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L-Methioninium nitrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.047
wR factor = 0.131
Data-to-parameter ratio = 8.2

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

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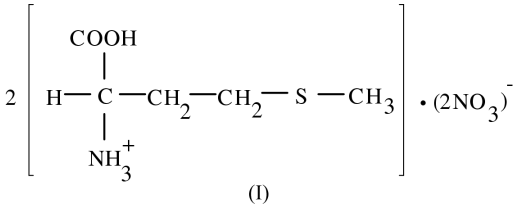
The asymmetric unit of the title compound, $C_5H_{12}NO_2S^+\cdot NO_3^-$, is composed of two crystallographically independent methioninium cations related by pseudosymmetry ($-x, \frac{1}{5} + y, \frac{1}{2} - z$) and two nitrate anions related by a pseudo-inversion centre at (0.50, 0.43, 0.25). In one of the residues, the straight side-chain conformation is *gauche* II–*trans*–*gauche* II, while in the other it is *gauche* II–*trans*–*trans*. In the crystal, the methioninium residues form N—H···O hydrogen-bonded molecular columns, which are interlinked by N—H···O and O—H···O hydrogen bonds involving the O atoms of the nitrate groups.

Comment

L-Methionine is one of the sulfur-containing amino acids. Apart from its role as a protein constituent and as an essential amino acid, methionine is also important as a donor of an active methyl group. The crystal structures of L-methionine (Torii & Iitaka, 1973), DL-methionine (α-form; Mathieson, 1952; Taniguchi *et al.*, 1980), L-methionine hydrochloride (Di Blasio *et al.*, 1977), DL-methionine nitrate (Mostad & Natarajan, 1985), bis(DL-methionine) dihydrogenphosphate (Asath Bahadur, 1992), bis(L-methioninium) sulfate (Srinivasan *et al.*, 2001) and L-methionine L-methioninium perchlorate (Sridhar *et al.*, 2002) have been reported. The present study of L-methionine reacted with nitric acid, (I), was undertaken to study the conformation and hydrogen-bonding pattern resulting from the presence of an inorganic acid.



$$2\left[\mathrm{H{-}\underset{\displaystyle NH_3^+}{\overset{\displaystyle COOH}{C}}{-}CH_2{-}CH_2{-}S{-}CH_3}\right]\cdot(2NO_3)^-$$

(I)

The asymmetric unit of (I) contains two crystallographically independent methioninium residues, 1 and 2, which are in the cationic form, and two nitrate anions (Fig. 1). The methioninium residues with their centroid at (0.50, 0.95, 0.25) are related by pseudosymmetry ($-x, \frac{1}{5} + y, \frac{1}{2} - z$). The deviation from this pseudosymmetry is large for atoms S21 and C25, as also evidenced from the different χ^3 angles. The two nitrate anions are related by a pseudo-inversion centre at (0.50, 0.43, 0.25).

The back-bone conformation angles ψ^1 for residues 1 and 2 are −27.6 (5) and −31.6 (5)°, respectively. Least-squares-

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plane calculations reveal that the deviations of the amino N atoms from the carboxyl groups are 0.64 (6) and 0.68 (6) Å for residues 1 and 2, respectively. This tendency for the C—N bond to twist is found in various amino acids (Lakshminarayanan *et al.*, 1967). All three possible rotational isomers are found to exist in the methioninium residues. In both the residues, the straight side-chain conformation angles χ^1 are in the *gauche* II form [−72.4 (5) and −66.6 (5)°], while χ^2 are in the *trans* form [−178.3 (3) and −178.5 (3)°]. However, angle χ^3 adopts a *gauche* II form [−85.7 (4)°] in residue 1 and a *trans* form [176.0 (3)°] in residue 2.

Both the methioninium residues have similar hydrogen-bonding features. The screw-related residues 1 are linked by N11—H11*C*···O1*A*(1−*x*, *y*−1/2, 1−*z*) hydrogen bonds to form a column-like structure around the 2_1 screw axis. Similarly, the screw-related residues 2 also form an independent molecular column around the 2_1 screw axis, through N21—H21*C*···O2*A*(1−*x*, *y*−1/2, −*z*) hydrogen bonds (Table 2). In the crystal, the molecular columns, formed independently by residues 1 and 2, are assembled alternately along the *c*-cell direction, and are interlinked by N—H···O and O—H···O hydrogen bonds involving the O atoms of the nitrate groups. The hydrophilic and hydrophobic groups are aggregated in two distinct regions in the crystal (Fig. 2).

Experimental

The title compound was crystallized by slow evaporation, at room temperature, from an aqueous solution containing a 1:1 stoichiometric ratio of L-methionine and nitric acid.

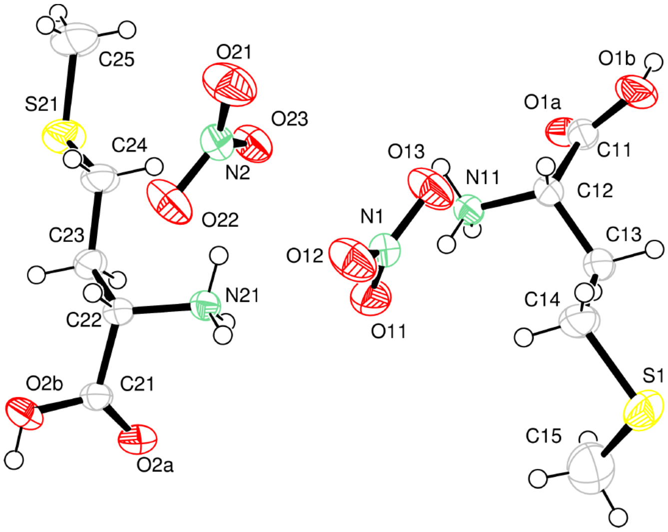

Figure 1
The structures of the two independent molecules of (I), showing the atomic numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

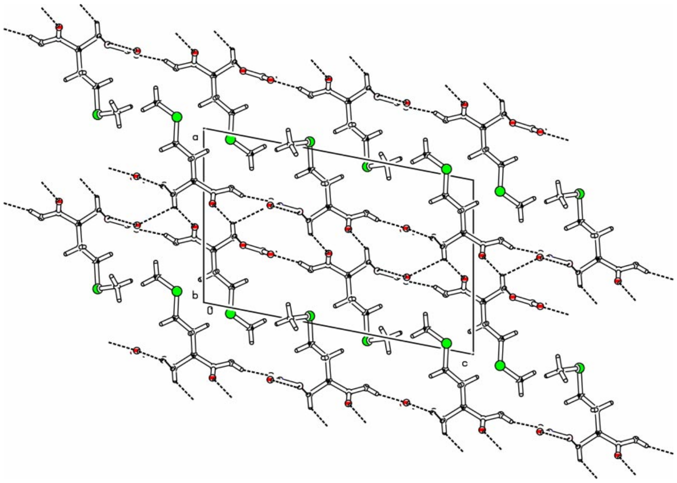

Figure 2
Packing of the molecules, viewed down the *b* axis.

Crystal data

$C_5H_{12}NO_2S^+ \cdot NO_3^-$
M_r = 212.23
Monoclinic, $P2_1$
a = 10.682 (2) Å
b = 5.577 (2) Å
c = 16.829 (6) Å
β = 100.92 (2)°
V = 984.3 (5) Å^3
Z = 4
D_x = 1.432 Mg m^{-3}
D_m = 1.43 Mg m^{-3}
D_m measured by flotation method in a mixture of carbon tetrachloride and xylene
Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 2.1–24.9°
μ = 0.33 mm^{-1}
T = 293 (2) K
Plate, colourless
0.5 × 0.3 × 0.2 mm

Data collection

Enraf–Nonis sealed-tube diffractometer
ω–2*θ* scans
Absorption correction: *ψ* scan (North *et al.*, 1968)
T_{min} = 0.892, T_{max} = 0.937
2028 measured reflections
1924 independent reflections
1671 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 24.9°
h = 0 → 12
k = 0 → 6
l = −19 → 19
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.131
S = 1.04
1924 reflections
235 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0999P)^2 + 0.1845P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.62 e Å^{-3}
$\Delta\rho_{min}$ = −0.36 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.194 (5)	O2*A*—C21	1.199 (5)
O1*B*—C11	1.299 (5)	O2*B*—C21	1.307 (5)
O1*A*—C11—C12—N11	−27.6 (5)	O2*A*—C21—C22—N21	−31.6 (5)
N11—C12—C13—C14	−72.4 (5)	N21—C22—C23—C24	−66.6 (5)
C12—C13—C14—S11	−178.3 (3)	C22—C23—C24—S21	−178.5 (3)
C13—C14—S11—C15	−85.7 (4)	C23—C24—S21—C25	176.0 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*B*—H1*B*···O23^{i}	0.82	1.90	2.663 (4)	156
O2*B*—H2*B*···O12^{ii}	0.82	1.85	2.615 (4)	154
N11—H11*C*···O1*A*^{iii}	0.89	2.08	2.859 (4)	145
N11—H11*A*···O13	0.89	2.50	2.934 (5)	111
N11—H11*A*···O11	0.89	2.22	3.072 (4)	161
N11—H11*B*···O13^{iv}	0.89	2.01	2.854 (5)	158
N21—H21*A*···O23	0.89	2.13	2.988 (4)	162
N21—H21*A*···O22	0.89	2.51	2.943 (5)	111
N21—H21*B*···O22^{iv}	0.89	2.00	2.840 (5)	157
N21—H21*C*···O2*A*^{v}	0.89	2.10	2.867 (4)	144
N21—H21*C*···O11	0.89	2.59	3.028 (4)	111

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

All H atoms were placed in geometrically calculated positions and included in the refinement in a riding-model approximation, with $U_{\rm iso}$ equal to $1.2U_{\rm eq}$ of the carrier atom ($1.5U_{\rm eq}$ for methyl and NH_3 H atoms).

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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