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The crystal structure of zwitterionic 3-aminoisonicotinic acid, $C_6H_6N_2O_2$

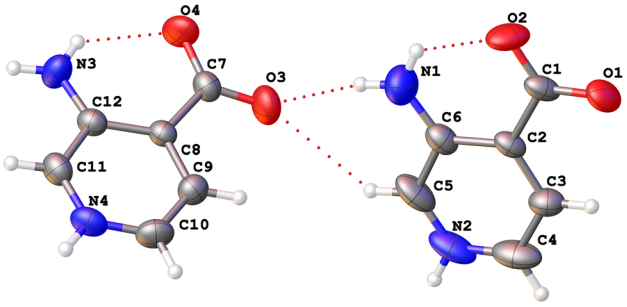

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.15 × 0.13 × 0.09 mm
Wavelength:	Cu *Kα* radiation (1.54184 Å)
μ:	0.99 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω-scans
θ_{max}, completeness:	71,5°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5419, 2278, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1330
$N(param)_{refined}$:	181
Programs:	CrysAlis^{PRO} [1], OLEX2 [2], SHELX [3, 4]

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Abstract

$C_6H_6N_2O_2$, monoclinic $P2_1/c$ (no. 14), a = 6.7909(2) Å, b = 23.9261(7) Å, c = 7.5103(2) Å, β = 95.265(2)°, V = 1215.12(6) Å^3, Z = 8, $R_{gt}(F)$ = 0.0574, w$R_{ref}(F^2)$ = 0.1439, T = 293.

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The crystal 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.

1 Source of materials

Method-1: A mixture of $FeSO_4{\cdot}7H_2O$ (0.1190 g) and 3-aminoisonicotinic acid (0.0690 g) was stirred in 15 mL aqueous solution for 6 h at 60 °C. Then the resulting mixture slowly cooled to room temperature was filtrated and volatilized in the air. The yellow stick crystals of the titled compound were isolated directly.

Method-2: Cadmium acetate dihydrate (0.0533 g) and 3-aminoisonicotinic acid (0.0552 g) in a mixture of H_2O (6 mL) and ethanol (3 mL) were sonicated for 1 h, then two drops of 1 mol/L HNO_3 were added into the mixture. The homogeneous mixture was sealed in a 20 mL solvothermal vial, and heated at 120 °C for 48 h, then cooled to room temperature at 5 °C/h. The powder XRD of obtained yellow stick crystals is identical to that prepared in the method-1.

2 Experimental details

Crystal data, data collection and structure refinement details are provided in Table 1. All hydrogen atoms were placed in calculated positions and refined using a riding-model approximation with C–H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, N–H = 0.86 Å and $U_{iso}(H) = 1.2U_{eq}(N)$.

3 Comment

Amino-functionalized isonicotinic acids are important medical intermediates and isoniazid derivatives in the synthesis and pharmacology [5]. In addition, as the one-center-acceptor–donor ligand they can react with the metal ion to construct a series of unique diamondoid network metal-organic frameworks (MOFs). For example, the acentric framework reported by Zhou et al. [6] exhibits potential 2nd-harmonic-generation response, ferroelectric behaviors

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.7517 (3)	0.78844 (11)	1.1216 (3)	0.0529 (6)
O2	0.7655 (3)	0.69649 (11)	1.1192 (3)	0.0599 (7)
N1	0.4589 (5)	0.63808 (13)	0.9789 (4)	0.0659 (9)
H1A	0.393541	0.608200	0.949171	0.079*
H1B	0.575262	0.635733	1.034047	0.079*
N2	0.1042 (3)	0.73829 (14)	0.8086 (3)	0.0583 (8)
H2	−0.012341	0.737810	0.753127	0.070*
C1	0.6792 (4)	0.74113 (14)	1.0819 (4)	0.0386 (7)
C2	0.4735 (3)	0.73988 (13)	0.9852 (3)	0.0329 (6)
C3	0.3766 (4)	0.78897 (14)	0.9390 (4)	0.0432 (7)
H3	0.436982	0.823053	0.968251	0.052*
C4	0.1877 (4)	0.78778 (19)	0.8483 (4)	0.0601 (9)
H4	0.121445	0.820798	0.816118	0.072*
C5	0.1904 (4)	0.69034 (18)	0.8498 (4)	0.0560 (10)
H5	0.124523	0.657174	0.818855	0.067*
C6	0.3790 (4)	0.68844 (14)	0.9391 (4)	0.0398 (7)
O3	0.2262 (3)	0.54899 (10)	0.8283 (3)	0.0542 (6)
O4	0.2557 (4)	0.45760 (10)	0.8737 (3)	0.0542 (6)
N3	0.2149 (4)	0.38967 (11)	0.5879 (3)	0.0510 (7)
H3A	0.206906	0.358277	0.531879	0.061*
H3B	0.210339	0.390469	0.701898	0.061*
N4	0.2533 (3)	0.48043 (12)	0.2136 (3)	0.0430 (6)
H4A	0.257206	0.476959	0.099979	0.052*
C7	0.2422 (4)	0.50017 (12)	0.7751 (3)	0.0348 (6)
C8	0.2440 (3)	0.49113 (12)	0.5756 (3)	0.0298 (6)
C9	0.2558 (4)	0.53756 (14)	0.4669 (4)	0.0381 (6)
H9	0.261222	0.573126	0.517130	0.046*
C10	0.2597 (4)	0.53129 (15)	0.2837 (4)	0.0458 (7)
H10	0.266691	0.562496	0.210724	0.055*
C11	0.2413 (4)	0.43485 (14)	0.3112 (4)	0.0395 (7)
H11	0.237271	0.400159	0.255112	0.047*
C12	0.2343 (4)	0.43735 (13)	0.4974 (3)	0.0335 (6)

and photoluminescence. Although the crystal structures of nicotinic acid and isonicotinic acid as pure organic room-temperature phosphorescences have been reported in the neutral form and zwitterion [7, 8], however, the crystal structure of amino-functionalized isonicotinic acid is not available. In our attempt to synthesize the MOFs containing the 3-aminoisonicotinic acid, we unexpectedly obtained the single-crystal of 3-aminoisonicotinic acid.

The determined results indicated that 3-aminoisonicotinic acid crystallizes as a zwitterion in the space group $P2_1/c$ without any other solvent molecules, which often were directly involved in the formation of hydrogen bonds or as the filler of void space. Its asymmetric unit includes two independent 3-aminoisonicotinic acids. The pyridine ring, the carboxylate group, and the $-NH_2$ group are in the same plane, similar to bis(4-aminopyridin-1-ium) iodide triiodide [9]. The existence of the zwitterionic form of 3-aminoisonicotinic acid is confirmed by the presence of an H atom bonded to the N1 or N4 atom in the difference Fourier map. All of the C–O band distances, less than 1.27 Å, also agree with this result. Specifically, the C1–O1, C1–O2, C7–O4, and C7–O3 bond distances are 1.259(4), 1.238(4), 1.258(3), and 1.242(3) Å, respectively. In the crystal of 3-aminoisonicotinic acid, all nitrogen and oxygen atoms are involved in N···O hydrogen bonds with distances in the range between 2.612(3) Å and 3.317(3) Å. The head-to-tail N2–H2···O2 and N2–H2···O1 interactions form one chain running parallel to the *a* axis, and the N···O distances are 3.025(4) Å and 2.738(4) Å, respectively. Another chain formed by very strong head-to-tail N4–H4A···O4 interactions with a N···O distance of 2.612(3) Å extends along the *c* axis. These two kinds of chains are mutually perpendicular and further interact by the N–H···O hydrogen bonds between carboxyl groups and neighboring amino groups. In addition, the weak C–H···O hydrogen bonds are also found in the crystal packing. The combination of these interactions builds an intricate three-dimensional assembly of a hydrogen bond network. Theoretical calculations at the ωB97XD/6–311++G** level have shown that in the gas phase the energy of the neutral form of 3-aminonicotinic acid is lower by about 92 kJ/mol than that of inner salt. However, in water the zwitterion becomes the favorable form with a difference in energy of 14 kJ/mol. From a structural point of view, zwitterion is stabilized by the strong head-to-tail N–H···O hydrogen bonds between the $-NH_2$ and carboxyl group. This is in agreement with the calculated changes in bond distance and other reported spectrophoto-chemical results in the case of 2-aminonicotinic acid with a similar structure [10].

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

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