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Bis(DL-methioninium) sulfate

N. Srinivasan,[a] B. Sridhar[b] and R. K. Rajaram[b]*

[a]Department of Physics, Thiagarajar College, Madurai - 625 009, India, and [b]Department of Physics, Madurai Kamaraj University, Madurai - 625 021, India

Correspondence e-mail: sshiya@yahoo.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
Disorder in solvent or counterion
R factor = 0.051
wR factor = 0.147
Data-to-parameter ratio = 7.8

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, $2\,C_5H_{12}NO_2S^+\cdot SO_4^{2-}$, the sulfate anions form strong hydrogen bonds with both the cations. A head-to-tail sequence is observed in both the molecules. The three sulfate anions on threefold axes link the amino-N atom through normal hydrogen bonds.

Comment

Methionine is one of the few amino acids containing sulfur; it also has straight-chain aliphatic α-amino acids. The crystal structure of DL-methionine (Mathieson, 1952), L-methionine (Torii & Iitaka, 1973), DL-methionine hydrochloride (Di Blasio *et al.*, 1977), DL-methionine nitrate (Mostad & Natarajan, 1985) and bis(DL-methionine dihydrogen phosphate) (Asath Bahadur, 1992) have already been reported. In the present study, the structure of bis(DL-methioninium) sulfate, (I), was determined

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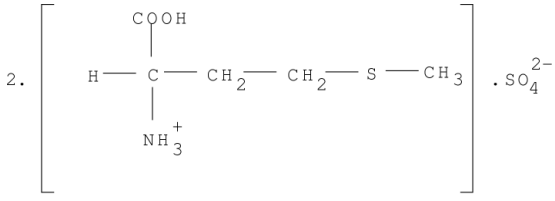

(I)

The two crystallographically independent methionine cations (*A* and *B*) have similar geometries (Fig. 1). The C^{γ} and S^{δ} atoms of molecule *B* are disordered. The minor contributing disordered atoms are denoted as primed atoms. The conformation angle ψ^2 is −148.5 (5) and 166.7 (4)° for molecules *A* and *B*, respectively, which agrees well with bis(DL-methionine dihydrogen phosphate). The χ^1 straight-chain conformation is in the *trans* form [−154.7 (5) & −159.6 (9)] for both the *A* and *B* molecules. The χ^2 conformation is in the *gauche* I form [63.1 (7)°] for molecule *A*, and in the *trans* [161.4 (10)°] and *gauche* I [75 (2)°] forms for the unprimed and primed atoms of molecule *B*. The χ^3 conformation is in the *gauche* I form [70.8 (7)°] for molecule *A*, and in the *gauche* II [−82 (2)°] and *gauche* I [70 (2)°] forms for the unprimed and primed atoms of molecule *B* (Lakshminarayanan *et al.*, 1967).

The carboxyl groups of the methionine cations *A* and *B* (Fig. 2 and Table 2) form strong hydrogen bonds with the sulfate anions. The three sulfate anions sitting on the threefold axis link the amino-N atom of both the molecules (*A* and *B*) and stabilize the structure. Bifurcated hydrogen bonds are

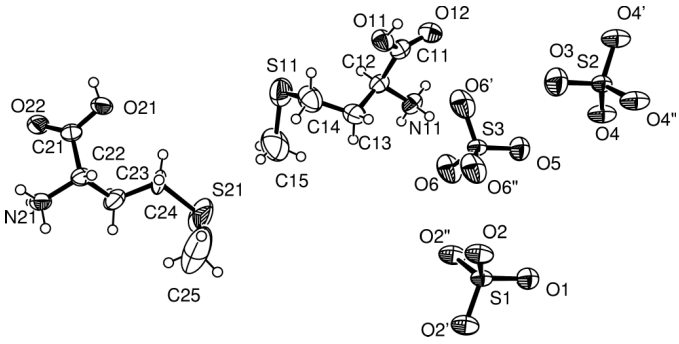

Figure 1
ORTEP (Johnson, 1976) plot of the molecular structures of the two independent DL-methionine cations showing the atomic numbering scheme with 50% probability displacement ellipsoids.

observed in the case of the amino-N atom and the sulfate- and carboxyl-O atoms of both the *A* and *B* molecules (Jeffrey & Saenger, 1991). The *A* and *B* molecules are both engaged in a head-to-tail sequence since the hydrogen bonds N11—H11*B*···O12($-y+1, x-y-1, z$) and N21—H21*B*···O22($-y, x-y-1, z$), connect the amino acids along *ab* plane (Vijayan, 1988).

Experimental

The title compound crystallized in an aqueous solution of methionine and sulfuric acid in the stoichiometric ratio of 2:1. The density of the sample was measured by flotation using a liquid mixture of carbon tetrachloride and xylene.

Crystal data

$2C_5H_{12}NO_2S^+\cdot SO_4^{2-}$
M_r = 396.49
Trigonal, *P*3
a = 10.281 (3) Å
b = 10.281 (3) Å
c = 14.788 (6) Å
V = 1353.5 (8) Å^3
Z = 3
D_x = 1.459 Mg m^{-3}
D_m = 1.454 Mg m^{-3}

D_m measured by flotation
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 14.5–23.4°
μ = 4.12 mm^{-1}
T = 293 (2) K
Needle, colourless
0.50 × 0.35 × 0.20 mm

Data collection

Enraf–Nonius sealed-tube diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.221, T_{max} = 0.438
2818 measured reflections
1786 independent reflections
1690 reflections with $I > 2\sigma(I)$

R_{int} = 0.066
θ_{max} = 70.0°
h = 0 → 12
k = −12 → 10
l = 0 → 17
25 standard reflections
every 3 reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.147
S = 1.09
1786 reflections
229 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1004P)^2 + 0.3922P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}
Flack parameter for absolute structure determination = −0.01 (3) (Flack, 1983)

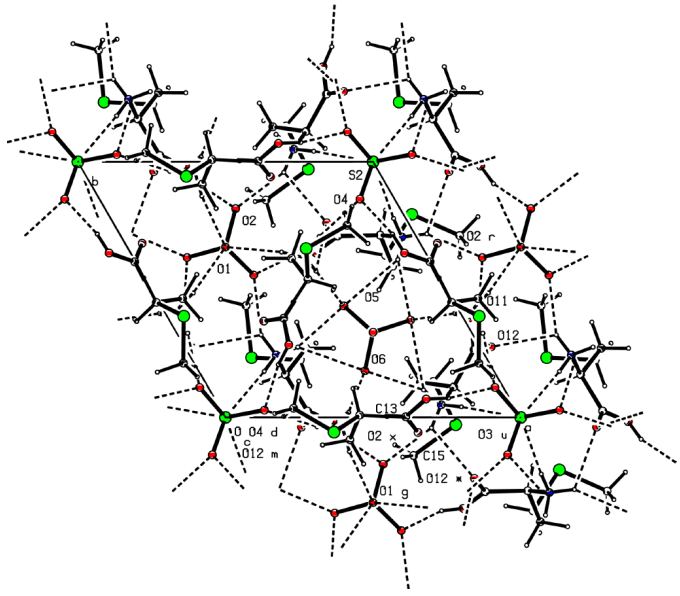

Figure 2
Packing diagram of the molecule viewed down the *a* axis

Table 1
Selected geometric parameters (Å, °).

O11—C11	1.312 (7)	O21—C21	1.289 (7)
O12—C11	1.198 (7)	O22—C21	1.202 (7)
O11—C11—C12—N11	−148.4 (5)	C21—C22—C23—C24′	53.6 (12)
N11—C12—C13—C14	−154.7 (5)	N21—C22—C23—C24	−159.6 (9)
C11—C12—C13—C14	84.5 (6)	C21—C22—C23—C24	80.1 (10)
C12—C13—C14—S11	63.1 (7)	C22—C23—C24—S21	161.4 (10)
C13—C14—S11—C15	70.8 (7)	C22—C23—C24′—S21′	74.6 (17)
O21—C21—C22—N21	166.7 (4)	C23—C24—S21—C25	−82.4 (15)
N21—C22—C23—C24′	173.9 (10)	C23—C24′—S21′—C25	70.0 (15)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H11···O2^{i}	0.82	1.79	2.569 (6)	158.9
N11—H11*A*···O3^{ii}	0.89	2.36	3.233 (7)	169.0
N11—H11*B*···O2^{ii}	0.89	2.16	2.964 (6)	150.6
N11—H11*B*···O12^{iii}	0.89	2.33	2.816 (6)	114.5
N11—H11*C*···O6	0.89	2.17	2.989 (8)	152.8
N11—H11*C*···O6^{iv}	0.89	2.49	3.209 (8)	138.0
O21—H21···O4^{v}	0.82	1.76	2.576 (5)	170.8
N21—H21*A*···O4^{vi}	0.89	2.11	2.956 (6)	159.1
N21—H21*B*···O1^{vii}	0.89	2.22	3.079 (6)	162.4
N21—H21*B*···O22^{viii}	0.89	2.65	3.083 (7)	110.8
N21—H21*C*···O6^{ix}	0.89	1.96	2.839 (7)	167.8

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

In molecule *B*, the atoms C24, S21 are disordered; the site-occupation factor for C24 and S21 is 0.58 (1), and for C24′ and S21′ is 0.42 (1). Since the geometry of these disordered atoms differs significantly from expected values, the distances were fixed by *DFIX* and the disordered group of atoms (with the associated H atoms) was treated using a split model. All H atoms were fixed by geometric

restraints using *HFIX*, and allowed to ride on the preceding 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.

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