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DL-Methioninium maleate

M. Alagar,[a] M. Subha Nandhini,[b] R. V. Krishnakumar[c] and S. Natarajan[b]*

[a]Department of Physics, Ayya Nadar Janaki Ammal College, Sivakasi 626 123, India, [b]Department of Physics, Madurai Kamaraj University, Madurai 625 021, India, and [c]Department of Physics, Thiagarajar College, Madurai 625 009, India

Correspondence e-mail: s natarajan50@yahoo.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.042
wR factor = 0.129
Data-to-parameter ratio = 14.0

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

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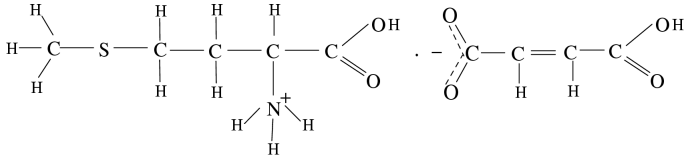
In the title compound, $C_5H_{12}NO_2S^+\cdot C_4H_3O_4^-$, the methionine molecule exists in the cationic form and the maleic acid molecule in the mono-ionized state. In the semi-maleate ion, there is an asymmetric intramolecular hydrogen bond between the carboxy OH group and an O atom of the other carboxylate group. There are no direct hydrogen-bonded interactions among the semi-maleate anions.

Comment

Methionine, an essential amino acid, is also a principal source of sulfur required by the body for normal metabolism and growth. The crystal structures of a number of complexes of methionine with inorganic acids and salts are already known. However, the present study, the crystal structure determination of a complex, (I), of methionine with maleic acid, appears to be the first of its kind involving methionine and a carboxylic acid. Recently, the crystal structures of several maleic acid complexes, namely glycinium maleate (Rajagopal, Krishnakumar, Mostad & Natarajan, 2001), L-alaninium maleate (Alagar, Krishnakumar, Subha Nandhini & Natarajan, 2001), β-alaninium maleate (Rajagopal, Krishnakumar & Natarajan, 2001), DL-valinium maleate (Alagar, Krishnakumar, Mostad & Natarajan, 2001) and L-phenylalaninium maleate (Alagar, Krishnakumar & Natarajan, 2001) have been reported from our laboratory.



(I)

Fig. 1 shows the molecular structure of the title compound, (I), with the atom-numbering scheme. The DL-methioninium molecule exists in the cationic form, with a protonated amino group and an uncharged carboxylic acid group. The maleic acid molecule exists in the mono-ionized state. The semi-maleate ion is essentially planar, as observed in the crystal structures of similar complexes. There is an asymmetric intramolecular hydrogen bond between atoms O3 and O5 of the semi-maleate ion, as was also observed in the crystal structures of maleic acid (James & Williams, 1974), glycinium maleate, L-alaninium maleate, DL-valinium maleate and β-alaninium maleate.

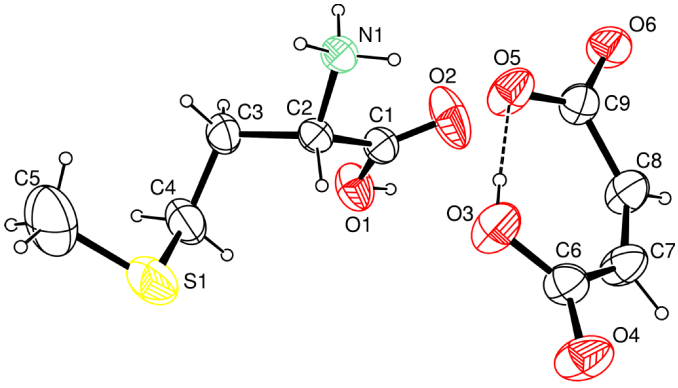


Figure 1
The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Fig. 2 shows the packing of molecules of (I), viewed down the *b* axis. The methioninium and semi-maleate ions aggregate in alternate columns parallel to the *a* axis. There are no direct hydrogen-bonded interactions among the semi-maleate ions. Rather they mediate interactions between the methionine molecules, in forming a double layer parallel to the *bc* plane. The methioninium cations, which are flanked on either sides of these layers, form alternating hydrophobic and hydrophilic layers. There are no hydrogen-bond interactions between these double layers. Interestingly, an inversion-related pair of maleate ions is seen surrounded by six neighbouring methioninium cations, as observed in *β*-alaninium oxalate monohydrate (Krishnakumar *et al.*, 2002). The mode of aggregation of molecules and the pattern of intermolecular interactions have some similarities with those observed in glycinium maleate, DL-valinium maleate and L-phenylalaninium maleate.

Experimental

Colourless single crystals of (I) were grown as transparent needles from a saturated aqueous solution containing DL-methionine and maleic acid in a 1:1 stoichiometric ratio.

Crystal data

$C_5H_{12}NO_2S^+\cdot C_4H_3O_4^-$
M_r = 265.28
Monoclinic, $P2_1/c$
a = 11.070 (2) Å
b = 5.746 (5) Å
c = 19.697 (14) Å
β = 102.34 (3)°
V = 1223.9 (14) Å^3
Z = 4
D_x = 1.440 Mg m^{-3}
D_m = 1.44 Mg m^{-3}

D_m measured by flotation in a xylene/bromoform mixture
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 16–24°
μ = 2.55 mm^{-1}
T = 293 (2) K
Needle, colourless
0.30 × 0.20 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.52, T_{max} = 0.77
2298 measured reflections
2192 independent reflections
2029 reflections with $I > 2\sigma(I)$

R_{int} = 0.013
θ_{max} = 68.0°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 6$
$l = -23 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity decay: none

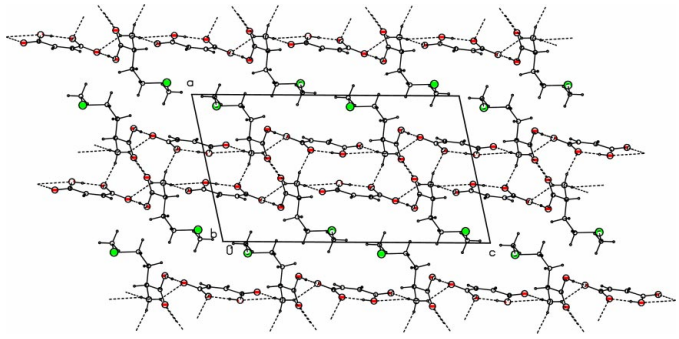


Figure 2
Packing diagram of the molecules of (I), viewed down the *b* axis.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.129
S = 0.93
2192 reflections
157 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0859P)^2 + 0.8155P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0036 (6)

Table 1
Selected geometric parameters (Å, °).

S1—C5	1.789 (4)	C3—C4	1.515 (3)
S1—C4	1.800 (3)	O3—C6	1.289 (3)
O1—C1	1.299 (3)	O4—C6	1.229 (2)
O2—C1	1.188 (2)	O5—C9	1.261 (2)
N1—C2	1.485 (2)	O6—C9	1.251 (2)
C1—C2	1.522 (3)	C6—C7	1.482 (3)
C2—C3	1.527 (3)	C8—C9	1.489 (3)
C5—S1—C4	100.40 (16)	O4—C6—O3	120.45 (18)
O2—C1—O1	124.22 (19)	O4—C6—C7	118.64 (19)
O2—C1—C2	121.52 (18)	O3—C6—C7	120.88 (17)
O1—C1—C2	114.22 (16)	C8—C7—C6	130.13 (19)
N1—C2—C1	106.38 (14)	C7—C8—C9	130.34 (18)
N1—C2—C3	112.10 (16)	O6—C9—O5	124.26 (19)
C1—C2—C3	114.77 (16)	O6—C9—C8	115.25 (18)
C4—C3—C2	113.06 (18)	O5—C9—C8	120.48 (17)
C3—C4—S1	114.88 (17)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O6^{i}	0.82	1.75	2.552 (3)	166.0
O3—H3···O5	0.82	1.64	2.459 (3)	176.6
N1—H1A···O4^{ii}	0.89	1.92	2.812 (3)	174.5
N1—H1B···O6^{iii}	0.89	2.19	2.973 (3)	147.0
N1—H1B···O2^{iii}	0.89	2.30	2.900 (2)	124.7
N1—H1C···O5	0.89	2.04	2.914 (3)	166.9
C2—H2A···O4^{iv}	0.98	2.50	3.233 (4)	131.5

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

The absolute configuration of DL-methioninium maleate was not established by the analysis but is known from the configuration of the starting reagents. The H atoms were placed at calculated positions

and were allowed to ride on their parent atoms with HFIX instructions using *SHELXL*97 (Sheldrick, 1997) defaults.

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, 1990); 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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