O8—V3—O7	107.9 (2)	N4—C7—C8	110.1 (4)
O9—V3—O1^{i}	111.4 (2)	N3—C8—C7	109.8 (4)
O8—V3—O1^{i}	110.2 (2)		
N1—C1—C2—N2	56.1 (6)	N3—C5—C6—N4	−57.8 (6)
C1—C2—N2—C3	−56.8 (6)	C5—C6—N4—C7	56.8 (6)
C2—N2—C3—C4	57.2 (6)	C6—N4—C7—C8	−56.5 (6)
N2—C3—C4—N1	−56.2 (6)	N4—C7—C8—N3	56.2 (6)
C3—C4—N1—C1	57.0 (6)	C7—C8—N3—C5	−59.2 (6)
C4—N1—C1—C2	−57.5 (6)	C8—N3—C5—C6	60.4 (6)

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

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N1—H18···O10	1.93 (4)	2.732 (6)	170 (6)
N1—H17···O3^{i}	1.96 (4)	2.806 (6)	173 (6)
N2—H19···O12^{i}	2.00 (4)	2.748 (6)	150 (6)
N2—H20···O11	2.05 (5)	2.799 (6)	149 (6)
N3—H21···O9^{ii}	2.30 (4)	3.098 (6)	174 (6)
N4—H23···O5	1.89 (4)	2.740 (6)	170 (6)
N4—H22···O3^{ii}	1.99 (4)	2.852 (6)	174 (6)
O10—H25···N3	1.89 (5)	2.737 (6)	162 (6)
O11—H26···O8	1.99 (5)	2.768 (6)	169 (6)
O11—H27···O4^{iii}	2.04 (5)	2.730 (6)	175 (8)
O12—H28···O6	2.04 (5)	2.765 (6)	168 (7)
O12—H29···O4^{iv}	2.11 (5)	2.770 (6)	155 (7)

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

Data reduction: *XP*21 (Pavelčík, unpublished). Program(s) used to solve structure: *XFPS* (Pavelčík, Sivý, Rizzoli & Andreetti, 1992). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1147). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$Me_2Cd(dabco)$

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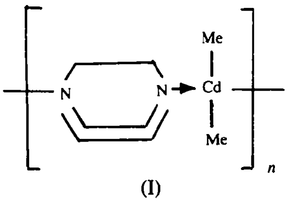
Abstract

The title compound, *catena*-poly[dimethylcadmium-μ-1,4-diazabicyclo[2.2.2]octane], $[Cd(CH_3)_2(C_6H_{12}N_2)]$, was synthesized and the crystal structure determined by X-ray diffraction methods. The complex was found to be a 1:1 linear polymer with four coordinated Cd atoms per unit cell. The Cd atom has distorted tetrahedral coordination.

Comment

The development of high-purity precursors for the preparation of II–VI semiconductor materials has been of critical importance for successful device fabrication. The realisation of techniques such as metal-organic chemical vapour deposition (MOCVD) and organometallic vapour-phase epitaxy (OMVPE) has been delayed by the inadequacy of the source materials available. We report here the synthesis and crystal structure of $Me_2Cd(dabco)$, (I) (where dabco is 1,4-diazabicyclo[2.2.2]octane), as a new MOCVD precursor (Bradley & Hursthouse, 1992; Jones & Rushworth, 1989).



(I)

The molecular structure and molecular arrangement in the unit cell are illustrated in Fig. 1. The complex consists of a 1:1 molecular adduct of dimethylcadmium bonded to dabco and has a linear polymeric structure. The Cd atom in the complex is coordinated in a distorted tetrahedral arrangement by two N atoms of two different dabco moieties and the C atoms of two methyl groups. The C—Cd—N bond angles [96.1 (1)–99.2 (1)°] are consistently some 9–10° smaller than the tetrahedral angle (Bradley & Dawes, 1990), whereas the C—Cd—C bond angle [155.9 (2)°] is 46° larger than the tetrahedral angle. The Cd—N distances [2.588 (4) and 2.669 (4) Å] are longer than would be expected for a regular dative interaction (Bradley & Hursthouse, 1992). This may be a result of steric repulsion between the methyl groups on the cadmium and the methylene groups of the dabco ligand. It may also be due to the hybridization of the atomic orbitals of cadmium. The formation of a 1:1 adduct with the dialkylcadmium as a Lewis acid involves the donation of electron density from the dabco molecule as a Lewis base into an sp^3-hybridized orbital of the metal (Bradley & Dawes, 1987).

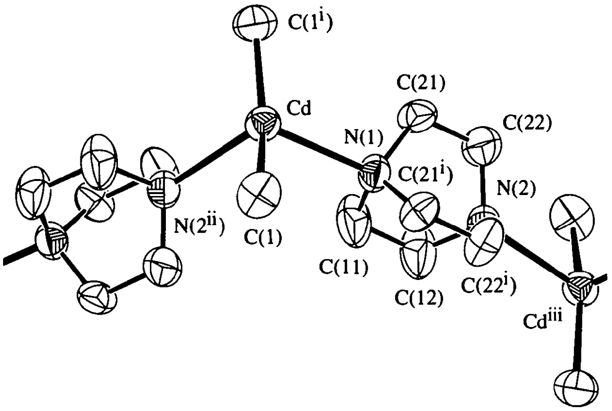


Fig. 1. The polymeric structure of the title compound showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

Dimethylcadmium was added dropwise to a stirred solution of dabco in diethyl ether. A white precipitate formed immediately. Crystals were obtained by recrystallization from benzene. The complex is much less air sensitive than the parent dimethylcadmium. All manipulations were carried out under superpurity N_2 with rigorous exclusion of air and moisture using a dry box and Schlenk techniques. Solvents were distilled from sodium benzophenone under N_2 and the single crystal was sealed in a Lindemann capillary also under N_2.

Crystal data

$[Cd(CH_3)_2(C_6H_{12}N_2)]$
$M_r = 254.65$
Orthorhombic
Pnma
$a = 12.193 (9)$ Å
$b = 12.821 (2)$ Å
$c = 6.685 (1)$ Å
$V = 1045$ Å^3
$Z = 4$
$D_x = 1.62$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 14.92–15.58°$
$\mu = 2.032$ mm^{-1}
$T = 298$ K
Column
2.0 × 0.1 × 0.1 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
2θ-ω scans
Absorption correction: ψ scan
$T_{min} = 0.852$, $T_{max} = 0.988$
1105 measured reflections
1105 independent reflections

866 observed reflections $[I > 3\sigma(I)]$
$\theta_{max} = 25°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 15$
3 standard reflections monitored every 60 reflections intensity decay: 0.5%

Refinement

Refinement on F
$R = 0.030$
$wR = 0.039$
$S = 1.23$
858 reflections
59 parameters
H-atom parameters not refined

$w = 1/\sigma^2(|F_o|)$
$(\Delta/\sigma)_{max} = 0.02$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement 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	0.20062 (3)	1/4	0.11438 (5)	3.78 (2)
N(1)	0.3756 (3)	1/4	−0.1046 (5)	3.8 (2)
N(2)	0.5482 (3)	1/4	−0.3278 (6)	3.8 (2)
C(1)	0.1909 (3)	0.4140 (4)	0.1791 (6)	5.4 (2)
C(11)	0.3457 (5)	1/4	−0.314 (1)	6.3 (3)
C(12)	0.4466 (5)	1/4	−0.4479 (9)	6.8 (4)
C(21)	0.4442 (3)	0.1582 (3)	−0.0642 (6)	4.9 (2)
C(22)	0.5456 (3)	0.1584 (3)	−0.1974 (7)	5.4 (2)

Table 2. *Selected geometric parameters* (Å, °)

Cd—C(1)	2.151 (5)	N(1)—C(21^{i})	1.469 (5)
Cd—C(1^{i})	2.151 (5)	N(2)—C(22)	1.463 (5)
Cd—N(1)	2.588 (4)	N(2)—C(22^{i})	1.463 (5)
Cd—N(2^{ii})	2.669 (4)	N(2)—C(12)	1.477 (7)
N(1)—C(11)	1.445 (7)	C(11)—C(12)	1.522 (8)
N(1)—C(21)	1.469 (5)	C(21)—C(22)	1.523 (5)
C(1)—Cd—C(1^{i})	155.9 (2)	C(21)—N(1)—Cd	111.5 (2)
C(1)—Cd—N(1)	99.2 (1)	C(22)—N(2)—C(22^{i})	106.8 (4)
C(1)—Cd—N(2^{ii})	96.1 (1)	C(22)—N(2)—C(12)	107.8 (3)
C(1^{i})—Cd—N(1)	99.2 (1)	C(22)—N(2)—Cd^{iii}	116.3 (2)
C(1^{i})—Cd—N(2^{ii})	96.1 (1)	C(22^{i})—N(2)—C(12)	107.8 (3)
N(1)—Cd—N(2^{ii})	99.7 (1)	C(22^{i})—N(2)—Cd^{iii}	116.3 (2)
C(11)—N(1)—C(21)	108.8 (3)	C(12)—N(2)—Cd^{iii}	101.2 (3)
C(11)—N(1)—C(21^{i})	108.8 (3)	N(1)—C(11)—C(12)	111.5 (5)
C(11)—N(1)—Cd	109.8 (3)	N(2)—C(12)—C(11)	111.0 (5)
C(21)—N(1)—C(21^{i})	106.5 (4)	N(1)—C(21)—C(22)	110.7 (3)
C(21^{i})—N(1)—Cd	111.5 (2)	N(2)—C(22)—C(21)	111.6 (3)

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

The structure was solved by direct methods and subsequent difference Fourier techniques and refined by full-matrix least-squares methods with anisotropic displacement factors for all non-H atoms. H atoms were located by difference Fourier techniques. All calculations were performed using the *TEXSAN* system of computer programs (Molecular Structure Corporation, 1985).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: OH1068). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Aquatris(dichloroacetato)ethanolbis(1,10-phenanthroline)lanthanum(III) and the Corresponding Samarium Complex

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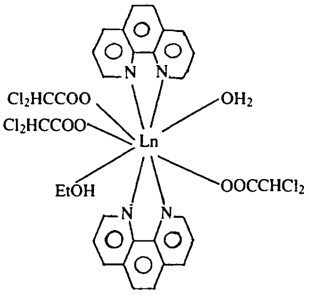
Abstract

The title complexes, $[La(CHCl_2CO_2)_3(C_{12}H_8N_2)_2(C_2H_5OH)(H_2O)]$ and $[Sm(CHCl_2CO_2)_3(C_{12}H_8N_2)_2(C_2H_5OH)(H_2O)]$, are isostructural. The La and Sm atoms are nine-coordinate with distorted tricapped trigonal prismatic coordination geometry. The average bond distances in the two structures are La—O(dichloroacetate) 2.470 (14), La—O(H_2O and C_2H_5OH) 2.59 (9), La—N 2.72 (2), Sm—O(dichloroacetate) 2.39 (3), Sm—O(H_2O and C_2H_5OH) 2.54 (13) and Sm—N 2.63 (4) Å. The complexes form one-dimensional intermolecular-hydrogen-bonded chains in a direction nearly parallel to the *a* axis. This stabilizes the crystal packing.

Comment

Rare earth dichloroacetates have been studied previously (Sing, Buhtra, Vaishnava & Misra, 1978; Spacu & Antonescu, 1969), particularly from the point of view of their preparation. However, a full understanding of the chemistry of these compounds is limited by the absence of structural information. Structural studies of lanthanide complexes involving carboxylate ligands have shown that the rare earth atoms have several types of coordination, usually with coordination numbers of eight or nine. In complexes containing the same ligands, the heavier rare earth atoms often coordinate to fewer ligands than the lighter ones. The carboxylate ligand has various modes of coordination to lanthanide atoms: monodentate, bidentate, bridging-bidentate or bridging-tridentate (Bone, Sowerby & Verma, 1978; Harrison, Giorgetti & Bunzle, 1985; Sawase, Koizumi, Suzuki, Shimoi & Ouchi, 1984). We have reported the synthesis and structure of dimeric $Gd(CCl_3COO)_3(phen)(EtOH)_2$ (phen = 1,10-phenanthroline) (Mao, Lu & Dong, 1989). As a part of our continuing study of dichloroacetate lanthanide complexes with a series of heterocyclic amine ligands, we have now synthesized and studied the complexes of lanthanide dichloroacetate with two 1,10-phenanthroline ligands (Ln from La to Yb), a series which includes more than one type of complex. The present paper describes the crystal structures of $[Ln(CHCl_2COO)_3(phen)_2(H_2O)(EtOH)]$ [Ln = La (1) or Sm (2)].



(1) Ln = La
(2) Ln = Sm

The two complexes are isostructural; the structure of the La complex is shown in Fig. 1. The central atom is nine-coordinate: four N atoms from two phenanthroline ligands, three O atoms from monodentate dichloroacetate (dca) ions, one O atom from ethanol and one O atom from water form a distorted tricapped trigonal prism. The atoms O(3), O(5), O(7), N(2), N(3) and N(4) form the prism with O(1), O(8) and N(1) capping the rectangular faces. The average bond distances in the two structures are: La—O(dca) 2.470 (14), La—O(H_2O and EtOH) 2.59 (9), La—N 2.72 (2), Sm—O(dca) 2.39 (3), Sm—O(H_2O and EtOH) 2.54 (13) and Sm—N 2.63 (4) Å. A comparison of the metal–ligand bond distances in the two complexes shows that the bonds

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