

## DL-Methioninium trichloroacetate at 123 K

K. Rajagopal,<sup>a</sup> R. V. Krishnakumar,<sup>b</sup> A. Mostad<sup>c</sup> and S. Natarajan<sup>d\*</sup>

<sup>a</sup>Department of Physics, Saraswathi Narayanan College, Madurai 625 022, India, <sup>b</sup>Department of Physics, Thiagarajar College, Madurai 625 009, India, <sup>c</sup>Department of Chemistry, University of Oslo, PO Box 1033 Blindern, N-0315 Oslo 3, Norway, and <sup>d</sup>Department of Physics, Madurai Kamaraj University, Madurai 625 021, India

Correspondence e-mail: s\_natarajan50@yahoo.com

## Key indicators

Single-crystal X-ray study  
 T = 123 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
 R factor = 0.029  
 wR factor = 0.092  
 Data-to-parameter ratio = 20.7

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

In the title compound,  $\text{C}_5\text{H}_{12}\text{NO}_2\text{S}^+\cdot\text{C}_2\text{Cl}_3\text{O}_2^-$ , the methionine molecule exists as a cation with a protonated amino group and an uncharged carboxylic acid group, while the trichloroacetic acid molecule exists as an anion. The assembly of methioninium and trichloroacetate ions, leading to layers parallel to the *ab* plane, is characterized by a strong  $\text{O}-\text{H}\cdots\text{O}$ -type hydrogen bond between the carboxylic acid and carboxylate groups of the respective ions. A head-to-tail hydrogen bond is also observed between the methioninium cations, in addition to  $\text{S}\cdots\text{Cl}$ ,  $\text{Cl}\cdots\text{Cl}$  and  $\text{Cl}\cdots\text{O}$  short contacts.

Received 25 November 2002

Accepted 2 December 2002

Online 19 December 2002

## Comment

Precise X-ray crystal structure investigations of proton-transfer complexes of the type *A*·*B*, where *A* is an amino acid and *B* is a carboxylic acid, are expected to provide useful information regarding biomolecular aggregation patterns. A number of crystal structures of amino acid–carboxylic acid complexes have already been elucidated, and their results indicate conservation of certain characteristic aggregation patterns involving the amino acid molecules. Also, systematic X-ray investigations of complexes involving halogens are expected to throw light on the role and importance of halogen–halogen interactions on biomolecular aggregation patterns. The present study reports the crystal structure of (I), a complex of methionine with trichloroacetic acid. The crystal structure of a complex of a dipeptide with trichloroacetic acid, *viz.* L-phenylalanylglycine trichloroacetate (Mitra & Subramanian, 1993), and that of DL-valinium trichloroacetate (Rajagopal *et al.*, 2002) have already been reported. Interestingly, the crystal structure of trichloroacetic acid in its native form remains unknown.

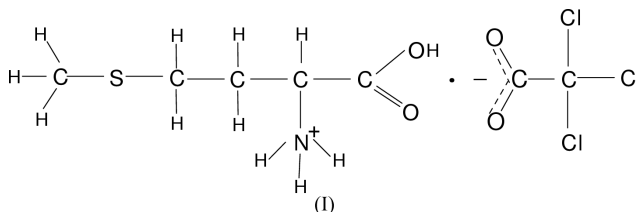
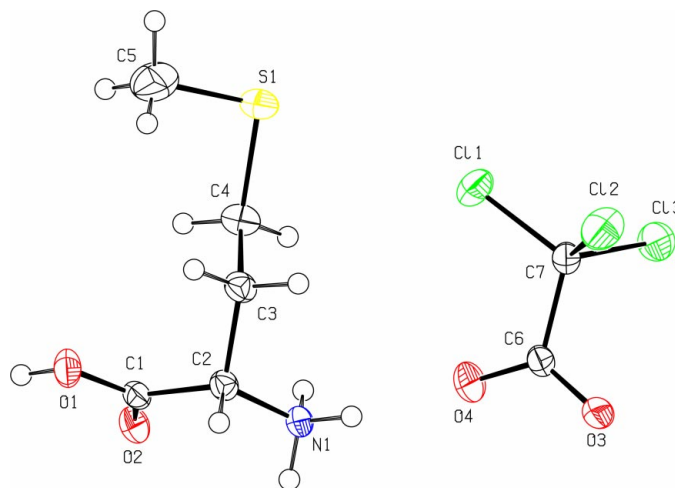
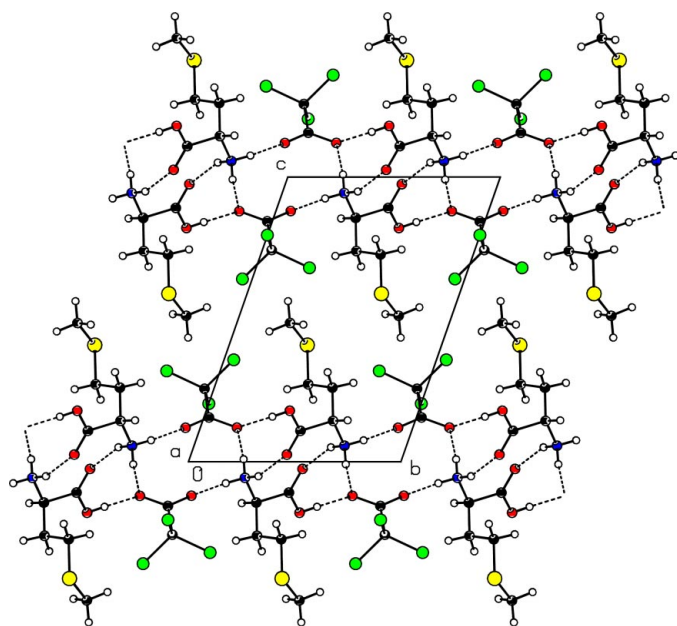


Fig. 1 shows the molecular structure of (I) with the atom-numbering scheme. Methionine exists in the cationic form with a protonated amino group and a neutral carboxylic acid group. The trichloroacetic acid moiety exists in the anionic state. The conformation of the methioninium cation is described by  $\psi^1$ ,  $\psi^2$ ,  $\chi^1$ ,  $\chi^2$  and  $\chi^3$ ; these are  $-2.7$  (2),  $177.2$  (1),  $66.1$  (2),  $179.5$  (1) and  $-70.2$  (2) $^\circ$ , respectively. These values differ significantly from those observed in DL-



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

methioninium maleate, *viz.* 26.6 (3),  $-155.6$  (2),  $-152.9$  (2), 73.9 (2) and 73.4 (2) $^\circ$  (Alagar *et al.*, 2002). The amino N atom deviates from the plane of the carboxyl group by only 0.069 (3) Å, in contrast to the value of 0.604 (3) Å observed in the case of DL-methioninium maleate. The side-chain atoms C2, C3, C4 and S1 lie in the same plane, with an r.m.s. deviation of 0.004 Å. The methyl atom C5 deviates by  $-1.662$  (4) Å (*trans* to the amino N atom) from this plane. In the case of DL-methioninium maleate, the methyl atom C5 deviates by 1.761 (5) Å and is *cis* with respect to the amino N atom. The angle between the plane defined by the carboxylic



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

acid and amino groups and the plane of the side-chain atoms (excluding C5) is 88.1 (1) $^\circ$  in the present structure, and is considerably different from that observed [59.3 (1) $^\circ$ ] in DL-methioninium maleate.

The packing of molecules of (I) in the unit cell, viewed down the *a* axis, is shown in Fig. 2. The C—O distances of the carboxylate group of the trichloroacetate anion are unequal [C6—O3 = 1.257 (2) Å and C6—O4 = 1.220 (2) Å], presumably due to the participation of O3 as acceptor in the formation of two hydrogen bonds and O4 in one. The assembly of methioninium and trichloroacetate ions, leading to layers parallel to the *ab* plane, is characterized by a strong O—H...O-type hydrogen bond between the carboxylic acid and carboxylate groups of respective ions. These layers have no hydrogen-bonded interactions between them and are held together by van der Waals interactions. In addition, a head-to-tail hydrogen bond is also observed between the methioninium cations. A few short contacts observed in the crystal structure are: S1...Cl1( $x - 1, y, z$ ) = 3.459 (2) Å, Cl2...Cl2( $-x + 2, -y + 2, -z + 1$ ) = 3.427 (2) Å and Cl3...O4( $x - 1, y, z$ ) = 3.249 (2) Å.

## Experimental

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

### Crystal data

$C_5H_{12}NO_2S^+ \cdot C_2Cl_3O_2^-$   
 $M_r = 312.60$   
Triclinic,  $P\bar{1}$   
 $a = 6.1359$  (12) Å  
 $b = 8.9746$  (18) Å  
 $c = 12.731$  (3) Å  
 $\alpha = 70.54$  (3) $^\circ$   
 $\beta = 85.95$  (3) $^\circ$   
 $\gamma = 85.08$  (3) $^\circ$   
 $V = 657.9$  (3) Å $^3$   
 $Z = 2$   
 $D_x = 1.578$  Mg m $^{-3}$

$D_m = 1.58$  Mg m $^{-3}$   
 $D_m$  measured by flotation in a mixture of xylene and bromoform  
Mo  $K\alpha$  radiation  
Cell parameters from 1024 reflections  
 $\theta = 1.7$ – $27.5$  $^\circ$   
 $\mu = 0.85$  mm $^{-1}$   
 $T = 123$  (2) K  
Prism, colourless  
 $0.5 \times 0.3 \times 0.2$  mm

### Data collection

Bruker SMART diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (SADABS; Bruker, 1998)  
 $T_{min} = 0.743, T_{max} = 0.843$   
7442 measured reflections  
2999 independent reflections

2628 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.019$   
 $\theta_{max} = 27.5$  $^\circ$   
 $h = -7 \rightarrow 7$   
 $k = -11 \rightarrow 11$   
 $l = -14 \rightarrow 16$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.029$   
 $wR(F^2) = 0.092$   
 $S = 1.17$   
2999 reflections  
145 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 0.4522P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.39$  e Å $^{-3}$   
 $\Delta\rho_{min} = -0.41$  e Å $^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

S1—C5	1.789 (3)	O2—C1	1.215 (2)
S1—C4	1.807 (2)	O3—C6	1.257 (2)
C11—C7	1.7634 (19)	O4—C6	1.220 (2)
C12—C7	1.761 (2)	C1—C2	1.521 (2)
C13—C7	1.786 (2)	C2—C3	1.537 (2)
N1—C2	1.493 (2)	C3—C4	1.527 (3)
O1—C1	1.304 (2)	C6—C7	1.565 (3)
C5—S1—C4	100.28 (12)	O4—C6—O3	127.07 (18)
O2—C1—O1	126.14 (17)	O4—C6—C7	117.98 (17)
O2—C1—C2	123.04 (17)	O3—C6—C7	114.94 (16)
O1—C1—C2	110.82 (16)	C6—C7—C12	109.80 (13)
N1—C2—C1	107.99 (14)	C6—C7—C11	112.47 (13)
N1—C2—C3	112.22 (15)	C12—C7—C11	108.67 (10)
C1—C2—C3	111.87 (15)	C6—C7—C13	107.04 (12)
C4—C3—C2	113.75 (15)	C12—C7—C13	109.97 (10)
C3—C4—S1	113.45 (14)	C11—C7—C13	108.86 (11)
O2—C1—C2—N1	−2.7 (2)	N1—C2—C3—C4	66.1 (2)
O1—C1—C2—N1	177.21 (14)	C1—C2—C3—C4	−55.4 (2)
O2—C1—C2—C3	121.28 (19)	C2—C3—C4—S1	179.46 (13)
O1—C1—C2—C3	−58.8 (2)	C5—S1—C4—C3	−70.20 (19)

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...O3 <sup>i</sup>	0.82	1.78	2.589 (2)	171
N1—H1A...O4 <sup>ii</sup>	0.89	1.90	2.771 (2)	164
N1—H1B...O2 <sup>iii</sup>	0.89	2.01	2.854 (2)	157
N1—H1C...O3 <sup>iv</sup>	0.89	1.89	2.749 (2)	163

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

All the H atoms were positioned geometrically and were allowed to ride on their respective parent atoms with *SHELXL97* (Sheldrick, 1997) defaults for bond lengths and displacement parameters.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; 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*.

KR thanks the UGC for the FIP programme. The authors thank the Council of Scientific and Industrial Research (CSIR), India for financial assistance. The authors also thank the UGC for the DRS programme and the Bio-informatics Centre, Madurai Kamaraj University, for providing the Cambridge Structural Database (Allen, 2002).

## References

- Alagar, M., Subha Nandhini, M., Krishnakumar, R. V. & Natarajan, S. (2002). *Acta Cryst. E* **58**, o396–o398.
- Allen, F. H. (2002). *Acta Cryst. B* **58**, 380–388.
- Bruker (1998). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (1999). *SMART-NT* and *SAINT-NT* (Version 5.0). Bruker AXS Inc., Madison, Wisconsin, USA.
- Mitra, S. N. & Subramanian, E. (1993). *Curr. Sci.* **65**, 980–983.
- Rajagopal, K., Krishnakumar, R. V., Mostad, A. & Natarajan, S. (2002). *Acta Cryst. E* **58**, o279–o281.
- Sheldrick, G. M. (1990). *Acta Cryst. A* **46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1999). *PLATON for Windows*. Utrecht University, The Netherlands.