

## DL-Threoninium oxalate

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## Key indicators

Single-crystal X-ray study

$T = 293$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å

$R$  factor = 0.053

w $R$  factor = 0.175

Data-to-parameter ratio = 9.4

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

In the title compound,  $\text{C}_4\text{H}_{10}\text{NO}_3^+\text{C}_2\text{HO}_4^-$ , the DL-threonine molecule exists as a cation and the oxalic acid molecule in the mono-ionized state. The molecules aggregate into infinite parallel layers which extend along the diagonal of the  $ac$  plane. These layers have no hydrogen-bonded interactions between them, only van der Waals interactions. The semi-oxalate ion deviates far from planarity. No classic 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 (Ramanadham *et al.*, 1973) diffraction investigations on the 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 racemic mixture of the crystals of D- and L- forms (Shoemaker *et al.*, 1950). A similar phenomenon has been observed in the case of L-allothreonine (Swaminathan & Srinivasan, 1975). The present study reports the crystal structure of a complex of DL-threonine with oxalic acid.

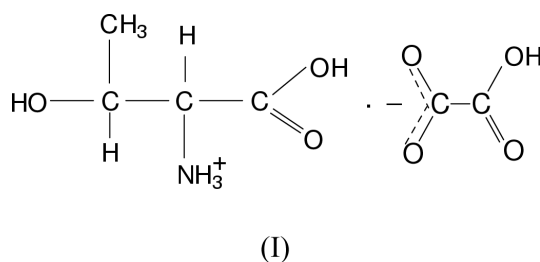
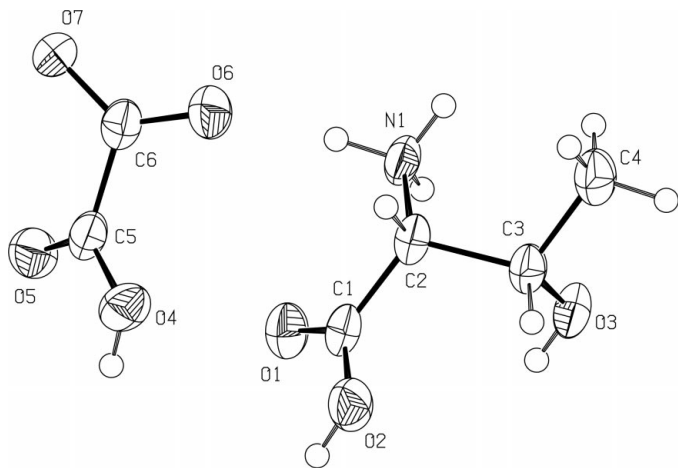


Fig. 1 shows the molecular structure of the title compound, (I), with the atom-numbering scheme. The amino acid exists in the cationic form with a positively charged amino group and a protonated carboxylic acid group. The torsion angles  $\Psi_1$  (N1—C2—C1—O1) and  $\Psi_2$  (N1—C2—C1—O2) describing the torsions of the two C—O bonds around C1—C2 are  $-2.5$  (4) and  $177.2$  (2)°, indicating that the carboxylic acid and the amino group lie in the same plane. Interestingly, L-threoninium cations exhibit a significant deviation from this planarity in the crystal structures of bis(L-threoninium) sulfate monohydrate (Sridhar *et al.*, 2001), O-phospho-L-threonine and O-phospho-DL-threonine (Maniukiewicz *et al.*, 1996). The

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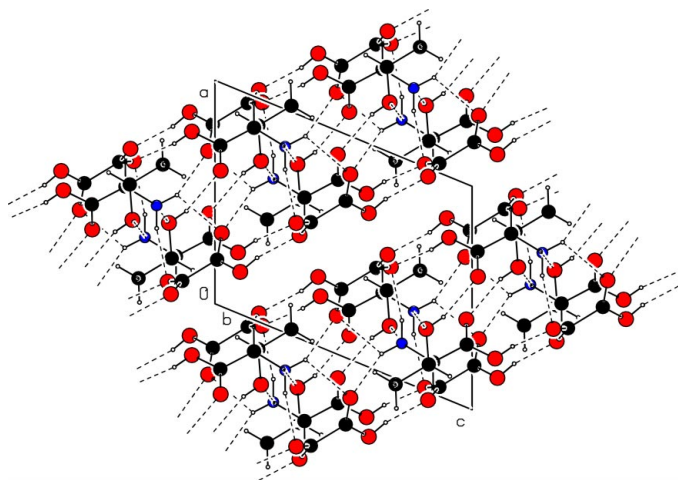
Online 27 July 2001



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

conformation of the molecule about the  $C^\alpha - C^\beta$  bond corresponds to the staggered ethane type. The sidechain conformation is described by the torsion angles  $\chi^{11}$ ,  $\chi^{12}$  and  $\chi^{13}$  of  $-59.0$  (3),  $60.1$  (3) and  $-178^\circ$ , respectively.

The oxalic acid molecule exists as a semi-oxalate anion. Unlike the crystal structures of other similar complexes, in the present case the semi-oxalate ion deviates far from planarity as the carboxyl groups are rotated by  $33.9$  (3) $^\circ$  with respect to the C5—C6 bond. The C—O distances in the carboxylate group of the semi-oxalate anion are unequal, presumably due to the participation of one atom (O6) in one hydrogen bond (O—H $\cdots$ O) and the other (O7) in two hydrogen bonds (O—H $\cdots$ O and N—H $\cdots$ O). Usually, the semi-oxalate ion has a tendency to be planar and the observed departure from planarity seems to be necessitated by requirements for optimum packing within the lattice.



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

Fig. 2 shows the packing of molecules of (I) viewed down the  $b$  axis. The semi-oxalate ions form hydrogen-bonded strings generated by the glide plane as in DL-arginine semi-oxalate complex (Chandra *et al.*, 1998). The threoninium and semi-oxalate ions are tied together by an infinite network of hydrogen bonds between them. The O3 (O $^y$ ) atom participates in the hydrogen-bonding network both as an acceptor and as a donor mediating the amino acid—amino acid interactions. No classic head-to-tail hydrogen bonds are observed in the crystal structure. The molecules aggregate into infinite parallel layers which extend along the diagonal of the  $ac$  plane. These layers have no hydrogen-bonded interactions between them, only van der Waals interactions.

## Experimental

Crystals of (I) were grown as fine transparent needles from a saturated aqueous solution containing DL-threonine and oxalic acid in stoichiometric ratio. The density was determined by flotation method using a liquid mixture of xylene and bromoform.

### Crystal data

$C_4H_{10}NO_3^+ \cdot C_2HO_4^-$   
 $M_r = 209.16$   
Monoclinic,  $P2_1/n$   
 $a = 8.325$  (5) Å  
 $b = 10.957$  (4) Å  
 $c = 10.363$  (4) Å  
 $\beta = 112.39$  (5) $^\circ$   
 $V = 874.0$  (7) Å $^3$   
 $Z = 4$   
 $D_x = 1.590$  Mg m $^{-3}$

$D_m = 1.61$  (2) Mg m $^{-3}$   
 $D_m$  measured by flotation  
Cu  $K\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta = 9-29^\circ$   
 $\mu = 1.30$  mm $^{-1}$   
 $T = 293$  (2) K  
Needle, colourless  
 $0.35 \times 0.21 \times 0.15$  mm

### Data collection

Enraf-Nonius CAD-4 diffractometer  
 $\omega-2\theta$  scans  
Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
 $T_{\min} = 0.76$ ,  $T_{\max} = 0.82$   
1605 measured reflections  
1605 independent reflections

1252 reflections with  $I > 2\sigma(I)$   
 $\theta_{\max} = 72.1^\circ$   
 $h = -10 \rightarrow 9$   
 $k = 0 \rightarrow 13$   
 $l = 0 \rightarrow 12$   
2 standard reflections  
frequency: 60 min  
intensity decay:  $<2\%$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.053$   
 $wR(F^2) = 0.175$   
 $S = 1.10$   
1605 reflections  
171 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1106P)^2 + 0.3459P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.36$  e Å $^{-3}$   
 $\Delta\rho_{\min} = -0.30$  e Å $^{-3}$

**Table 1**  
Hydrogen-bonding and short-contact geometry (Å,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H2 $\cdots$ O7 $^i$	0.82	1.67	2.483 (4)	168
O3—H3 $\cdots$ O1 $^{ii}$	0.82	2.05	2.854 (4)	165
O4—H4 $\cdots$ O6 $^i$	0.82	1.82	2.623 (4)	167
N1—H1A $\cdots$ O5 $^{iii}$	0.89	2.08	2.810 (4)	138
N1—H1A $\cdots$ O5 $^{iv}$	0.89	2.55	3.065 (3)	118
N1—H1B $\cdots$ O6	0.89	2.63	3.217 (3)	125
N1—H1B $\cdots$ O3 $^v$	0.89	2.09	2.895 (3)	151
N1—H1C $\cdots$ O7 $^{iv}$	0.89	2.18	3.060 (4)	168
C2—H2A $\cdots$ O6	0.98	2.55	3.174 (4)	122

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

The H atoms were placed at calculated positions and were allowed to ride on their respective parent atoms with *HFIX* instructions using *SHELXL97* (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: *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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