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# *catena*-Poly[diaquacadmium(II)-$\mu$-(diethyl dichloromethylenebisphosphonato)-$\kappa^3O,O':O''$-tetraaquacadmium(II)-$\mu$-(diethyl dichloromethylenebisphosphonato)-$\kappa^3O:O',O''$]

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**Key indicators**

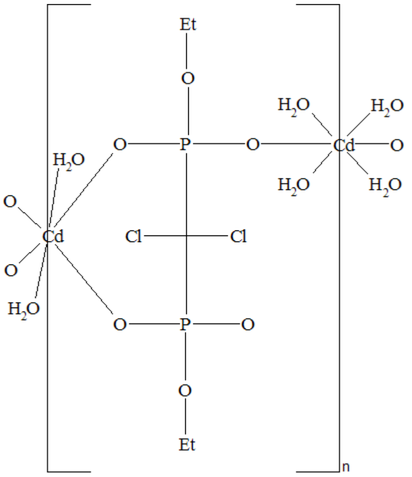
Single-crystal X-ray study
$T$ = 150 K
Mean $\sigma$(C–C) = 0.004 Å
$R$ factor = 0.026
$wR$ factor = 0.072
Data-to-parameter ratio = 19.3

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

The title compound, $[Cd(C_5H_{10}Cl_2O_6P_2)(H_2O)_3]_n$, is isomorphous with the Zn and Mg complexes of the $(Cl_2CP_2O_6Et_2)^{2-}$ ligand. The structure can be described as centrosymmetric octahedral Cd atoms with two symmetrically chelating $[Cl_2C(PO_3Et)_2]^{2-}$ ligands, connected into polymeric chains along the [110] direction by further octahedral Cd atoms.

## Comment

Recent investigations of the chemistry of metal bisphosphonates have focused on the properties of solid materials, due to their practical applications in ion exchange, sorption, catalysis, *etc*. (Clearfield, 1998; Zhang & Clearfield, 1997; Alberti *et al.*, 1996; Snover *et al.*, 1996). To study the solid materials, several metal complexes of methylenebisphosphonate, $[H_2C(PO_3H)_2]^{2-}$, and its analogues etidronate, $[(CH_3)(HO)C(PO_3H)_2]^{2-}$, and alendronate, $[(NH_3CH_2CH_2CH_2)(HO)C(PO_3H)_2]^{2-}$, including some Cd complexes, have been prepared and characterized (Serre & Férey, 2002; Barthelet *et al.*, 2000; Sergienko *et al.*, 1998; El Messbahi *et al.*, 2000; Dufau *et al.*, 1995).



(I)

Previously, we reported the structures of the Ca, Sr and Ba complexes of clodronate, $[Cl_2C(PO_3H)_2]^{2-}$, which is a halogenated analogue of methylenebisphosphonate (Kontturi *et al.*, 2004*a*,*b*,*c*). We have also reported some alkaline earth metal complexes of its two symmetrical dialkyl ester derivatives $[Cl_2C(PO_3Et)_2]^{2-}$ and $[Cl_2C(PO_3Pr^i)_2]^{2-}$ (Kontturi *et al.*, 2002, 2005*a*). The Zn and Cd complexes of clodronate and its diisopropyl ester derivative, and the Zn complex of the diethyl ester derivative of clodronate, have also been prepared and are being published (Kontturi *et al.*, 2005, 2005*b*). We report here the preparation and crystal structure of the Cd complex

$[Cd(Cl_2CP_2O_6Et_2)(H_2O)_3]_n$, (I), of the diethyl ester derivative of clodronate.

The title compound is isomorphous with the Mg and Zn complexes of the diethyl ester derivative of clodronate (Kontturi *et al.*, 2002, 2005*b*). The structure is best described as monomeric units consisting of octahedral Cd1 atoms with two symmetrically chelating $[Cl_2C(PO_3Et)_2]^{2-}$ ligands, connected into polymeric chains along the [110] direction by octahedral Cd2 atoms. The metal atoms Cd1 and Cd2 in the asymmetric unit are both on centres of symmetry, having Cd—O bond lengths of 2.221 (2)–2.332 (2) Å. The $[Cl_2C(PO_3Et)_2]^{2-}$ ligands are chelated to Cd1, forming a six-membered chelate ring, and connected to Cd2 through one O atom. The chains are connected to each other by hydrogen bonds [O···O/Cl = 2.718 (3)–3.462 (2) Å and 125–179°].

The FT–IR and solid-state $^{31}P$ NMR analysis of the title compound and of the isomorphous Mg and Zn complexes (Kontturi *et al.*, 2002, 2005*b*) reveal some changes in the spectra, due to the different metal atoms. In the FT–IR spectra, changes are observed in the 1340–980 cm$^{-1}$ region, attributed to the stretching vibrations of the phosphonate $PO_3$ groups; the main signals in that region are shifted to lower frequencies from Mg to Cd. In the $^{31}P$ NMR spectra it can be seen that the signals of the phosphonate groups of the Cd complex ($\delta_P$ 8.7 and 2.1) are shifted downfield when compared with the signals of the Zn and Mg complexes ($\delta_P$ 6.2 and −1.2, and 5.8 and −1.2, respectively). This can be explained by the steric effect of Cd; the average P—Cd distance 3.83 Å is longer than average P—Zn and P—Mg distances of 3.68 Å.

## Experimental

Compound (I) was prepared by the gel method (Kontturi *et al.*, 2004*c*) from $(C_5H_{10}NH_2)_2Cl_2C(PO_3Et)_2$ (0.13 mmol/0.45 ml $H_2O$, pH 5.8) and $Cd(NO_3)_2\cdot4H_2O$ (0.13 mmol/0.45 ml $H_2O$, pH 5.0) by mixing them together, followed by the addition of tetramethoxysilane (TMOS) [$V_{tot}(H_2O)$ = 0.9 ml, pH 5.2; *V*(TMOS) = 0.1 ml]. After the gel formation, acetone (1.0 ml) was added above the gel and (I) crystallized as colourless plate-like crystals. Analysis found for (I): C 13.0, H 3.60, Cd 24.5%; calculated for $C_5H_{16}CdCl_2O_9P_2$: C 12.9, H 3.47, Cd 24.2%. IR (KBr pellet, cm$^{-1}$, characteristic region): 1209 (*s*), 1114 (*s*), 1096 (*s*), 1049 (*bs*), 961 (*s*), 868 (*s*), 763 (*m*). $^{31}P$ CP/MAS NMR: $\delta_P$ 8.7 and 2.1. $^{113}Cd$ CP/MAS NMR: $\delta_{Cd}$ 4.4 and −9.0. TGA: 333–853 K, 42.1% ($C_5H_{16}Cl_2O_3$ 41.9%).

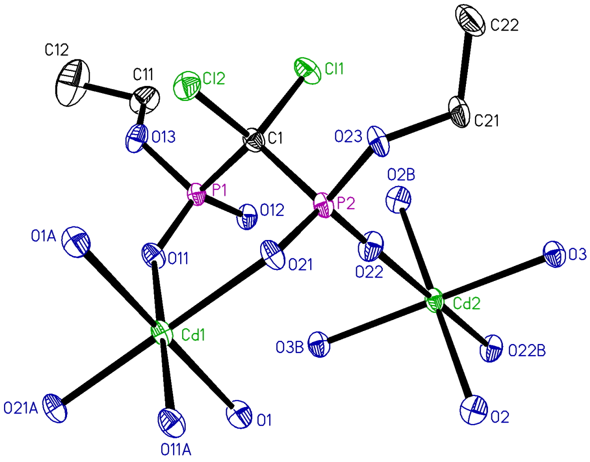


**Figure 1**
The structure of the asymmetric unit of (I), together with additional atoms to complete the coordination of cadmium, showing displacement ellipsoids at the 50% probability level and the atom-numbering scheme. Atoms labelled with the suffixes A and B are at the symmetry positions (−*x*, −*y*, 1 − *z*) and (1 − *x*, 1 − *y*, 1 − *z*), respectively. For clarity, H atoms have been omitted.

### *Crystal data*

$[Cd(C_5H_{10}Cl_2O_6P_2)(H_2O)_3]$
$M_r$ = 465.42
Triclinic, $P\overline{1}$
*a* = 7.5437 (2) Å
*b* = 8.5071 (2) Å
*c* = 11.8973 (4) Å
α = 97.4564 (12)°
β = 97.4929 (11)°
γ = 91.4131 (12)°
*V* = 749.92 (4) Å$^3$
*Z* = 2
$D_x$ = 2.061 Mg m$^{-3}$
$D_m$ = 2.03 (2) Mg m$^{-3}$
$D_m$ measured by flotation in cyclohexane/bromoform
Mo *K*α radiation
Cell parameters from 6546 reflections
θ = 2.4–27.5°
μ = 2.06 mm$^{-1}$
*T* = 150 (2) K
Thick plate, colourless
0.25 × 0.25 × 0.10 mm

### *Data collection*

Nonius KappaCCD diffractometer
φ scans and ω scans with κ offsets
Absorption correction: multi-scan (*XPREP* in *SHELXTL*; Bruker, 1998)
$T_{min}$ = 0.627, $T_{max}$ = 0.821
6546 measured reflections
3422 independent reflections
3041 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.017
$\theta_{max}$ = 27.5°
*h* = −9 → 9
*k* = −11 → 10
*l* = −15 → 15

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.072
*S* = 0.97
3422 reflections
177 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.2P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.57 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.86 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cd1—O21 | 2.2331 (17) | P1—O12 | 1.4968 (17) |
| Cd1—O11 | 2.2806 (16) | P1—O11 | 1.4979 (17) |
| Cd1—O1 | 2.3316 (17) | P1—O13 | 1.5747 (18) |
| Cd2—O22 | 2.2206 (17) | P1—C1 | 1.853 (2) |
| Cd2—O2 | 2.2847 (18) | P2—O22 | 1.4799 (18) |
| Cd2—O3 | 2.3124 (17) | P2—O21 | 1.4932 (18) |
| Cl1—C1 | 1.798 (2) | P2—O23 | 1.5797 (17) |
| Cl2—C1 | 1.788 (2) | P2—C1 | 1.864 (3) |
| | | | |
| Cl2—C1—Cl1 | 107.92 (12) | Cl2—C1—P2 | 108.36 (12) |
| Cl2—C1—P1 | 109.40 (12) | Cl1—C1—P2 | 109.91 (12) |
| Cl1—C1—P1 | 108.07 (12) | P1—C1—P2 | 113.06 (12) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1*A*···O12$^{i}$ | 0.85 | 2.15 | 2.925 (2) | 152 |
| O1—H1*B*···O3$^{ii}$ | 0.85 | 2.01 | 2.858 (2) | 179 |
| O2—H2*A*···Cl1$^{ii}$ | 0.85 | 2.76 | 3.4622 (19) | 141 |
| O2—H2*A*···O12$^{ii}$ | 0.85 | 2.33 | 2.906 (2) | 125 |
| O2—H2*B*···O23$^{iii}$ | 0.85 | 1.94 | 2.784 (2) | 170 |
| O3—H3*A*···O11$^{iv}$ | 0.85 | 1.94 | 2.761 (2) | 161 |
| O3—H3*B*···O12$^{ii}$ | 0.85 | 1.92 | 2.718 (3) | 157 |

Symmetry codes: (i) 1 − *x*, −*y*, 1 − *z*; (ii) 1 − *x*, 1 − *y*, 1 − *z*; (iii) −*x*, 1 − *y*, 1 − *z*; (iv) *x*, 1 + *y*, *z*.

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The H atoms of the ethyl groups were placed at calculated positions and those of the water molecules were located in difference maps, with C—H distances in the range 0.98–0.99 Å and O—H distances of 0.85 Å, and with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O,C).

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXL97*.

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