O1W	0.67497(8)	0.0030(2)	0.51679(5)	0.0383(3)
H1Wa	0.6528(11)	−0.128(3)	0.5374(7)	0.0575(5)*
H1Wb	0.7379(5)	0.021(3)	0.5283(8)	0.0575(5)*

geometry and refined isotropically ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{O})$, for all H atoms) using a riding model.

Comment

In 1973, Fusao and Akira reported the single crystal structure of picolinic acid [5]. Thereafter, the structures of many derivatives of picolinic acid such as 2,5-pyridinedicarboxylic acid, 2,6-pyridinedicarboxylic acid [6], 2,4,6-pyridinetricarboxylic acid [7] and 2,3,5,6-pyridinetetracarboxylic acid [8] have been reported successively. Furthermore the crystal structure of picolinic acid *N*-oxide has been studied [9]. Some

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derivatives like thiol [10], trifluoromethoxyl [11], phosphonoalkyl [12], acylamino [13] or other substituent groups have although been reported [14–16]. However, there are only two nitro-substituted picolinic acids that have been studied: 4-nitropicolinic acid monohydrate and 2-carboxylic acid-4-nitropyridine-1-oxide.

The title compound 5-nitropicolinic acid crystallizes in C2/c together with one water molecule, giving the molecule formula of C₆H₆N₂O₅. All of the atoms are nearly co-planar, except the two oxygen atoms from the nitro group. The two C–O bond lengths of the carboxyl group are 1.215 and 1.305 Å, indicating that the oxygen from the longer one is protonated. Two 5-nitropicolinic acid molecules are bridged by two water molecules by two O–H···O hydrogen bonds to form a dimer. These dimers are linked with O–H···N hydrogen bonds to a two-dimensional structure. All bond lengths and angles of 5-nitropicolinic acid are normal and comparable with its analogues [17–19].

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