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The crystal structure of 5-carboxy-2-(hydroxymethyl)-1*H*-imidazol-3-ium-4-carboxylate, C₆H₈N₂O₆

Table 1: Data collection and handling.

Crystal:	Yellow platelet
Size:	0.56 × 0.14 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.16 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	28.3°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	9388, 1919, 0.020
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1567
$N(\text{param})_{\text{refined}}$:	148
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

Source of material

The compound was synthesized in analogy to a published procedure [7]. 0.1 mol of *o*-phenylenediamine and 0.1 mol of glycolic acid were placed in a round bottomed flask and refluxed in 100 mL of 4 M HCl solution for 2 h. The resultant dark blue solution was neutralised with aqueous ammonia and the resultant light purple precipitate was filtered on a Buchner funnel. The precipitate was recrystallised from boiling ethanol. A small amount of the purified compound was dissolved in aqueous ethanol, and crystals suitable for single crystal X-ray diffraction were obtained after slow evaporation of the mother liquor.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å for aromatic carbon atoms, C–H 0.99 Å for the methylene group) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$.

The H atom of the hydroxyl groups was allowed to rotate with a fixed angle around the C–O bond to best fit the experimental electron density (HFIX 147 in the SHELX program suite [3]), with $U(\text{H})$ set to $1.5U_{\text{eq}}(\text{O})$.

Both nitrogen-bound H atoms as well as the H atoms of the water molecule and the H atom of the carboxyl group were located on a difference Fourier map and refined freely. The position of the aforementioned carboxyl H atom was

<https://doi.org/10.1515/ncrs-2020-0593>

Received November 12, 2020; accepted December 30, 2020;

published online February 15, 2021

Abstract

C₆H₈N₂O₆, monoclinic, $P2_1/c$ (no. 14), $a = 7.4709(4)$ Å, $b = 14.2051(9)$ Å, $c = 7.3198(4)$ Å, $\beta = 97.096(4)^\circ$, $V = 770.86(8)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0346$, $wR_{\text{ref}}(F^2) = 0.0946$, $T = 200$ K.

CCDC no.: 2053160

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
O1	0.46258 (14)	0.88897 (7)	0.73947 (15)	0.0252 (2)
O2	0.69777 (13)	0.83834 (7)	0.60857 (14)	0.0232 (2)
O3	0.82914 (14)	0.68678 (7)	0.54187 (15)	0.0244 (2)
H3	0.770 (3)	0.7617 (19)	0.575 (3)	0.069 (8)*
O4	0.77886 (14)	0.53446 (7)	0.58178 (15)	0.0282 (3)
O5	0.05073 (15)	0.63360 (8)	0.93659 (16)	0.0316 (3)
H5	0.069176	0.635310	1.052092	0.047*
O6	0.10691 (14)	0.85018 (7)	0.82943 (17)	0.0281 (3)
N1	0.33934 (15)	0.70842 (8)	0.78531 (16)	0.0178 (2)
N2	0.46211 (15)	0.57430 (8)	0.73756 (16)	0.0179 (2)
C1	0.32162 (17)	0.61548 (9)	0.79985 (18)	0.0178 (3)
C2	0.49649 (17)	0.72716 (9)	0.71056 (18)	0.0166 (3)
C3	0.57351 (17)	0.64241 (9)	0.68025 (18)	0.0166 (3)
C4	0.16598 (19)	0.56707 (10)	0.8709 (2)	0.0250 (3)
H4A	0.098421	0.529769	0.770846	0.030*
H4B	0.211449	0.523413	0.971424	0.030*
C5	0.55545 (18)	0.82539 (9)	0.68500 (18)	0.0179 (3)
C6	0.73946 (18)	0.61706 (9)	0.59758 (19)	0.0194 (3)
H1	0.254 (3)	0.7565 (15)	0.815 (3)	0.041 (5)*
H2	0.485 (3)	0.5086 (17)	0.736 (3)	0.046 (6)*
H6A	0.019 (2)	0.8416 (15)	0.892 (3)	0.052 (6)*
H6B	0.151 (3)	0.9033 (9)	0.864 (3)	0.047 (6)*

refined approximately midway between the two O atoms, suggesting H atom disorder.

Comment

Chelate ligands have found widespread use in coordination chemistry due to the increased stability of coordination compounds they can form in comparison to monodentate ligands. The stability of these compounds is enhanced further if the denticity of the ligand is increased upon incorporation of more and more potential donor sites [8]. Especially dicarboxylic acids are interesting in this aspect as chemical factors such as pH values could have an influence on the protonation/deprotonation of acidic functional groups and fine-tune the denticity of the resulting ligand species. One such example are imidazole-dicarboxylic acids that can be synthesized according to a published procedure [7]. In continuation of our studies of the structures of poly-functional carboxylic acids [9–15] the title compound was synthesized. To ensure the successful generation of the desired compound, the molecular and crystal structure of the latter was determined. Structural information about barium salts of the title compound has been published earlier [16]. Furthermore, the structures of three related compounds have been reported in the literature [17–19].

The structure solutions shows the presence of an imidazole-4,5-dicarboxylic acid bearing a hydroxymethyl substituent in the 2-position. Furthermore, one molecule of solvent water is present in the asymmetric unit. The acid is present in a zwitterionic form with one of the carboxyl groups having protonated the imine-type nitrogen atom. The hydrogen atom of the remaining carboxyl group is disordered over both carboxyl moieties. C–N bond lengths are measured at 1.3303(17)–1.3811(17) Å which is in good agreement with other compounds found in the Cambridge Structural Database [20]. Intracyclic angles cover a range of 106.74(11)–109.15(11)° with the largest two angles found on the pnicogen atoms.

In the crystal, classical hydrogen bonds of the N–H...O and O–H...O type are present. The hydrogen bonds stemming from the protons on the water molecule invariably employ one of the carboxylate-type oxygen atoms as acceptor. The carboxyl groups are linked by an intramolecular hydrogen bond. The N–H supported hydrogen bonds see either the oxygen atom of the water molecule or another carboxyl group oxygen atom as acceptor. The hydroxymethyl group gives rise to a hydrogen bond to the water molecule. In terms of graph-set analysis [21, 22], the descriptor for the hydrogen bonds is $S(6)DDDDC_1^1(6)$ at the unitary level. Furthermore one C–H...O contact whose range falls by more than 0.1 Å below the sum of van-der-Waals radii is observed between one of the hydrogen atoms of the methylene group and a carboxylate oxygen atom as acceptor. The graph-set descriptor for the latter contact is $C_1^1(7)$ at the unitary level. In total, the molecular species present in the asymmetric unit are connected to a three-dimensional network. π -Stacking is not a stabilizing feature of the crystal structure with the shortest distance in between two centers of gravity measured at 4.5719(8) Å.

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

Research funding: The corresponding author thanks the National Research Foundation for financial support.

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

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