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Key indicators

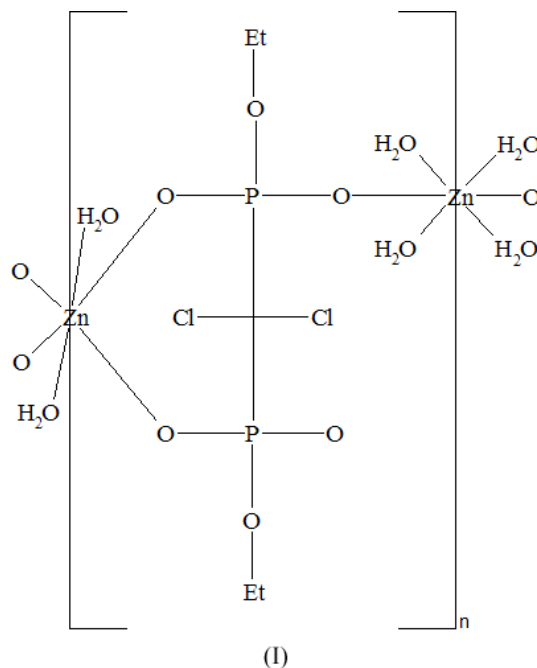
Single-crystal X-ray study
 $T = 120$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.020
 wR factor = 0.053
Data-to-parameter ratio = 18.0For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**catena-Poly[diacquazinc(II)- μ -(diethyl dichloro-
methylenebisphosphonato)- $\kappa^3\text{O},\text{O}':\text{O}''$ -tetraqua-
zinc(II)- μ -(diethyl dichloromethylenebisphos-
phonato)- $\kappa^3\text{O}:\text{O}',\text{O}''$]**The title structure, $[\text{Zn}(\text{C}_5\text{H}_{10}\text{Cl}_2\text{O}_6\text{P}_2)(\text{H}_2\text{O})_3]_n$, consists of one-dimensional chains. The structure is best described as centrosymmetric monomeric units consisting of octahedral Zn atoms with two symmetrically chelating $[\text{Cl}_2\text{C}(\text{PO}_3\text{Et})_2]^{2-}$ ligands, connected into polymeric chains along the [110] direction by further octahedral Zn atoms.

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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 bisphosphonates, including some Zn complexes of methylenebisphosphonate, $[\text{H}_2\text{C}(\text{PO}_3\text{H})_2]^{2-}$, and its analogues etidronate, $[(\text{CH}_3)(\text{HO})\text{C}(\text{PO}_3\text{H})_2]^{2-}$, and alendronate, $[(\text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_2)(\text{HO})\text{C}(\text{PO}_3\text{H})_2]^{2-}$, have been prepared and characterized (Serre & Férey, 2002; Barthelet *et al.*, 2000; Barthelet, Merlier *et al.*, 2002; Barthelet, Riou & Férey, 2002; Sergienko *et al.*, 1998, 2000; Song *et al.*, 2001; Dufau *et al.*, 1995).Previously, we reported the structures of Ca, Sr and Ba complexes of clodronate, $[\text{Cl}_2\text{C}(\text{PO}_3\text{H})_2]^{2-}$, 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 deriva-

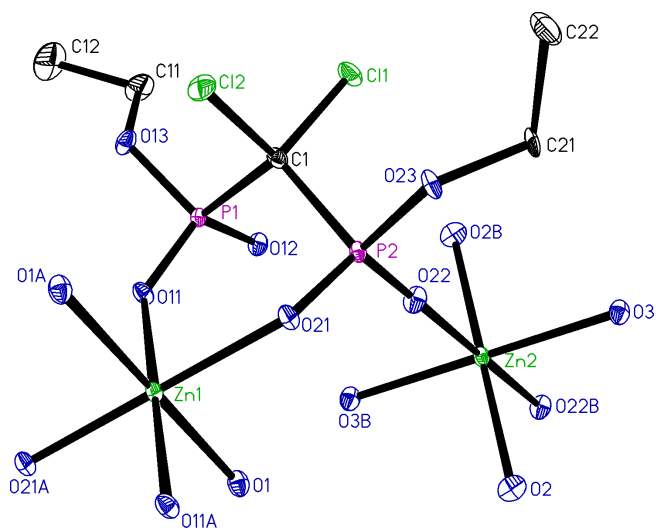


Figure 1
The structure of the asymmetric unit of (I), together with additional atoms to complete the coordination of zinc, showing displacement ellipsoids at the 50% probability level and the atom-numbering scheme. Atoms labelled with the suffixes A and B are at the symmetry positions $(-x, -y, 1-z)$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

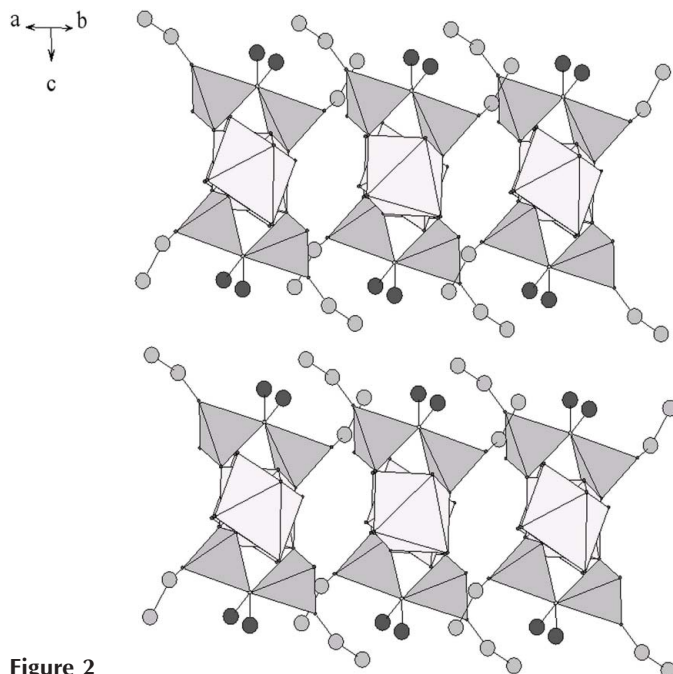


Figure 2
Packing of compound (I), along the [110] direction, showing the layer-like arrangement of the chains. Key: light grey octahedra: Zn; medium grey tetrahedra: phosphonate.

tives $[\text{Cl}_2\text{C}(\text{PO}_3\text{Et})_2]^{2-}$ and $[\text{Cl}_2\text{C}(\text{PO}_3\text{Pr}^i)_2]^{2-}$ (Kontturi *et al.*, 2002; Kontturi, Peräniemi *et al.*, 2005). The Zn and Cd complexes of clodronate and its diisopropyl ester derivative have also been prepared (Kontturi, Laurila *et al.*, 2005). We report here the preparation and crystal structure of the Zn complex $[\text{Zn}(\text{Cl}_2\text{CP}_2\text{O}_6\text{Et}_2)(\text{H}_2\text{O})_3]_n$, (I), of the diethyl ester derivative of clodronate.

The title compound is isomorphous with the previously reported Mg complex of the diethyl ester derivative of

clodronate (Kontturi *et al.*, 2002). The structure is best described as monomeric units consisting of octahedral Zn1 atoms with two symmetrically chelating $[\text{Cl}_2\text{C}(\text{PO}_3\text{Et})_2]^{2-}$ ligands, connected into polymeric chains along the [110] direction by octahedral Zn2 atoms. In the asymmetric unit, metal atoms Zn1 and Zn2 lie on centres of symmetry (Fig. 1), having Zn–O bond lengths of 2.057 (1)–2.154 (1) Å. The $[\text{Cl}_2\text{C}(\text{PO}_3\text{Et})_2]^{2-}$ ligands are chelated to Zn1, forming a six-membered chelate ring, and connected to atom Zn2 through one O atom. Thus, three of the four unsubstituted phosphonate O atoms of the $[\text{Cl}_2\text{C}(\text{PO}_3\text{Et})_2]^{2-}$ ligands are involved in metal coordination, the fourth being unbound.

In the crystal structure, one-dimensional chains are connected in a layer-like structure parallel to the (001) plane by O–H...O hydrogen bonds $[\text{O}\cdots\text{O} = 2.6895(17)\text{--}2.9749(17)\text{ Å}]$ and O–H...Cl hydrogen bonds $[\text{O}\cdots\text{Cl} = 3.3723(13)\text{ Å}]$ (Table 2), with the ethyl groups pointing into the space between these layers (Fig. 2).

Experimental

The title compound was prepared by the gel method (Kontturi *et al.*, 2004c) by mixing $(\text{C}_5\text{H}_{10}\text{NH}_2)_2\text{Cl}_2\text{C}(\text{PO}_3\text{Et})_2$ (0.25 mmol/0.45 ml H_2O , pH 5.8) and $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.50 mmol/0.45 ml H_2O , pH 4.4). In addition, tetramethoxysilane (TMOS) was added [$V_{\text{tot}}(\text{H}_2\text{O}) = 0.9\text{ ml}$, pH 4.7; $V(\text{TMOS}) = 0.1\text{ ml}$]. After the gel formation, acetone (1.0 ml) was added above the gel and the compound crystallized as colourless plates. Analysis found for (I): C 14.4, H 3.90, Zn 15.4%; calculated for $\text{C}_5\text{H}_{16}\text{Cl}_2\text{O}_9\text{P}_2\text{Zn}$: C 14.4, H 3.85, Zn 15.6%. IR (KBr pellet, cm^{-1} , characteristic region): 1244 (s), 1209 (s), 1130 (s), 1059 (bs), 1021 (s), 962 (s), 868 (s), 764 (s). ^{31}P -CP/MAS NMR: δ_P 6.2 and -1.2 . TGA: 323–863 K 47.0% ($\text{C}_5\text{H}_{16}\text{Cl}_2\text{O}_3$ 46.6%).

Crystal data

$[\text{Zn}(\text{C}_5\text{H}_{10}\text{Cl}_2\text{O}_6\text{P}_2)(\text{H}_2\text{O})_3]$
 $M_r = 418.39$
 Triclinic, $P\bar{1}$
 $a = 7.3809(1)\text{ Å}$
 $b = 8.3383(1)\text{ Å}$
 $c = 11.8498(2)\text{ Å}$
 $\alpha = 94.659(1)^\circ$
 $\beta = 97.724(1)^\circ$
 $\gamma = 93.244(1)^\circ$
 $V = 718.597(18)\text{ Å}^3$
 $Z = 2$
 $D_x = 1.934\text{ Mg m}^{-3}$

$D_m = 1.90(1)\text{ Mg m}^{-3}$
 D_m measured by flotation in cyclohexane/bromofrom
 Mo $K\alpha$ radiation
 Cell parameters from 13 591 reflections
 $\theta = 2.5\text{--}27.0^\circ$
 $\mu = 2.34\text{ mm}^{-1}$
 $T = 120(2)\text{ K}$
 Plate, colourless
 $0.20 \times 0.15 \times 0.08\text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ scans and ω scans with κ offsets
 Absorption correction: multi-scan (XPREP in SHELXTL; Bruker, 1998)
 $T_{\text{min}} = 0.652$, $T_{\text{max}} = 0.835$
 13 591 measured reflections

3136 independent reflections
 2852 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$
 $\theta_{\text{max}} = 27.0^\circ$
 $h = -8 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.053$
 $S = 1.07$
 3136 reflections
 174 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0245P)^2 + 0.3604P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.46\text{ e Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.55\text{ e Å}^{-3}$

Table 1
Selected geometric parameters (Å, °).

Zn1—O21	2.0568 (11)	P1—O11	1.4959 (12)
Zn1—O11	2.1043 (11)	P1—O12	1.4982 (12)
Zn1—O1	2.1535 (12)	P1—O13	1.5757 (12)
Zn2—O22	2.0580 (12)	P1—C1	1.8517 (16)
Zn2—O2	2.0902 (12)	P2—O22	1.4829 (12)
Zn2—O3	2.1154 (12)	P2—O21	1.4937 (12)
Cl1—C1	1.7947 (16)	P2—O23	1.5813 (11)
Cl2—C1	1.7874 (17)	P2—C1	1.8655 (17)
Cl2—C1—Cl1	108.03 (9)	Cl2—C1—P2	108.30 (8)
Cl2—C1—P1	109.76 (9)	Cl1—C1—P2	110.57 (9)
Cl1—C1—P1	109.05 (8)	P1—C1—P2	111.08 (8)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1B \cdots O12 ⁱ	0.85	2.11	2.9293 (16)	161
O1—H1A \cdots O3 ⁱⁱ	0.87	2.11	2.9377 (17)	160
O2—H2A \cdots Cl1 ⁱⁱ	0.85	2.79	3.3723 (13)	128
O2—H2A \cdots O12 ⁱⁱ	0.85	2.22	2.9749 (17)	149
O2—H2B \cdots O23 ⁱⁱⁱ	0.85	1.89	2.7348 (16)	174
O3—H3B \cdots O11 ^{iv}	0.85	2.04	2.8194 (16)	153
O3—H3A \cdots O12 ⁱⁱ	0.85	1.84	2.6895 (17)	176

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

H atoms of the ethyl groups were placed in calculated positions, with C—H distances of 0.99 (methylene) and 0.98 Å (methyl). They were included in the refinement in a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. H atoms of the aqua ligands were located in difference maps and placed at optimized positions, with O—H distances of ~ 0.85 Å, using a riding-model approximation with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The position of atom H1A was not optimized, since the original O—H distance was close to the ideal value of 0.85 Å.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduc-

tion: *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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