

A hydrated complex of DL-alanine with cadmium chloride

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$

H-atom completeness 78%

R factor = 0.048

wR factor = 0.133

Data-to-parameter ratio = 16.4

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

In the title complex, *catena*-poly[[[dicadmium(II)]- μ -DL-alanine-di- μ -chloro] monohydrate], $\{[\text{CdCl}_2(\text{C}_3\text{H}_7\text{NO}_2)] \cdot \text{H}_2\text{O}\}_n$, the DL-alanine molecules exist in the zwitterionic form. The Cd atoms lie on inversion centers and are coordinated by four Cl atoms and two carboxyl O atoms, forming a distorted octahedral environment. These octahedra are linked through Cl–Cl edges and are bridged by the carboxyl groups of the alanine residues, forming a one-dimensional polymer chain that extends along [100].

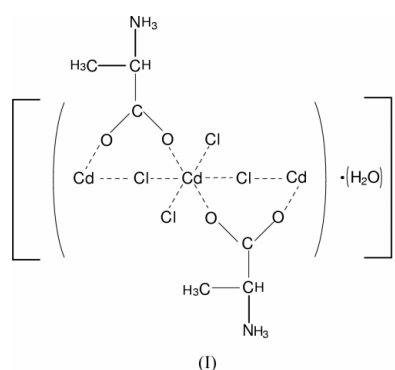
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Comment

Halagenocadmium–amino acid complexes are interesting, as cadmium is a naturally occurring metallic element, chemically similar to zinc. Cadmium is found to occur naturally in at least one protein, metallothionein (Kagi & Vallee, 1960). A precise determination of the crystal structure of DL-alanine itself was recently carried out in our laboratory (Subha Nandhini *et al.*, 2001). The present study reports the crystal structure of a complex of DL-alanine with cadmium chloride, *viz.* *catena*-poly[[[dicadmium(II)]- μ -DL-alanine-di- μ -chloro] monohydrate], (I). The crystal structures of complexes of cadmium chloride with glycine (Thulasidhass & Mohana Rao, 1980), L-proline (Yukawa *et al.*, 1983) and hydroxy-L-proline (Yukawa *et al.*, 1982), L-alanine (Schaffers & Keszler, 1993), sarcosine (Krishnakumar *et al.*, 1996) and β -alanine (Subha Nandhini *et al.*, 2002) have already been reported.



The DL-alanine molecules exist as zwitterions. The torsion angles involving the C1–C2 bond [-3.4 (4), 177.7 (3), -125.2 (3) and 55.9 (4) $^\circ$; see Table 1] observed in (I) are distinctly different from those observed in DL-alanine [16.3 (2), -164.0 (2), -105.7 (2) and 74.0 (2) $^\circ$; Subha Nandhini *et al.*, 2001]. The conformation of the alanine molecule about the N–C bond corresponds to the staggered-ethane type.

In the crystal structures of the majority of the complexes, the Cd atom has a tetrahedral coordination (Bürgi, 1973;

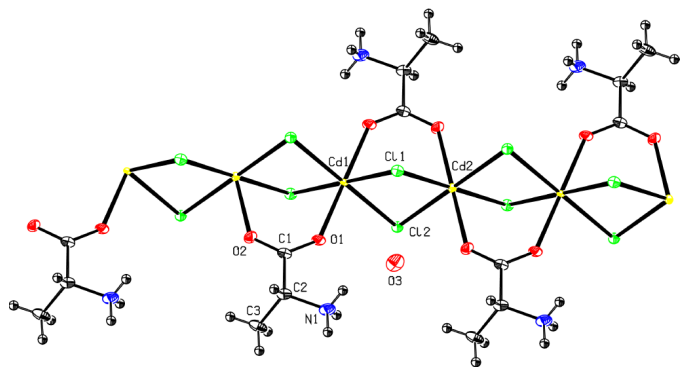


Figure 1
An ORTEP (Johnson & Burnett, 1996) view of title complex, showing part of the polymeric chain and the atom-numbering scheme for the contents of the asymmetric unit. The displacement ellipsoids are drawn at the 50% probability level.

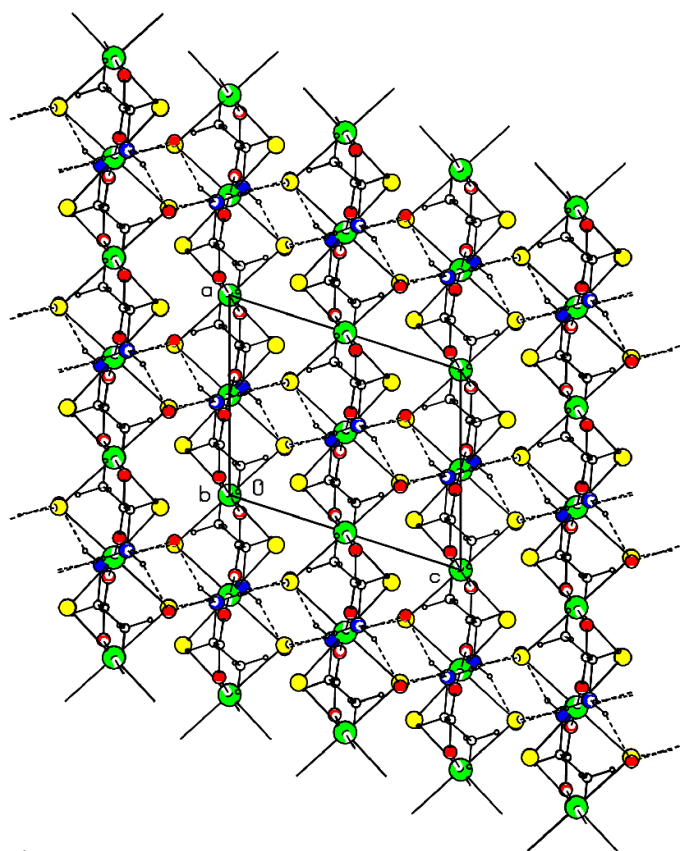


Figure 2
Packing of the molecules in the unit cell, viewed down the *b* axis.

Liptrot, 1974). In (I), each Cd atom lies on an inversion center and is coordinated by four Cl atoms and two carboxyl O atoms, forming distorted octahedra. The four Cl atoms which coordinate to a Cd atom form a square plane. These square planes extend along the shorter axis, *a*. The dihedral angle between adjacent square planes is $34.8(1)^\circ$. These square planes are spanned by the carboxyl O atoms, which complete the coordination around the Cd atom. These polyhedra fuse directly by sharing Cl–Cl edges, forming one-dimensional polymeric chains in the [100] direction. The water O atom does not participate in coordination with cadmium. The

metal–ligand coordination observed in this structure is remarkably similar to those observed in the crystal structures of complexes of CdCl_2 with L-alanine, L-proline, hydroxy L-proline and β -alanine, and distinctly different from glycine– CdCl_2 and sarcosine– CdCl_2 .

Selected interatomic distances are listed in Table 1. The mean Cd–Cl distance, $2.61(1) \text{ \AA}$, is in agreement with the corresponding distances reported in the structures of complexes of CdCl_2 with β -alanine [$2.619(5) \text{ \AA}$], L-alanine [$2.61(1) \text{ \AA}$], L-proline [$2.615(3) \text{ \AA}$], 4-hydroxy-L-proline [$2.620(2) \text{ \AA}$], glycine [$2.543(6) \text{ \AA}$] and sarcosine [$2.589(1) \text{ \AA}$]. The Cd–Cl distances also agree well with those observed in other simple organic complexes of CdCl_2 , viz. $2.60(1)$ and $2.65(1) \text{ \AA}$ for $\text{CdCl}_2 \cdot 4\text{H}_2\text{O}$ (Leligny & Monier, 1979) and CdCl_2 dipyridine (Paulus, 1969), respectively. The Cd–Cl distances reported for CdCl_2 diimidazole (Flook *et al.*, 1973), viz. $2.706(2)$ and $2.731(2) \text{ \AA}$, are longer compared to those in the present structure.

The crystal structure of (I) is illustrated in Fig. 2 and the hydrogen bonds that stabilize it are listed in Table 2. There are no direct interactions between the alanine molecules. The adjacent polymeric chains are interconnected through N–H \cdots O and N–H \cdots Cl hydrogen bonds. The water atom O3 is involved in short contacts with Cl1 [$3.234(3) \text{ \AA}$], Clⁱⁱ [$3.166(3) \text{ \AA}$] and O2ⁱⁱ [$3.030(4) \text{ \AA}$] [symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $1 + x, y, z$].

Experimental

Colourless single crystals of the title complex were grown as transparent plates, using a mixture of water and acetone, containing DL-alanine and cadmium chloride in a stoichiometric ratio.

Crystal data

$[\text{CdCl}_2(\text{C}_3\text{H}_7\text{NO}_2)] \cdot \text{H}_2\text{O}$
 $M_r = 290.42$
 Monoclinic, $P2_1/c$
 $a = 7.1190(15) \text{ \AA}$
 $b = 14.408(3) \text{ \AA}$
 $c = 8.6396(13) \text{ \AA}$
 $\beta = 107.98(2)^\circ$
 $V = 842.9(3) \text{ \AA}^3$
 $Z = 4$
 $D_x = 2.289 \text{ Mg m}^{-3}$
 $D_m = 2.29 \text{ Mg m}^{-3}$

D_m measured by flotation in a mixture of carbon tetrachloride and bromoform
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 19\text{--}32^\circ$
 $\mu = 3.18 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Transparent plate, colourless
 $0.18 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Enraf–Nonius sealed-tube diffractometer
 ω – 2θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.639$, $T_{\max} = 0.728$
 1797 measured reflections
 1541 independent reflections
 1469 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.095$
 $\theta_{\text{max}} = 25.3^\circ$
 $h = -8 \rightarrow 8$
 $k = 0 \rightarrow 17$
 $l = -9 \rightarrow 10$
 2 standard reflections
 frequency: 60 min
 intensity decay: 0.1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.134$
 $S = 1.15$
 1541 reflections
 94 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.096P)^2 + 1.0634P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 2.57 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -2.89 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.265 (2)	Cd2—Cl1	2.6397 (11)
Cd1—Cl2	2.5697 (10)	O1—C1	1.241 (4)
Cd1—Cl1	2.6635 (9)	O2—C1	1.256 (4)
Cd2—O2 ⁱ	2.352 (3)	N1—C2	1.500 (5)
Cd2—Cl2	2.5669 (8)	C1—C2	1.532 (5)
		C2—C3	1.501 (5)
O1—Cd1—O1 ⁱ	180	Cl2—Cd2—Cl2 ⁱⁱⁱ	180
O1—Cd1—Cl2	87.73 (7)	O2 ⁱ —Cd2—Cl1	91.59 (7)
O1 ⁱ —Cd1—Cl2	92.27 (7)	O2 ⁱⁱ —Cd2—Cl1	88.41 (7)
Cl2—Cd1—Cl2 ⁱ	180	Cl2—Cd2—Cl1	89.02 (3)
O1—Cd1—Cl1	93.33 (7)	Cl2 ⁱⁱⁱ —Cd2—Cl1	90.98 (3)
O1 ⁱ —Cd1—Cl1	86.67 (7)	Cl1—Cd2—Cl1 ⁱⁱⁱ	180
Cl2—Cd1—Cl1	88.44 (3)	O1—C1—O2	127.7 (3)
Cl2 ⁱ —Cd1—Cl1	91.56 (3)	O1—C1—C2	116.1 (3)
Cl1—Cd1—Cl1 ⁱ	180	O2—C1—C2	116.2 (3)
O2 ⁱ —Cd2—O2 ⁱⁱ	180	N1—C2—C3	109.2 (3)
O2 ⁱ —Cd2—Cl2	91.27 (7)	N1—C2—C1	108.4 (3)
O2 ⁱⁱ —Cd2—Cl2	88.73 (7)	C3—C2—C1	113.9 (3)
O1—C1—C2—N1	−3.4 (4)	O1—C1—C2—C3	−125.2 (3)
O2—C1—C2—N1	177.7 (3)	O2—C1—C2—C3	55.9 (4)

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

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1A \cdots O3	0.89	2.05	2.900 (5)	158
N1—H1B \cdots O3 ⁱ	0.89	2.03	2.901 (5)	166
N1—H1C \cdots Cl1 ⁱⁱ	0.89	2.46	3.270 (3)	152

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

H atoms were placed at calculated positions and were allowed to ride on their respective parent atoms, with C—H = 0.97 or 0.98 Å and N—H = 0.89 Å, with $U_{iso} = 1.5U_{eq}(\text{parent atom})$ for the methyl and amino group, and $U_{iso} = 1.2U_{eq}(\text{parent atom})$ for the rest. No satisfactory H-atom positions were found for the water O atom. Hence, the structure was refined without them. The highest peaks in the final difference map were located at distances less than 0.92 Å from the Cd atoms.

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) and *ORTEPIII* (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL97*.

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