Guang Huang*

The crystal structure of 2-amino-3-carboxypyridin-1-ium iodide hemihydrate, $C_6H_8IN_2O_{2.5}$

<https://doi.org/10.1515/ncrs-2021-0204>

Received May 23, 2021; accepted June 17, 2021;
published online July 14, 2021

Abstract

$C_6H_8IN_2O_{2.5}$, monoclinic, $P2_1/n$ (no. 13), $a = 9.8300(4)$ Å, $b = 5.3338(2)$ Å, $c = 17.4040(8)$ Å, $\beta = 105.493(2)^\circ$, $V = 879.36(6)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0139$, $wR_{\text{ref}}(F^2) = 0.0306$, $T = 150(2)$ K.

CCDC no.: 2090565

The asymmetric unit of the title 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 commercially available and used as received. An amount of 1.38 g (0.10 mol)

*Corresponding author: Guang Huang, Sino–Portugal Belt and Road Joint Laboratory on Science of Cultural Heritage Conservation, City University of Macau, Macau, P. R. China; and Southern Marine Science and Engineering Guangdong Laboratory (Zhuhai), Zhuhai, Guangdong, P. R. China, E-mail: ghuang@cityu.mo. <https://orcid.org/0000-0002-9171-3641>

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.25 × 0.15 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	3.61 mm ^{−1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	26.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9344, 1802, 0.027
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1667
$N(\text{param})_{\text{refined}}$:	109
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

2-aminonicotinic acid was mixed with 5 mL deionized water and 5 mL 40% hydroiodic acid. The solution was stirred for 30 min, then filtered. Several days later, a large number of colorless block crystals of the title compound were harvested, yield 78% (based on 2-aminonicotinic acid).

Experimental details

The structure was solved by direct methods with the SHELXS program. All H-atoms from C and N atoms were positioned with idealized geometry and refined isotropically ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$) using a riding model with C–H = 0.95 Å and N–H = 0.88 Å. The H-atom of the carboxylic group was positioned based on a difference electron density peak and refined isotropically with the distance of O2–H2A = 0.84 Å. The H-atom from O_{water} was located based on a difference electron density peak and refined freely with a distance of O1W–H1WA = 0.82 Å ($U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$).

Comment

The N atoms of 2-aminonicotinic acid are ready to be protonated and its crystal structure indicates it is preferred to crystallize as inner salts [5–7]. There are various salts of the 2-aminonicotinic acid, such as nitrate, hydrochloride, dihydrogenphosphate, sulfate, perchlorate

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

Atom	x	y	z	U _{iso} */U _{eq}
C1	0.7297 (2)	0.2244 (4)	0.49638 (12)	0.0233 (4)
C2	0.6925 (2)	0.4314 (3)	0.43771 (11)	0.0195 (4)
C3	0.7939 (2)	0.5837 (4)	0.42147 (12)	0.0232 (4)
H3	0.890331	0.554152	0.447902	0.028*
C4	0.7587 (2)	0.7815 (4)	0.36695 (12)	0.0260 (4)
H4	0.829807	0.884976	0.355846	0.031*
C5	0.6208 (2)	0.8214 (4)	0.33053 (12)	0.0256 (4)
H5	0.594390	0.955764	0.293724	0.031*
C6	0.5477 (2)	0.4761 (4)	0.39741 (11)	0.0207 (4)
I1	0.93578 (2)	0.71135 (2)	0.66484 (2)	0.02275 (5)
N1	0.51953 (18)	0.6717 (3)	0.34593 (10)	0.0224 (4)
H1	0.430810	0.703382	0.321120	0.027*
N2	0.44045 (18)	0.3395 (3)	0.40588 (11)	0.0268 (4)
H2A	0.353855	0.376613	0.378475	0.032*
H2B	0.455659	0.211288	0.438917	0.032*
O1	0.64255 (16)	0.1108 (3)	0.52111 (10)	0.0331 (4)
O2	0.86643 (14)	0.1751 (3)	0.51909 (9)	0.0253 (3)
H2	0.881736	0.059259	0.553009	0.038*
O1W	0.250000	0.8468 (4)	0.250000	0.0269 (5)
H1W	0.216 (3)	0.938 (5)	0.2779 (15)	0.040*

and polyoxometalates [8–14]. But the single crystal structure of its hydroiodide salt has not been reported.

The asymmetric unit consists of one 2-amino-3-carboxypyridin-1-ium cation, one iodide anion and one half of a water molecule (see the Figure). All the bond lengths of the title compound are comparable with its analogues. When the pyridine is protonated, the carboxyl and the amino groups are kept neutral. There is an intra-molecular hydrogen bond in the structure formed by the hydrogen bond N2–H2B···O1. The organic cation, the iodide anion as well as the water molecule are linked by hydrogen bonds to generate a one dimensional chain.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: None declared.

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. SAINT v8.37A; Bruker AXS Inc: Madison, Wisconsin, USA, 2015.
2. Sheldrick G. Using phases to determine the space group. *Acta Crystallogr.* 2018, *A74*, a353.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Bourhis L. J., Dolomanov O. V., Gildea R. J., Howard J. A. K., Puschmann H. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment—Olex2 dissected. *Acta Crystallogr.* 2015, *A71*, 59–75.
5. Dobson A. J., Gerkin R. E. 2–Aminonicotinic acid. *Acta Crystallogr.* 1997, *C53*, 1427–1429.
6. Pawluko A., Starosta W., Leciejewicz J., Natkaniec I., Nowak D. The molecular structure and dynamics of 2-aminopyridine-3-carboxylic acid by X-ray diffraction at 100 K, inelastic neutron scattering, infrared, Raman spectroscopy and from first principles calculations. *Chem. Phys. Lett.* 2007, *437*, 32–37.
7. Grishanov D. A., Navasardyan M. A., Medvedev A. G., Lev O., Prikhodchenko P. V., Churakov A. V. Hydrogen peroxide insular dodecameric and pentameric clusters in peroxosolvate structures. *Angew. Chem. Int. Ed.* 2017, *56*, 15241–15245.
8. Berrah F., Bouacida S., Roisnel T. 2–Amino-3-carboxypyridinium nitrate. *Acta Crystallogr.* 2011, *E67*, o2057–o2058.
9. Bouchene R., Bouacida S., Berrah F., Daran J.-C. 2–Amino-3-carboxypyridinium chloride hemihydrate. *Acta Crystallogr.* 2012, *E68*, o1493–o1494.
10. Akriche S., Rzaigui M. 2–Amino-3-carboxypyridinium dihydrogenphosphate. *Acta Crystallogr.* 2007, *E63*, o3460.
11. Ma Y.-H., Ge S.-W., Shen Y., Sun B.-W. Novel perchlorate and sulphate salts of 2-aminonicotinic acid: synthesis, characterization, thermal studies and Hirshfeld surface analysis. *Chin. J. Struct. Chem.* 2016, *35*, 7–15.
12. Berrah F., Ouakkaf A., Bouacida S., Roisnel T. Bis(2-amino-3-carboxypyridinium) sulfate trihydrate. *Acta Crystallogr.* 2011, *E67*, o953–o954.
13. Berrah F., Bouacida S., Anana H., Roisnel T. 2–Amino-3-carboxypyridinium perchlorate. *Acta Crystallogr.* 2012, *E68*, o1601–o1602.
14. Wang D.-X., Liu H.-B., Chen Y.-G., Wei S. Protonated 2-aminonicotinic acid as charge complement in POM-based inorganic-organic hybrids: synthesis, crystal structure and characterization. *J. Cluster Sci.* 2015, *26*, 1567–1576.