Crystal structure of 2-ethyl-2-hydroxybutyric acid, at 200 K, $C_6H_{12}O_3$

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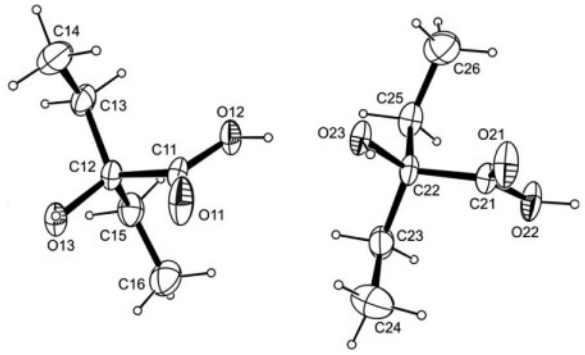

Abstract

$C_6H_{12}O_3$, triclinic, $P\bar{1}$ (no. 2), a = 6.7695(5) Å, b = 10.9645(8) Å, c = 11.2349(9) Å, α = 98.322(4)°, β = 107.359(3)°, γ = 104.064(4)°, V = 750.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.0442, $wR_{ref}(F^2)$ = 0.1229, T = 200 K.

Table 1. Data collection and handling.

Crystal:	colourless rods, size 0.104×0.144×0.452 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.93 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$2\theta_{max}$:	56.7°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13059, 3683
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2467
$N(param)_{refined}$:	171
Programs:	SHELX, WinGX, MERCURY, PLATON [15–18]

Source of material

The title compound was obtained commercially (ACROS). Crystals suitable for the diffraction study were obtained upon slow sublimation of the compound at room temperature.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.99 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2U_{eq}(C). The H atoms of the methyl groups were allowed to rotate with a fixed H–C–C angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [15]), with U_{iso}(H) set to 1.5U_{eq}(C). The H atoms of the hydroxyl groups were allowed to rotate with a fixed H–O–C angle around the C–O bond to best fit the experimental electron density (HFIX 147 in the SHELX program suite [15]), with U_{iso}(H) set to 1.5U_{eq}(O).

Discussion

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. Hydroxycarboxylic acids are particularly interesting in this aspect as they offer two hydroxyl groups of markedly different acidity as potential bonding partners. Upon varying the substitution pattern on the hydrocarbon backbone, the acidity of the respective hydroxyl groups can be finetuned over a wide range and they may serve as probes for establishing the rules in which pK_a range coordination to various central atoms of variable Lewis acidity can be observed. At the beginning of a comprehensive study about a series of homo- and heteroleptic coordination compounds derived from simple α-hydroxy- carboxylic acids, the title compound was chosen as a starting point as it has already shown its potential to act as a chelating, dianionic ligand towards ruthenium [1, 2] and chromium [3] as well as a chelating and bridging dianionic ligand towards vanadium [4]. For the latter metal, a mixed coordination behaviour, namely chelating-dianionic as well as chelating-monoan-ionic, have been reported in one single compound [5]. The crystal structures of several other α-hydroxycarboxylic acids have recently been published by one of us [6–11]. The title compound is a symmetrically-substituted derivative of glycolic acid. The asymmetric unit contains two complete molecules. The least-squares planes as defined by the non-hydrogen atoms of the alkyl chains on the one hand and the α-hydroxycarboxylic "backbone" on the other hand enclose angles of 88.03(3)° and 89.02(9)°, respectively, for the two different molecules. The C–O bond lengths found in the carboxyl groups encountered among the the two molecules of 1.2016(17) Å and 1.2019(16) Å for the carbonyl-type oxygen atom and 1.3185(16) Å and 1.3190(16) Å towards the acidic hydroxyl group do not differ significantly. A similar picture is found for the two carbon-oxygen bonds involving the alcoholic hydroxyl group with 1.4296(15) Å and 1.4309(16) Å, respectively. In comparison to other α-hydroxy- carboxylic acids whose metrical parameters have been deposited with the Cambridge Structural Database [12] the latter values are found to be in good agreement with the most common ones observed. The comparison to a specific series of previously-published comparable members of this compound class also shows good agreement for the discussed bonds [6–11]. In the crystal, classical hydrogen bonds of the O–H···O type are observed that involve all double-bonded oxygen atoms as well as both alcoholic hydroxyl groups as acceptors. The latter ones serve as the endpoint of hydrogen bonds established by the carboxyl groups and act as donors towards the carbonyl-type oxygen atoms. The pattern formed involves dimeric units created from the two different molecules present in the asymmetric unit upon action of the alcoholic hydroxyl groups. In terms of graph-set analysis [12, 13], the descriptor for the pattern observed are $R^2_2(10)$ rings (first level) and $R^4_4(12)$ rings (second level). In total, the molecules are connected to strands along [101].

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(12)	2*i*	0.3930	0.2595	0.4506	0.048
H(13)	2*i*	0.9034	0.4113	0.7945	0.043
H(22)	2*i*	0.0695	0.2966	–0.0744	0.055
H(23)	2*i*	0.2666	0.3936	0.3238	0.040
H(13A)	2*i*	0.4791	0.1078	0.6921	0.040
H(13B)	2*i*	0.6893	0.1302	0.8152	0.040
H(14A)	2*i*	0.4395	0.3056	0.7781	0.070
H(14B)	2*i*	0.6524	0.3304	0.9005	0.070
H(14C)	2*i*	0.4391	0.2140	0.8768	0.070
H(15A)	2*i*	0.9367	0.1192	0.6864	0.042
H(15B)	2*i*	0.7157	0.0740	0.5659	0.042
H(16A)	2*i*	1.0251	0.1455	0.5063	0.073
H(16B)	2*i*	1.0771	0.2870	0.5921	0.073
H(16C)	2*i*	0.8612	0.2284	0.4680	0.073
H(23A)	2*i*	0.5438	0.2180	0.2699	0.043
H(23B)	2*i*	0.4798	0.2207	0.1217	0.043
H(24A)	2*i*	0.7797	0.4000	0.2501	0.089
H(24B)	2*i*	0.6327	0.4471	0.3238	0.089
H(24C)	2*i*	0.5809	0.4464	0.1750	0.089
H(25A)	2*i*	0.1273	0.0651	0.0908	0.038
H(25B)	2*i*	0.1793	0.0745	0.2409	0.038
H(26A)	2*i*	–0.1899	0.1220	0.0752	0.069
H(26B)	2*i*	–0.1359	0.1392	0.2265	0.069
H(26C)	2*i*	–0.1950	–0.0012	0.1366	0.069

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(11)	2*i*	0.6678(2)	0.4213(1)	0.6046(1)	0.0642(8)	0.0296(6)	0.0234(5)	0.0171(5)	–0.0021(5)	0.0074(4)
O(12)	2*i*	0.4570(2)	0.22111(9)	0.50177(9)	0.0359(6)	0.0344(5)	0.0200(5)	0.0105(5)	–0.0004(4)	0.0093(4)
O(13)	2*i*	0.9352(2)	0.34223(9)	0.78192(9)	0.0333(5)	0.0298(5)	0.0179(5)	0.0094(4)	0.0016(4)	0.0060(4)
O(21)	2*i*	0.0872(2)	0.4118(1)	0.11681(9)	0.0558(7)	0.0358(6)	0.0211(5)	0.0248(5)	0.0036(5)	0.0074(4)
O(22)	2*i*	0.1311(2)	0.2606(1)	–0.01968(9)	0.0512(7)	0.0498(7)	0.0146(5)	0.0286(6)	0.0085(5)	0.0110(4)
O(23)	2*i*	0.2445(2)	0.31392(9)	0.31854(8)	0.0376(6)	0.0274(5)	0.0134(4)	0.0128(5)	0.0050(4)	0.0048(4)
C(11)	2*i*	0.6229(2)	0.3065(1)	0.5950(1)	0.0323(7)	0.0302(7)	0.0129(6)	0.0117(6)	0.0069(5)	0.0063(5)
C(12)	2*i*	0.7507(2)	0.2437(1)	0.6899(1)	0.0297(7)	0.0268(7)	0.0172(6)	0.0093(6)	0.0042(5)	0.0072(5)
C(13)	2*i*	0.6066(3)	0.1747(2)	0.7575(1)	0.0392(8)	0.0369(8)	0.0236(7)	0.0094(7)	0.0093(6)	0.0150(6)
C(14)	2*i*	0.5274(3)	0.2641(2)	0.8350(2)	0.050(1)	0.061(1)	0.0389(9)	0.0181(9)	0.0254(8)	0.0192(8)
C(15)	2*i*	0.8388(3)	0.1501(2)	0.6213(2)	0.0400(8)	0.0367(8)	0.0292(8)	0.0194(7)	0.0081(7)	0.0084(6)
C(16)	2*i*	0.9613(3)	0.2079(2)	0.5397(2)	0.049(1)	0.071(1)	0.0376(9)	0.030(1)	0.0220(8)	0.0147(9)
C(21)	2*i*	0.1463(2)	0.3187(1)	0.0954(1)	0.0293(7)	0.0289(7)	0.0160(6)	0.0094(6)	0.0045(5)	0.0060(5)
C(22)	2*i*	0.2492(2)	0.2536(1)	0.1982(1)	0.0311(7)	0.0298(7)	0.0128(6)	0.0138(6)	0.0045(5)	0.0058(5)
C(23)	2*i*	0.4827(2)	0.2646(2)	0.2059(2)	0.0346(8)	0.0513(9)	0.0257(7)	0.0209(7)	0.0087(6)	0.0129(7)
C(24)	2*i*	0.6321(3)	0.4016(2)	0.2419(2)	0.036(1)	0.070(1)	0.070(1)	0.0099(9)	0.019(1)	0.019(1)
C(25)	2*i*	0.1158(3)	0.1124(1)	0.1693(1)	0.0449(9)	0.0286(7)	0.0217(7)	0.0143(7)	0.0076(6)	0.0061(6)
C(26)	2*i*	–0.1223(3)	0.0912(2)	0.1502(2)	0.047(1)	0.0402(9)	0.044(1)	0.0026(8)	0.0164(8)	0.0054(8)

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