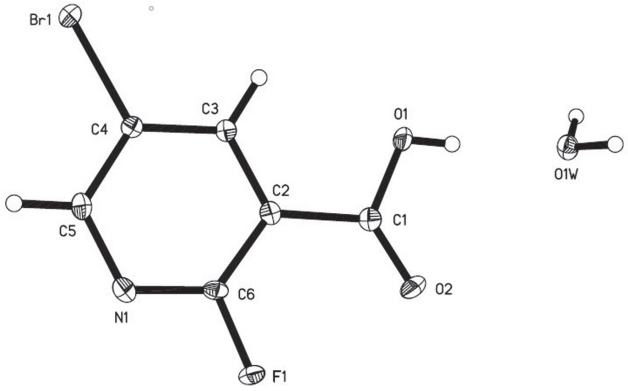
Bin Cai*, Yu-Ning Meng, Meng-En Zhu, Xi-Shuang Yao and Gang Chen

The crystal structure of 5-bromo-2-fluoronicotinic acid monohydrate, $C_6H_5BrFNO_3$



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Abstract

$C_6H_5BrFNO_3$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 3.9894(4)$ Å, $b = 13.6128(11)$ Å, $c = 14.7495(12)$ Å, $V = 801.00(12)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0213$, $wR_{ref}(F^2) = 0.0465$, $T = 150(2)$ 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 the starting materials were used as received without further purification. 5-Bromo-2-fluoronicotinic acid (2.20 g, 10 mmol) was added to a solution with 10 mL THF and 0.5 mL double-destilled water under room temperature, stirred for 30 min, then filtered. The filtrate was let evaporate in air. Several days later, colorless block crystals were obtained, yield 73.2% (based on 5-bromo-2-fluoronicotinic acid).

***Corresponding author: Bin Cai,** School of Chemistry and Chemical Engineering, Zhoukou Normal University, Zhoukou, Henan 466001, P.R. China, e-mail: caib@actinide.org. https://orcid.org/0000-0002-3573-5651

Yu-Ning Meng, Meng-En Zhu, Xi-Shuang Yao and Gang Chen: School of Chemistry and Chemical Engineering, Zhoukou Normal University, Zhoukou, Henan 466001, P.R. China

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.28 × 0.15 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	5.11 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6092, 1436, 0.037
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1345
$N(param)_{refined}$:	112
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Br1	0.44512(10)	0.13585(3)	0.59935(3)	0.02082(13)
C1	0.6521(10)	0.5242(3)	0.6165(3)	0.0197(10)
C2	0.6962(10)	0.4239(3)	0.6573(3)	0.0165(9)
C3	0.5648(10)	0.3411(3)	0.6161(2)	0.0149(8)
H3	0.442340	0.346722	0.561112	0.018*
C4	0.6132(9)	0.2502(3)	0.6557(3)	0.0151(9)
C5	0.7842(10)	0.2426(3)	0.7366(3)	0.0194(9)
H5	0.810919	0.179897	0.764002	0.023*
C6	0.8707(10)	0.4083(3)	0.7381(3)	0.0177(9)
F1	1.0187(7)	0.48277(16)	0.78116(16)	0.0275(6)
H1	0.460(14)	0.570(4)	0.519(3)	0.041*
N1	0.9144(9)	0.3226(3)	0.7777(2)	0.0207(8)
O1	0.4767(10)	0.5183(2)	0.5402(2)	0.0328(9)
O2	0.7598(8)	0.5990(2)	0.6473(2)	0.0331(8)
O1W	0.3974(7)	0.6911(2)	0.46422(18)	0.0218(7)
H1WA	0.236161	0.731199	0.478597	0.033*
H1WB	0.420241	0.689679	0.405587	0.033*

Experimental details

The structure was solved by direct methods with the SHELXS-2018 program. All H-atoms from C atoms were positioned with idealized geometry and refined isotropically ($U_{iso}(H) = 1.2U_{eq}(C)$ using a riding model with C—H = 0.95 Å). The H-atom from O1 atom was positioned at a Q peak and refined isotropically ($U_{iso}(H) = 1.5U_{eq}(O)$ with O1—H1 = 0.773 Å). The H1WA and H1WB were positioned with Q peaks information and refined isotropically

with distances fixed as O1W—H1WA = O1W—H1WA = 0.870 Å (U_{iso}(H) = 1.5U_{eq}(O)).

Comment

To date, some single-crystal stuctures of mono- or multi-halogen-substituted nicotinic acids (although called pyridine-3-carboxylic acid) have been reported, including 6-fluoronicotinic acid [5], 2-chloro-pyridine-3-carboxylic acid [6], 2-chloro-6-(trifluoromethoxy)nicotinic acid and 6-chloro-2-(trifluoromethoxy)nicotinic acid [7], 6-chloro-nicotinic acid [8], 2-bromo-pyridine-3-carboxylic acid [9], and 5-bromonicotinic acid [10]. However, to the best of our knowledge, the single-crystal stucture of a mixed halogen-substituted nicotinic acid has not been reported.

The title compound crystalizes in the orthorhombic space group $P2_12_12_1$ (no. 19) with the formula of $C_6H_5BrFNO_3$. The asymmetric unit is made of one 5-bromo-2-fluoronicotinic acid and one water molecule. All the atoms of 5-bromo-2-fluoronicotinic acid are nearly co-planar. The bond lengths of C—F and C—Br are 1.334 and 1.888 Å, respectively. The carboxyl group is protonated and the N atom from the pyridine is not protonated, which is confirmed by the X-ray diffraction. There is an one-dimensional water molecular chain constructed by hydrogen bond O1W—H1WA···O1W, which are linked by hydrogen bonds O1—H1···O1W and O1W—H1WB···N1 to generate a three-dimensional supramolecular structure. All the bond lengths are similar to their analogues [6–10].

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