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Key indicators

Single-crystal X-ray study
T = 105 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.036
wR factor = 0.105
Data-to-parameter ratio = 32.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

DL-Valinium perchlorate

The title compound, $\text{C}_5\text{H}_{12}\text{NO}_2^+\cdot\text{ClO}_4^-$, crystallizes in the triclinic space group $P\bar{1}$ with four valinium cations and four perchlorate anions in the asymmetric unit. In the crystal, three of the four crystallographically independent valinium residues are linked to the perchlorate anions *via* $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. The fourth residue, on the other hand, forms $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with an inversion-related residue, thereby forming a dimer. Both class I and class III hydrogen-bonding patterns are observed. All the four residues have similar *gauche* II–*gauche* I side-chain conformations.

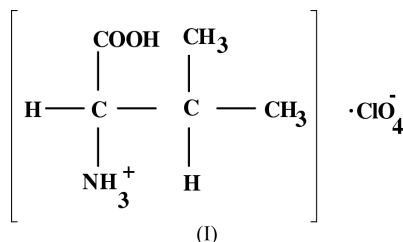
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Comment

Valine is a branched-chain amino acid. Generally branched-chain amino acids (BCAA) such as leucine, isoleucine and valine play a vital role in tissue repair and also provide energy directly to muscle tissue. The crystal structures of L-valine hydrochloride (Parthasarathy, 1966; Ando *et al.*, 1967), L-valine hydrochloride monohydrate (Rao, 1969), DL-valine (Mallikarjunan & Rao, 1969; Dalhus & Görbitz, 1996a), L-valine (Torri & Iitaka, 1970; Dalhus & Görbitz, 1996b), DL-valine nitrate (Rao & Parthasarathy, 1974), L-valine nitrate (Srinivasan *et al.*, 1997) and L-valine L-valinium perchlorate monohydrate (Pandiarajan *et al.*, 2001) have been reported. In the present study, the crystal structure of DL-valinium perchlorate, (I), was undertaken. Recently, a closely related crystal structure of DL-valinium nitrate, in the triclinic space group $P\bar{1}$ with $z = 8$, was solved in our laboratory (Srinivasan *et al.*, 2002).



The asymmetric unit contains four crystallographically independent valinium residues (I, II, III and IV) and four independent perchlorate anions (1, 2, 3 and 4). The Cl–O bond distances and O–Cl–O bond angles show nearly ideal tetrahedral geometry. The C–O distances and O–C–C angles show the existence of the carboxyl group in all four valinium residues. The backbone torsion angle ψ^1 indicates a *cis* conformation for all four valinium residues. The deviations of α -amino nitrogen atoms N1, N2, N3 and N4 from the corresponding carboxyl planes are 0.052 (2), 0.022 (2), 0.477 (2) and 0.006 (2) Å, respectively. This tendency of the C–N bond to twist is commonly found in amino acids (Lakshminarayanan *et al.*, 1967). All three possible side-chain

rotamers (*gauche I/gauche II*, *gauche I/trans* and *gauche II/trans*) are observed for valine residues in crystals (Torri & Iitaka, 1970). In the present structure, the torsion angles χ^{11} and χ^{12} are *gauche II* and *gauche I*, respectively, for all four valinium residues.

Only 11 of the 16 O atoms in the perchlorate anions take part in hydrogen bonding. The perchlorate anions connect the carboxyl group of valinium residues I, II and IV by O—H...O hydrogen bonding. Interestingly, in residue III, the carboxyl O atom forms a rather strong O—H...O [2.638 (1) Å] hydrogen bond with its inversion-related equivalent, resulting in a dimer. Since the H atom, H3B, is closer to the donor carboxyl O atom, it may be termed an asymmetric hydrogen bond (Olovsson *et al.*, 2001). Further, the H atom shows a *syn-syn* orientation with respect to the donor and acceptor carboxyl groups [H3B—O3B—C31—O3A is -0.6 (14)° and H3B...O3Bⁱⁱⁱ—C31ⁱⁱⁱ—O3Aⁱⁱⁱ is -4.2 (4)°; symmetry code: (iii) 2—*x*, 1—*y*, —*z*]. This type of *syn-syn* orientation is also found in betaine betainium oxalate (Rodrigues *et al.*, 2001).

The amino N atoms of residues I and III form N—H...O hydrogen bonds with carboxyl groups of neighbouring valinium residues, as well as O atoms of the surrounding perchlorate anions. In contrast, the amino N atoms of residues II and IV interact only with perchlorate anions. A class I hydrogen-bonding pattern, with three two-centered hydrogen bonds, is observed for residues I and III. Chelated and three-centered hydrogen bonds are observed in residues II and IV, leading to a class III hydrogen-bonding pattern, with two three-centered and one two-centered hydrogen bonds (Jeffrey & Saenger, 1991). The aggregation of hydrophilic double layers, stacked between hydrophobic double layers parallel to the *bc* plane at *x* = 0 plane, is observed. Similar aggregation patterns are also observed in DL-valinium nitrate (Srinivasan *et al.*, 2002).

Experimental

The title compound was crystallized by slow evaporation from an aqueous solution of DL-valine and perchloric acid in a 1:1 stoichiometric ratio.

Crystal data

C ₅ H ₁₂ NO ₂ ⁺ ·ClO ₄ [−]	$D_m = 1.50 \text{ Mg m}^{-3}$
$M_r = 217.61$	D_m measured by flotation in a mixture of carbon tetrachloride and xylene
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.3005$ (6) Å	Cell parameters from 8152 reflections
$b = 13.0905$ (8) Å	$\theta = 2.5\text{--}35.0^\circ$
$c = 14.6105$ (9) Å	$\mu = 0.41 \text{ mm}^{-1}$
$\alpha = 81.288$ (2)°	$T = 105$ (2) K
$\beta = 88.4473$ (19)°	Plate, colorless
$\gamma = 75.9648$ (19)°	$0.70 \times 0.50 \times 0.15 \text{ mm}$
$V = 1889.1$ (2) Å ³	
$Z = 8$	
$D_x = 1.530 \text{ Mg m}^{-3}$	

Data collection

Bruker SMART CCD diffractometer	15604 independent reflections
ω scans	12138 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.020$
$T_{\text{min}} = 0.76$, $T_{\text{max}} = 0.94$	$\theta_{\text{max}} = 35.1^\circ$
35831 measured reflections	$h = -16 \rightarrow 16$
	$k = -21 \rightarrow 21$
	$l = -23 \rightarrow 23$

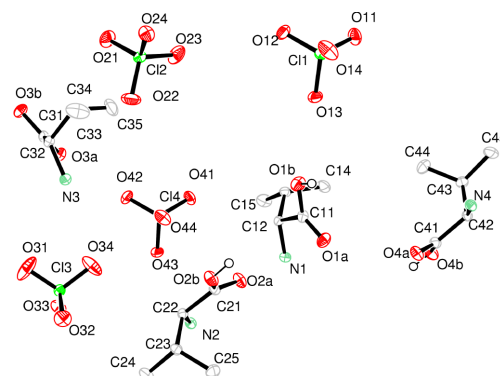


Figure 1

The structures of the four independent valinium cations and four perchlorate anions of the title compound, showing 50% probability displacement ellipsoids (Johnson, 1976) and the atom-numbering scheme.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.105$
 $S = 1.02$
 15604 reflections
 485 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.6779P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} = 0.002$$

$$\Delta\rho_{\text{max}} = 0.78 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.54 \text{ e \AA}^{-3}$$

Table 1

Selected geometric parameters (Å, °).

O1A—C11	1.2132 (14)	O3A—C31	1.2248 (13)
O1B—C11	1.3161 (14)	O3B—C31	1.3064 (13)
O2A—C21	1.2141 (13)	O4A—C41	1.2121 (14)
O2B—C21	1.3209 (13)	O4B—C41	1.3262 (14)
O1A—C11—C12—N1	2.09 (14)	O3A—C31—C32—N3	−20.98 (14)
N1—C12—C13—C14	−73.50 (12)	N3—C32—C33—C34	−64.56 (13)
N1—C12—C13—C15	52.77 (12)	N3—C32—C33—C35	62.85 (13)
O2A—C21—C22—N2	1.11 (14)	O4A—C41—C42—N4	0.30 (15)
N2—C22—C23—C24	−53.19 (12)	N4—C42—C43—C44	−75.99 (12)
N2—C22—C23—C25	72.66 (12)	N4—C42—C43—C45	49.37 (12)

Table 2

Hydrogen-bonding 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>
O1B—H1B...O34 ⁱ	0.86 (2)	1.89 (2)	2.7503 (14)	177 (2)
N1—H1A...O24 ⁱⁱ	0.89	2.15	2.8349 (13)	133
N1—H1C...O2A	0.89	2.15	2.8670 (12)	137
N1—H1D...O12 ⁱⁱ	0.89	2.27	2.9264 (13)	130
O2B—H2B...O44 ⁱ	0.87 (2)	1.88 (2)	2.7395 (12)	175 (2)
N2—H2A...O13 ^v	0.89	2.19	2.9124 (13)	138
N2—H2A...O12 ⁱ	0.89	2.51	3.3055 (13)	149
N2—H2C...O23 ⁱ	0.89	2.02	2.8695 (13)	159
N2—H2D...O24 ⁱⁱ	0.89	2.15	2.9234 (13)	145
N2—H2D...O43	0.89	2.31	2.9731 (13)	132
O3B—H3B...O3A ⁱⁱⁱ	0.90 (2)	1.74 (2)	2.6381 (11)	174 (2)
N3—H3A...O1A ⁱ	0.89	2.09	2.9288 (12)	158
N3—H3D...O33 ^{iv}	0.89	2.25	2.9745 (13)	139
N3—H3C...O42	0.89	2.10	2.9546 (13)	161
O4B—H4B...O14 ⁱⁱ	0.86 (2)	1.93 (2)	2.7913 (13)	172 (2)
N4—H4A...O43 ^v	0.89	2.20	2.9049 (12)	135
N4—H4A...O42 ^v	0.89	2.51	3.3032 (13)	148
N4—H4C...O13 ⁱⁱ	0.89	2.16	2.8827 (13)	138
N4—H4C...O33 ^v	0.89	2.32	2.9834 (13)	132
N4—H4D...O31 ⁱ	0.89	1.95	2.8208 (14)	165

Symmetry codes: (i) 1—*x*, 1—*y*, 1—*z*; (ii) *x*, *y*—1, *z*; (iii) 2—*x*, 1—*y*, —*z*; (iv) 1—*x*, 1—*y*, —*z*; (v) *x*, *y*, 1+*z*; (vi) 1—*x*, 1—*y*, 2—*z*.

The carboxyl H atoms (H1B, H2B, H3B and H4B) were located from a difference Fourier map and refined isotropically (O—H = 0.86–0.90 Å). All other H atoms were placed in geometrically calculated positions and included in the refinement in a riding-model approximation, with U_{iso} equal to $1.2U_{\text{eq}}$ of the carrier atom. The O atoms of perchlorate anion 3 have slightly higher U_{iso} values compared to the other three perchlorate anions. Attempts to refine these O atoms with a split model resulted in site-occupation factors for major and minor components of 0.93 and 0.07. However, due to unsuccessful convergence, the refinement of this split model could not be confirmed and hence is not reported.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

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