

Dichlorobis(DL-valine)zinc(II)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.053
wR factor = 0.137
Data-to-parameter ratio = 16.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $[\text{ZnCl}_2(\text{C}_5\text{H}_{11}\text{NO}_2)_2]$, the Zn atom lies on the twofold axis within the unit cell, with two symmetrically related valine molecules coordinating to it as ligands. The observed asymmetry of the carboxylate group is most likely a result of the participation of only one of the carboxyl O atoms in the coordination environment. Zinc has a distorted tetrahedral environment with twofold-related Cl atoms and two carboxyl O atoms, one each from the twofold-related valine molecules in the asymmetric unit.

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Comment

Valine, an essential amino acid, is often found in the interior of protein molecules due to its hydrophobic nature and thus plays a key role in determining their three-dimensional structure. Structural data on simple valine–inorganic salt complexes seem to be very limited. Apart from the present study which reports the crystal structure of (I), a complex of DL-valine with ZnCl_2 , namely dichlorobis(DL-valine)zinc(II), the structure of DL-valine with CaCl_2 (Glowiak & Ciunik, 1978) remains the only other complex that has been reported so far. Zinc, which competes successfully with cadmium for protein-binding sites, also plays an important biological role in the form of a structural motif called zinc fingers. Interestingly, zinc finger motifs are characteristic of certain proteins that have an affinity to bind to DNA. Recently, the crystal structures of trichloro(sarcosinio)zinc(II) monohydrate (Krishnakumar *et al.*, 2001) and dichlorobis(sarcosinato)zinc(II) (Subha Nandhini *et al.*, 2001) have been reported.

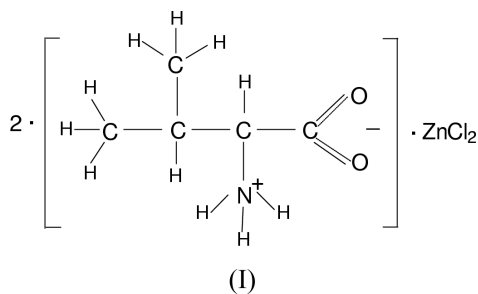


Fig. 1 shows the molecular structure and the atom-numbering scheme adopted. The Zn atom lies on the twofold axis within the unit cell with two symmetrically related valine molecules coordinating to it as ligands. Valine exists as a zwitterion, as expected, with C1–O1 and C1–O2 bond distances of 1.252 (3) and 1.233 (3) Å, respectively. This observed asymmetry of the carboxylate group is most likely a result of the participation of only one of the carboxyl O atoms

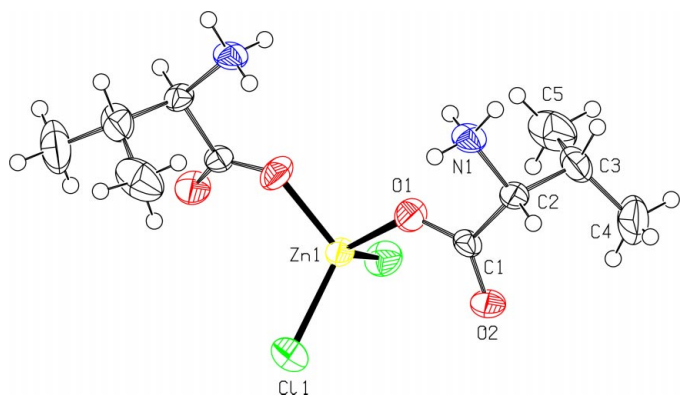


Figure 1
The structure of (I), with 50% probability displacement ellipsoids.

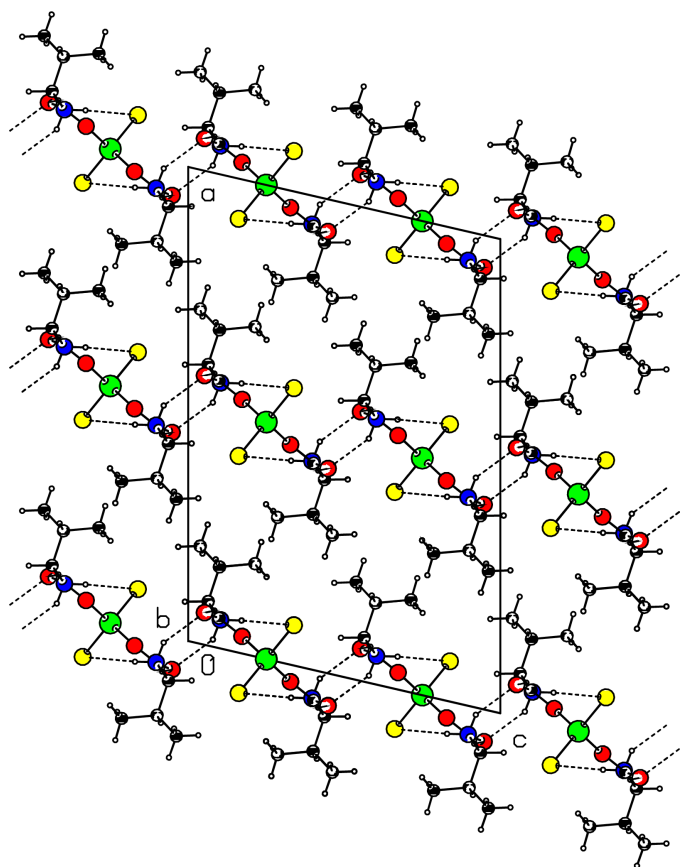


Figure 2
Packing of the molecules of (I) viewed down the *b* axis.

(O1) in the coordination environment. The carboxylate group is quite planar and the amino nitrogen deviates from this plane by 0.486 (4) Å, leading to the twisting of the C–N bond out of the plane of the carboxyl group by 19.9 (3)°. The conformation of the valine molecule determined by the internal rotational angles ψ_2 [–19.4 (3)°], χ_{11} [–164.4 (3)°] and χ_{12} [70.5 (3)°] agree well with the values observed for the monoclinic form of DL-valine (Mallikarjunan & Rao, 1969) and for the triclinic form of DL-valine (Dalhus & Gorbitz, 1996).

Zinc is known to have both tetrahedral and octahedral coordination in crystal structures (Cingi *et al.*, 1972). In the present structure, zinc has a distorted tetrahedral environment with twofold related Cl atoms and two carboxyl O atoms, one each from the twofold-related valine molecules in the asymmetric unit. Similar metal–ligand coordination is observed in the crystal structures of glycine with ZnCl₂ (Hariharan *et al.*, 1989) and L-proline with ZnCl₂ (Yukawa *et al.*, 1985). However, in the complexes of ZnCl₂ with L-histidine (Foster *et al.*, 1993) and sarcosine (Krishnakumar *et al.*, 2001), the Zn atom exhibits a different coordination environment with one of the carboxyl O and three Cl atoms participating in it. Interestingly, in both these structures, the amino acid exists in an unusual cationic form.

Fig. 2 shows the packing of the molecules of (I) viewed down the *b* axis. The valine molecules coordinating to Zn through O1 form a linear chain characterized by a head-to-tail hydrogen bond between the centrosymmetrically related valine molecules and an N–H···Cl hydrogen bond. The linear chain, on either side, is flanked by the hydrophobic side chains of valine leading to alternating polar and non-polar regions along the *a* axis. This chain forms an infinite two-dimensional layered network parallel to the *bc* plane through head-to-tail hydrogen bonds between translationally related valine molecules along the *b* axis. O1 of the carboxyl group does not participate in the hydrogen bonding network and the strengths of the two head-to-tail hydrogen bonds involving O2 are nearly equal. Though the metal–ligand coordination observed in (I) is similar to those observed in some amino acid–ZnCl₂ complexes, the crystal structure itself does not bear any similarities with them.

Experimental

Colourless single crystals of (I) were grown from a saturated aqueous solution containing DL-valine and ZnCl₂ in a 1:1 stoichiometric ratio.

Crystal data

[ZnCl₂(C₅H₁₁NO₂)₂]
 $M_r = 370.57$
 Monoclinic, *C2/c*
 $a = 19.997$ (2) Å
 $b = 6.2259$ (10) Å
 $c = 13.5028$ (10) Å
 $\beta = 103.02$ (2)°
 $V = 1637.9$ (3) Å³
 $Z = 4$
 $D_x = 1.503$ Mg m^{–3}
 $D_m = 1.52$ Mg m^{–3}

D_m measured by flotation in a mixture of xylene and bromoform
 Cu $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 15$ –27°
 $\mu = 5.19$ mm^{–1}
 $T = 293$ (2) K
 Plate, colourless
 0.24 × 0.18 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω –2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.40$, $T_{\max} = 0.60$
 1526 measured reflections
 1435 independent reflections
 1394 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$
 $\theta_{\text{max}} = 67.9^\circ$
 $h = -24 \rightarrow 23$
 $k = 0 \rightarrow 7$
 $l = -15 \rightarrow 16$
 2 standard reflections every 100 reflections
 intensity decay: <2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.137$
 $S = 1.11$
 1435 reflections
 87 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.1048P)^2 + 1.3333P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.06 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.89 \text{ e } \text{\AA}^{-3}$

Table 1
 Selected geometric parameters (\AA , $^\circ$).

Zn1—O1	1.9500 (18)	C2—C1	1.529 (3)
Zn1—C11	2.2430 (8)	C2—C3	1.535 (4)
N1—C2	1.492 (3)	C3—C4	1.522 (5)
O1—C1	1.252 (3)	C3—C5	1.526 (5)
O2—C1	1.233 (3)		
O1—Zn1—O1 ⁱ	91.77 (12)	C4—C3—C5	111.2 (3)
O1—Zn1—C11 ⁱ	110.88 (7)	C4—C3—C2	110.7 (3)
O1—Zn1—C11	115.94 (7)	C5—C3—C2	112.5 (3)
N1—C2—C1	107.9 (2)	O2—C1—O1	127.6 (2)
N1—C2—C3	110.5 (2)	O2—C1—C2	118.4 (2)
C1—C2—C3	112.3 (2)	O1—C1—C2	114.0 (2)
N1—C2—C3—C4	-164.4 (3)	N1—C2—C1—O2	159.6 (2)
C1—C2—C3—C4	75.0 (4)	C3—C2—C1—O2	-78.4 (3)
N1—C2—C3—C5	70.5 (3)	N1—C2—C1—O1	-19.4 (3)
C1—C2—C3—C5	-50.1 (3)	C3—C2—C1—O1	102.6 (3)

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

Table 2
 Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A \cdots O2 ⁱ	0.89	2.03	2.837 (3)	151
N1—H1B \cdots Cl1 ⁱⁱ	0.89	2.59	3.370 (2)	146
N1—H1C \cdots O2 ⁱⁱⁱ	0.89	2.19	2.972 (3)	146

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

The H atoms were placed at calculated positions and were allowed to ride on their respective parent atoms 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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