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Dichlorobis(DL-proline-κO)zinc(II)

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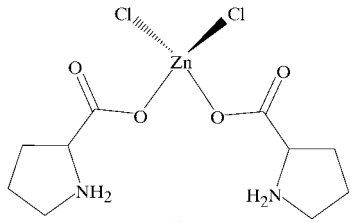
The title compound, $[ZnCl_2(C_5H_9NO_2)_2]$, crystallizes in the centrosymmetric space group *C*2/*c* with the Zn atom on a twofold axis. The two proline residues in any one complex thus have the same absolute configuration. Hydrogen bonding links the molecules into linear chains, which run in the crystallographic *b* direction. The proline residues within any one chain also have an identical absolute configuration.

Comment

Zn^{2+} ions play an essential role in the regulation and catalytic activity of biological systems (Fraústo da Silva & Williams, 1991). To obtain a deeper insight into the interaction of metal ions with amino acids, neutral salts can be studied. Such neutral salts are formed by the interaction of neutral zwitterionic amino acids with metal salts, *e.g.* $CaCl_2$, $SrCl_2$, $BaCl_2$ and LiCl (Pfeiffer & Wittka, 1915). The crystal structures of neutral salts of Zn^{2+} with DL-penicillamine (Bell & Sheldrick, 1984), D-penicillamine (Bell & Sheldrick, 1984), L-proline (Yukawa *et al.*, 1985), sarcosine (Subha Nandhini *et al.*, 2001), L-*t*-leucine (Hoffmüller *et al.*, 1999), glycine (Hariharan *et al.*, 1989), DL-valine (Nandhini *et al.*, 2001) and DL-alanine (Subha Nandhini *et al.*, 2002) have already been reported. In all cases, the Zn^{2+} ions are tetrahedrally four-coordinate, with two halogenides and two O atoms of two negatively charged carboxylates as donors. The halogenides act as acceptors of hydrogen bonds, which are donated by the positively charged ammonium groups.

In the structure of dichlorobis(L-proline)zinc(II) (Yukawa *et al.*, 1985), the Zn complex contains two independent L-proline residues. The five-membered ring of one of these residues has an envelope conformation on C4 and a C—N—C^{α}—C torsion angle of −0.8 (5)°, while the other has a twist conformation on the C3—C4 bond, with a C—N—C^{α}—C torsion angle of 11.0 (4)°. From quantum chemical calculations, it is known that the torsion angle of the carboxylate group is correlated with the ring puckering (Ramek *et al.*, 1997). This correlation can also be found in the crystal structures of 83 proline complexes (133 residues) obtained from the Cambridge Structural Database (April 2002 release; Allen, 2002), as shown by a plot of the C—N—C^{α}—C ring torsion angles *versus* the N—C^{α}—C—O torsion angles (Fig. 1). A negative value for the C—N—C^{α}—C torsion angle results in a positive deviation from 0° for the N—C^{α}—C—O torsion angle, while a positive value results in a negative deviation. In dichlorobis(L-proline)zinc(II), the N—C^{α}—C—O torsion angles are −15.2 (5) and 20.9 (5)°, respectively, thus fitting badly into the correlation. The two independent proline residues also differ in their C—O—Zn angles, which are 122.4 (3) and 116.5 (3)°, respectively. For comparison with these data, we prepared the title racemic compound, dichlorobis(DL-proline)zinc(II), (I), and present its structure here.



(I)

Compound (I) crystallizes in the centrosymmetric space group *C*2/*c*. The Zn atom is located on a twofold axis in a distorted tetrahedral environment (Fig. 2). Both proline ligands of one complex consequently have the same absolute configuration, either *R* or *S*. Conformation analysis of the five-membered ring according to the method of Evans & Boeyens (1989) results in coefficients of 59 and 41% for the envelope and twist conformations, respectively, indicating an intermediate form. The C5—N1—C2—C3 torsion angle is 21.05 (14)° and the O1—C1—C2—N1 torsion angle is −9.81 (16)°, which is perfectly in line with the above-mentioned correlation between these two torsion angles. The

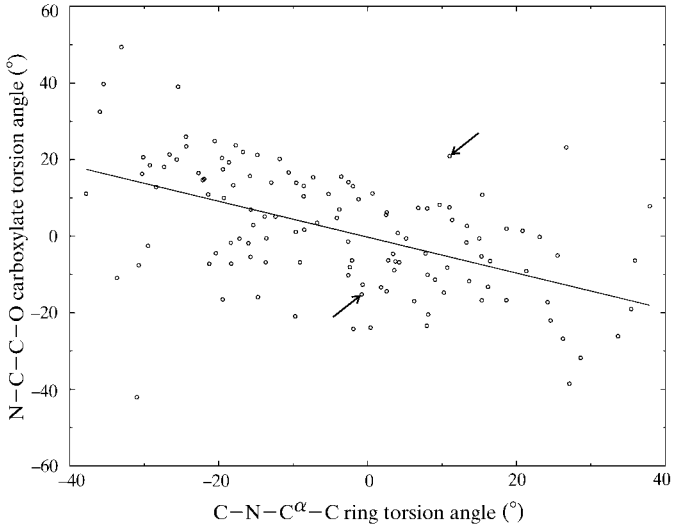


Figure 1
The correlation between the C—N—C^{α}—C and N—C—C—O torsion angles in 83 crystal structures containing proline (133 observations). The two independent proline residues of dichlorobis(L-proline)zinc(II) (Yukawa *et al.*, 1985) are marked with arrows.

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C1—O1—Zn1 angle of 128.29 (9)° is significantly larger than the corresponding angles in the L-proline complex. As expected, the C1—O1 bond length of the coordinated O atom is significantly longer than the C1—O2 bond of the non-coordinated O atom (Table 1).

Both H atoms of the ammonium group are involved in hydrogen bonding (Table 2). Atom H1*A* forms a bifurcated hydrogen bond, with atom O1 of the same proline residue and atom Cl1^{i} as acceptors [symmetry code: (i) x, $1 + y$, z]. The angle sum at H1*A* is 355 (2)°. Atom H1*B* forms an intermolecular hydrogen bond to atom O2^{i}. Due to the hydrogen bonding, a linear chain is formed in the direction of the crystallographic *b* axis (Fig. 3). Because translation is the only symmetry operation in the generation of these chains, all proline residues within one chain have the same configuration. Of course, in the racemic centrosymmetric crystal, there are the same number of chains with *R*-proline as with *S*-proline residues.

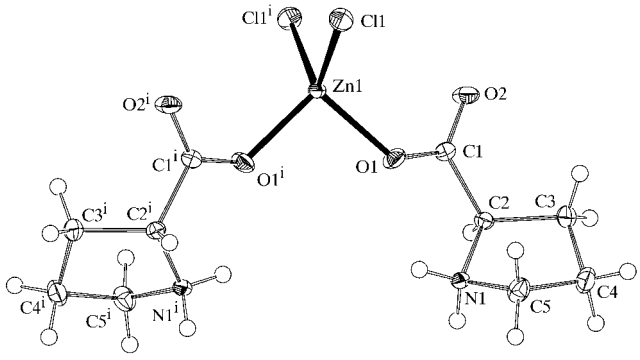

Figure 2
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. A complex containing two *R*-proline residues is shown [symmetry code: (i) $1 - x$, y, $\frac{3}{2} - z$].

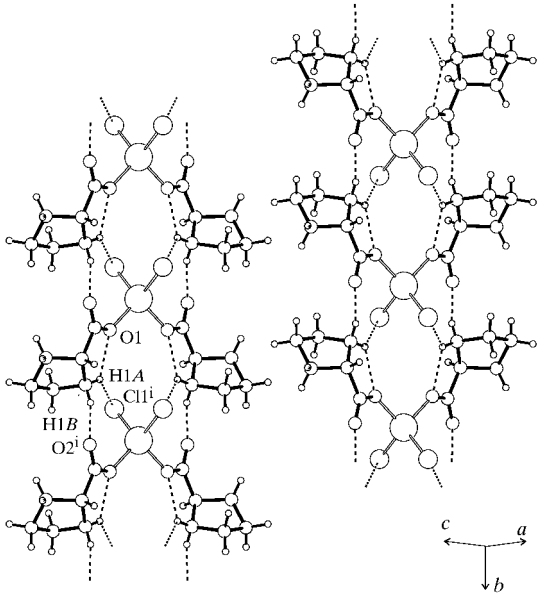

Figure 3
Hydrogen-bond formation in the crystal structure of (I). The proline residues in the chain on the left-hand side have the *R* configuration, while those on the right-hand side have the *S* configuration [symmetry code: (i) x, $1 + y$, z].

Partial separation of chiral molecules in a racemic crystal has been reported previously for the structure of *N*-acetyl-DL-alanine methyl ester (Müller & Lutz, 2001), where the hydrogen-bonded chains consist of one *R* and two *S* molecules, or *vice versa*. A complete separation of the *R* and *S* forms would lead to a mixture of enantiopure crystals, as in the famous example of sodium ammonium tartrate (Pasteur, 1848). Indeed, we observed this separation in a crystallization experiment, where we obtained a crystalline powder of dichlorobis(L-proline)zinc(II) and dichlorobis(D-proline)-zinc(II). The structure of the powder was analyzed by comparison of the measured powder pattern with that calculated from the single-crystal coordinates (Yukawa *et al.*, 1985). This powder was later used as seed crystals for the crystallization of the racemic compound, (I). It seems that, in this case, the conditions of the crystallization experiment control which product is obtained, not the nature of the seed crystals.

Experimental

DL-Proline (0.502 g; 99%, ACROS Organics) and $ZnCl_2$ (0.297 g; 98%, Fluka Chimica) were dissolved in a minimum amount of water. The solution was heated to 363 K and cooled slowly to room temperature, yielding a viscous oil. As seed crystals, a mixture of previously obtained dichlorobis(L-proline)zinc(II) and dichlorobis-(D-proline)zinc(II) powder was added. After standing for 6 h, transparent colourless crystals of (I) were obtained of a size suitable for the diffraction experiment. The product can also be obtained by crystallization from aqueous ethanol.

Crystal data

$[ZnCl_2(C_5H_9NO_2)_2]$
$M_r = 366.53$
Monoclinic, $C2/c$
$a = 18.6705$ (8) Å
$b = 5.9427$ (2) Å
$c = 13.3961$ (4) Å
$\beta = 104.637$ (4)°
$V = 1438.10$ (9) Å^3
$Z = 4$
$D_x = 1.693$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 96 reflections
$\theta = 3.8$–$22.6°$
$\mu = 2.09$ mm^{-1}
$T = 150$ (2) K
Needle, colourless
0.30 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1997)
$T_{min} = 0.58$, $T_{max} = 0.73$
12 791 measured reflections
1648 independent reflections
1485 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 27.5°$
$h = -24 \rightarrow 23$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.018$
$wR(F^2) = 0.048$
$S = 1.08$
1648 reflections
95 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0233P)^2 + 1.2477P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	1.9625 (10)	N1—C2	1.5008 (18)
Zn1—Cl1	2.2429 (4)	C1—C2	1.5243 (19)
O1—C1	1.2763 (16)	C2—C3	1.5458 (19)
O2—C1	1.2334 (17)	C3—C4	1.530 (2)
N1—C5	1.4967 (19)	C4—C5	1.518 (2)
O2—C1—C2—N1	170.55 (12)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl1^{i}	0.876 (19)	2.755 (18)	3.3721 (13)	128.6 (14)
N1—H1A···O1	0.876 (19)	2.117 (18)	2.6014 (16)	114.2 (14)
N1—H1B···O2^{i}	0.88 (2)	1.90 (2)	2.7498 (16)	163.8 (17)

Symmetry code: (i) $x, 1+y, z$.

H atoms on N atoms were refined freely with isotropic displacement parameters. All remaining H atoms were placed in geometrically idealized positions, with C—H distances in the range 0.99–1.00 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVAL*14 (Duisenberg, 1998) and *SORTAV* (Blessing, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1157). Services for accessing these data are described at the back of the journal.

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