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The crystal structure of 3-amino-5-carboxypyridin-1-ium perchlorate monohydrate, $C_6H_9ClN_2O_7$

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Abstract

$C_6H_9ClN_2O_7$, triclinic, $P\bar{1}$ (no. 2), $a = 6.8667(4)$ Å, $b = 7.5196(4)$ Å, $c = 10.0908(5)$ Å, $\alpha = 74.237(2)^\circ$, $\beta = 81.603(3)^\circ$, $\gamma = 88.888(3)^\circ$, $V = 495.95(5)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0377$, $wR_{ref}(F^2) = 0.0902$, $T = 150(2)$ K.

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The asymmetric unit of the title 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.

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Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.15 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.41 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	26.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	12,649, 2054, 0.072
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1609
$N(param)_{refined}$:	149
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

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

Atom	x	y	z	U_{iso}^*/U_{eq}
C1	0.1938 (3)	−0.2739 (3)	0.6848 (2)	0.0201 (5)
C2	0.2139 (3)	−0.0704 (3)	0.6168 (2)	0.0171 (5)
C3	0.2667 (3)	−0.0091 (3)	0.4740 (2)	0.0181 (5)
H3	0.286515	−0.096305	0.420772	0.022*
C4	0.2912 (3)	0.1804 (3)	0.4068 (2)	0.0195 (5)
C5	0.2590 (3)	0.3016 (3)	0.4909 (2)	0.0206 (5)
H5	0.272691	0.431174	0.450083	0.025*
C6	0.1855 (3)	0.0557 (3)	0.6956 (2)	0.0200 (5)
H6	0.150678	0.015737	0.793892	0.024*
Cl1	0.68697 (8)	0.21373 (7)	0.87046 (6)	0.01990 (16)
N1	0.2089 (3)	0.2353 (2)	0.62844 (19)	0.0213 (4)
H1	0.190000	0.315350	0.678280	0.026*
N2	0.3484 (3)	0.2445 (3)	0.2676 (2)	0.0301 (5)
H2A	0.365850	0.364063	0.228915	0.036*
H2B	0.368185	0.166698	0.216015	0.036*
O1	0.2351 (3)	−0.3857 (2)	0.61864 (17)	0.0323 (4)
O2	0.1300 (3)	−0.3156 (2)	0.81855 (16)	0.0258 (4)
H2	0.137636	−0.430011	0.853099	0.039*
O3	0.5590 (3)	0.1041 (2)	0.82217 (19)	0.0332 (4)
O4	0.7986 (3)	0.3422 (3)	0.7533 (2)	0.0443 (5)
O5	0.5694 (3)	0.3152 (3)	0.9539 (2)	0.0366 (5)
O6	0.8201 (2)	0.0957 (2)	0.95093 (17)	0.0243 (4)
O1W	0.1691 (2)	0.3292 (2)	0.90705 (17)	0.0237 (4)
H1WA	0.276046	0.300689	0.944213	0.036*
H1WB	0.083147	0.244687	0.956493	0.036*

Source of material

5-Aminopyridine-3-carboxylic acid (0.138 g, 1 mmol) was added to a solution of 10 mL concentrated perchloric acid (70%) under room temperature and stirred for 15 min. The

mixture was filtered and left to evaporate naturally. A few days later, colorless block crystals of 3-amino-5-carboxypyridinium perchlorate monohydrate were harvested, yield 78% (based on 5-aminopyridine-3-carboxylic acid [APCA]).

Experimental details

The structure was solved by direct methods with the SHELXS program. All H-atoms from C atoms and N atoms were positioned with idealized geometry and refined isotropically ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$) using a riding model with C–H = 0.95 Å and N–H = 0.879 and 0.88 Å. The H2, H1WA and H1WB were positioned based on difference electron density peaks and refined with the distance restraints of O2–H2 = 0.84 Å, O1W–H1WA = 0.87 Å and O1W–H1WB = 0.87 Å, respectively ($U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$).

Comment

5-Aminopyridine-3-carboxylic acid and its deprotonated derivatized anions are known as multi-functional ligands to build various metal (Co(II), Zn(II), Cu(II), Cd(II), Pb(II) and Y(III)) complexes [5–10] and heterometallic complexes (Cu(II)–Ti(IV) and Cu(II)–In(III)) [11–13] with excellent applications. However, to date, the single-crystal structure of 5-aminopyridine-3-carboxylic acid or any of its salts have not been reported.

The title compound crystallises in $P\bar{1}$. The asymmetric unit of the title compound consists of one N-protonated 5-carboxypyridinium cation, one perchlorate anion, and one crystal water molecule. All the atoms of the 3-aminopyridine moiety are nearly co-planar, but the free carboxyl group is slightly twisted. All the bond lengths of C–C, C–N and C–O are normal, which are comparable to their analogues [14, 15]. There are two kinds of one-dimensional chains: one is constructed by the hydrogen bond N1–H1...O1 and the other is constructed by the hydrogen bonds O1W–H1WA...O5 and O1W–H1WB...O6. The hydrogen bonds N2–H2A...O4 and N2–H2A...O4 link the aforementioned chains to generate a three-dimensional supramolecular structure.

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