N-Dichloroacetyl-DL-valine–water (1/0.41)

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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean σ(C–C) = 0.003 Å

Disorder in solvent or counterion

R factor = 0.040

wR factor = 0.095

Data-to-parameter ratio = 17.9

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

In the title compound, $C_7H_{11}Cl_2NO_3\cdot0.41H_2O$, the D and L forms are linked by N—H···O and C—H···O hydrogen bonds to form centrosymmetric dimers. These hydrogen bonds form rings of graph-set motif $R_2^2(14)$, $R_2^2(10)$ and $R_2^1(6)$. The dimers are linked together by O—H···O hydrogen bonds to form two-dimensional molecular networks.

Comment

Valine is an important amino acid and the structures of L-valine (Torii & Iitaka, 1970), DL-Valine (Mallikarjunan & Rao, 1969) L-valine hydrochloride (Ando *et al.*, 1967), DL-valine hydrochloride (Blasio *et al.*, 1977) and L-valine L-valinium perchlorate monohydrate (Pandiarajan *et al.*, 2001) have been reported. The structures of the model peptides N-acetyl-D,L-valine (Carroll *et al.*, 1990) and N-carboxy-L-valine anhydride (Kanazawa *et al.*, 1984) have also been reported. We report here the structure of the title compound, (I), a valine derivative.

(I)
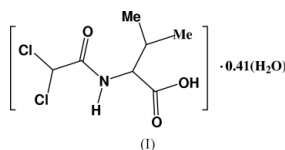
The C1—C2—N1—C3 torsion angle, which describes the planarity of the peptide unit, is 176.95 (17)°. The torsion angle φ_1 (C4—C3—N1—C2) is −128.83 (19)°. The torsion angles around the C3—C4 and C3—C5 bonds (Fig. 1 and Table 1) are comparable to those observed for DL-valine hydrochloride (Blasio *et al.*, 1977). In the crystal structure, the enantiomers are linked by centrosymmetric N1—H1A···O3[i] and C1—H1···O3[i] hydrogen bonds (symmetry codes as in Table 2) to form dimers. In a dimer, the N—H···O and C—H···O hydrogen bonds form rings of graph-set motif (Etter, 1990) $R_2^2(10)$ and $R_2^2(14)$, respectively. In addition, the N—H···O and C—H···O hydrogen bonds together form a ring of graph-set motif $R_2^1(6)$ (Fig. 2). The dimers are linked together by O2—H2···O1[ii] hydrogen bonds to form two-dimensional molecular networks parallel to the *bc* plane.

Experimental

L-valine and dichloroacetic acid in 1:1 molar ratio were mixed together and kept at 443 K for 5 h. Racemization occurred in the synthesis. The resulting solution was kept at room temperature overnight to obtain the title compound. Single crystals suitable for an X-ray diffraction study were obtained by recrystallizing the title compound from 70% aqueous ethanol.
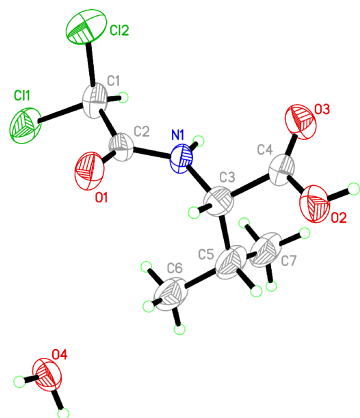
Figure 1
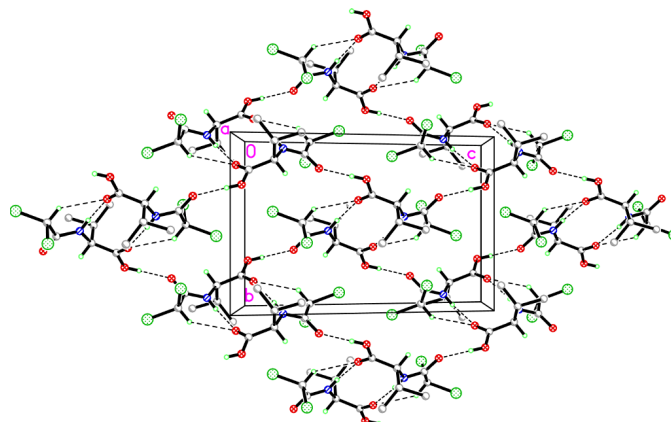The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

Figure 2
A view of the hydrogen-bonded network parallel to the *bc* plane. Solvent water molecules with partial occupancy have been omitted.

Crystal data

$C_7H_{11}Cl_2NO_3 \cdot 0.41H_2O$	$D_x = 1.403$ Mg m^{-3}
$M_r = 235.45$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 785
$a = 9.298$ (2) Å	reflections
$b = 9.011$ (1) Å	$\theta = 2.6–19.5°$
$c = 13.990$ (2) Å	$\mu = 0.57$ mm^{-1}
$\beta = 108.07$ (1)°	$T = 293$ (2) K
$V = 1114.3$ (3) Å^3	Prism, colorless
$Z = 4$	$0.28 \times 0.15 \times 0.15$ mm

Data collection

Bruker SMART Apex CCD area-detector diffractometer	2417 independent reflections
	1788 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.016$
Absorption correction: multi-scan	$\theta_{max} = 27.0°$
(*SADABS*; Sheldrick, 1996)	$h = -11 \rightarrow 11$
$T_{min} = 0.90$, $T_{max} = 0.91$	$k = -11 \rightarrow 11$
6265 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0388P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$	$+ 0.1217P]$
$wR(F^2) = 0.095$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.14$	$(\Delta/\sigma)_{max} < 0.001$
2417 reflections	$\Delta\rho_{max} = 0.30$ e Å^{-3}
135 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

C1—C2	1.527 (3)	C3—C5	1.542 (3)
C2—O1	1.208 (2)	C4—O3	1.188 (2)
C2—N1	1.319 (2)	C4—O2	1.308 (2)
C3—N1	1.445 (2)	C5—C7	1.482 (3)
C3—C4	1.502 (3)	C5—C6	1.509 (3)
N1—C3—C4—O3	−14.7 (3)	N1—C3—C5—C6	−62.1 (2)
C5—C3—C4—O3	110.1 (2)	C4—C3—C5—C6	173.93 (18)
N1—C3—C4—O2	166.68 (16)	O1—C2—N1—C3	−0.5 (3)
C5—C3—C4—O2	−68.5 (2)	C1—C2—N1—C3	176.95 (17)
N1—C3—C5—C7	63.7 (2)	C4—C3—N1—C2	−128.83 (19)
C4—C3—C5—C7	−60.3 (2)	C5—C3—N1—C2	106.7 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···O3^i	0.86	2.03	2.876 (2)	169
O2—H2···O1^{ii}	0.82	1.85	2.667 (2)	178
C1—H1···O3^i	0.98	2.57	3.371 (3)	139
C3—H3···O1	0.98	2.36	2.769 (3)	104

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

A solvent water O atom with partial occupancy was found in the asymmetric unit. The occupancy of this atom was initially refined and later fixed at 0.41 (1) (the standard uncertainty for the refined value was 0.4113). This atom lies at a distance of 2.239 (5) Å from O2($1 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$). The positional and isotropic displacement parameters of solvent water H atoms were refined [O—H = 0.84 (5) and 0.93 (7) Å and U_{iso}(H) = 0.08 (2) and 0.034 (14) Å^2, respectively]. All other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of 0.82–0.98 Å, with isotropic displacement parameters 1.2 to 1.5 times U_{eq} of the parent atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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