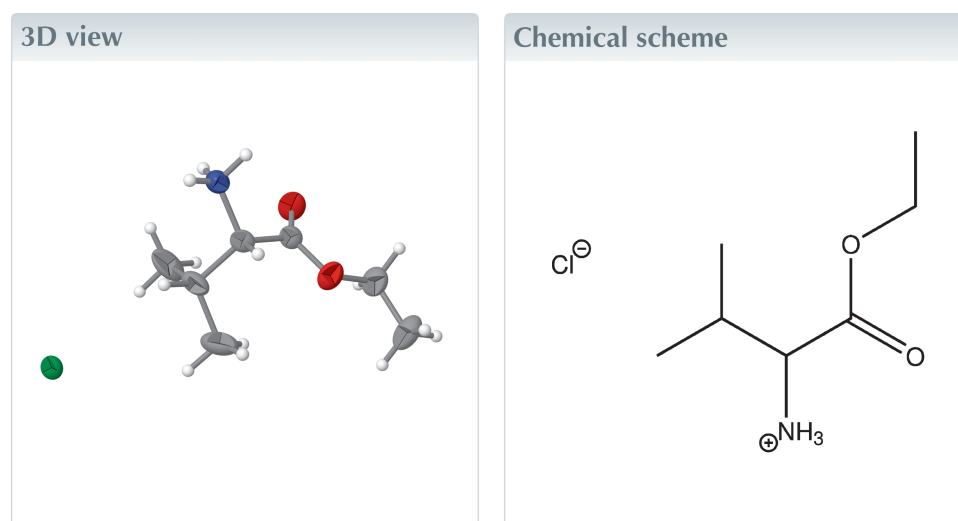


L-Valine ethyl ester hydrochloride

Erin Van Rooyen, Eric Cyriel Hosten and Richard Betz*

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The title compound [systematic name: (2*S*)-1-ethoxy-3-methyl-1-oxobutan-2-aminium chloride], $C_7H_{16}NO_2^+ \cdot Cl^-$, is the hydrochloride salt of the ethyl ester of L-valine. In the crystal, classical hydrogen bonds of the $N-H \cdots Cl$ type are observed alongside $C-H \cdots O$ and $C-H \cdots Cl$ contacts, connecting the entities of the asymmetric unit into sheets lying perpendicular to the crystallographic *a* axis.



Structure description

Amino acids play a pivotal role in the human metabolism and represent a crucial macronutrient class at the centre of all higher life. Natural representatives of this compound class appear as the L-configured stereoisomers in organisms and give rise to the chiral nature of proteins (McMurry, 2008). As a result of their bidentate nature, they have found ample use as chelating ligands in transition-metal chemistry whose denticity can be fine-tuned by varying the pH of the reaction mixture under investigation (Gade, 1998). Potential donor sites on certain amino acid side chains can further diversify the bonding behaviour and give rise to unique bonding patterns. One way to simplify the variety of bonding modes to be encountered is to block the acid group by means of esterification (Becker *et al.*, 2000). At the onset of a study around the coordination and condensation behaviour of amino acids and certain derivatives thereof towards selected transition metals and main group elements, the metrical parameters of starting materials need to be established to allow for comparative studies regarding the influence of binding on bond lengths and angles. Structural information for the ethyl ester hydrochlorides of phenylglycine (Brunner *et al.*, 2021), nitroso cysteine (Yi *et al.*, 2005, 2016), glycine (He *et al.*, 2010), cysteine (Haas, 1965; Gorbitz, 1989; Defonsi Lestard *et al.*, 2013) is apparent in the literature. Furthermore, we have elucidated the molecular and crystal structures of the methyl ester hydrochloride salt of L-valine (Betz *et al.*, 2011), metacholine chloride (Muller *et al.*, 2021), as well as the hydrochloride salt of benzylglycine (Hosten *et al.*, 2011). As an extension of these studies, we now report the structure of the title compound, $C_7H_{16}NO_2^+ \cdot Cl^-$ (**1**).

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H11···Cl1 ⁱ	0.91 (3)	2.34 (4)	3.192 (3)	157 (3)
N1–H12···Cl1 ⁱⁱ	0.81 (4)	2.38 (4)	3.133 (3)	155 (3)
N1–H13···Cl1 ⁱⁱⁱ	0.94 (3)	2.19 (3)	3.122 (2)	175 (3)
C2–H2···O2 ^{iv}	1.00	2.40	3.377 (3)	165
C7–H7B···Cl1 ^v	0.98	2.82	3.760 (4)	160

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z$; (ii) $-x+1, y-\frac{1}{2}, -z$; (iii) $x-1, y, z$; (iv) $x, y-1, z$; (v) $-x+1, y+\frac{1}{2}, -z+1$.

The structure solution shows a derivative of L-valine with the carboxyl group converted into the ethyl ester (Fig. 1). The absolute structure in space group $P2_1$ is well established and, as expected, the stereogenic atom C2 has an *S* configuration. The amino group shows protonation whose positive charge has been counterbalanced by a chloride anion. The ethyl side chain, the carboxyl group as well as the nitrogen-bearing carbon atom are close to co-planar with the largest deviation from the least-squares plane as defined by the non-hydrogen atoms of the aforementioned moieties is 0.104 (2) Å for the ethereal oxygen atom. Selected torsion angles include $O1-C1-C2-N1 = 148.9 (2)^\circ$, $C1-C2-C3-C4 = -64.3 (4)^\circ$ and $C1-O1-C6-C7 = -170.3 (3)^\circ$. Otherwise, all bond lengths and angles are found to be in good agreement with values for comparable compounds whose metrical parameters have been deposited with the Cambridge Structural Database (Groom *et al.*, 2016).

In the crystal of (**I**), classical hydrogen bonds of the N–H···Cl type are observed as well as C–H···O and C–H···Cl contacts whose range falls by more than 0.1 Å below the sum of van der Waals radii of the atoms participating in them (Table 1). These are established by all the nitrogen-bound hydrogen atoms as donors in the case of the classical hydrogen bonds (which generate [010] chains), as well as the hydrogen atom of the stereocentre and the ketonic oxygen atom in case of the C–H···O contacts. The chlorine-supported C–H interactions stem from one of the hydrogen atoms of the methyl group in the ester side chain. In terms of graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995), the descriptor for these interactions is $DDDDC^1_1(4)$ on the unary

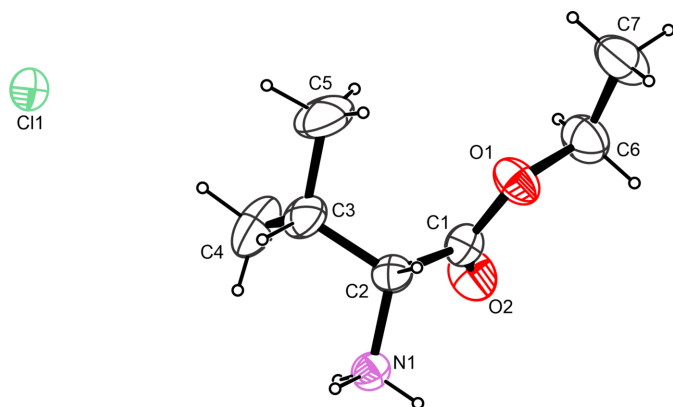


Figure 1
The molecular structure of (**I**) with displacement ellipsoids drawn at the 50% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_{16}NO_2^+ \cdot Cl^-$
M_r	181.66
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	200
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.7222 (7), 5.3577 (4), 10.1105 (8)
β (°)	93.499 (3)
<i>V</i> (Å ³)	525.66 (7)
<i>Z</i>	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.33
Crystal size (mm)	0.24 × 0.20 × 0.16
Data collection	
Diffractometer	Bruker D8 Quest CCD, software APEX5
Absorption correction	Multi-scan (SADABS; Krause <i>et al.</i> , 2015)
T_{min} , T_{max}	0.681, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30362, 2592, 2378
R_{int}	0.050
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.666
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.094, 1.11
No. of reflections	2592
No. of parameters	115
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.39, -0.19
Absolute structure	Flack x determined using 983 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	0.037 (17)

Computer programs: APEX2 and SAINT (Bruker, 2014), SHELXS7 (Sheldrick 2008), ORTEP-3 for Windows (Farrugia, 2012), Mercury (Macrae *et al.*, 2020), SHELXL2019/3 (Sheldrick, 2015) and PLATON (Spek, 2020).

level. In total, the entities of the asymmetric unit are connected to sheets lying perpendicular to the crystallographic

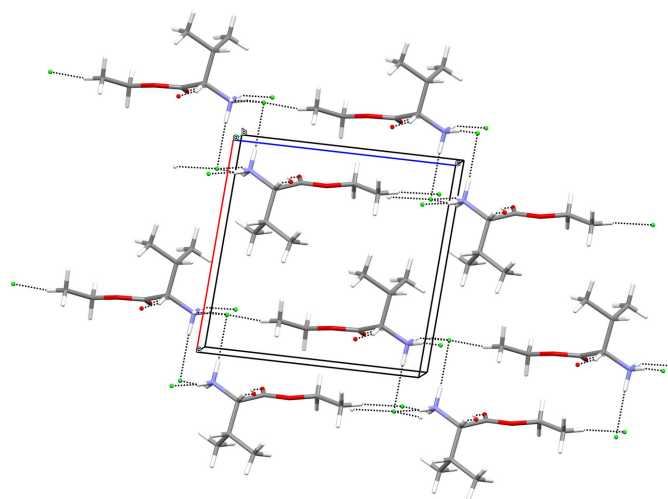


Figure 2
Intermolecular contacts (black dashed lines) in (**I**), viewed approximately along [010].

a axis with the chloride anions forming channels along the crystallographic *b*-axis direction (Fig. 2).

Synthesis and crystallization

The compound was obtained commercially (Fluka). Crystals suitable for the diffraction study were obtained upon prolonged storage of the compound at room temperature in a tightly sealed glass bottle.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2025). **10**, x251047 [<https://doi.org/10.1107/S2414314625010478>]

L-Valine ethyl ester hydrochloride

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(2S)-1-Ethoxy-3-methyl-1-oxobutan-2-aminium chloride

Crystal data

$C_7H_{16}NO_2^+ \cdot Cl^-$	$F(000) = 196$
$M_r = 181.66$	$D_x = 1.148 \text{ Mg m}^{-3}$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 9.7222 (7) \text{ \AA}$	Cell parameters from 9975 reflections
$b = 5.3577 (4) \text{ \AA}$	$\theta = 3.0\text{--}28.3^\circ$
$c = 10.1105 (8) \text{ \AA}$	$\mu = 0.33 \text{ mm}^{-1}$
$\beta = 93.499 (3)^\circ$	$T = 200 \text{ K}$
$V = 525.66 (7) \text{ \AA}^3$	Block, colourless
$Z = 2$	$0.24 \times 0.20 \times 0.16 \text{ mm}$

Data collection

Bruker D8 Quest CCD, software APEX5 diffractometer	2592 independent reflections
φ and ω scans	2378 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Krause <i>et al.</i> , 2015)	$R_{\text{int}} = 0.050$
$T_{\text{min}} = 0.681$, $T_{\text{max}} = 0.746$	$\theta_{\text{max}} = 28.3^\circ$, $\theta_{\text{min}} = 2.0^\circ$
30362 measured reflections	$h = -12 \rightarrow 12$
	$k = -7 \rightarrow 7$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 0.1046P]$
$wR(F^2) = 0.094$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2592 reflections	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
115 parameters	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
1 restraint	Absolute structure: Flack x determined using 983 quotients $[(I^-)-(I)]/[(I^+)+(I)]$ (Parsons <i>et al.</i> , 2013)
Primary atom site location: structure-invariant direct methods	Absolute structure parameter: 0.037 (17)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The carbon-bound H atoms were placed in calculated positions (C—H = 0.99 Å for the methylene group, C—H = 1.00 Å for the methine groups) and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The H 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 (Sheldrick, 2015), with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. All three nitrogen-bound H atoms were located in a difference Fourier map and refined freely.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.1799 (2)	0.5810 (6)	0.42612 (16)	0.0430 (4)
O2	0.1606 (2)	0.9078 (4)	0.2891 (2)	0.0476 (5)
N1	0.14778 (19)	0.5828 (6)	0.07661 (19)	0.0315 (4)
H11	0.175 (3)	0.734 (6)	0.048 (3)	0.028 (8)*
H12	0.163 (3)	0.488 (7)	0.017 (4)	0.041 (10)*
H13	0.052 (3)	0.590 (8)	0.084 (3)	0.042 (7)*
C1	0.1815 (2)	0.6913 (5)	0.3087 (3)	0.0323 (5)
C2	0.2186 (2)	0.5065 (5)	0.2043 (3)	0.0315 (5)
H2	0.182912	0.338817	0.228863	0.038*
C3	0.3750 (3)	0.4843 (6)	0.1889 (3)	0.0446 (7)
H3	0.388485	0.353065	0.120594	0.053*
C4	0.4394 (3)	0.7226 (8)	0.1406 (5)	0.0696 (11)
H4A	0.426621	0.856780	0.204623	0.104*
H4B	0.395174	0.769270	0.054479	0.104*
H4C	0.538125	0.695948	0.131565	0.104*
C5	0.4487 (4)	0.3945 (9)	0.3184 (4)	0.0709 (11)
H5A	0.542475	0.341653	0.301441	0.106*
H5B	0.398092	0.253446	0.353508	0.106*
H5C	0.452595	0.530938	0.383063	0.106*
C6	0.1598 (4)	0.7340 (7)	0.5419 (3)	0.0513 (8)
H6A	0.064320	0.799024	0.538592	0.062*
H6B	0.224035	0.877473	0.544488	0.062*
C7	0.1861 (4)	0.5768 (10)	0.6606 (3)	0.0615 (9)
H7A	0.121992	0.435409	0.657131	0.092*
H7B	0.172734	0.676039	0.740249	0.092*
H7C	0.280990	0.514478	0.663367	0.092*
Cl1	0.82750 (5)	0.58922 (7)	0.08644 (5)	0.03471 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0631 (11)	0.0339 (9)	0.0324 (8)	0.0021 (11)	0.0057 (7)	−0.0014 (10)
O2	0.0681 (14)	0.0269 (10)	0.0487 (11)	0.0080 (9)	0.0104 (10)	0.0010 (9)
N1	0.0311 (9)	0.0284 (10)	0.0351 (9)	0.0023 (12)	0.0015 (7)	−0.0016 (14)
C1	0.0301 (12)	0.0309 (12)	0.0361 (13)	−0.0009 (10)	0.0032 (9)	0.0002 (10)
C2	0.0329 (12)	0.0247 (11)	0.0368 (13)	0.0029 (9)	0.0013 (9)	0.0004 (9)
C3	0.0333 (13)	0.0491 (16)	0.0509 (16)	0.0153 (12)	−0.0007 (11)	−0.0099 (13)
C4	0.0291 (15)	0.074 (3)	0.107 (3)	0.0004 (16)	0.0145 (17)	0.009 (2)
C5	0.058 (2)	0.083 (3)	0.069 (2)	0.030 (2)	−0.0199 (17)	−0.005 (2)

C6	0.0631 (19)	0.054 (2)	0.0368 (15)	0.0060 (15)	0.0050 (13)	-0.0086 (14)
C7	0.080 (2)	0.072 (2)	0.0323 (13)	-0.018 (3)	0.0029 (13)	-0.001 (2)
Cl1	0.0342 (3)	0.0331 (3)	0.0373 (3)	0.0006 (3)	0.00536 (19)	-0.0008 (3)

Geometric parameters (Å, °)

O1—C1	1.327 (3)	C4—H4A	0.9800
O1—C6	1.452 (4)	C4—H4B	0.9800
O2—C1	1.192 (3)	C4—H4C	0.9800
N1—C2	1.483 (3)	C5—H5A	0.9800
N1—H11	0.91 (3)	C5—H5B	0.9800
N1—H12	0.81 (4)	C5—H5C	0.9800
N1—H13	0.94 (3)	C6—C7	1.476 (5)
C1—C2	1.507 (4)	C6—H6A	0.9900
C2—C3	1.543 (4)	C6—H6B	0.9900
C2—H2	1.0000	C7—H7A	0.9800
C3—C4	1.516 (5)	C7—H7B	0.9800
C3—C5	1.531 (5)	C7—H7C	0.9800
C3—H3	1.0000		
C1—O1—C6	118.7 (3)	C3—C4—H4B	109.5
C2—N1—H11	113.3 (19)	H4A—C4—H4B	109.5
C2—N1—H12	112 (2)	C3—C4—H4C	109.5
H11—N1—H12	105 (3)	H4A—C4—H4C	109.5
C2—N1—H13	110.6 (18)	H4B—C4—H4C	109.5
H11—N1—H13	107 (3)	C3—C5—H5A	109.5
H12—N1—H13	108 (3)	C3—C5—H5B	109.5
O2—C1—O1	124.8 (3)	H5A—C5—H5B	109.5
O2—C1—C2	124.6 (2)	C3—C5—H5C	109.5
O1—C1—C2	110.6 (2)	H5A—C5—H5C	109.5
N1—C2—C1	108.1 (2)	H5B—C5—H5C	109.5
N1—C2—C3	110.0 (2)	O1—C6—C7	108.0 (3)
C1—C2—C3	113.6 (2)	O1—C6—H6A	110.1
N1—C2—H2	108.3	C7—C6—H6A	110.1
C1—C2—H2	108.3	O1—C6—H6B	110.1
C3—C2—H2	108.3	C7—C6—H6B	110.1
C4—C3—C5	111.0 (3)	H6A—C6—H6B	108.4
C4—C3—C2	113.4 (2)	C6—C7—H7A	109.5
C5—C3—C2	110.6 (3)	C6—C7—H7B	109.5
C4—C3—H3	107.2	H7A—C7—H7B	109.5
C5—C3—H3	107.2	C6—C7—H7C	109.5
C2—C3—H3	107.2	H7A—C7—H7C	109.5
C3—C4—H4A	109.5	H7B—C7—H7C	109.5
C6—O1—C1—O2	-4.0 (4)	N1—C2—C3—C4	57.1 (4)
C6—O1—C1—C2	173.9 (2)	C1—C2—C3—C4	-64.3 (4)
O2—C1—C2—N1	-33.1 (3)	N1—C2—C3—C5	-177.5 (3)
O1—C1—C2—N1	148.9 (2)	C1—C2—C3—C5	61.2 (4)

O2—C1—C2—C3	89.3 (3)	C1—O1—C6—C7	-170.3 (3)
O1—C1—C2—C3	-88.7 (3)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H11 \cdots C11 ⁱ	0.91 (3)	2.34 (4)	3.192 (3)	157 (3)
N1—H12 \cdots C11 ⁱⁱ	0.81 (4)	2.38 (4)	3.133 (3)	155 (3)
N1—H13 \cdots C11 ⁱⁱⁱ	0.94 (3)	2.19 (3)	3.122 (2)	175 (3)
C2—H2 \cdots O2 ^{iv}	1.00	2.40	3.377 (3)	165
C7—H7B \cdots C11 ^v	0.98	2.82	3.760 (4)	160

Symmetry codes: (i) $-x+1, y+1/2, -z$; (ii) $-x+1, y-1/2, -z$; (iii) $x-1, y, z$; (iv) $x, y-1, z$; (v) $-x+1, y+1/2, -z+1$.