Crystal structure of iminodiacetic acid monomethyl ester monohydrate, $C_5H_9NO_4 \cdot H_2O$

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Abstract

$C_5H_9NO_5$, monoclinic, $P2_1/c1$ (No. 14), $a = 5.212 \text{ \AA}$, $b = 16.881 \text{ \AA}$, $c = 10.116 \text{ \AA}$, $\beta = 119.09^\circ$, $V = 777.8 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.058$, $wR_{\text{ref}}(F^2) = 0.180$, $T = 293 \text{ K}$.

Source of material

A mixture of iminodiacetic acid (16.8 g, 0.13 mol), thionyl chloride (30.9 g, 0.26 mol) and methanol (85 ml) was placed in a 250 ml round bottomed flask fitted with a reflux condenser and a silica guard tube. The mixture was stirred and heated under reflux for 4 hours. The solution was then washed with water/dichloromethane and the organic layer dried with anhydrous Na_2SO_4 , evaporated under reduced pressure and left to crystallise from dichloromethane/*n*-hexane. The (methoxycarbonylmethylamino)-acetic acid was obtained with 15% yield. Melting point: 411 K – 413 K. Ft-IR (cm^{-1} ; group): (1643; C=O ketone form), (3503; N—H).

Experimental details

The structure was solved by direct methods. The hydrogen atoms of the main residue were placed at calculated positions and refined as riding using the SHELXL-97 defaults [1]. The crystal structure contains one water molecule disordered over three positions, sum of the their freely refined occupancies is 1.00(3). The isotropic temperature factors of the three water O atoms were constrained to be equal, the water H atoms could not be located.

Discussion

Iminodiacetic acid and its derivatives are important compounds in coordination chemistry. The presence of two close carboxylic groups makes this molecule and its derivatives excellent ion coordination agents. This property has been fully exploited in the preparation of modified polymers and resins for ion capture, both for analytical [2–4] or industrial uses [5,6]. In medical related sci-

ences, iminodiacetic acid derivatives are used as solid phase supports for peptide synthesis [7] and as base for chemical libraries in combinatorial chemistry [8]. Iminodiacetic acid is also of great importance in organic chemistry, namely on the synthesis of maleimides [9] and 3,4 di-substituted pyrroles [10] by Friedman method. Following the preparation of the manganese complex of -octaphenyl-porphyrin for our studies of metalloporphyrin-based oxidation of hydrocarbons [11], we synthesised several iminodiacetic derivatives as pyrrole precursors, amongst them, the title compound. The conformation of the zwitterion is close to that found in the second polymorph form of iminodiacetic acid, IMDA2 [12].

The C4 atom is gauche to C1 when the ion is viewed along N—C3 and with C3 trans to C2 when viewed along N—C1. The formal negative charge is spread over the carboxylate group O3—C4—O4 (C—O distances are: $d(\text{C4—O3}) = 1.250(2) \text{ \AA}$, $d(\text{C4—O4}) = 1.243(3) \text{ \AA}$). The bond distances of the carboxylic acid group indicate one double bond ($d(\text{C2=O2}) = 1.196(3) \text{ \AA}$) and one single bond ($d(\text{C2—O1}) = 1.326(3) \text{ \AA}$). The substituted half of the iminodiacetic acid molecule is approximated planar with C1, C2, O1, O2, C5 lying in a plane (rms deviation from L.S. plane $0.02 \text{ \AA}$), the nitrogen atom is $0.186(3) \text{ \AA}$ away from that plane. The zwitterions are bonded together by hydrogen bonds forming layers. The nitrogen atom donates its two hydrogen atoms to the oxygen atoms of the carboxylate groups of neighbouring molecules (N—H1...O3ⁱ: $2.670(3) \text{ \AA}$, 176.2° , $i: x+1, -y-1/2, z+1/2$; N—H2...O4ⁱⁱ: $2.986(3) \text{ \AA}$, 139.0° , $ii: x+1, y, z$). Using graph-set analysis [13] one recognises at the unitary level, chains of degree 5 running along the [100] and [201] directions. In the second polymorph form of iminodiacetic acid, one of the N—H...O bonds also forms a chain of degree 5 while the other displays only discrete patterns [13].

Table 1. Data collection and handling.

Crystal:	colourless prism, size $0.08 \times 0.10 \times 0.42 \text{ mm}$
Wavelength:	Cu K_α radiation ($1.54180 \text{ \AA}$)
μ :	11.06 cm^{-1}
Diffractionmeter, scan mode:	Enraf-Nonius Mach 3, $\omega/2\theta$
$2\theta_{\text{max}}$:	144.88°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	3178, 1550
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1346
$N(\text{param})_{\text{refined}}$:	105
Programs:	SHELXS-97 [14], SHELXL-97 [1], PLATON [15], ORTEPII [16]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U _{iso}
H(1)	4e		0.2298	-0.2714	0.0139	0.046
H(2)	4e		0.068	-0.2617	-0.1494	0.046
H(3A)	4e		-0.2163	-0.2497	0.0166	0.053
H(3B)	4e		-0.0718	-0.175	-0.0127	0.053
H(1A)	4e		0.0202	-0.3839	0.0122	0.059
H(1B)	4e		-0.2386	-0.3672	-0.1514	0.059
H(5A)	4e		0.4343	-0.5215	-0.1719	0.134
H(5B)	4e		0.1993	-0.5872	-0.2020	0.134
H(5C)	4e		0.1343	-0.5210	-0.3230	0.134
O(5)	4e	0.130(4)	0.550(5)	0.009(2)	-0.005(3)	0.094(2)
O(6)	4e	0.52(1)	0.555(2)	0.0818(4)	-0.0402(6)	0.094(2)
O(7)	4e	0.35(1)	0.428(3)	0.0718(5)	-0.0459(9)	0.094(2)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O(4)	4e	-0.6515(3)	-0.18125(9)	-0.2033(2)	0.0389(8)	0.0613(9)	0.0532(9)	0.0119(6)	0.0237(7)	0.0033(6)
O(3)	4e	-0.4241(3)	-0.2340(1)	-0.3201(1)	0.0307(7)	0.079(1)	0.0331(7)	0.0045(6)	0.0136(6)	-0.0018(6)
O(2)	4e	0.2703(4)	-0.3746(1)	-0.2031(2)	0.067(1)	0.065(1)	0.102(2)	-0.0070(8)	0.061(1)	-0.0080(9)
O(1)	4e	0.0978(4)	-0.4835(1)	-0.1469(2)	0.077(1)	0.0514(9)	0.076(1)	-0.0004(8)	0.044(1)	0.0006(8)
N	4e	0.0526(3)	-0.2774(1)	-0.0686(2)	0.0271(7)	0.054(1)	0.0325(8)	-0.0002(6)	0.0138(6)	0.0027(6)
C(4)	4e	-0.4379(4)	-0.2128(1)	-0.2053(2)	0.0305(9)	0.047(1)	0.0374(9)	-0.0005(7)	0.0166(8)	0.0018(7)
C(3)	4e	-0.1625(4)	-0.2258(1)	-0.0537(2)	0.034(1)	0.063(1)	0.034(1)	0.0023(8)	0.0158(8)	-0.0032(8)
C(1)	4e	-0.0286(4)	-0.3617(1)	-0.0857(3)	0.038(1)	0.055(1)	0.061(1)	-0.0028(8)	0.0282(9)	0.0051(9)
C(2)	4e	0.1325(4)	-0.4059(1)	-0.1516(2)	0.034(1)	0.053(1)	0.050(1)	-0.0010(8)	0.0173(8)	0.0013(9)
C(5)	4e	0.2279(9)	-0.5324(2)	-0.2167(4)	0.111(3)	0.065(2)	0.100(2)	0.010(2)	0.058(2)	-0.009(2)

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