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Refinement of the crystal structure of L-valinemethylester hydrochloride, $C_6H_{13}NO_2 \cdot HCl$, *at 200 K*

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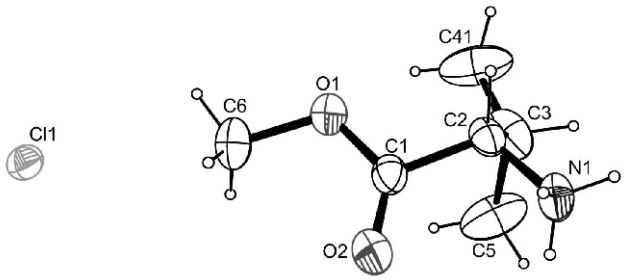

Abstract

$C_6H_{14}ClNO_2$, orthorhombic, $P2_12_12_1$ (no. 19), a = 5.9023(2) Å, b = 7.2617(2) Å, c = 21.5387(7) Å, V = 923.2 Å^3, Z = 4, $R_{gt}(F)$ = 0.026, $wR_{ref}(F^2)$ = 0.070, T = 200 K.

Source of material

The compound was obtained commercially (Fluka). Crystals suitable for the X-ray diffraction study were taken directly from the provided compound.

Experimental details

Carbon-bound H atoms were placed in calculated positions (d(C—H) = 1.00 Å for methine groups) and were included in the refinement in the riding model approximation, with U(H) set to 1.2 U_{eq}(C). The hydrogen atoms of the methyl groups were allowed to rotate with a fixed angle around the C—C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [1]). The nitrogen-bound H atoms were located on a difference Fourier map and refined freely. The Flack parameter of –0.02(5) confirms *syn* configuration.

The disorder affecting C41/C42 is based on the two possible orientations of the methyl and the hydrogen atom bonded to their common carrier atom C3. The difference in energy of these two possible orientations seems to be low enough to allow the presence of both rotational isomers in the solid state. A careful analysis of the thermal parameters of carbon atom C5 shows no indication for a disorder model that should be applied to this atom.

Discussion

Amino acids are an important class of biomolecules. Their molecular set-up of an amino group in α-position to a carboxylic acid group denotes them as an important class of chelate ligands offering a *N*,*O*-set of donor atoms for a vast variety of main group elements and transition metals. Depending on the pH-value, they may act as mono- or bidentate ligands capable of forming five-membered chelate rings. Furthermore, they may act as strictly neutral as well as anionic or cationic ligands. Although a number of studies focussed on the complexation behaviour of amino acids has been conducted, the knowledge about the coordination behaviour of the esters of amino acids is scant. Although the crystal structure of the title compound has been deposited with the Cambridge Structural Database as a private communication [2], no thorough discussion pertaining thereof is apparent in the literature. At the beginning of a bigger study aimed at gathering knowledge about the coordination behaviour of amino acid esters, we therefore determined the crystal structure of the title compound to allow for comparative studies in envisioned coordination compounds.

The title compound is the hydrochloride of the methyl ester of L-valine. Protonation took place on the amino group. The asymmetric carbon atom is (*S*)-configured. One of the methyl groups on the backbone of the amino acid is disordered over two positions with occupancies of 0.69:0.31 which is similar to the findings of Jaeger et al., where a ratio of 0.72:0.28 was given among the deposited data [2]. Protonation of the amino group prevents resonance in the amide moiety which becomes apparent by a C=O bond length of only 1.194(2) Å and a bond length of d(C(NH$_3$)—C(O$_2$)) = 1.521(2) Å. While these two bond lengths obtained in this low-temperature study are invariably longer than the ones obtained earlier at room temperature – Jaeger et al. reported values of approximately 1.18 Å and 1.51 Å, respectively [2] – the other bond legths in the title compound are not affected to a significant degree by the change of temperature.

In the crystal structure, all hydrogen atoms of the NH_3^+ substituent act as donors in hydrogen bonds that invariably have chloride anions as acceptor. Apart from these classical hydrogen bonds, C–H···Cl contacts can be observed whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating. The latter contacts are supported by one of the hydrogen atoms on the methyl group on the backbone of the amino acid that does not show disorder. The chloride anions therefore serve as fourfold acceptors. In total, these hydrogen bonds connect the components of the title compound to infinte strands along the crystallographic a axis with the hydrophobic parts of the molecule forming the outside lining of these strands. A description of the hydrogen bonding system in terms of graph-set analysis [3,4] necessitates a *DDD* descriptor on the unitary level for the classical hydrogen bonds while the C–H···Cl contacts can be described by a *D* descriptor on the same level.

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Table 1. Data collection and handling.

Crystal:	colourless block, size 0.289 × 0.324 × 0.511 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.64 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ/ω
$2\theta_{max}$:	56.58°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8759, 2277
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2207
$N(param)_{refined}$:	117
Programs:	SHELXS-97, SHELXL-97 [1], ORTEP-3 [5], Mercury [6], PLATON [7]

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

Atom	Site	Occ.	x	y	z	U_{iso}
H(71)	4*a*		0.617(3)	0.331(2)	0.5337(9)	0.048(5)
H(72)	4*a*		0.728(3)	0.231(2)	0.5785(9)	0.040(4)
H(73)	4*a*		0.498(3)	0.274(3)	0.5874(9)	0.044(5)
H(2)	4*a*		0.8506	0.5150	0.5915	0.038
H(3)	4*a*		0.5058	0.6429	0.5500	0.063
H(41A)	4*a*	0.686	0.5324	0.9129	0.5927	0.114
H(41B)	4*a*	0.686	0.7786	0.8240	0.5844	0.114
H(41C)	4*a*	0.686	0.6625	0.8294	0.6515	0.114
H(42A)	4*a*	0.314	0.4961	0.8697	0.5354	0.093
H(42B)	4*a*	0.314	0.5609	0.6845	0.4992	0.093
H(42C)	4*a*	0.314	0.7512	0.7952	0.5367	0.093
H(51)	4*a*		0.2069	0.7171	0.6124	0.106
H(52)	4*a*		0.3249	0.6190	0.6705	0.106
H(53)	4*a*		0.2453	0.4990	0.6122	0.106
H(61)	4*a*		0.9174	0.4072	0.7813	0.087
H(62)	4*a*		0.6990	0.5343	0.7915	0.087
H(63)	4*a*		0.9463	0.6246	0.7904	0.087

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

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*a*		0.8316(2)	0.5541(2)	0.70570(4)	0.0505(6)	0.0579(6)	0.0301(5)	–0.0160(5)	–0.0038(4)	–0.0002(4)
O(2)	4*a*		0.6337(2)	0.2933(2)	0.69689(5)	0.0653(8)	0.0543(6)	0.0332(5)	–0.0170(6)	–0.0057(5)	0.0080(4)
N(1)	4*a*		0.6229(2)	0.3129(2)	0.57292(5)	0.0240(5)	0.0602(7)	0.0254(5)	0.0080(5)	–0.0009(5)	–0.0043(5)
C(1)	4*a*		0.7154(2)	0.4290(2)	0.67504(6)	0.0266(5)	0.0438(7)	0.0269(5)	0.0019(5)	–0.0005(4)	0.0001(5)
C(2)	4*a*		0.6964(2)	0.4802(2)	0.60678(6)	0.0222(5)	0.0471(7)	0.0267(6)	0.0053(5)	0.0026(4)	0.0043(5)
C(3)	4*a*		0.5363(3)	0.6443(3)	0.59566(8)	0.0416(8)	0.068(1)	0.0472(8)	0.0248(8)	0.0048(6)	0.0171(8)
C(41)	4*a*	0.686(4)	0.6348(5)	0.8153(3)	0.6069(2)	0.041(1)	0.036(1)	0.150(3)	0.001(1)	0.003(2)	0.016(2)
C(42)	4*a*	0.314	0.591(2)	0.7591(7)	0.5362(2)	0.104(5)	0.047(3)	0.035(3)	0.028(3)	0.009(3)	0.012(2)
C(5)	4*a*		0.3086(3)	0.6175(3)	0.6253(1)	0.0290(7)	0.054(1)	0.129(2)	0.0071(7)	0.0069(9)	–0.026(1)
C(6)	4*a*		0.8501(4)	0.5279(3)	0.77273(7)	0.069(1)	0.075(1)	0.0298(7)	–0.014(1)	–0.0102(7)	–0.0035(7)
Cl(1)	4*a*		0.88621(5)	0.64219(5)	0.92912(1)	0.0280(1)	0.0489(2)	0.0290(1)	–0.0064(1)	0.0004(1)	–0.0018(1)

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