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L-Valine L-valinium perchlorate monohydrate

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In the title compound, $C_5H_{12}NO_2^+\cdot ClO_4^-\cdot C_5H_{11}NO_2\cdot H_2O$, the valine as a zwitterion and valinium are bonded through a strong O—H···O hydrogen bond. Their ammonium groups and the perchlorate ion are held together by hydrogen bonds. Both valine and valinium show *gauche*-II forms.

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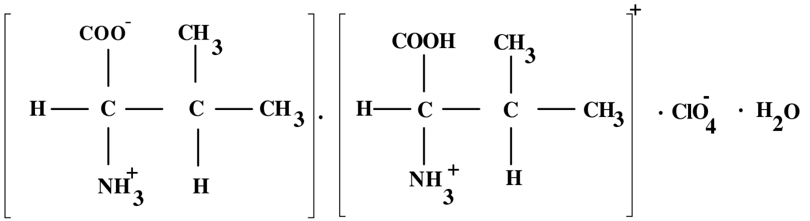
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.037
wR factor = 0.110
Data-to-parameter ratio = 7.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Valine is an essential amino acid. The crystal structures of L-valine (Torri & Iitaka, 1970), DL-valine (Mallikarjunan & Rao, 1969), L-valine hydrochloride monohydrate (Rao, 1969), L-valine hydrochloride (Parthasarathy, 1966; Ando *et al.*, 1967), DL-valine hydrochloride (Di Blasio *et al.*, 1977) and L-valine nitrate (Srinivasan & Rajaram, 1997) have been reported. In the present study, (I), the structure of valine reacted with perchloric acid was undertaken.



(I)

All three possible rotational isomers of the valine molecule, *viz. trans, gauche*-I, *gauche*-II have been found in the crystalline state (Torri & Iitaka, 1970). In (I), both valine and valinium molecules are in the *gauche*-II form. The amino N atom deviates from the carboxyl plane by 0.050 (6) Å in the valine molecule and 0.024 (7) Å in the valinium molecule, which corresponds to the twisting of the C—N bond out of the plane of the carboxyl group by 3.5 (4)° in valine and −1.8 (5)° in the valinium molecule. This tendency of twisting of the C—N bond is found in various amino acids (Lakshminarayanan *et al.*, 1967).

The valine and valinium molecules are bonded through a strong O—H···O hydrogen bond [O2*B*···O1*B* distance 2.562 (4) Å]. The perchlorate ion plays a vital role in forming hydrogen bonds with valine and valinium molecules, and stabilizing the structure. The water molecule links the ammonium group of the valinium molecule with perchlorate. A bifurcated hydrogen bond is observed in the case of the water molecule with perchlorate O atoms (Jeffrey & Saenger, 1991). The valine molecule is engaged in a head-to-tail straight (*S*2) sequence since the N11—H11*A*···O1*B*(*x*, *y* + 1, *z*) hydrogen bond connects two amino acids separated by a unit cell along the *b* axis, and a zigzag (*Z*1) sequence since N11—

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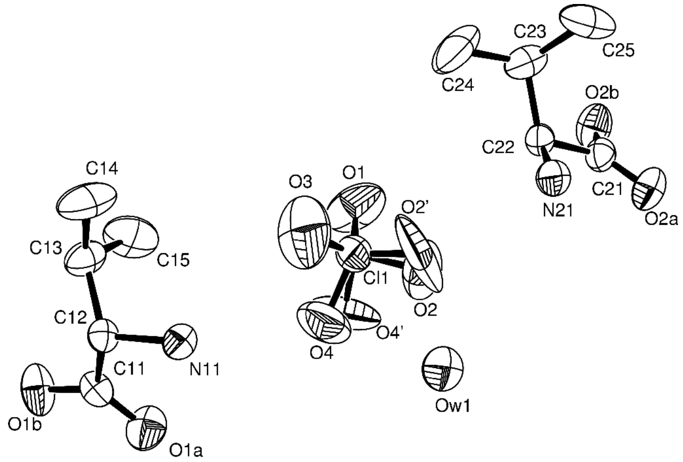

Figure 1
The molecular structure of (I) with the atom-numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

H11*C*···O2*A*($1-x$, $y+\frac{1}{2}$, $1-z$) connects two 2_1-related amino acids (Vijayan, 1988).

Experimental

Colorless needle-shaped crystals of (I) were obtained by the slow evaporation of an aqueous solution of L-valine and perchloric acid in a stoichiometric ratio of 2:1.

Crystal data

$C_5H_{12}NO_2^+ \cdot ClO_4^- \cdot C_5H_{11}NO_2 \cdot H_2O$
$M_r = 352.77$
Monoclinic, $P2_1$
$a = 11.235$ (3) Å
$b = 5.8312$ (14) Å
$c = 13.0948$ (19) Å
$\beta = 91.282$ (16)°
$V = 857.7$ (3) Å^3
$Z = 2$
$D_x = 1.366$ Mg m^{-3}
$D_m = 1.369$ Mg m^{-3}
D_m measured by flotation in carbon tetrachloride–xylene
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 8.1$–13.7°
$\mu = 0.27$ mm^{-1}
$T = 293$ (2) K
Needle, colorless
0.25 × 0.23 × 0.13 mm

Data collection

Enraf–Nonius sealed-tube diffractometer
ω–2θ scans
1751 measured reflections
1665 independent reflections
1481 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.011$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 6$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.110$
$S = 1.17$
1665 reflections
228 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2 + 0.1320P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.030 (6)
Absolute structure: Flack (1983)
Flack parameter = 0.06 (11)

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.225 (4)	O2*A*—C21	1.197 (4)
O1B—C11	1.268 (4)	O2*B*—C21	1.305 (5)
O1*A*—C11—C12—N11	3.5 (4)	O2*A*—C21—C22—N21	−1.8 (5)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11*A*···O1*B*$^{\rm i}$	0.89	1.95	2.727 (4)	145
N11—H11*B*···O3$^{\rm i}$	0.89	2.51	3.113 (6)	126
N11—H11*B*···O4$^{\rm i}$	0.89	2.53	3.37 (3)	159
N11—H11*C*···O2*A*$^{\rm ii}$	0.89	2.28	2.886 (4)	125
O2*B*—H2*B*···O1*B*	0.82	1.74	2.562 (4)	175
N21—H21*A*···O2$'^{\rm iii}$	0.89	2.38	2.87 (3)	115
N21—H21*A*···O1$^{\rm iv}$	0.89	2.63	3.156 (6)	118
N21—H21*B*···O*W*1$^{\rm ii}$	0.89	1.98	2.818 (5)	157
N21—H21*C*···O4$^{\rm ii}$	0.89	2.13	3.013 (11)	169
N21—H21*C*···O4$'^{\rm ii}$	0.89	2.26	3.13 (2)	168
O*W*1—H*W*1···O4$^{\rm i}$	0.80 (5)	2.45 (7)	3.050 (12)	133 (6)
O*W*1—H*W*1···O4$'^{\rm i}$	0.80 (5)	2.57 (7)	3.24 (3)	143 (6)
O*W*1—H*W*1···O2	0.80 (5)	2.63 (6)	3.115 (15)	120 (6)
O*W*1—H*W*1···O2′	0.80 (5)	2.63 (7)	3.18 (4)	127 (6)
O*W*1—H*W*2···O1*A*	0.89 (5)	1.93 (5)	2.806 (4)	167 (5)

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

There is a positional disorder of the perchlorate O atoms. The site-occupation factors of O2 and O4 are 0.65 (5), and those of O2′ and O4′ 0.35 (5). The disorder is possibly due to the onset of rotational disorder of the perchlorate ion. The H atoms of the water molecule were located from difference Fourier maps and refined, while all the other H atoms were refined with geometrical restraints using *HFIX*.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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