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Bis(DL-methioninium) sulfate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.007 Å
Disorder in main residue
R factor = 0.061
wR factor = 0.178
Data-to-parameter ratio = 12.7

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

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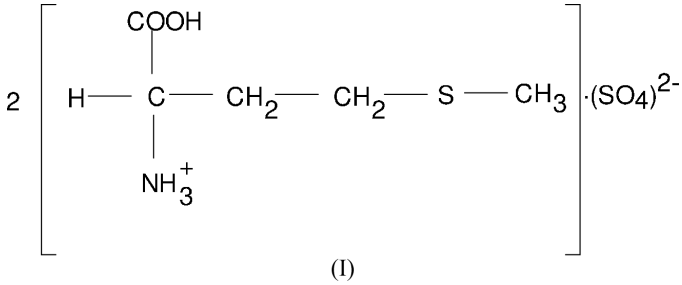
In the title compound, $2C_5H_{12}NO_2S^+\cdot SO_4^{2-}$, the sulfate anion forms a strong O—H···O hydrogen bond with a methioninium residue. The S atom (S^{δ}) of the methioninium residue is disordered. The packing reveals aggregation of the methioninium cations as a cylindrical cage along the *c* axis.

Comment

DL-Methionine is sulfur-containing amino acid, which is considered to be an indispensable dietary nutrient. 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-methioninium nitrate (Mostad & Natarajan, 1985), bis(DL-methionine) dihydrogen phosphate (Asath Bahadur, 1992), bis(L-methioninium) sulfate (Srinivasan *et al.*, 2001), L-methionine L-methioninium perchlorate (Sridhar *et al.*, 2002) and L-methioninium nitrate (Pandiarajan *et al.*, 2002) have been reported. The present study of the reaction product of DL-methionine with sulfuric acid, (I), was undertaken to study the conformation and hydrogen-bonding pattern.



(I)

The asymmetric unit of (I) contains one methioninium cation and two sulfate anions sitting on sites of symmetry 3 and $\overline{3}$, *viz.* (0, 0, *z*) and ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{3}$), respectively. The S atom (S^{δ}) of the methioninium cation is disordered over two positions. The unequal C—O bond distances and O—C—C bond angles clearly show the existence of a carboxylic group in the methioninium residue (Table 1). The backbone conformation angles, ψ^1 and ψ^2, are −18.9 (5) and 161.9 (3)°, respectively. The side-chain conformation angle for the major disorder component of the methioninium cation is *trans-trans-gauche* II, while it is *trans-gauche* I-*gauche* I for the minor component.

One of the sulfate anions (S3) forms a strong O—H···O hydrogen bond with the methioninium cation. The amino N atom of the methioninium cation forms N—H···O hydrogen bonds with the sulfate anion. In addition, this N atom also forms an intermolecular hydrogen bond with a symmetry-related O atom of the carboxylic group. A class III hydrogen

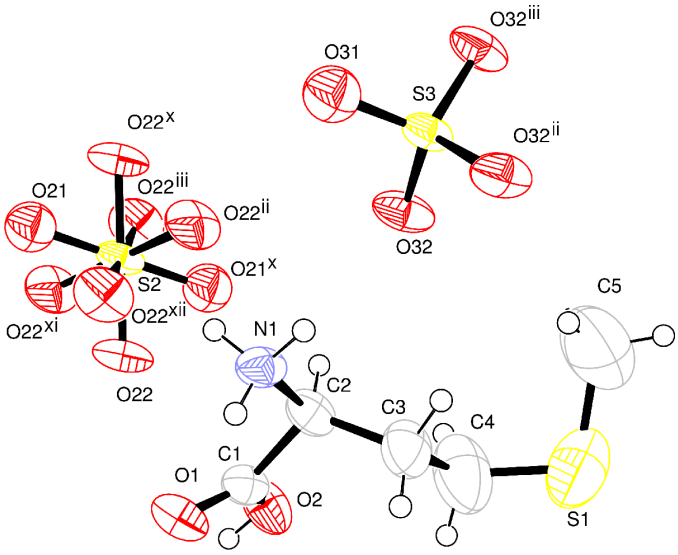


Figure 1
The structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976). One of the sulfate anions is disordered across a $\overline{3}$ site. [Symmetry codes: (ii) $-x, x-y, z$; (iii) $y, -x, z$; (x) $\frac{1}{3}-x, \frac{2}{3}-y, \frac{2}{3}-z$; (xi) $\frac{1}{3}-y, \frac{2}{3}-x+y, \frac{2}{3}-z$; (xii) $x-y+\frac{1}{3}, x+\frac{2}{3}, \frac{2}{3}-z$.]

bonding pattern is observed, involving one two-centred and two three-centred hydrogen bonds (Jeffrey & Saenger, 1991).

The packing diagram viewed down the *c* axis clearly depicts the aggregation of the methioninium cations, as a cylindrical cage, which is occupied by the sulfate anions having site symmetry 3 and $\overline{3}$. The methioninium cations, linked through O—H···O and N—H···O hydrogen bonds, form the cylindrical cage. A similar cylindrical cage aggregation along the *c* axis is observed in bis(L-methioninium) sulfate (Srinivasan *et al.*, 2001), in which the included compound, the sulfate anion, sitting on the threefold axis, does not have any potential donor in its vicinity to allow it to interact with the methioninium cation through hydrogen bonding. Each sulfate anion is surrounded by six methioninium cations as a cylindrical cage (Fig. 3). Such cylindrical cages are aggregated in the *ab* plane. The hydrophilic layers at $z = \frac{1}{3}$ are stacked between hydrophobic layers at $z = \frac{1}{6}$.

Experimental

The title compound was crystallized from an aqueous solution of methionine and sulfuric acid in the stoichiometric ratio 2:1 by slow evaporation.

Crystal data

$2C_5H_{12}NO_2S^+\cdot SO_4^{2-}$
$M_r = 396.49$
Trigonal, $R\overline{3}$
$a = 10.233\ (5)$ Å
$c = 44.494\ (5)$ Å
$V = 4035\ (3)$ Å^3
$Z = 9$
$D_x = 1.467$ Mg m^{-3}
$D_m = 1.465$ Mg m^{-3}
D_m measured by flotation using a mixture of carbon tetrachloride and xylene
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 9.7$–$15.5°$
$\mu = 0.45$ mm^{-1}
$T = 293\ (2)$ K
Block, colourless
0.30 × 0.20 × 0.15 mm

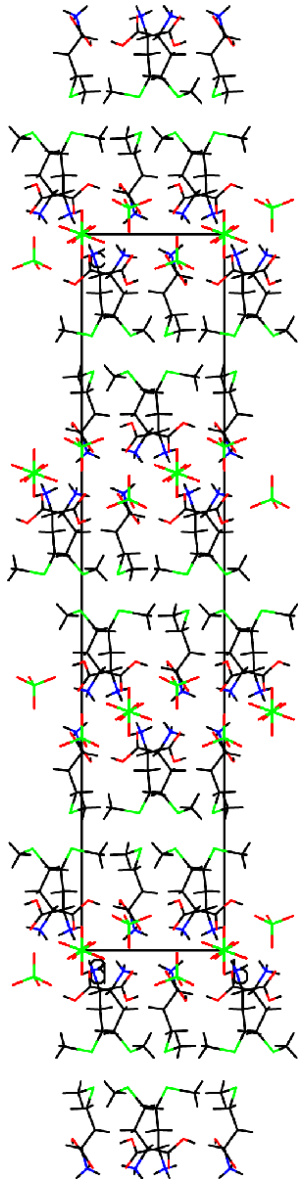


Figure 2
Partial packing of the ions, viewed down the *a* axis.

Data collection

Nonius MACH3 four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.897$, $T_{max} = 0.935$
5569 measured reflections
1584 independent reflections
1332 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 25.0°$
$h = -12 \rightarrow 10$
$k = -1 \rightarrow 12$
$l = -52 \rightarrow 52$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.178$
$S = 1.13$
1576 reflections
124 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.085P)^2 + 13.3806P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.003$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: none

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.198 (5)	O2—C1	1.303 (5)
O1—C1—C2	121.8 (3)	O2—C1—C2	113.3 (3)
O1—C1—C2—N1	−18.9 (5)	C2—C3—C4—S1′	74.1 (7)
O2—C1—C2—N1	161.9 (3)	C2—C3—C4—S1	153.2 (5)
N1—C2—C3—C4	−167.7 (5)	C5—S1′—C4—C3	66.7 (7)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O32^{i}	0.82	1.78	2.570 (4)	162
N1—H1*A*···O31^{ii}	0.89	2.30	3.179 (4)	172
N1—H1*B*···O22^{iii}	0.89	1.92	2.772 (7)	160
N1—H1*B*···O22^{iv}	0.89	2.11	2.862 (7)	141
N1—H1*C*···O32	0.89	2.10	2.895 (4)	148
N1—H1C···O1^{v}	0.89	2.41	2.924 (4)	117

Symmetry codes: (i) $1-x+y, 1-x, z$; (ii) $\frac{4}{3}-x, -\frac{1}{3}-y, \frac{2}{3}-z$; (iii) $\frac{1}{3}+x-y, x-\frac{1}{3}, \frac{2}{3}-z$; (iv) $1-y, x-y, z$; (v) $1-x+y, -x, z$.

The S atom (S^{δ}) of the methioninium cation is disordered; the site occupancy factors for the disordered positions S1 and S1′ were refined to 0.56 (1) and 0.44 (1), respectively. Since the S—C distances involving the disordered S atom differed significantly from the expected value, they were restrained to 1.79 (1) Å. The U_{ij} components of atoms C4 and C5 were approximated to isotropic behaviour. Since atom S2 lies on a $\overline{3}$ axis, the O atoms of this sulfate anion are disordered across the inversion centre. All the H atoms were placed in calculated positions [O—H = 0.82 Å, N—H = 0.89 Å and C—H = 0.96–0.97 Å] and included in the refinement in a riding-model approximation, with U_{iso}(H) equal to $1.5U_{eq}$ of the carrier atom. Eight reflections were omitted from the final refinement due to large diffences between F_o and F_c.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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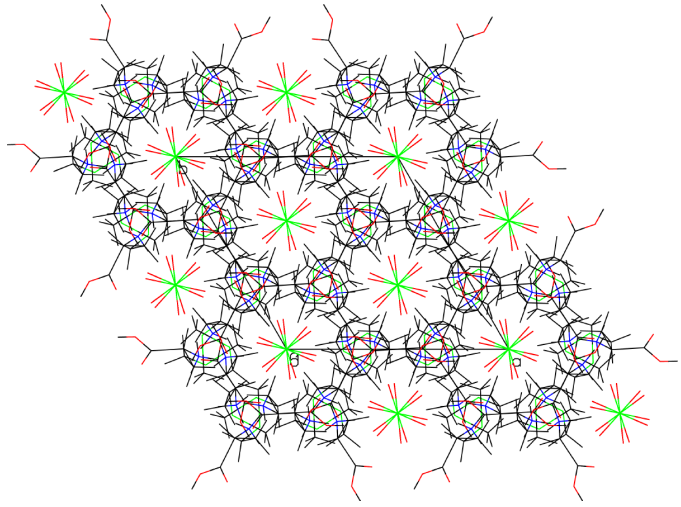

Figure 3
Packing of the ions, viewed down the *c* axis.

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