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The crystal structure of 3-carboxy-5-methylpyridin-1-ium-2-carboxylate, $C_8H_7NO_4$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.25 × 0.20 × 0.10 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.13 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	26.4°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	16801, 1535, 0.054
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1232
$N(\text{param})_{\text{refined}}$:	124
Programs:	Bruker [1], SHELX [2], Olex2 [3, 4]

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.64456(11)	0.60483(10)	0.3572(2)	0.0185(4)
C2	0.57641(11)	0.54590(10)	0.2991(2)	0.0193(4)
C3	0.48719(12)	0.57573(10)	0.2442(3)	0.0209(4)
H3	0.440601	0.536278	0.202793	0.025*
C4	0.46354(11)	0.66047(10)	0.2475(2)	0.0213(4)
C5	0.53321(11)	0.71583(10)	0.3099(3)	0.0221(4)
H5	0.520538	0.774471	0.316246	0.027*
C6	0.74984(12)	0.59518(10)	0.4117(3)	0.0214(4)
C7	0.58749(12)	0.45027(10)	0.2888(3)	0.0220(4)
C8	0.36724(12)	0.69144(11)	0.1864(3)	0.0275(4)
H8A	0.350907	0.668437	0.053986	0.041*
H8B	0.367708	0.753040	0.179692	0.041*
H8C	0.320339	0.673036	0.285753	0.041*
H1	0.6642(16)	0.7239(14)	0.392(3)	0.037(6)*
N1	0.61841(10)	0.68633(9)	0.3613(2)	0.0202(3)
O1	0.79312(8)	0.66138(8)	0.4425(2)	0.0287(3)
O2	0.78408(8)	0.52211(8)	0.4220(2)	0.0311(3)
O3	0.52042(9)	0.40893(8)	0.2325(2)	0.0309(3)
O4	0.66619(9)	0.41579(7)	0.3451(2)	0.0317(4)
H4	0.707325	0.453275	0.362039	0.047*

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Abstract

$C_8H_7NO_4$, orthorhombic, *Pccn* (no. 56), $a = 14.1361(10)$ Å, $b = 15.8923(12)$ Å, $c = 6.6410(6)$ Å, $V = 1491.9(2)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.0406$, $wR_{\text{ref}}(F^2) = 0.1155$, $T = 150(2)$ 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.

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Source of material

All reagents were purchased and used without further purification. The title compound was synthesized in a THF solution: solid 5-methylpyridine-2,3-dicarboxylic acid (1.81 g,

10 mmol) was dissolved in 25 mL THF solution and stirred under room temperature for 15 min. The mixed solution was filtered, sealed with perforated parafilm and let evaporate slowly at room temperature. Colorless crystals were harvested after several days, yield: 86.5% (based on 5-methylpyridine-2,3-dicarboxylic acid).

Experimental details

The structure was solved by direct methods with the SHELXS program. All H-atoms from C atoms and O atoms were positioned with idealized geometry and refined isotropically ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$) using a riding model with C–H = 0.95 Å, N–H = 0.90 Å and O–H = 0.84 Å, respectively.

Comment

Pyridine-2,3-dicarboxylic acid and their analogues are easily to form inner salts, such as 3-carboxypyridin-1-ium-2-carboxylate, which have been reported elsewhere [5–10]. Here we report the crystal structure of 3-carboxy-5-methylpyridin-1-ium-2-carboxylate.

As shown in the figure, the title compound, 3-carboxy-5-methylpyridin-1-ium-2-carboxylate crystallizes as the inner salt form of the 5-methylpyridine-2,3-dicarboxylic acid. All non-hydrogen atoms are nearly coplanar. The N atom from the pyridine ring is protonated and the carboxyl group in 2-position is deprotonated [5–7]. There are two kinds of hydrogen bonds: O–H...O and N–H...O. The intermolecular hydrogen bond N–H...O(01) connects two molecules to generate a dimer. Furthermore there is one intramolecular hydrogen bond (see the figure). All bond lengths and angles of the 3-carboxy-5-methylpyridin-1-ium-2-carboxylate are comparable to its analogues [5–7].

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