thank Mr Li Xi-Guang for making single-crystal diffraction measurements and for help with preparation of the drawing.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55845 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1022]

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Structure of $CdCl_2.C_3H_7NO_2$

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Abstract

catena-Poly[cadmium-di-μ-chloro-μ-L-alanine-*O*:*O*′], $CdCl_2.C_3H_7NO_2$, has been synthesized and structurally characterized. The Cd atom occupies a distorted octahedral environment of four Cl atoms and two O atoms. These octahedra are linked through Cl···Cl edges and bridged by carboxyl groups of the alanine molecules to form one-dimensional rods that extend along [010].

Comment

We have recently crystallized several new complexes incorporating the amino acid L-alanine; this work is part of an effort in examining and modelling the optical second-order nonlinearities of compounds containing a carboxyl group as the principal chromophore. In this contribution we describe the structure of the adduct formed between this acid and cadmium chloride.

Crystals were grown by dissolving a 1:1 molar ratio of $CdCl_2.2.5H_2O$ (Aldrich, 98%) and L-alanine (Aldrich, 99%) in warm distilled water. The solution was set aside at room temperature, and crystals formed upon slow evaporation of the solvent. Structure-solution data are provided in the experimental details. Positional parameters and equivalent isotropic displacement coefficients are listed in Table 1.

As seen in Fig. 1, the Cd atoms bind to four Cl atoms and two O atoms in a distorted octahedral environment. The octahedra are spanned by the carboxyl group of the alanine molecule and fuse directly by sharing Cl1···Cl2 edges to form one-dimensional chains that extend along the *b* axis. If the carboxyl group is regarded as a single atom, the condensation of octahedra may be considered to result from a sharing of triangular faces as occurs in the chains of the compound $CsNiCl_3$ (Tiščenko, 1955) and related derivatives. We derive this description, in part, from the lack of coplanarity between adjacent $CdCl_4$ planes. The angle between these planes is 145.7 (1)° which compares with the angle 114° for similar planes in the structure of $CsNiCl_3$.

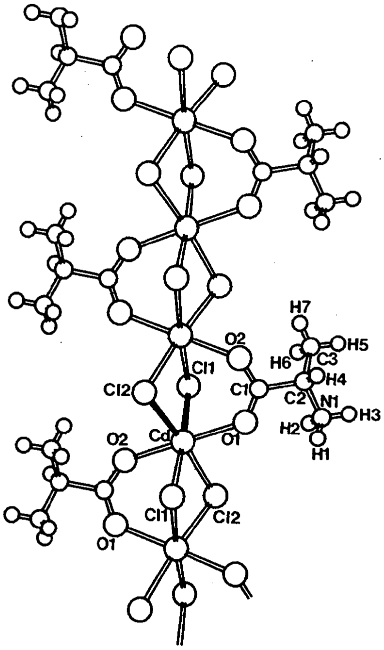

Fig. 1. Labelled sketch of the one-dimensional chain of edge-sharing $CdCl_2$ units bridged by $C_3H_7NO_2$ molecules. The interactions Cd—Cl1′ and Cd—Cl2′ are indicated by filled bonds.

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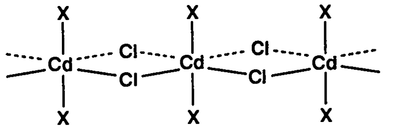
The angle in the present chain structure is actually intermediate to those found in the face-sharing chain and the more common Cl-bridged strings (1). In these chains the Cd atoms are bridged through Cl···Cl edges, and monodentate *X* ligands occupy *trans* vertices in the distorted octahedron about each Cd atom. Such structures have been reported for the *X* ligands: pyridine (Paulus, 1969), urea (Nardelli, Cavalca & Fava, 1957), H_2O (Leligny & Monier, 1979), cyandiamide (Villa, Coghi, Mangio, Nardelli & Pellizzi, 1971), and imidazole (Flook, Freeman, Hug & Rosalky, 1973).



(1)

A packing diagram is depicted in Fig. 2, where adjacent chains are seen to be crystallographically related by the C_2 rotation axis. The interchain distances N···Cl1 = 3.224 (8) and N···O2 = 2.83 (1) Å as well as the intrachain distances N···O1 = 2.63 (1) Å indicate the presence of hydrogen bonding.

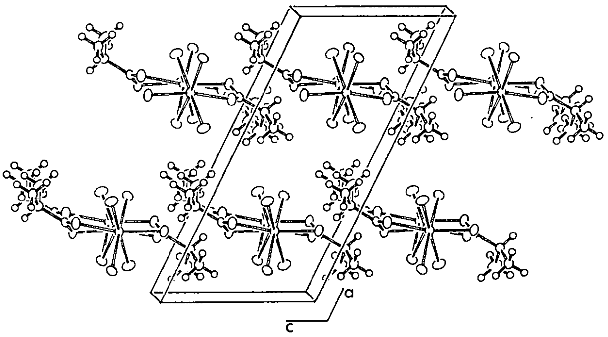


Fig. 2. Packing diagram of $CdCl_2.C_3H_7NO_2$ as viewed along the [010] direction; the unit cell of the structure is outlined.

Selected interatomic distances and angles are listed in Table 1. The average Cd—Cl distance, 2.61 (1) Å, compares to similar distances of 2.60 (1) and 2.65 Å in the compounds $CdCl_2.4H_2O$ (Leligny & Monier, 1979) and $CdCl_2$.2(pyridine) (Paulus, 1969), respectively, and contrasts to the longer distances of 2.706 (2) and 2.731 (2) Å reported for $CdCl_2$.2(imidazole) (Flook, Freeman, Hug & Rosalky, 1973). The average Cd—O distance, 2.33 (4) Å, compares to the value 2.33 Å calculated from crystal radii (Shannon, 1976) for a six-coordinate Cd atom. Considerable deviations from the orthogonal angles of an octahedron are evident from consideration of Table 2; the largest excursion is represented by the angle of 82.9 (2)° for Cl1′—Cd—O1. The O1—Cd—O2 angle is distorted to 168.7 (8)° by opposing rotations of the neighboring carboxyl groups approximately along the *c* axis as seen in the packing diagram.

The distances and angles in the alanine ligand compare favorably to those of the crystallized molecule. Bridging of the Cd atoms by the carboxyl group affords an O1—C1—O2 angle of 127.6 (7)° that is slightly wider than the 125.6° angle for O1—C1—O2 in an L-alanine molecule (Simpson & Marsh, 1966). As noted above, pairs of carboxyl groups in adjacent chains are related by a C_2 rotation. Because the plane normals of the groups are canted with respect to the rotation axis (*b*), an interplanar angle of 27.6° is observed.

Experimental

Crystal data

$[CdCl_2(C_3H_7NO_2)]$
$M_r = 272.4$
Monoclinic
$C2$
$a = 16.240$ (2) Å
$b = 7.272$ (1) Å
$c = 7.987$ (2) Å
$\beta = 116.44$ (1)°
$V = 844.7$ (2) Å^3
$Z = 4$
$D_x = 2.14$ Mg m^{-3}
Mo $K\alpha$ radiation

$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 15$-18°
$\mu = 3.155$ mm^{-1}
$T = 296$ K
Plate
0.35 × 0.20 × 0.08 mm
Colourless
Crystal source: aqueous solution of $CdCl_2.2.5H_2O$/L-$C_3H_7NO_2$

Data collection

Rigaku AFC-6*R* diffractometer
ω-2θ scans
Absorption correction: empirical
$T_{min} = 0.63$, $T_{max} = 1.44$
2120 measured reflections
2008 independent reflections
1900 observed reflections
$[F_o^2 > 3\sigma(F_o^2)]$

$R_{int} = 0.046$
$\theta_{max} = 37.5$°
$h = -27 \rightarrow 27$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 13$
3 standard reflections monitored every 200 reflections
intensity variation: 3.5%

Refinement

Refinement on F
Final $R = 0.063$
$wR = 0.088$
$S = 1.95$
1900 reflections
81 parameters
H-atom parameters not refined

$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 2.072$ e Å^{-3}
$\Delta\rho_{min} = -1.404$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cd	0.24399 (4)	0.2755	0.48899 (7)	1.83 (2)
Cl1	0.3733 (1)	0.0347 (5)	0.5409 (3)	2.17 (5)
Cl2	0.1283 (2)	0.0117 (4)	0.3200 (3)	2.60 (6)
O1	0.2177 (5)	0.3773 (9)	0.1974 (9)	2.3 (2)
O2	0.2392 (6)	0.176 (1)	0.7653 (9)	2.5 (2)
N	0.3836 (6)	−0.096 (1)	1.165 (1)	2.2 (2)
C1	0.2804 (5)	0.036 (1)	0.861 (1)	1.8 (2)
C2	0.3350 (6)	0.073 (1)	1.075 (1)	2.0 (2)
C3	0.4028 (8)	0.234 (1)	1.113 (2)	3.2 (3)

Table 2. *Geometric parameters* (Å, °)

Cd—Cl1	2.621 (3)	C1—O2	1.27 (1)
Cd—Cl1	2.614 (3)	C1—C2	1.56 (1)
Cd—Cl2	2.603 (3)	C2—N	1.47 (1)
Cd—Cl2	2.600 (3)	C2—C3	1.54 (1)
Cd—O1	2.295 (6)	O1—O2	2.26 (1)
Cd—O2	2.357 (7)	Cl1—Cl2	3.566 (3)
C1—O1	1.25 (1)	Cl1—Cl2	3.646 (3)
Cl1—Cd—Cl2	86.1 (1)	Cl2—Cd—O2	90.2 (2)
Cl1—Cd—Cl2	88.57 (7)	O1—Cd—O2	168.7 (3)
Cl1—Cd—Cl2	98.96 (7)	O1—C1—O2	127.6 (7)
Cl1—Cd—Cl2	86.3 (1)	O1—C1—C2	118.2 (7)
Cl1—Cd—O1	98.6 (2)	O2—C1—C2	114.2 (7)
Cl1—Cd—O1	82.9 (2)	C1—C2—C3	110.9 (7)
Cl1—Cd—O2	90.3 (2)	N—C2—C1	108.0 (7)
Cl1—Cd—O2	88.9 (2)	N—C2—C3	111.0 (8)
Cl2—Cd—O1	97.0 (2)	Cd—Cl1—Cd	88.15 (6)
Cl2—Cd—O1	86.9 (2)	Cd—Cl2—Cd	88.83 (7)
Cl2—Cd—O2	86.7 (2)		

In the refinement, $\Sigma w(|F_o|-|F_c|)^2$ was minimized. The weighting scheme used was $w=1/\sigma^2(F_o^2)$ in which $\sigma(F_o^2) = [C+1/4(t_c/t_b)\times(b_1+b_2) + (pI)^2]^{1/2}$ where C is the total number of counts per peak, t_c is the time spent counting peak density, t_b is the time spent counting one side of background, b_1 is the high-angle background count, b_2 is the low-angle background count, p is the fudge factor and $I = C-1/2(t_c/t_b)(b_1 + b_2)$.

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Structure of Monomeric Hydrated Manganese(III) Tetra(4-*N*-methylpyridyl)porphyrin Pentachloride

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Abstract

The structure of the title compound, diaqua{2,7,12,17-tetrakis(1-methyl-4-pyridyl)-21,22,23,24-tetraazapentacyclo[16.2.1.1^{3,6}.1^{8,11}.1^{13,16}]tetracosa-1(21),2,4,6(22),7,9,11(23),12,14,16(24),17,19-dodecaene-N^{21},N^{22},N^{23},N^{24}}manganese(III) pentachloride heptahydrate, Mn-tmpyp, is the second example of a planar diaqua-ligated metalloporphyrin with an extensive anion–water network which interdigitates between successive layers of porphyrins. The Mn atoms have near octahedral geometry: Mn—N1 2.012 (5), Mn—N2 2.013 (5), Mn—O1 2.221 (5) Å, N1—Mn—O1 90.2 (2), N2—Mn—O1 89.1 (2)°. The pyridyl planes are inclined by 65.0° (C11–C12–C13–N12–C14–C15) and 71.2° (C16–C17–C18–N11–C19–C20) with respect to the least-squares plane through the porphyrin.

Comment

The reactions of iron(III) and manganese(III) tetraarylporphyrins have been extensively employed to model the chemistry of haem enzymes and to develop new oxidation catalysts (Meunier, 1986; Mansuy, 1987; Mansuy, Battioni & Battioni, 1989). The [Mn^{III}(tmpyp)]$^{5+}$ structure is isomorphous with

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