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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.001 \text{ \AA}$
R factor = 0.034
wR factor = 0.093
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>.

DL-Threoninium maleate at 150 K

In the title compound, $\text{C}_4\text{H}_{10}\text{NO}_3^+ \cdot \text{C}_4\text{H}_3\text{O}_4^-$, the threonine molecule exists as a cation and the maleic acid molecule exists in the mono-ionized state. In the semi-maleate ion, there is an intramolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond. The molecules aggregate into infinite parallel layers which extend in the $(0\bar{2}2)$ plane. These layers have no hydrogen-bonded interactions between them, only van der Waals interactions. The semi-maleate ion is essentially planar. The structure is stabilized by $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, in addition to weak $\text{C}-\text{H} \cdots \text{O}$ interactions. No classical head-to-tail hydrogen bonds are observed.

Comment

Threonine, an essential amino acid necessary to maintain nitrogen equilibrium in the adult human, is a significant constituent of many common plant and milk proteins. It does not undergo transamination and is also potentially glucogenic. X-ray (Shoemaker *et al.*, 1950) and neutron (Ramanatham *et al.*, 1973) diffraction investigations on crystals of the L isomer have already been carried out. Recently, a precise determination of the crystal structure of L-threonine at 12 K (Janczak *et al.*, 1997) was reported. However, the crystal structure of its racemate is not yet known since, on crystallization, DL-threonine produces a mixture of crystals of the D and L forms (Shoemaker *et al.*, 1950). A similar phenomenon has been observed in the case of L-allothreonine (Swaminathan & Srinivasan, 1975). Recently, the crystal structures of DL-threoninium oxalate (Subha Nandhini *et al.*, 2001), glycinium maleate (Rajagopal, Krishnakumar, Mostad & Natarajan, 2001), β -alaninium maleate (Rajagopal, Krishnakumar & Natarajan, 2001), sarcosinium maleate (Rajagopal *et al.*, 2002) and L-alaninium maleate (Alagar *et al.*, 2001) have been reported. The present study reports the crystal structure of DL-threoninium maleate, (I), a complex of DL-threonine with maleic acid.

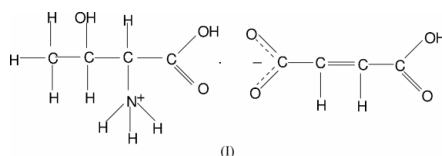


Fig. 1 shows the molecular structure of (I) with the atom-numbering scheme. The threonine molecule exists in the cationic form with a positively charged amino group and an uncharged carboxylic acid group. The torsion angles χ^1 ($\text{N1}-\text{C2}-\text{C1}-\text{O1}$) and χ^2 ($\text{N1}-\text{C2}-\text{C1}-\text{O2}$), describing the torsions of the two C—O bonds around C1—C2, are 45.02 (10) and -136.12 (10) $^\circ$, respectively, indicating that the carboxylic acid and amino groups of the threoninium cation exhibit a

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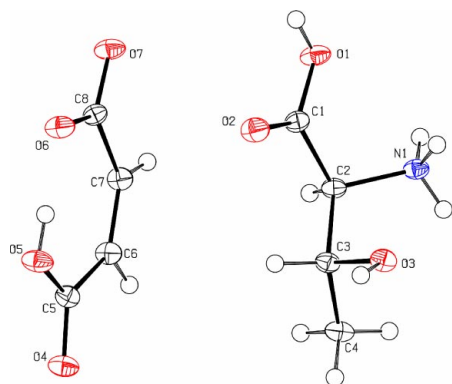


Figure 1
The molecular structure of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids.

significant deviation from planarity, as observed in similar structures, *viz.* bis(L-threoninium) sulfate monohydrate (Sridhar *et al.*, 2001), *O*-phospho-L-threonine and *O*-phospho-DL-threonine (Maniukiewicz *et al.*, 1996). Interestingly, in the structure of DL-threoninium oxalate, the torsion angles of the DL-threoninium cation are 177.2 (2) and -2.5 (4) $^\circ$, indicating that the carboxylic acid and amino groups lie in the same plane.

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. In the semi-maleate ion, the intramolecular hydrogen bond between atoms O5 and O6 is found to be asymmetric, as in the crystal structures of maleic acid (James & Williams, 1974), and the above-mentioned glycinium maleate, β -alaninium maleate and L-alaninium maleate. However, in the crystal structures of complexes of maleic acid with DL- and L-arginine (Ravishankar *et al.*, 1998) and L-histidine and L-lysine (Pratap *et al.*, 2000), this intramolecular hydrogen bond between carboxylic acid groups is symmetric, with the H atom shared between the two O atoms.

Fig. 2 shows the packing of (I), viewed down the *a* axis. The threoninium and semi-maleate ions are linked together by an infinite network of hydrogen bonds. Atom O3 participates in the hydrogen-bonding network, both as an acceptor and as a donor, mediating the amino acid–amino acid and amino acid–maleic acid interactions. No classical head-to-tail hydrogen bonds are observed in the crystal structure. The semi-maleate ions do not have direct hydrogen-bond interactions among themselves, except for a weak C–H \cdots O hydrogen bond which links them into infinite chains along the *a* axis. The molecules aggregate into parallel layers which extend in the (0 $\bar{2}2$) plane. These layers have no hydrogen-bonded interactions between them, only van der Waals interactions. The structure is stabilized by an infinite network of N–H \cdots O and O–H \cdots O hydrogen bonds (Table 2).

Experimental

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

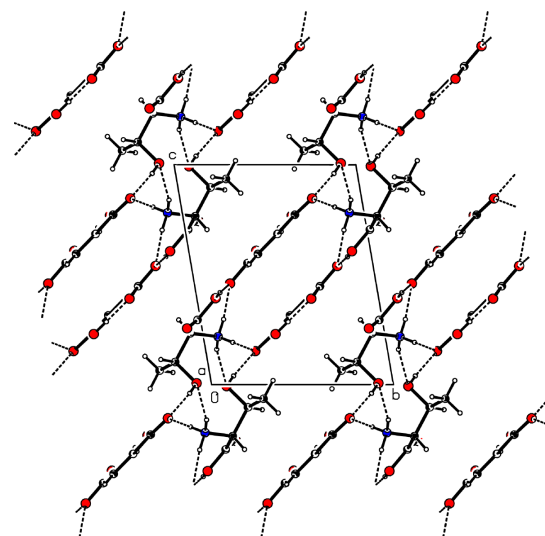


Figure 2
Packing of the molecules of (I), viewed down the *a* axis.

Crystal data

$C_4H_{10}NO_3^+ \cdot C_4H_3O_4^-$
 $M_r = 235.19$
Triclinic, $P\bar{1}$
 $a = 5.8050$ (12) \AA
 $b = 8.4310$ (17) \AA
 $c = 10.740$ (2) \AA
 $\alpha = 98.88$ (3) $^\circ$
 $\beta = 105.17$ (3) $^\circ$
 $\gamma = 91.68$ (3) $^\circ$
 $V = 499.90$ (19) \AA^3
 $Z = 2$
 $D_x = 1.563$ Mg m^{-3}

$D_m = 1.57$ Mg m^{-3}
 D_m measured by flotation in a mixture of xylene and bromoform
Mo $K\alpha$ radiation
Cell parameters from 1024 reflections
 $\theta = 2.0$ – 28.3 $^\circ$
 $\mu = 0.14$ mm^{-1}
 $T = 150$ (2) K
Prism, colorless
 $0.5 \times 0.5 \times 0.3$ mm

Data collection

Bruker SMART diffractometer
 ω scans
Absorption correction: none
7459 measured reflections
2468 independent reflections
2366 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$
 $\theta_{\text{max}} = 28.4$ $^\circ$
 $h = -7 \rightarrow 7$
 $k = -11 \rightarrow 11$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.093$
 $S = 1.07$
2468 reflections
195 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.1504P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.42$ e \AA^{-3}
 $\Delta\rho_{\text{min}} = -0.32$ e \AA^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.061 (9)

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1–C1	1.3133 (12)	O5–C5	1.2899 (12)
O2–C1	1.2091 (13)	O6–C8	1.2747 (12)
O4–C5	1.2327 (13)	O7–C8	1.2406 (13)
O2–C1–O1	124.61 (9)	O1–C1–C2	112.13 (9)
O2–C1–C2	123.26 (9)		
O2–C1–C2–N1	-136.12 (10)	O5–C5–C6–C7	-1.63 (17)
O1–C1–C2–N1	45.02 (10)	C6–C7–C8–O7	-176.44 (10)
O4–C5–C6–C7	178.22 (10)	C6–C7–C8–O6	3.42 (16)

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1 \cdots O7 ⁱ	0.89 (2)	1.70 (2)	2.598 (1)	177 (2)
O3—H3O \cdots O4 ⁱⁱ	0.87 (2)	1.91 (2)	2.771 (1)	166 (2)
O5—H5 \cdots O6	0.84	1.56	2.400 (1)	180
N1—H1N \cdots O4 ⁱⁱⁱ	0.92 (2)	1.96 (2)	2.848 (1)	162 (1)
N1—H2N \cdots O3 ^{iv}	0.87 (2)	2.14 (2)	2.968 (1)	160 (2)
N1—H3N \cdots O7 ^v	0.92 (2)	1.96 (2)	2.870 (1)	171 (2)
C6—H6 \cdots O6 ^{vi}	0.96 (2)	2.59 (2)	3.328 (2)	133 (1)
C7—H7 \cdots O1 ^v	0.95 (2)	2.58 (2)	3.489 (2)	162 (1)

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

All the H atoms, except H5, were located in a difference Fourier map and were refined isotropically. Atom H5 was positioned geometrically with O—H = 0.84 Å and refined as riding, with $U(H5)$ constrained to be $1.5U_{eq}(O5)$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

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