DL-Valinium nitrate

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The asymmetric unit of the title compound, $C_5H_{12}NO_2^+\cdot NO_3^-$, consists of four valinium cations and four nitrate anions. The valinium residues are related to one another by pseudo-twofold symmetry and pseudo-translation. The nitrate anions are related by a pseudo-*c*-glide and pseudo-translation. The crystal structure is stabilized by N—H$\cdots$O and O—H$\cdots$O hydrogen bonds.

Comment

Valine is one of the essential amino acids. The crystal structures of L-valine hydrochloride (Parthasarathy, 1966; Ando *et al.*, 1967), L-valine hydrochloride monohydrate (Rao, 1969), DL-valine (Mallikarjunan & Rao, 1969), L-valine (Torii & Iitaka, 1970), L-valinium nitrate (Srinivasan *et al.*, 1997) and L-valine L-valininium perchlorate monohydrate (Pandiarajan *et al.*, 2001) have been reported. The structure of DL-valinium nitrate was solved in $P2_1/c$ (Rao & Parthasarathy, 1974) and refined to an R value of 0.12. However, our preliminary crystallographic investigation on DL-valinium nitrate indicated a triclinic cell. Hence the crystal structure determination of the title compound, (I), was undertaken.
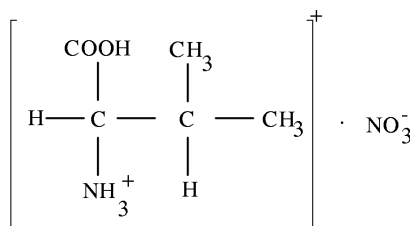
(I)

The collected intensity data, in the present study, confirm the triclinic system. The transformation to the monoclinic primitive cell reported by Rao & Parthasarathy (1974) requires $H = h$; $K = k/2$ and $L = k/2 + l$; thus hkl reflections with k odd have to be systematically weak. In fact, the intensity data showed that the reflections with k odd are not weak. Another transformation (012/0$\bar{1}$0/100) to a monoclinic *C*-centred cell is possible; however, one of the cell angles differs by 0.25° from 90°. Thus no higher symmetry has been overlooked in the present study.

The geometry of four crystallographically independent valinium residues (*A*, *B*, *C* and *D*; Fig. 1) are similar in geometry and agree well with DL-valine hydrochloride (Di Blasio *et al.*, 1977). The residues *A* and *C* are related to *B* and *D*, respectively, by a pseudo-twofold symmetry rotation around (1/2, y, 1/4) and a translation of 1/6 along the y axis.
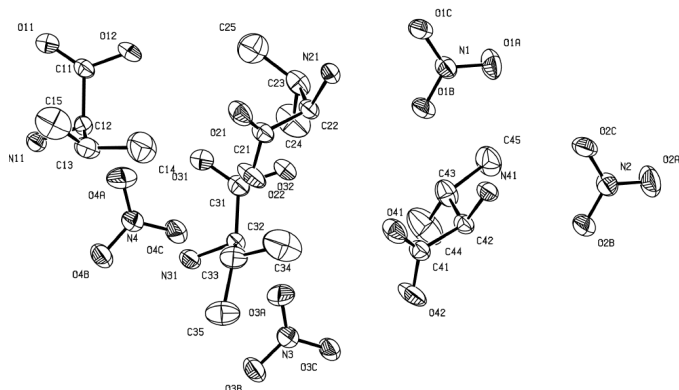
Figure 1
View of the four cations and four anions in the asymmetric unit of (I) showing the numbering schemes; displacement ellipsoids are drawn at the 50% probability level (Johnson, 1976). H atoms have been omitted for clarity.

Figure 2
Packing of the ions viewed down the b axis.

Residues A and B are related to C and D, respectively, by a pseudo-translation of half the unit cell along the b axis. The pseudosymmetry present in the structure looks credible in view of the difference in the conformations of the $C(H)(CH_3)_2$ moieties (Fig. 2). The geometry of the four nitrate anions (I, II, III and IV) is similar and they exhibit pseudosymmetric features. Anions I and II are related to III and IV, respectively, by a pseudo-c-glide with a mirror plane at $y = 0$. Anions I and III are related to II and IV, respectively, by a pseudo-translation of half the unit cell along the b axis.

Generally in valine residues, all three possible rotational isomers, *viz. trans, gauche*-I and *gauche*-II, have been found in the crystalline state (Torii & Iitaka, 1970). For the valinium residues A, B, C and D, the conformation angles ψ^1 are 19.9 (4), 22.6 (4), 33.1 (4) and 32.6 (4)°, respectively. The branched-chain conformation angle χ^{11} [159.0 (3), 160.7 (3), 174.3 (3) and 177.4 (3)°] of the four valinium residues indicates the *trans* form. However, the conformation angle χ^{12} indicates the *gauche*-II form [−74.5 (4) and −73.3 (4)°] for residues A and B, and the *gauche*-I form [52.2 (4) and 54.6 (4)°] for residues C and D. The absence of higher perfect symmetry in the crystal may be due to this difference in the conformation angle χ^{12}.

All four residues have strikingly similar hydrogen-bonding patterns due to the presence of the pseudosymmetry (Fig. 3 and Table 1). The nitrate anions are involved in strong O—H···O and N—H···O hydrogen bonds with the valinium residues and as a result the corresponding acceptor O atoms have relatively weak covalent bonds with the N atoms. The amino N atoms of the valinium residues are also involved in relatively weak N—H···O hydrogen bonds with the nitrate anions. Chelated three-centered hydrogen bonds of amino nitrogen with nitrate O atoms, besides three-centered hydrogen bonds of the amino nitrogen with carboxyl (head-to-tail sequence) and nitrate O atoms are observed in the structure (Jeffrey & Saenger, 1991). The aggregation of the double layered hydrophilic groups about the $x = 0$ plane is such that these groups are involved in an extensive two-dimensional hydrogen-bonding network. The hydrophobic zone ($x = 1/2$) is sandwiched between the double-layered hydrophilic groups.
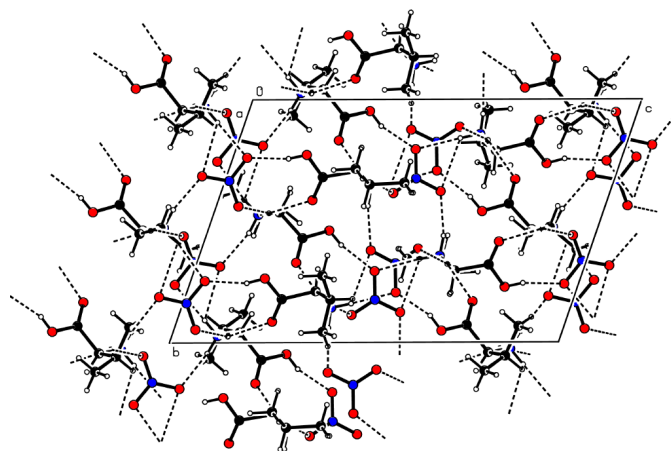
Experimental

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

Crystal data

$C_5H_{12}NO_2^+ \cdot NO_3^-$	$D_m = 1.375$ Mg m^{-3}
$M_r = 180.17$	D_m measured by flotation using a
Triclinic, $P\bar{1}$	mixture of carbon tetrachloride
$a = 9.5695 (10)$ Å	and xylene
$b = 11.2104 (16)$ Å	Cu $K\alpha$ radiation
$c = 17.537 (3)$ Å	Cell parameters from 25
$\alpha = 108.52 (3)°$	reflections
$\beta = 104.14 (2)°$	$\theta = 15.2–23.8°$
$\gamma = 90.25 (2)°$	$\mu = 1.08$ mm^{-1}
$V = 1722.9 (4)$ Å^3	$T = 293 (2)$ K
$Z = 8$	Needle, colorless
$D_x = 1.389$ Mg m^{-3}	$0.45 \times 0.30 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.012$
ω–2θ scans	$\theta_{max} = 63.5°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \to 10$
	$k = -12 \to 11$
$T_{min} = 0.712$, $T_{max} = 0.851$	$l = -19 \to 19$
5768 measured reflections	3 standard reflections
5409 independent reflections	frequency: 60 min
4447 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0809P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$+ 1.5449P]$
$wR(F^2) = 0.180$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} = 0.001$
5409 reflections	$\Delta\rho_{max} = 0.43$ e Å^{-3}
435 parameters	$\Delta\rho_{min} = -0.31$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.0049 (4)

Table 1
Selected geometric parameters (Å, °).

N1—O1A	1.226 (3)	N4—O4B	1.246 (3)
N1—O1B	1.249 (3)	N4—O4C	1.272 (4)
N1—O1C	1.266 (4)	O11—C11	1.199 (4)
N2—O2A	1.222 (4)	O12—C11	1.312 (4)
N2—O2B	1.246 (3)	O21—C21	1.197 (4)
N2—O2C	1.268 (4)	O22—C21	1.315 (4)
N3—O3A	1.224 (4)	O31—C31	1.204 (4)
N3—O3B	1.251 (3)	O32—C31	1.315 (4)
N3—O3C	1.268 (4)	O41—C41	1.204 (4)
N4—O4A	1.218 (4)	O42—C41	1.314 (4)
O11—C11—C12—N11	19.9 (4)	O31—C31—C32—N31	33.1 (4)
N11—C12—C13—C15	−74.5 (4)	N31—C32—C33—C34	174.3 (3)
N11—C12—C13—C14	159.0 (3)	N31—C32—C33—C35	52.2 (4)
O21—C21—C22—N21	22.6 (4)	O41—C41—C42—N41	32.6 (4)
N21—C22—C23—C25	−73.3 (4)	N41—C42—C43—C45	54.6 (4)
N21—C22—C23—C24	160.7 (4)	N41—C42—C43—C44	177.4 (3)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O12—H12···O1C[i]	0.82	1.87	2.636 (3)	155
N11—H11B···O21[ii]	0.89	2.18	2.907 (3)	138
N11—H11B···O4A[iii]	0.89	2.53	3.014 (4)	115
N11—H11C···O4B[iv]	0.89	1.97	2.843 (4)	168
N11—H11A···O3C[v]	0.89	2.02	2.914 (4)	179
N11—H11A···O3B[v]	0.89	2.46	3.048 (4)	124
O22—H22···O4C[v]	0.82	1.84	2.628 (3)	160
N21—H21C···O2B[iv]	0.89	1.96	2.840 (4)	168
N21—H21A···O1C	0.89	2.01	2.899 (3)	178
N21—H21A···O1B	0.89	2.50	3.061 (4)	122
N21—H21B···O31[vi]	0.89	2.20	2.920 (4)	138
N21—H21B···O2A[vii]	0.89	2.45	2.968 (4)	117
O32—H32···O2C[viii]	0.82	1.88	2.660 (3)	160
N31—H31B···O41[ii]	0.89	2.13	2.885 (4)	143
N31—H31B···O3A[ii]	0.89	2.47	2.963 (4)	116
N31—H31A···O4C	0.89	2.08	2.946 (4)	165
N31—H31A···O4B	0.89	2.50	3.019 (4)	118
N31—H31C···O3B[v]	0.89	1.97	2.835 (4)	163
O42—H42···O3C	0.82	1.91	2.667 (4)	152
N41—H41B···O11[ix]	0.89	2.11	2.877 (4)	144
N41—H41B···O1A[vii]	0.89	2.54	3.011 (4)	114
N41—H41C···O1B	0.89	1.97	2.832 (4)	163
N41—H41A···O2C	0.89	2.09	2.954 (3)	165
N41—H41A···O2B	0.89	2.47	3.004 (4)	119

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

The structure is twinned (twin matrix $\overline{1}00/010/0\overline{1}\overline{1}$) with a twinning factor of 0.140 (2). All H atoms were fixed by geometrical constraints and were allowed to ride on the parent atom.

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.
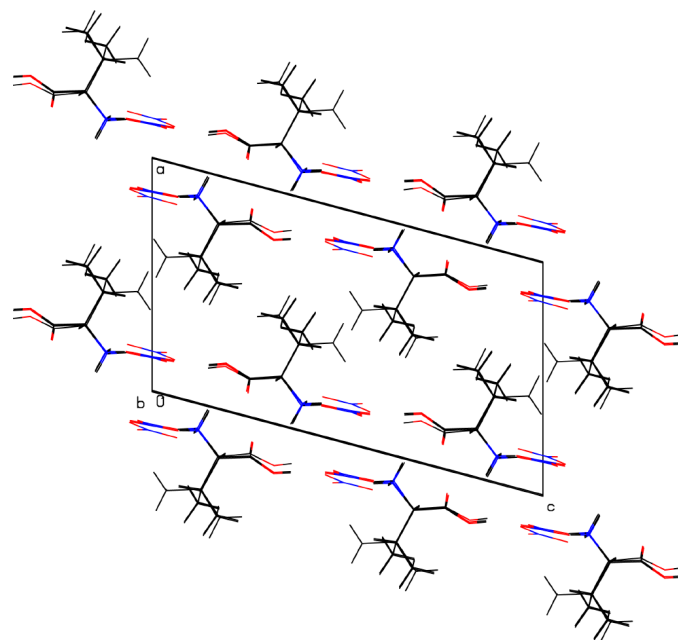
Figure 3
Packing of the ions viewed down the *a* axis.

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