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DL-Valinium trichloroacetate at 123 K

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In the title compound, $C_5H_{12}NO_2^+\cdot C_2Cl_3O_2^-$, the valine molecule is in a cationic state and the trichloroacetic acid is in the anionic state. In the crystal, the intermolecular N—H···O and O—H···O hydrogen bonds link the molecules to form an infinite two-dimensional network parallel to (001).

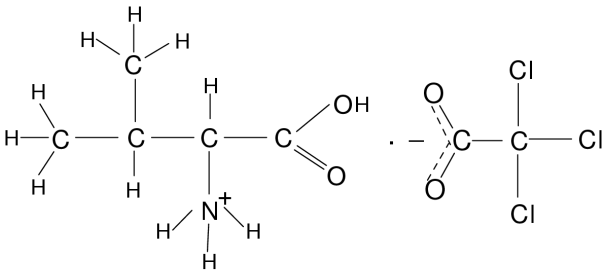
Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.033
wR factor = 0.083
Data-to-parameter ratio = 19.2

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

Comment

In our laboratory, we have been elucidating the crystal structures of proton-transfer complexes of the type *A.B*, where *A* is an amino acid and *B* is a carboxylic acid which is believed to have existed in the pre-biotic earth (Miller & Orgel, 1974; Kvenvolden *et al.*, 1971). A brief survey of the Cambridge Structural Database (Allen & Kennard, 1993) revealed a scarcity of precise crystallographic data on amino acid–halogenoacetic acid complexes. We report here the crystal structure of a complex of DL-valine with trichloroacetic acid, namely, DL-valinium trichloroacetate, (I). Systematic X-ray investigations of such compounds are expected to throw light on the importance of halogen–halogen interactions on biomolecular aggregation patterns. The crystal structure of a complex of a dipeptide with trichloroacetic acid, L-phenylalanylglycine trichloroacetate has already been reported (Mitra & Subramanian, 1993). The crystal structure of trichloroacetic acid remains unknown.



(I)

In (I), the valine molecule is in a cationic state with a positively charged amino group and an uncharged carboxylic acid group. The trichloroacetic acid exists in the anionic state with a negatively charged carboxylate group (Fig. 1). The carboxylate group of valine is planar, and the amino N atom deviates from this plane by 0.528 (1) Å, leading to the twisting of the C—N bond out of the plane of the carboxyl group by 21.9 (1)°. The conformation of the valine molecule, determined by the internal rotation angles ψ^2 [−22.4 (2)], χ^{11} [−162.9 (1)] and χ^{12} [70.9 (1)°], agrees well with the values observed for the monoclinic form of DL-valine (Mallikarjunan & Rao, 1969) and for the triclinic form of DL-valine (Dalhus &

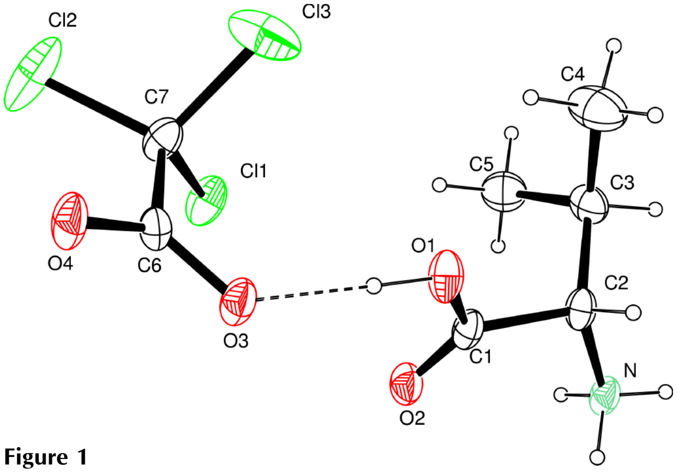


Figure 1
The molecular structure of (I), showing the atom-numbering scheme, with probability displacement ellipsoids drawn at the 50% level.

Görbitz, 1996). However, in DL-valinium maleate (Alagar *et al.*, 2001), χ^{11} [57.1 (2)°] deviates significantly from that observed in the present study. In the crystal, the valine and the trichloroacetic acid molecules are alternately linked by O—H···O and N—H···O hydrogen bonds to form infinite one-dimensional chains along [110]. The inversion-related chains are interlinked by N—H···O hydrogen bonds to form an infinite two-dimensional network parallel to (001). In this network, the D and L isomers exist as centrosymmetrically hydrogen-bonded dimers (Table 2).

Experimental

Single crystals of (I) were grown from a saturated aqueous solution containing DL-valine and trichloroacetic acid in the stoichiometric ratio 1:1.

Crystal data

$C_5H_{12}NO_2^+\cdot C_2Cl_3O_2^-$
$M_r = 280.53$
Triclinic, $P\overline{1}$
$a = 7.2380\ (14)$ Å
$b = 8.4150\ (17)$ Å
$c = 10.303\ (2)$ Å
$\alpha = 106.50\ (3)^\circ$
$\beta = 97.50\ (3)^\circ$
$\gamma = 95.80\ (3)^\circ$
$V = 590.2\ (2)$ Å^3
$Z = 2$
$D_x = 1.578$ Mg m^{-3}
$D_m = 1.60$ Mg m^{-3}
D_m measured by flotation in bromoform and xylene
Mo $K\alpha$ radiation
Cell parameters from 1024 reflections
$\theta = 2.5\text{–}23.0^\circ$
$\mu = 0.77$ mm^{-1}
$T = 123\ (2)$ K
Prismatic, colourless
$0.50 \times 0.40 \times 0.15$ mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{\min} = 0.68$, $T_{\max} = 0.89$
7923 measured reflections
3537 independent reflections
3204 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 30.7^\circ$
$h = -9 \rightarrow 10$
$k = -11 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.083$
$S = 1.04$
3537 reflections
184 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 0.3602P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.61$ e Å^{-3}
$\Delta\rho_{\min} = -0.59$ e Å^{-3}

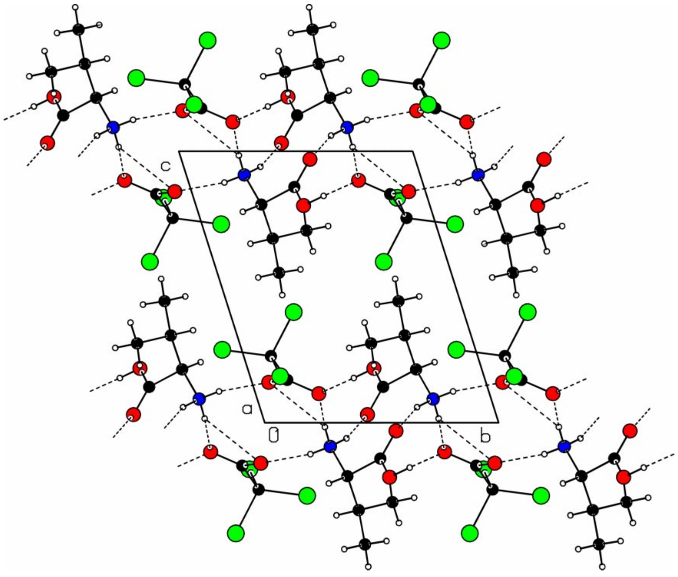


Figure 2
Packing of the molecules of (I), viewed down the *a* axis.

Table 1
Selected geometric parameters (Å, °).

Cl1—C7	1.7747 (14)	N—C2	1.4953 (17)
Cl2—C7	1.7580 (14)	C1—C2	1.5197 (17)
Cl3—C7	1.7749 (17)	C2—C3	1.5320 (19)
O1—C1	1.3150 (16)	C3—C5	1.525 (2)
O2—C1	1.2136 (17)	C3—C4	1.531 (2)
O3—C6	1.2538 (15)	C6—C7	1.5578 (18)
O4—C6	1.2300 (15)		
O2—C1—O1	125.57 (11)	O4—C6—O3	127.11 (12)
O2—C1—C2	122.27 (11)	O4—C6—C7	117.64 (11)
O1—C1—C2	112.15 (11)	O3—C6—C7	115.22 (11)
N—C2—C1	107.11 (11)	C6—C7—Cl2	112.03 (9)
N—C2—C3	111.25 (10)	C6—C7—Cl1	111.82 (9)
C1—C2—C3	112.46 (10)	Cl2—C7—Cl1	108.40 (8)
C5—C3—C4	111.94 (15)	C6—C7—Cl3	105.78 (9)
C5—C3—C2	112.10 (11)	Cl2—C7—Cl3	109.62 (8)
C4—C3—C2	111.28 (13)	Cl1—C7—Cl3	109.13 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H10···O3	0.89 (3)	1.72 (3)	2.601 (2)	169 (2)
N—H2N···O4$^{\rm i}$	0.84 (2)	1.93 (2)	2.761 (2)	169.6 (19)
N—H1N···O3$^{\rm ii}$	0.89 (2)	1.94 (2)	2.804 (2)	163.6 (19)
N—H3N···O2$^{\rm iii}$	0.90 (2)	2.00 (2)	2.871 (2)	162.5 (17)

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

All the H atoms were located from a difference Fourier map and were included in the refinement with isotropic displacement parameters. The ranges of C—H and N—H bond lengths are 0.96 (3)–0.98 (2) Å and 0.84 (2)–0.90 (2) Å, respectively, and the O—H distance is 0.89 (3) Å.

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