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Structures of Bisphosphonate Metal Complexes: Zinc and Cadmium Complexes of Clodronate and Its Partial Ester Derivatives

Mervi Kontturi,*,[†] Elina Laurila,[†] Riikka Mattsson,[†] Sirpa Peräniemi,[‡] Jouko J. Vepsäläinen,[‡] and Markku Ahlgrén[†]

Departments of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101 Joensuu, Finland, and University of Kuopio, P.O. Box 1627, FIN-70211 Kuopio, Finland

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Four new zinc and cadmium bisphosphonates $[\{NaZn(Cl_2CP_2O_6H)(H_2O)_5\}]_n$ (**1**), $[\{Cd_2(Cl_2CP_2O_6)(H_2O)_4\}\cdot H_2O]_n$ (**2**), $[\{Zn(Cl_2CP_2O_6Pr^i{}_2)(H_2O)_3\}\cdot H_2O]_n$ (**3**), and $[\{Cd_2(Cl_2CP_2O_6Pr^i{}_2)_2(MeOH)_2(H_2O)_2\}\cdot H_2O]_2$ (**4**) have been prepared and their crystal structures determined by single-crystal X-ray diffractometry. Two bisphosphonate ligands were used: clodronate, (dichloromethylene)bis(phosphonate) and its symmetrical *P*,*P*′-diisopropyl ester derivative. The structure of the Zn complex **1** is three-dimensional, consisting of one-dimensional Zn–clodronate chains connected to the three-dimensional network by Na^+ ions. The structure of Cd complex **2** consists of double layers, and a unique bond was found between the Cd^{2+} cation and a Cl atom of clodronate. Zn complex **3** consists of one-dimensional chains, but the binding of the bisphosphonate ligands is unique: in **3** the bisphosphonate ligand is only bidentate. Compound **4** is a tetramer, and hydrogen bonds hold the tetramers together, forming a layered structure.

Introduction

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.[1−4] To study the solid materials, several metal complexes of bisphosphonates, including Zn and Cd complexes, have been prepared and characterized. Usually, the structures are polymeric consisting of chains, layers, pillared layers, or three-dimensional networks, but monomeric structures have also been found.[5−21] The structural properties are dependent on the length and rigidity of the organic group connected to the phosphonate groups and on the number of donor atoms and degree of protonation of the phosphonate group.[1−4] To affect these properties, organic templates are also used in the preparation of complexes. In

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* Author to whom correspondence should be addressed. E-mail: mervi.kontturi@joensuu.fi. Tel.: +358-13-251 3377. Fax: +358-13-251 3390.

[†] University of Joensuu.

[‡] University of Kuopio.

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the case of methylenebis(phosphonate) MBP, $[H_2C(PO_3H)_2]^{2-}$, and its analogues etidronate, $[(CH_3)(HO)C(PO_3H)_2]^{2-}$, and alendronate, $[(NH_3CH_2CH_2CH_2)(HO)C(PO_3H)_2]^{2-}$, some Zn and Cd complexes have already been reported.[14−21]

Previously, we reported the structures of polymeric Ca and Ba complexes[22,23] and a monomeric Sr complex[24] of clodronate, $[Cl_2C(PO_3H)_2]^{2-}$, as well as alkaline earth metal complexes of *P*,*P*′-diethyl (dichloromethylene)bis(phosphonate), $[Cl_2C(PO_3Et)_2]^{2-}$,[25] and Mg and Ca complexes of *P*,*P*′-diisopropyl (dichloromethylene)bis(phosphonate), $[Cl_2C(PO_3Pr^i)_2]^{2-}$.[26] The results showed that clodronate and its ester derivatives produce both molecular and polymeric structures with metals, and moreover, the structures of the metal complexes indicate that the dimensionalities of the structures decrease with increasing size of the alkyl substituent.[22−23,25−26] We have also succeeded to prepare Zn and Cd complexes of the diethyl ester derivative of clodronate, and the structures proved to be one-dimensional chains and isomorphous with the Mg complex of the same ligand.[27] Here we report the structures of the Zn and Cd complexes of clodronate $[\{NaZn(Cl_2CP_2O_6H)(H_2O)_5\}]_n$ (**1**) and $[\{Cd_2(Cl_2CP_2O_6)(H_2O)_4\}\cdot H_2O]_n$ (**2**) and the Zn and Cd complexes of the *P*,*P*′-diisopropyl (dichloromethylene)bis(phosphonate) $[\{Zn(Cl_2CP_2O_6Pr^i{}_2)(H_2O)_3\}\cdot H_2O]_n$ (**3**) and $[\{Cd_2(Cl_2CP_2O_6Pr^i{}_2)_2(MeOH)_2(H_2O)_2\}\cdot H_2O]_2$ (**4**).

Experimental Section

Materials and Methods. Reagents used for the synthesis and characterization of compounds **1**−**4** were analytical reagent grade. Infrared spectra were recorded on a Nicolet Magna-IR spectrometer 750 with the KBr pellet technique. ^{31}P- and ^{113}Cd-CP/MAS NMR experiments were performed at 161.98 MHz (^{31}P) and 88.74 MHz (^{113}Cd) on a Bruker AMX 400 spectrometer equipped with a double-tuned Bruker MAS 400 SB-BL 7 probe. The ^{31}P-MAS NMR experiment for **2** was measured at 109.36 MHz on a Chemagnetics CMX Infinity 270 spectrometer. The external standards were hydroxyapatite, sturyldiphenylphosphine (for **2**), and $Cd(NO_3)_2\cdot 4H_2O = -100.0$ ppm. Thermal analyses were performed in a nitrogen atmosphere at a temperature range of 25−700 °C with a heating rate of 5 °C/min on a Mettler Toledo TGA/SDTA851^e thermobalance.

Preparation of Compounds 1−**4.** Syntheses and characterization of the disodium salts of clodronate $Na_2[CCl_2(PO_3H)_2]\cdot 4H_2O$ and its diisopropyl ester derivative $Na_2[Cl_2C(PO_3Pr^i)_2]$ have been reported earlier.[28−30] The Zn and Cd complexes of these compounds were crystallized using gel method A or B. In method A, bisphosphonate and metal salt are dissolved in water separately and warmed to 40 °C in a water bath. Certain portions of the solutions are then mixed together, and if necessary, the pH is adjusted with 0.02−1.0 M NaOH. The tetramethoxysilane (TMOS, 10−20 vol %) is added, the two-phase system is shaken until homogeneous, and the emulsion is left to form a gel. Then a precipitant, acetone, is added above the gel. In method B, only the bis(phosphonate) is placed into the gel, and the metal is offered as a metal salt solution of known concentration by placing it above the gel. If needed, a pure TMOS-gel layer (0.5 mL, 20% v/v) can be added between the native gel and the precipitant (method A) or metal salt solution (method B) to slow the crystallization.

Compound **1** was prepared from $Na_2[CCl_2(PO_3H)_2]\cdot 4H_2O$ (0.015 mmol/0.40 mL of H_2O, pH 4.3) and $Zn(NO_3)_2\cdot 6H_2O$ (0.030 mmol/0.40 mL of H_2O, pH 4.5) using method A [$V_{tot}(H_2O) = 0.8$ mL, pH 2.5; V(TMOS) = 0.2 mL]. A solution of acetone and water (1:1, 1.0 mL) was used as the precipitant, and the colorless, slatelike crystals were formed above the gel. Anal. Found (calcd) for $CH_{11}Cl_2NaO_{11}P_2Zn$, **1**: C, 2.96 (2.86); H, 2.50 (2.64); Zn, 15.7 (15.6); Na 5.58 (5.47). IR (KBr pellet, cm^{-1}, characteristic region): 1146 s, 1085 m, 1001 s, 930 s b, 804 s, 760 s, 661 s, 631 s. ^{31}P-CP/MAS NMR: δ_P 11.9 and 10.1 ppm. TGA: 30−210 °C, 21.0% (5H_2O, 21.4%); 210−670 °C, 20.3% (2Cl, C, H, 20.0%).

Compound **2** was prepared from $Na_2[CCl_2(PO_3H)_2]\cdot 4H_2O$ (0.006 mmol/0.45 mL of H_2O, pH 4.5) and $Cd(NO_3)_2\cdot 4H_2O$ (0.011 mmol/0.45 mL of H_2O, pH 4.7) using method A with a pH adjustment [$V_{tot}(H_2O) = 0.9$ mL, pH adjusted from 3.0 to 3.9−4.2; V(TMOS) = 0.1 mL]. A pure TMOS-gel layer [$V(H_2O) = 0.45$ mL, V(TMOS) = 0.05 mL] was used between the gel and the precipitant acetone ($V = 1.0$ mL). The colorless, slatelike crystals formed above the gel. Anal. Found (calcd) for $CH_{10}Cd_2Cl_2O_{11}P_2$, **2**: C, 2.11 (2.16); H, 1.81 (1.81); Cd, 40.2 (40.5). IR (KBr pellet, cm^{-1}, characteristic region): 1120 vs b, 1089 vs, 1012 s, 978 s, 866 m, 750 m. ^{31}P-CP/MAS NMR: δ_P 14.3 and 10.8 ppm. ^{113}Cd-CP/MAS NMR: δ_{Cd} 28.3 and 17.4 ppm. TGA: 30−170 °C, 16.5% (5H_2O, 16.2%); 170−590 °C, 14.9% (2Cl, C, 14.9%).

Compound **3** was prepared with method B, placing the $Na_2[Cl_2C(PO_3Pr^i)_2]$ (0.15 mmol/0.90 mL of H_2O, pH 6.8) in the gel [V(TMOS) = 0.1 mL]. A pure TMOS-gel layer was added above the original gel [$V(H_2O) = 0.45$ mL, V(TMOS) = 0.05 mL]. After gel formation, $Zn(NO_3)_2\cdot 6H_2O$ was added above the gel layers as a metal salt solution (6.2 mmol/1.0 mL of H_2O, pH 3.0). The colorless, platelike crystals formed on the gel−liquid border. Anal. Found (calcd) for $C_7H_{22}Cl_2O_{10}P_2Zn$, **5**: C, 18.2 (18.1); H, 4.42 (4.77); Zn, 13.7 (14.1). IR (KBr pellet, cm^{-1}, characteristic region): 1248 s, 1203 vs, 1126 vs, 1081 s, 1011 s, 897 m, 868 m, 828 m, 770 w, 746 w. ^{31}P-CP/MAS NMR: δ_P 4.7 and 0.2 ppm. TGA: 40−130 °C, 15.5% (4H_2O, 15.5%); 130−600 °C, 36.2% (2Pr^i, 2Cl, C, 36.4%).

Compound **4** was prepared from $Na_2[Cl_2C(PO_3Pr^i)_2]$ (0.16 mmol/0.40 mL of H_2O, pH 7.0) and $Cd(NO_3)_2\cdot 4H_2O$ (0.16 mmol/0.40 mL of H_2O, pH 5.5) with method A [$V_{tot}(H_2O) = 0.8$ mL; pH 5.0; V(TMOS) = 0.2 mL]. Acetone ($V = 1.0$ mL) was used as the precipitant, and the colorless crystals formed in the gel in the shape of diamonds. Anal. Found (calcd) for $C_{32}H_{84}Cd_4Cl_8O_{34}P_8$, **6**: C, 19.2 (19.3); H, 4.36 (4.25); Cd, 22.8 (22.6). IR (KBr pellet, cm^{-1}, characteristic region): 1228 b vs, 1175 m, 1145 m, 1122 s, 1087 vs, 990 vs, 890 m, 855 m, 752 w, 738 w.

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Table 1. Crystallographic and Structure Refinement Data for **1**−**4**

	1	**2**	**3**	**4**
formula	$CH_{11}Cl_2NaO_{11}P_2Zn$	$CH_{10}Cd_2Cl_2O_{11}P_2$	$C_7H_{22}Cl_2O_{10}P_2Zn$	$C_{32}H_{84}Cd_4Cl_8O_{34}P_8$
fw	420.30	555.73	464.46	1993.95
cryst system	orthorhombic	triclinic	triclinic	monoclinic
space group	Pnma	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
T, K	120(2)	120(2)	150(2)	150(2)
a, Å	7.8054(1)	5.6551(2)	7.0256(2)	13.9504(1)
b, Å	14.1138(2)	9.5290(2)	9.5328(3)	12.3418(1)
c, Å	11.2885(2)	12.3693(4)	14.3501(3)	21.0920(2)
α, deg		78.056(2)	75.735(1)	
β, deg	90	82.530(2)	83.738(2)	94.1647(4)
γ, deg		74.997(2)	71.109(2)	
V, Å^3	1243.58(3)	627.83(3)	880.82(4)	3621.88(5)
Z	4	2	2	2
ρ_{obsd}, g cm^{-3} [a]	2.20(5)	2.90(4)	1.72(1)	1.79(2)
ρ_{calcd}, g cm^{-3}	2.24	2.94	1.75	1.83
μ(Mo Kα), mm^{-1}	2.743	4.113	1.920	1.709
F(000)	840	528	476	1992
cryst size, mm^3	0.15 × 0.15 × 0.15	0.25 × 0.25 × 0.05	0.30 × 0.20 × 0.03	0.15 × 0.15 × 0.15
θ range, deg	2.89−26.00	3.05−25.49	4.13−26.00	1.91−26.00
reflcns collcd	16 566	10 689	9149	54 179
unique reflcns	1274	2335	3419	7102
R_{int}	0.0572	0.0796	0.0549	0.0370
R_1 [b]	0.0435	0.0324	0.0357	0.0239
wR_2 [c]	0.0951	0.0859	0.0892	0.0602
GOF on F^2	1.194	1.077	1.047	1.072

[a] Measured by flotation at room temperature. [b] $R_1 = [\Sigma||F_o| - |F_c||]/[\Sigma|F_o|]$ $[I \geq 2\sigma(I)]$. [c] $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$ (all data).

^{31}P- CP/MAS NMR: δ_P 9.0, 5.8 and 1.6 ppm. ^{113}Cd-CP/MAS NMR: δ_{Cd} 3.2, 0.9, −12.7 and −17.6 ppm. TGA: 40−95 °C, 12.1% (3H_2O, 2MeOH, 11.8%); 95−590 °C, 34.0% (2Pr^i, 2Cl, C, 33.9%).

Single-Crystal X-ray Diffraction. Single crystals were used for structural determinations on a Nonius Kappa CCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å). Denzo and Scalepack programs were used for cell refinements and data reduction.[31] The structures were solved using direct methods with SHELXS 97, and structural refinements were carried out with SHELXL 97.[32] Crystallographic data are summarized in Table 1. The hydrogen atoms of the isopropyl groups were placed at calculated positions, and the hydrogen atoms of the water molecules and hydroxyl groups were placed from the difference maps with $U_{iso}(H) = 1.5U_{eq}(O)$. The aqua ligand O3 in **1** is disordered (70/30), and no allowance was made for the H atoms of the O3′.

Results

The compounds were characterized with single-crystal X-ray analysis, and spectral properties were determined in IR and ^{31}P and ^{113}Cd CP/MAS NMR studies. The IR spectra of all compounds showed a series of strong bands in the 1300−900 cm^{-1} region, which were attributed to the stretching vibrations of the phosphonate PO_3 groups; for the metal complexes of clodronate **1** and **2**, this region was narrower. In all spectra there were also two bands in the 870−740 cm^{-1} region, which might be attributed to the asymmetric and symmetric ν(P−C−P) vibrations. Broad bands around 3000 cm^{-1} caused by the O−H stretching vibrations indicated the presence of water molecules. Moreover, protonated phosphonate oxygen atoms in **1** and methanol molecules in **4** exhibited bands in the same area. In the spectra of **3** and **4** there were bands caused by the isopropyl groups in the 1485−1442 and 1390−1362 cm^{-1} regions.

^{31}P CP/MAS NMR spectra can be explained on the basis of the X-ray crystal structures of the compounds. In **1** the P atoms of the phosphonate groups are in different chemical environments, due to the partly protonated O atoms and the Na$^+$ ions occupying the every second crystallographic place, affording two partly overlapping signals at 11.9 and 10.1 ppm. For **2**, two signals at 14.3 and 10.8 ppm were observed due to the different environments of the P atoms: one phosphonate group is coordinated to three Cd^{2+} cations and the other to four Cd^{2+} cations. In compound **3** both phosphonate groups are coordinated to one Zn^{2+} cation, but the environments are different due to a lattice water molecule, which is closer to P1 (4.63 Å) than to P2 (6.65 Å) and causes distortion in the isopropyl group of P1; two signals at 4.7 and 0.2 ppm were also observed.

Compound **4** has a structure different from that of the previous structures, **1**−**3**, since it contains two independent ligands, and three chemical shifts were found at 9.0, 5.8 and 1.6 ppm (intensities 2:1:1). According to the X-ray structure, the phosphonate groups of ligand 1 are identical, being coordinated to Cd1 and Cd2. On the other hand, phosphorus atoms of ligand 2 are in unequal environments since one phosphonate group is coordinated to two different metal cations, Cd1 and Cd2, while the other is only coordinated to Cd1. The structural results were also verified using ^{113}Cd-NMR spectroscopy. The observed results were expected: compounds **2** and **4** have two different Cd^{2+} cations. Due to second-order effects and complex couplings to neighboring atoms, the fine structures of the ^{113}Cd NMR spectra were difficult to assign.

The thermal stability of compounds **1**−**4** was studied with thermogravimetry. Analysis showed that in each case the

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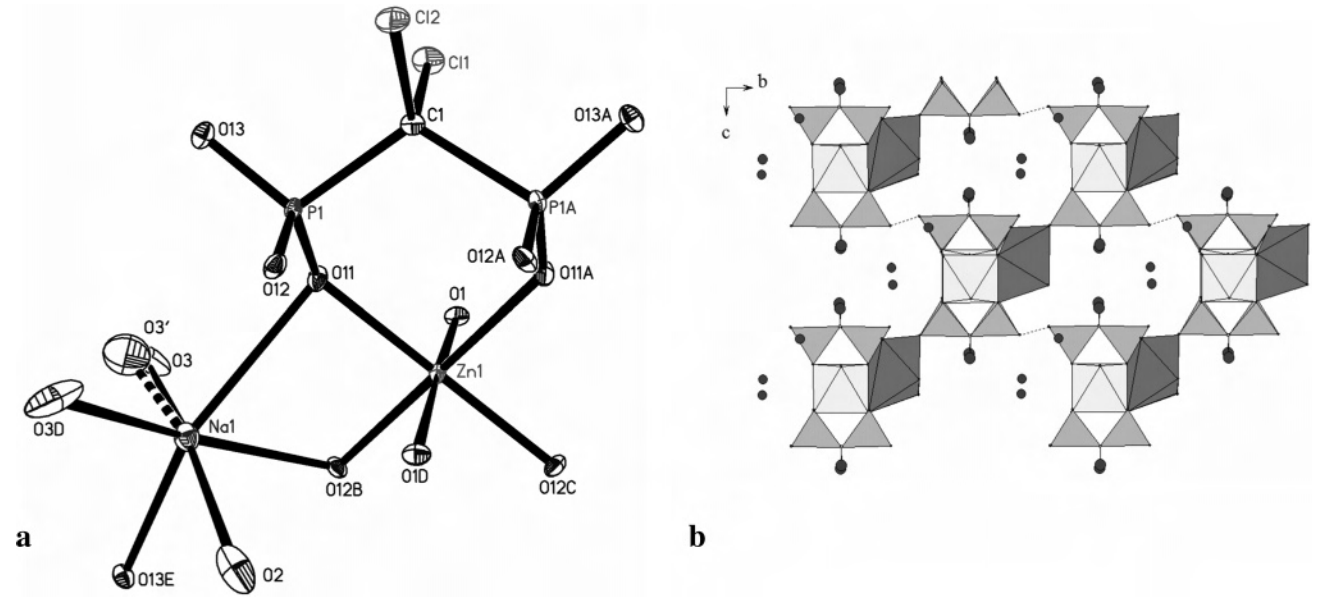

Figure 1. (a) Structure of **1** with thermal ellipsoids (50%) and numbering scheme and (b) a layerlike presentation (along the *bc*-plane) of the packing of **1** in the direction of the *a*-axis (light gray octahedron, Zn; medium gray tetrahedron, phosphonate; dark gray octahedron, Na). For clarity, hydrogen atoms are omitted. Atoms labeled with the suffixes A−E are at the following respective symmetry positions: *x*, 1.5 − *y*, *z*; *x* + 0.5, *y*, 0.5 − *z*; *x* + 0.5, 1.5 − *y*, 0.5 − *z*; *x* − 0.5, *y*, 0.5 − *z*; 0.5 − *x*, 1 − *y*, *z* + 0.5.

Table 2. Selected Bond Distances (Å) for **1** and **2**[a]

compd **1**				compd **2**			
Zn1−O12A	2.041(3)	Na1−O3	2.272(7)	Cd1−O11	2.273(3)	Cd2−Cl2	2.940(1)
Zn1−O11	2.062(3)	Na1−O2	2.309(5)	Cd1−O23A	2.285(3)	Cd2−O13	2.235(3)
Zn1−O1	2.218(4)	Na1−O12A	2.360(4)	Cd1−O1	2.293(3)	Cd2−O21	2.367(3)
		Na1−O13E	2.367(4)	Cd1−O2	2.317(3)	Cd2−O12B	2.194(3)
		Na1−O3B	2.542(7)	Cd1−O3	2.249(3)	Cd2−O22B	2.214(3)
		Na1−O11	2.713(5)	Cd1−O4	2.283(3)	Cd2−O21C	2.231(3)

[a] Symmetry transformations used to generate equivalent atoms for **1**: A, *x* + 0.5, *y*, 0.5 − *z*; B, *x* − 0.5, *y*, 0.5 − *z*; C, *x*, 1.5 − *y*, *z*; D, *x* + 0.5, 1.5 − *y*, 0.5 − *z*; E, 0.5 − *x*, 1 − *y*, *z* + 0.5. Symmetry transformations for **2**: A, *x*, *y* − 1, *z*; B, *x* + 1, *y*, *z*; C, 1 − *x*, 1 − *y*, 1 − *z*.

decomposition process took place in two steps. The first loss of weight occurred at about 30−200 °C for **1** and **2** and at about 40−120 °C for **3** and **4**, due to the evaporation of water molecules and in the case of **4** also to evaporation of methanol molecules. The second observed loss of weight contained several overlapping steps, beginning at around 200 °C for **1** and **2** and at around 120 °C for **3** and **4**. This was related to the loss of Cl atoms in **1** and **2** and to loss of Cl atoms and alkyl groups in **3** and **4**. The decomposition process terminated at about 700 °C by the loss of the carbon atoms, and the results indicate that the final residues were metal polyphosphates $M(PO_3)_2$.

Description of Structure 1. The structure of **1**, $[\{NaZn(Cl_2CP_2O_6H)(H_2O)_5\}]_n$, is best described as one-dimensional chains of Zn^{2+} cations and $Cl_2CP_2O_6H^{3-}$ and aqua ligands, connected to a three-dimensional network by Na^+ cations located between the chains. In the asymmetric unit (Figure 1a), there is one octahedral Zn^{2+} cation located on a mirror plane, having Zn−O distances of 2.042(3)−2.246(4) Å (Table 2). Two $Cl_2CP_2O_6H^{3-}$ ligands chelate to Zn^{2+} in trans-positions, and the remaining two axial sites are occupied by μ-aqua ligands; both $Cl_2CP_2O_6H^{3-}$ and aqua ligands connect Zn^{2+} to adjacent Zn^{2+} cations. The Na^+ ions, originating from the disodium clodronate, occupy every second crystallographic site, leaving additional space within the structure. The Na^+ ions are in an octahedral environment, being coordinated by three O atoms of three different $Cl_2CP_2O_6H^{3-}$ ligands and three aqua ligands [Na−O = 2.264(7)−2.714(4) Å], one of them, O3, being disordered (70/30). The $Cl_2CP_2O_6H^{3-}$ ligand is coordinated to metal cations, providing four O atoms: it forms two six-membered chelate rings with Zn^{2+} cations and acts as mono- and triatomic bridges between Zn^{2+} and Na^+ cations. The remaining two O atoms are partly protonated: adjacent $Cl_2CP_2O_6H^{3-}$ ligands share one hydrogen atom, positioned between two oxygen atoms with a very short O···O distance, 2.459(6) Å. There are also intramolecular hydrogen bonds in the structure, O···O distances being 2.656(4)−3.015(4) Å and the angles 143−163°. The three-dimensional network carries channels in the direction of the *a*-axis, as presented in the packing diagram, Figure 1b.

Description of Structure 2. Compound **2**, $[\{Cd_2(Cl_2CP_2O_6)(H_2O)_4\}\cdot H_2O]_n$, consists of Cd^{2+} cations, $Cl_2C(PO_3)_2{}^{4-}$ and aqua ligands connected to double layers parallel to the (001) plane. In the asymmetric unit there are two crystallographically independent Cd^{2+} cations (Figure 2a), both having distorted octahedral geometry. The binding sites around Cd1 are occupied by two phosphonate O atoms and four aqua ligands, the Cd−O bond lengths being 2.248(3)−2.317(5) Å (Table 2). The coordination sphere of Cd2 consists of three $Cl_2C(PO_3)_2{}^{4-}$ ligands: one is coordinated monodentally, the other one is chelated forming a six-

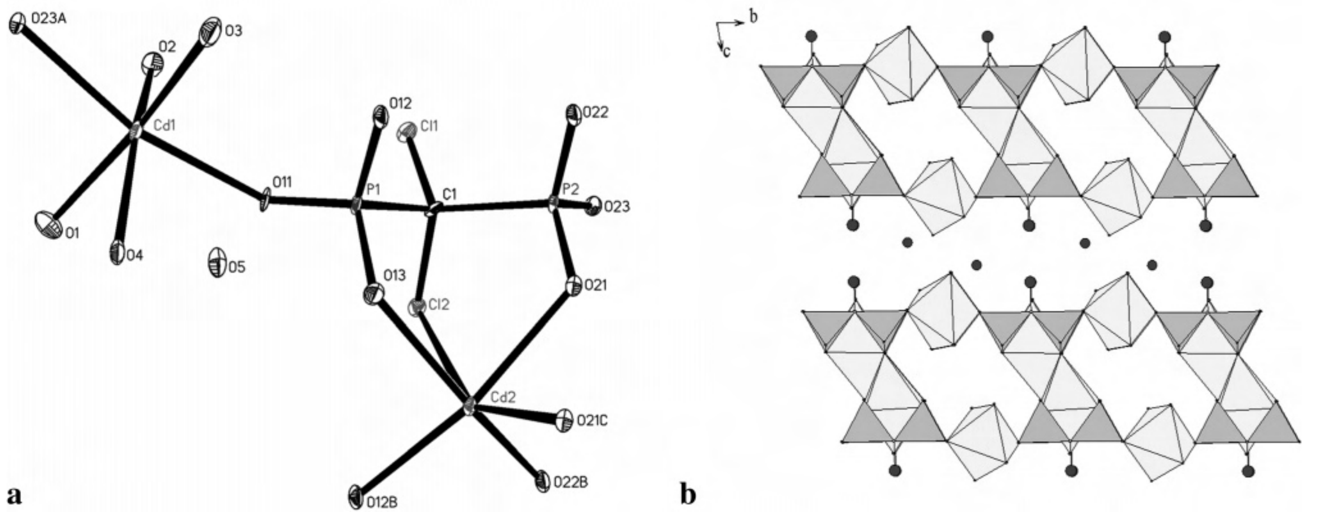

Figure 2. (a) Asymmetric unit of **2** with thermal ellipsoids (50%) and the numbering scheme and (b) packing of the layers of **2** in the direction of the *a*-axis (light gray octahedron, Cd; medium gray tetrahedron, phosphonate). Atoms labeled with the suffixes A−C are at the following respective symmetry positions: $x, y - 1, z$; $-x, 1 - y, 1 - z$; $1 - x, 1 - y, 1 - z$. For clarity, hydrogen atoms are omitted.

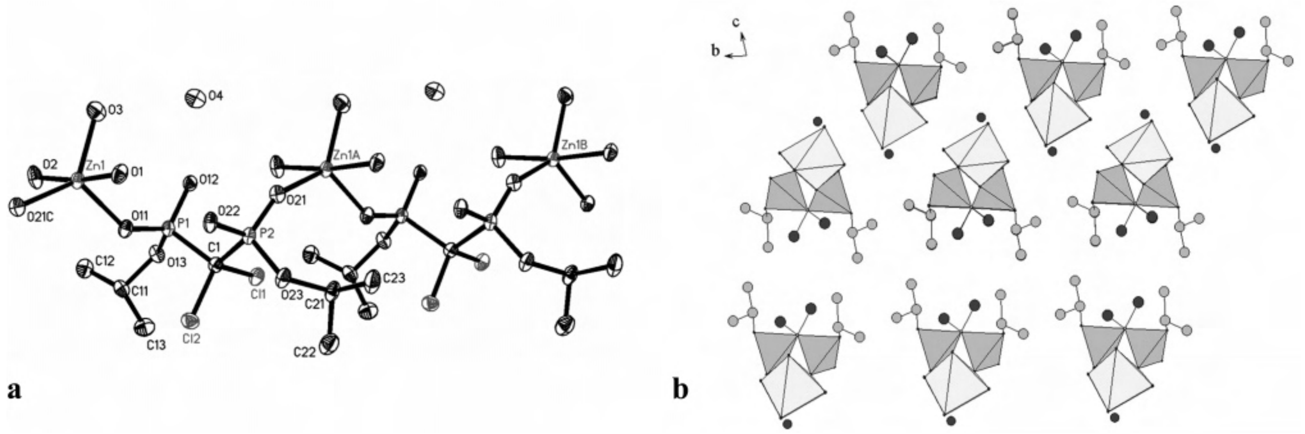

Figure 3. (a) Part of the chain structure of **3** with thermal ellipsoids (50%) and numbering scheme and (b) packing of **3** (light gray octahedron, Zn; medium gray tetrahedron, phosphonate) in the direction of the *a*-axis. For clarity, hydrogen atoms are omitted. Atoms labeled with the suffixes A and C are at the symmetry positions $x - 1, y, z$ and $x + 1, y, z$, respectively.

membered chelate ring, and the third one is chelated by two O atoms and one chlorine atom, forming five- and six-membered chelate rings. The Cd−Cl(C) bond is unique and has not been reported previously. The Cd2−O bond distances are 2.194(3)−2.367(3) Å, and the Cd2−Cl2 bond distance is 2.940(1) Å. On the other hand, there is only one type of $Cl_2C(PO_3)_2^{4-}$ ligand in the structure of **2**, this ligand being coordinated to five Cd^{2+} cations through six O atoms and one Cl atom, acting as a chelating and bridging ligand. The P−O(Cd) bond distances are normal at 1.514(3)−1.530(3) Å, and no noticeable change is observed in the C−Cl2 distance of the coordinated Cl2 atom. The double layers of **2** are held together by hydrogen bonds, the O···O distances being 2.700(4)−2.871(5) Å (angles 144−175°). There are channels within the layers and a void between the layers, as presented in Figure 2b.

Description of Structure 3. Compound **3**, $[\{Zn(Cl_2CP_2O_6Pr^i_2)(H_2O)_3\}\cdot H_2O]_n$, consists of Zn^{2+} cations, $Cl_2C(PO_3Pr^i)_2^{2-}$ and aqua ligands, and lattice water molecules connected to infinite polymeric chains along the [100] direction. The Zn^{2+} cation is five-coordinated by two $Cl_2C(PO_3Pr^i)_2^{2-}$ ligands and three aqua ligands (Figure 3a). The Zn−O bond lengths are 1.965(2)−2.092(2) Å (Table 3), and the Zn^{2+} cation adopts a trigonal bipyramidal geometry. The $Cl_2C(PO_3Pr^i)_2^{2-}$ ligand is coordinated to two Zn^{2+} cations, providing only one O atom to each. The polymeric chains of **3** are connected by hydrogen bonds [O···O 2.682(3)−2.920(3) Å, 137−172°] to a layerlike construction along the (001) plane, isopropyl groups pointing to the interlayer section (Figure 3b). The void between the layers is small, as the isopropyl groups fill the space.

Table 3. Selected Bond Distances (Å) for **3** and **4**[a]

compd 3		compd 4			
Zn1−O11	1.964(2)	Cd1−O11	2.246(2)	Cd2−O12	2.276(2)
Zn1−O21C	2.004(2)	Cd1−O21	2.211(2)	Cd2−O22	2.274(2)
Zn1−O1	2.091(2)	Cd1−O31	2.449(2)	Cd2−O32	2.230(2)
Zn1−O2	2.031(2)	Cd1−O1	2.284(2)	Cd2−O2	2.288(2)
Zn1−O3	2.011(3)	Cd1−O31A	2.318(2)	Cd2−O3	2.290(2)
		Cd1−O41A	2.232(2)	Cd2−O4	2.285(2)

[a] Symmetry transformations used to generate equivalent atoms: for **3** (C), $x + 1, y, z$; for **4** (A), $-x, 1 - y, -z$.

Description of Structure 4. Compound **4**, $[\{Cd_2(Cl_2CP_2O_6Pr^i_2)_2(MeOH)_2(H_2O)_2\}\cdot H_2O]_2$, consists of tetramers

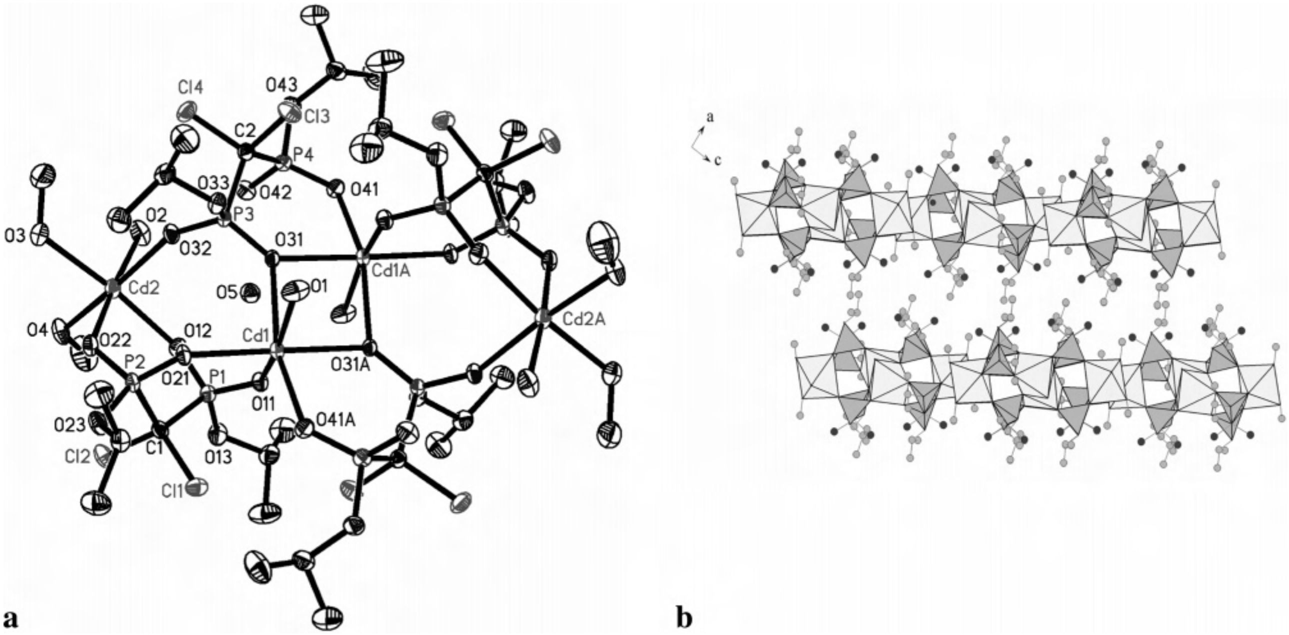

Figure 4. (a) Structure of the tetramer of compound **4** with thermal ellipsoids (50%) and numbering scheme and (b) packing of **4** in the direction of the *b*-axis (light gray octahedron, Cd; medium gray tetrahedron, phosphonate). For clarity, hydrogen atoms are omitted. Atoms labeled with the suffix A are at the symmetry position $-x$, $1 - y$, $-z$.

formed by Cd^{2+} cations and by $Cl_2C(PO_3Pr^i)_2^{2-}$, methanol, and aqua ligands (Figure 4a). The structure is similar to the previously published structure of the Ca complex of the same ligand.[26] There are two crystallographically independent, octahedral Cd^{2+} cations [Cd−O = 2.211(2)−2.449(2) Å, Table 3] in the asymmetric unit, connected to each other by three triatomic bridges formed by $Cl_2C(PO_3Pr^i)_2^{2-}$ ligands. There are two chelating $Cl_2C(PO_3Pr^i)_2^{2-}$ ligands around Cd1, forming six-membered chelate rings in cis-positions. The fifth coordination site is occupied by a μ-phosphonate O atom connecting Cd1 to the adjacent Cd1 atom, and the sixth site is occupied by an aqua ligand. The Cd1 atoms form a square plane around a center of symmetry with two bridging phosphonate O atoms, and the Cd2 atoms are above and below this plane. The coordination sphere of Cd2 contains one chelating $Cl_2C(PO_3Pr^i)_2^{2-}$ ligand, forming a six-membered chelate ring, and one $Cl_2C(PO_3Pr^i)_2^{2-}$ ligand, which provides only one O atom to Cd2. One aqua ligand and two methanol molecules occupy the rest of the coordination sites. Hydrogen bonds [O···O 2.729(3)−3.071(3) Å, 105−177°] hold the tetramers together, forming a layered structure parallel to the ($\bar{1}01$) plane. The isopropyl groups and chlorine atoms of the $Cl_2C(PO_3Pr^i)_2^{2-}$ ligands and CH_3 groups of the methanol ligands point to the interlayer section (Figure 4b).

Discussion

Previously, some Zn and Cd complexes of methylenebis(phosphonate) MBP, $[H_2C(PO_3H)_2]^{2-}$, and its analogues etidronate, $[(CH_3)(HO)C(PO_3H)_2]^{2-}$, and alendronate, $[(NH_3CH_2CH_2CH_2)(HO)C(PO_3H)_2]^{2-}$, have been reported.[14−21] The structures of these metal complexes are either molecular (monomers and dimers)[17,18,21] or polymeric chains, layers, or three-dimensional networks.[14−16,19−21] The new metal compounds **1**−**4**, and also the Zn and Cd complexes of the (dichloromethylene)bis(phosphonic acid) *P*,*P′*-diethyl ester,[27] are different from the Zn and Cd complexes of MBP and its derivatives etidronate and alendronate.[14−21] The structures of the Zn complexes of clodronate and its ester derivatives are all different, one-dimensional single-chains, and the structure of the Cd complex of clodronate is two-dimensional and double-layered, while the structures of the Cd complexes of the ester derivatives are a one-dimensional chain and a tetramer.[27]

The different ligands and also the methods of preparation obviously cause the structural differences between the previously described Zn and Cd complexes[14−21] and compounds **1**−**4**. The previous compounds were prepared by hydrothermal synthesis[16,19,21] or by evaporation,[17−18,20−21] and to obtain the crystallizable product, in some cases pH adjustment or templates were used in the preparation.[15−19] On the contrary, compounds **1**−**4** were produced using an easily controllable gel method. The advantages of this method, in addition to the possibility to control the conditions, are the small amounts of starting materials needed, the perfectly shaped crystals formed, and the purity of the compounds obtained. Most of the compounds (**1**, **3**, **4**) were prepared without adjustment of pH; while in the case of **2**, the pH had to be adjusted to 4 to obtain suitable crystals for X-ray measurements.

The overall structures of the previously described Zn and Cd complexes and the compounds **1**−**4** are different, but there are also similarities among the compounds. The chain construction found in **1** is also found in the layered, mixed Zn/V complex of MBP,[14] and the double layers of **2** consist of double chains, which are also found in a Zn complex of etidronate.[19] In addition, the binding mechanism of the ligands and coordination spheres of the metals are similar.

The bisphosphonate ligands have high affinity to form chelate rings with metal cations; MBP, etidronate, and alendronate as well as clodronate and its ester derivatives all form six-membered chelate rings with Zn^{2+} and Cd^{2+} cations.[14−21,27] The only exception is compound **3**, in which the bisphosphonate ligand is coordinated terminally to two different metal cations and is not chelated. Another interesting binding mechanism of clodronate was also found: clodronate coordinated to a metal cation through its chlorine atom, forming a unique Cd−Cl(C) bond in compound **2**. Only some M−Cl(C) bonds, but not Cd−Cl(C) bonds, have been described previously. The distance of this bond in **2** is 0.67 Å longer than the average Cd−O coordination bond, and in other similar metal chromophores $CoClO_5$ and $NiClO_5$ the difference is 0.55[33] and 0.46 Å, respectively.[34]

It has been proposed that to produce three-dimensional structures all the phosphonate oxygen atoms of the bisphosphonate ligand must be involved in metal coordination.[5] Therefore, the alkyl substituents in the ester derivatives of clodronate might reduce the dimensionality of the complex structure. In the Zn complexes of MBP, all six phosphonate O atoms are involved in coordination and three-dimensional structures are found.[15,16] In the case of Zn and Cd complexes of etidronate and alendronate, four phosphonate O atoms and the hydroxyl O atom are involved and polymeric, but not three-dimensional, structures are obtained.[17−21] In compound **1**, clodronate provides all six O atoms to Zn^{2+} and Na^{+} and the structure is, indeed, three-dimensional. In **2**, clodronate donates all six O atoms and a chlorine atom to metals, compound **2** being a two-dimensional double layer. In the case of the ester derivatives of clodronate, the diethyl ester derivative donates three[27] and the diisopropyl ester derivative two (in **3**) or four (in **4**) unsubstituted O atoms to metals, also producing polymeric structures. In addition, a two-dimensional structure is achieved in **3** and **4** through hydrogen bonding: two-dimensional layers are formed from the chains of **3** and from the tetramers of **4**. The organic ester groups are pointing to the interlayer region, forcing the layers apart and increasing the interlayer distance.

Altogether, the structures of the Zn and Cd complexes of clodronate and its ester derivatives, together with the previously published structures, indicate that the dimensionalities of the structures decrease with increasing size of the alkyl substituent.On the other hand, it can be assumed that esterification of clodronate does not totally prevent the formation of the polymeric structures, but it could increase the porosity of the structure by increasing the distance between the structural units.[22−23,25−27]

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Supporting Information Available: Crystallographic data for compounds **1**−**4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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