

DL-Threoninium trichloroacetate

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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 = 0.033
 wR factor = 0.085
Data-to-parameter ratio = 12.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_4\text{H}_{10}\text{NO}_3^+ \cdot \text{C}_2\text{Cl}_3\text{O}_2^-$, (I), the amino acid molecule exists in the cationic form, with a positively charged amino group and an uncharged carboxylic acid group. The trichloroacetic acid molecule exists in the anionic state. The threoninium cations and the trichloroacetate anions form hydrogen-bonded double layers, linked together by a network of $\text{N}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds and extended along the b axis. These double layers have no hydrogen-bonded interactions between them. No classic head-to-tail hydrogen bonds are observed in (I).

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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, we have reported the crystal structures of DL-threoninium maleate (Rajagopal *et al.*, 2004), DL-threoninium oxalate (Subha Nandhini *et al.*, 2001), DL-valinium trichloroacetate (Rajagopal *et al.*, 2002), DL-methioninium trichloroacetate (Rajagopal, Krishnakumar, Mostad & Natarajan, 2003a), β -alaninium trichloroacetate (Rajagopal, Krishnakumar, Subha Nandhini, Mostad & Natarajan, 2003), L-prolinium trichloroacetate (Rajagopal, Krishnakumar, Mostad & Natarajan, 2003b) and L-phenylalaninium trichloroacetate monohydrate (Rajagopal, Krishnakumar, Subha Nandhini, Cameron & Natarajan, 2003). The crystal structure of trichloroacetic acid itself was determined only recently in our laboratory (Rajagopal, Mostad *et al.*, 2003). The present study, which reports the crystal structure of DL-threoninium trichloroacetate, (I), a complex of DL-threonine with trichloroacetic acid, is part of a series of X-ray investigations on proton-transfer complexes of amino acid-trichloroacetic acid. The results of these investigations will be useful in the understanding of ionization states, biomolecular interactions and characteristic aggregation patterns.

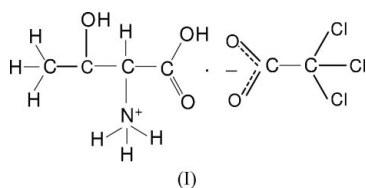


Fig. 1 shows the molecular structure of (I) with the atom-numbering scheme. The asymmetric unit of (I) comprises two threoninium cations, which are related through the pseudo-symmetry operation $(\frac{1}{2} + x, 1 - y, z)$, and two trichloroacetate anions, related to each other through the pseudo-symmetry operation $(\frac{1}{2} - x, \frac{3}{2} - y, 1 - z)$. The threonine molecules in (I) exist in the cationic form, with a positively charged amino group and an uncharged carboxylic acid group. The trichloroacetic acid is in the anionic state. The conformation angles ψ^1 and ψ^2 for the two DL-threoninium cations, describing the torsions of the two C—O bonds around C1—C2, are $-175.2(2)$ and $4.9(3)^\circ$, and $177.5(2)$ and $-2.5(3)^\circ$, respectively, indicating that the carboxylic acid and amino groups of the threoninium cations lie in the same planes. This is in agreement with the values reported for DL-threoninium oxalate [$177.2(2)$ and $-2.5(4)^\circ$; Subha Nandhini *et al.*, 2001].

Fig. 2 shows the packing of the molecules of (I), viewed down the *a* axis. The threoninium cations and trichloroacetate anions are linked together by an infinite network of hydrogen bonds. Atoms O3A and O3B participate in the hydrogen-bonding network as both acceptors and donors, mediating the amino acid–amino acid interactions. No classic head-to-tail hydrogen bonds are observed in the crystal structure of (I), as observed in similar structures, *viz.* DL-threoninium maleate and DL-threoninium oxalate. The molecules aggregate into parallel layers which extend along the *b* axis. 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...O and O—H...O hydrogen bonds (Table 2). The aggregation pattern observed in (I) is similar to those observed in DL-threoninium maleate and DL-threoninium oxalate.

Experimental

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

Crystal data

$C_4H_{10}NO_3^+ \cdot C_2Cl_3O_2^-$
 $M_r = 282.50$
 Monoclinic, $P2_1$
 $a = 10.3290(11) \text{ \AA}$
 $b = 10.4271(11) \text{ \AA}$
 $c = 10.7795(11) \text{ \AA}$
 $\beta = 103.115(12)^\circ$
 $V = 1130.7(2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.660 \text{ Mg m}^{-3}$
 $D_m = 1.65 \text{ Mg m}^{-3}$

D_m measured by flotation in xylene–bromoform
 Mo $K\alpha$ radiation
 Cell parameters from 3441 reflections
 $\theta = 1.9\text{--}25.0^\circ$
 $\mu = 0.81 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Block, colourless
 $0.40 \times 0.30 \times 0.25 \text{ mm}$

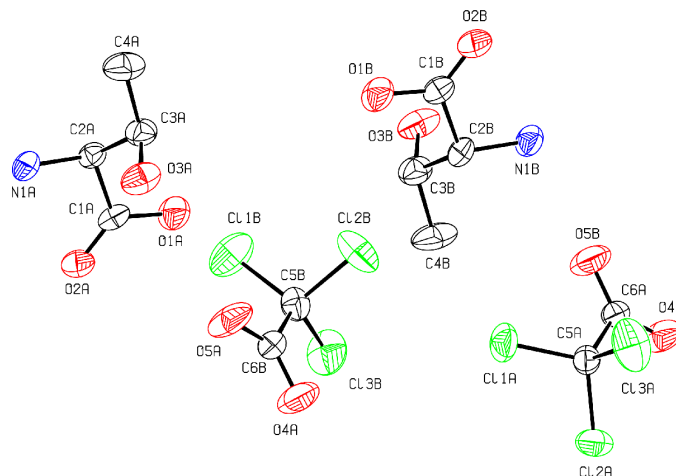


Figure 1

The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

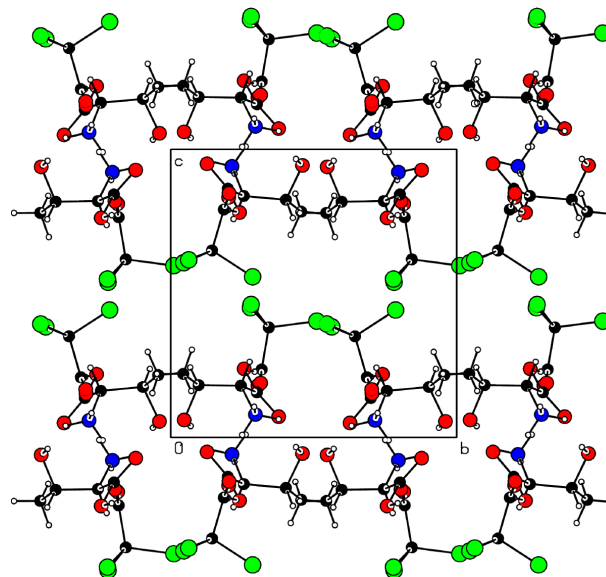


Figure 2

The crystal packing of (I), viewed down the *a* axis.

Data collection

Bruker SMART APEX CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1998)
 $T_{\min} = 0.734$, $T_{\max} = 0.812$
 6904 measured reflections

4451 independent reflections
 4159 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$
 $\theta_{\max} = 28.0^\circ$
 $h = -13 \rightarrow 9$
 $k = -13 \rightarrow 13$
 $l = -11 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.085$
 $S = 1.05$
 4451 reflections
 277 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.2061P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.25 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

C11A—C5A	1.766 (3)	O3B—C3B	1.413 (4)
C12A—C5A	1.745 (3)	O4B—C6A	1.226 (3)
C13A—C5A	1.769 (3)	O5B—C6A	1.202 (3)
C11B—C5B	1.762 (3)	N1A—C2A	1.477 (3)
C12B—C5B	1.766 (3)	N1B—C2B	1.484 (3)
C13B—C5B	1.760 (3)	C1A—C2A	1.510 (4)
O1A—C1A	1.306 (3)	C2A—C3A	1.539 (4)
O2A—C1A	1.198 (3)	C3A—C4A	1.502 (5)
O3A—C3A	1.429 (4)	C5A—C6A	1.555 (4)
O4A—C6B	1.200 (4)	C1B—C2B	1.517 (4)
O5A—C6B	1.226 (3)	C2B—C3B	1.536 (4)
O1B—C1B	1.303 (3)	C3B—C4B	1.505 (5)
O2B—C1B	1.208 (3)	C5B—C6B	1.555 (4)
O2A—C1A—O1A	126.5 (3)	O2B—C1B—O1B	126.7 (3)
O2A—C1A—C2A	122.3 (2)	O2B—C1B—C2B	122.3 (2)
O1A—C1A—C2A	111.2 (2)	O1B—C1B—C2B	111.1 (2)
N1A—C2A—C1A	108.4 (2)	N1B—C2B—C1B	107.5 (2)
N1A—C2A—C3A	111.2 (2)	N1B—C2B—C3B	111.7 (2)
C1A—C2A—C3A	113.3 (2)	C1B—C2B—C3B	113.0 (2)
O3A—C3A—C4A	107.2 (2)	O3B—C3B—C4B	107.1 (3)
O3A—C3A—C2A	110.1 (2)	O3B—C3B—C2B	111.2 (2)
C4A—C3A—C2A	112.9 (3)	C4B—C3B—C2B	112.3 (3)
C6A—C5A—C12A	112.33 (18)	C6B—C5B—C13B	111.6 (2)
C6A—C5A—C11A	111.75 (19)	C6B—C5B—C11B	111.5 (2)
C12A—C5A—C11A	109.13 (14)	C13B—C5B—C11B	108.95 (16)
C6A—C5A—C13A	107.13 (18)	C6B—C5B—C12B	106.74 (19)
C12A—C5A—C13A	108.99 (16)	C13B—C5B—C12B	108.94 (16)
C11A—C5A—C13A	107.33 (14)	C11B—C5B—C12B	109.02 (17)
O5B—C6A—O4B	126.6 (3)	O4A—C6B—O5A	126.2 (3)
O5B—C6A—C5A	117.5 (2)	O4A—C6B—C5B	118.0 (3)
O4B—C6A—C5A	115.8 (2)	O5A—C6B—C5B	115.7 (3)
O2A—C1A—C2A—N1A	4.9 (3)	O2B—C1B—C2B—N1B	−2.3 (3)
O1A—C1A—C2A—N1A	−175.3 (2)	O1B—C1B—C2B—N1B	177.5 (2)
O2A—C1A—C2A—C3A	128.8 (3)	O2B—C1B—C2B—C3B	−126.0 (3)
O1A—C1A—C2A—C3A	−51.4 (3)	O1B—C1B—C2B—C3B	53.8 (3)
N1A—C2A—C3A—O3A	54.9 (3)	N1B—C2B—C3B—O3B	−54.4 (3)
C1A—C2A—C3A—O3A	−67.4 (3)	C1B—C2B—C3B—O3B	67.0 (3)
N1A—C2A—C3A—C4A	−64.8 (3)	N1B—C2B—C3B—C4B	65.6 (3)
C1A—C2A—C3A—C4A	172.8 (3)	C1B—C2B—C3B—C4B	−173.0 (3)
C12A—C5A—C6A—O5B	149.4 (3)	C13B—C5B—C6B—O4A	27.0 (4)
C11A—C5A—C6A—O5B	26.3 (3)	C11B—C5B—C6B—O4A	149.1 (3)
C13A—C5A—C6A—O5B	−91.0 (3)	C12B—C5B—C6B—O4A	−91.9 (3)
C12A—C5A—C6A—O4B	−31.0 (3)	C13B—C5B—C6B—O5A	−156.3 (3)
C11A—C5A—C6A—O4B	−154.1 (3)	C11B—C5B—C6B—O5A	−34.2 (3)
C13A—C5A—C6A—O4B	88.6 (3)	C12B—C5B—C6B—O5A	84.7 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1A—H1A...O5A ⁱ	0.82	1.82	2.571 (3)	152
O3A—H3A...O2B ⁱⁱ	0.82	2.03	2.824 (3)	163
O1B—H1B...O4B ⁱⁱⁱ	0.82	1.81	2.597 (3)	160
O3B—H3B...O2A ^{iv}	0.82	1.98	2.780 (3)	167
N1A—H1A1...O3A ^v	0.89	2.11	2.926 (3)	151
N1A—H1A2...O4A ^{vi}	0.89	1.85	2.724 (3)	167
N1A—H1A3...O4B ^v	0.89	1.98	2.841 (3)	162
N1B—H1B1...O5A ^{vii}	0.89	1.94	2.798 (3)	161
N1B—H1B2...O5B	0.89	1.87	2.756 (3)	171
N1B—H1B3...O3B ^{iv}	0.89	2.25	3.015 (3)	144

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

All H atoms were treated as riding on their respective parent atoms, with N—H = 0.89, O—H = 0.82 and C—H = 0.96–0.98 Å, and with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C,N})$ or $1.5U_{\text{eq}}(\text{C,O})$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; 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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