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L-Methionine L-methioninium perchlorate monohydrate

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Key indicators

Single-crystal X-ray study
T = 105 K
Mean σ(C–C) = 0.002 Å
R factor = 0.029
wR factor = 0.086
Data-to-parameter ratio = 40.1

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

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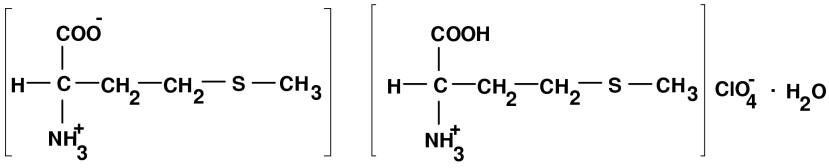
In the title compound, $C_5H_{12}NO_2S^+\cdot ClO_4^-\cdot C_5H_{11}NO_2S\cdot H_2O$, the L-methionine and L-methioninium residues are linked by a strong O···O hydrogen bond [2.500 (1) Å]. The methionine residue adopts a *trans–gauche* I–*gauche* I conformation, while the methioninium residue has a *gauche* II–*trans–gauche* I conformation. The methioninium residues in the crystal are engaged in straight (*S*1) head-to-tail hydrogen bonding, thus forming infinite chains along the *b* axis.

Comment

Methionine is a sulfur-containing amino acid which is essential for normal metabolism, growth and maintenance of body tissues. As part of our ongoing research programme of studying the conformation and hydrogen-bonding features of amino acids in the presence of inorganic acids, *e.g.* perchloric acid, the crystal structures of L-phenylalanine L-phenylalaninium perchlorate (Srinivasan & Rajaram, 1997), L-valine L-valinium perchlorate monohydrate (Pandiarajan *et al.*, 2001*a*), hydrogen bis[L-lysinium(+)] dichloride perchlorate (Srinivasan *et al.*, 2001), β-alaninium perchlorate (Pandiarajan *et al.*, 2001*b*), D-phenylglycinium perchlorate (Ramaswamy *et al.*, 2001) and bis(L-proline) hydrogen (1+) perchlorate (Pandiarajan *et al.*, 2002) have been solved. In this paper, the crystal structure of the product of reaction of L-methionine with perchloric acid is reported.



(I)

The asymmetic unit of the title salt, (I), contains a neutral methionine residue, a methioninium cation, a perchlorate anion and a water molecule (Fig. 1). The C—O bond distances [1.259 (1) and 1.260 (1) Å] and O—C—C angles [116.20 (9) and 117.51 (9)°] of the methionine residue indicate a deprotonated carboxylate group, whilst the methioninium residue is unsymmetrical [C—O 1.216 (1) and 1.305 (1) Å, and O—C—C 122.3 (1) and 111.34 (9)°], owing to the protonation of one of the O atoms.

The backbone conformation angles ψ^1 are 3.8 (1) and −21.6 (2)° for the methionine and methioninium residues, respectively; the deviation of the amino N atom from the planar carboxyl group is 0.098 (2) Å for the methionine and

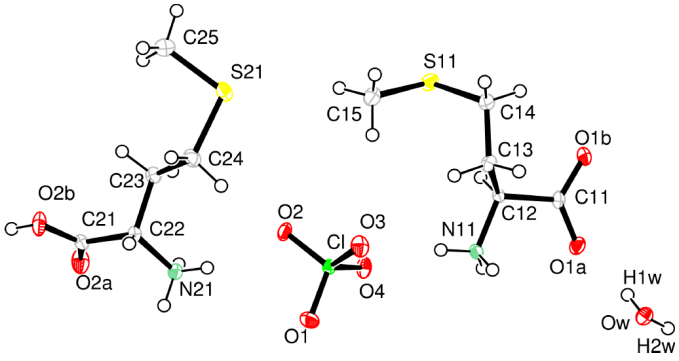


Figure 1
The molecular structure of the title compound, with the atom-numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

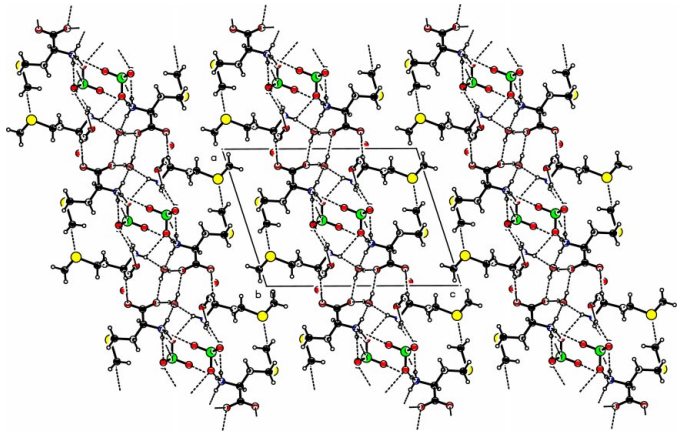


Figure 2
Packing diagram of the title molecule, viewed down the *b* axis.

−0.483 (2) Å for the methioninium residue. The side-chain conformation for the methionine residue is *trans–gauche* I–*gauche* I and for the methioninium residue it is *gauche* II–*trans–gauche* I.

In the perchlorate anion, the Cl—O distances and angles show nearly ideal tetrahedral symmetry; the anion plays a vital role in hydrogen bonding with the amino acid residues.

The packing diagram of the crystal of the title compound, viewed down the *b* axis, is shown in Fig. 2. The methionine and methioninium residues are interlinked by a strong O—H···O hydrogen bond [O2*B*—H2*B*···O1*B*^{iii} 2.500 (1) Å, symmetry code: (iii) 1+*x*, *y*−2, *z*]. Atom H2*B* is in a *syn* orientation with respect to both the donor carboxyl group of the methioninium residue and the acceptor carboxylate group of the methionine residue; the torsion angles H2*B*—O2*B*—C21—O2*A* and H2*B*—O1*B*^{iii}—C11^{iii}—O1*A*^{iii} are 2.6 and −24.0°, respectively. This kind of *syn–syn* conformation is also found in betaine betainium oxalate (Rodrigues *et al.*, 2001).

Interestingly, the methionine residue shows a class I hydrogen-bonding pattern, having three two-centered N—H···O bonds, while the methioninium residue shows a class II pattern, having a one three-centered and two two-centered hydrogen bonds (Jeffrey & Saenger, 1991). The amino N atom of the methionine residue forms two-centered hydrogen bonds with a solvent water molecule and also with the O atom of the perchlorate anion, the latter hydrogen bond giving rise to infinite chains along the *b* axis. The methioninium residue shows a similar hydrogen-bonding pattern, forming, in addition, a straight (*S*1) head-to-tail sequence along the *b* axis. The water molecule, as a donor, links two symmetry-related methionine residues; it adopts a 2*A*-1/1*D* tetrahedral configuration (Jeffrey & Saenger, 1991).

Experimental

The title compound was crystallized by slow evaporation from an aqueous solution of L-methionine and perchloric acid in a 2:1 stoichiometric ratio.

Crystal data

$C_5H_{12}NO_2S^+\cdot ClO_4^-\cdot C_5H_{11}NO_2S\cdot H_2O$	D_m = 1.472 Mg m^{-3}
M_r = 416.89	D_m measured by flotation in carbon tetrachloride and xylene
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
a = 11.3720 (15) Å	Cell parameters from 7529 reflections
b = 5.5876 (8) Å	θ = 2.7–37.6°
c = 15.323 (2) Å	μ = 0.48 mm^{-1}
β = 107.782 (5)°	T = 105 (2) K
V = 927.1 (2) Å^3	Plate, colorless
Z = 2	0.8 × 0.4 × 0.2 mm
D_x = 1.493 Mg m^{-3}	

Data collection

Bruker SMART CCD diffractometer	9018 independent reflections
ω scans	8635 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	R_{int} = 0.022
T_{min} = 0.677, T_{max} = 0.913	θ_{max} = 37.6°
17119 measured reflections	$h = -19 \rightarrow 18$
	$k = -9 \rightarrow 9$
	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.1368P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.029	$(\Delta/\sigma)_{max}$ = 0.002
$wR(F^2)$ = 0.086	$\Delta\rho_{max}$ = 0.62 e Å^{-3}
S = 1.07	$\Delta\rho_{min}$ = −0.60 e Å^{-3}
9018 reflections	Absolute structure: Flack (1983); 3692 Friedel pairs
225 parameters	Flack parameter = 0.05 (3)
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.2587 (13)	O2*A*—C21	1.2156 (14)
O1*B*—C11	1.2596 (13)	O2*B*—C21	1.3060 (14)
O1*B*—C11—O1*A*	126.29 (9)	O2*A*—C21—O2*B*	126.30 (11)
O1*B*—C11—C12	116.20 (9)	O2*A*—C21—C22	122.32 (10)
O1*A*—C11—C12	117.51 (9)	O2*B*—C21—C22	111.34 (9)
O1*A*—C11—C12—N11	3.82 (12)	O2*A*—C21—C22—N21	−21.62 (15)
N11—C12—C13—C14	−153.83 (9)	N21—C22—C23—C24	−84.52 (11)
C12—C13—C14—S11	65.58 (11)	C22—C23—C24—S21	171.84 (7)
C13—C14—S11—C15	67.02 (9)	C23—C24—S21—C25	58.75 (10)

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

D—H···A	D—H	H···A	D···A	D—H···A
N11—H11A···OW^{i}	0.89	2.00	2.818 (1)	153
N11—H11B···O3	0.89	2.18	3.042 (1)	164
N11—H11C···O4^{ii}	0.89	2.08	2.962 (1)	171
O2B—H2B···O1B^{iii}	0.82	1.71	2.500 (1)	163
N21—H21A···O2	0.89	2.20	2.909 (1)	137
N21—H21A···O2A^{ii}	0.89	2.57	3.189 (2)	127
N21—H21B···O3^{i}	0.89	2.21	3.044 (1)	155
N21—H21C···OW^{iv}	0.89	2.01	2.798 (1)	147
OW—H1W···O1A	0.80 (2)	1.92 (3)	2.706 (1)	169 (2)
OW—H2W···O1A^{v}	0.82 (2)	1.95 (2)	2.759 (1)	168 (2)

Symmetry codes: (i) $x, y-1, z$; (ii) $x, 1+y, z$; (iii) $1+x, y-2, z$; (iv) $1-x, y-\frac{3}{2}, 1-z$; (v) $-x, \frac{1}{2}+y, 1-z$.

The H atoms of the water molecule were located and refined isotropically (O—H = 0.79–0.83 Å). All other H atoms were placed in geometrically calculated positions and included in the refinement in the riding-model approximation, with U_{iso} equal to $1.2U_{eq}$ of the carrier atom ($1.5U_{eq}$ for methyl and NH_3 H atoms).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; 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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References

Bruker (1998). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Jeffrey, G. A. & Saenger, W. (1991). *Hydrogen Bonding in Biological Structures*. Berlin, Heidelberg, New York: Springer-Verlag.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Pandiarajan, S., Sridhar, B. & Rajaram, R. K. (2001*a*). *Acta Cryst.* E**57**, o466–o468.

Pandiarajan, S., Sridhar, B. & Rajaram, R. K. (2001*b*). *Acta Cryst.* E**57**, o1130–o1132.

Pandiarajan, S., Sridhar, B. & Rajaram, R. K. (2002). *Acta Cryst.* E**58**, o74–o76.

Ramaswamy, S., Sridhar, B., Ramakrishnan, V. & Rajaram, R. K. (2001). *Acta Cryst.* E**57**, o1149–o1151.

Rodrigues, V. H., Paixão, J. A., Costa, M. M. R. R. & Matos Beja, A. (2001). *Acta Cryst.* C**57**, 213–215.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Spek, A. L.(1999). *PLATON* for Windows. Utrecht University, The Netherlands.

Srinivasan, N. & Rajaram, R. K. (1997). *Acta Cryst*, C**53**, 1711–1713.

Srinivasan, N., Sridhar, B. & Rajaram, R. K. (2001). *Acta Cryst.* E**57**, o875–o877.