

Synthesis and Crystal Structures of Three Zinc (Chloromethyl)phosphonates

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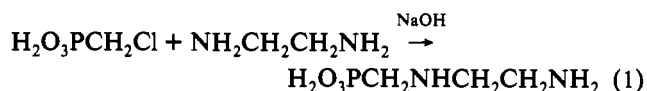
Reaction of zinc compounds with (chloromethyl)phosphonic acid yielded three novel layered compounds. $\text{Zn}(\text{O}_3\text{-PCH}_2\text{Cl})\cdot\text{H}_2\text{O}$ was prepared from zinc acetate and the phosphonic acid at 70 °C. It is monoclinic, space group $P2_1/n$, with $a = 4.781(2)$ Å, $b = 19.816(8)$ Å, $c = 5.6975(8)$ Å, $\beta = 91.91(2)^\circ$, and $Z = 4$. This compound has a layered structure similar to that of $\text{Zn}(\text{O}_3\text{PC}_6\text{H}_5)\cdot\text{H}_2\text{O}$.¹ Addition of urea to the reaction mixture yielded another layered product in which urea is coordinated to zinc through oxygen. The compound is monoclinic, $P2_1/c$, with $a = 5.040(3)$ Å, $b = 8.522(3)$ Å, $c = 17.401(2)$ Å, $\beta = 89.80(2)^\circ$, and $Z = 4$. The zinc atom is tetrahedrally coordinated by three phosphonate oxygens and one from urea. The phosphonate oxygens bridge across two zinc atoms forming a chain of eight-membered rings running parallel to the a -axis. The chains are linked together through hydrogen bonding along the b -axis to form the layers. $\text{Zn}_2\text{Cl}(\text{O}_3\text{PCH}_2\text{Cl})(\text{HO}_3\text{PCH}_2\text{Cl})\cdot 3\text{H}_2\text{O}$ was prepared at 60 °C from a mixture of ZnCl_2 and (chloromethyl)phosphonic acid. The crystals are orthorhombic, $Pbca$, with $a = 19.500(4)$ Å, $b = 17.686(3)$ Å, $c = 8.198(1)$ Å, and $Z = 8$. Zinc atoms are both tetrahedrally and octahedrally coordinated. The latter type of Zn atoms are joined in a cluster of two by bridging phosphonate oxygens forming four-membered rings. Each of these Zn atoms is bridged in the opposite direction by phosphonate groups to tetrahedrally coordinated Zn atoms. The octahedra are completed by three water molecules. A chlorine atom is bonded directly to the tetrahedral zinc. The phosphonate bridging of metal atoms forms 14-membered rings and 12-membered rings in addition to the 4-membered rings. Each of the interlayer distances are determined by the way in which the chloromethyl group is situated in the interlamellar space.

Introduction

Recent studies¹⁻³ in our laboratory have dealt with the synthesis and crystal structures of di- and trivalent layered metal phosphonates. Related studies have been carried out by Mallouk et al.⁴⁻⁶ Our interest in these compounds stems from the recognition, demonstrated with group IV phosphonates,⁷⁻⁹ that one can prepare functionalized derivatives exhibiting interesting complexing and sorption behavior. For example, the sulfonated mixed derivative zirconium phenylphosphonate phosphate, $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{-H})_x(\text{HPO}_4)_{2-x}$, exhibits high selectivities for the larger alkaline earth ions.¹⁰ In fact, quantitative precipitation of large charged complexes is possible.¹¹ Similarly, amino derivatives of the type $\text{Zr}(\text{O}_3\text{PCH}_2(\text{NHCH}_2\text{CH}_2)_n\text{NH}_2)_2$ can complex, in a supramolecular manner, large polyvalent anions such as $\text{Fe}(\text{CN})_6^{4-}$, PtCl_4^{2-} , etc.¹² The amino groups upon protonation cause the layers to swell allowing free access of the exchanging ions to the interlayer space. The exchange capacity can be controlled by the number of amino groups protonated.

Preparation of the layered metal aminophosphonates entails refluxing of a metal nitrate or chloride solution with an amino

phosphonic acid. The amino phosphonic acids are prepared by reaction 1. In the case of divalent metals, the amino phosphonates



form gels from which it is difficult to recover the solid metal amino phosphonate. It occurred to us that an alternative route would allow easier recovery of the desired product. This procedure involves the initial preparation of $\text{M}^{\text{II}}\text{O}_3\text{PCH}_2\text{Cl}$ followed by reaction with ethylene diamine. Burwell and Thompson¹³ have shown that interlayer chemical rxns can be carried out with phosphonates. They prepared $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{COOH})_2$ and found this compound to be unreactive to acylation. However, by adding NH_3 they were able to form the ammonium ion intercalation product, which then formed an acid chloride by the action of SOCl_2 on the ammonium salt. This result is indicative that simple interlayer condensation reactions are possible. In this paper we describe the preparation of zinc (chloromethyl)phosphonates as a prelude to describing potential interlayer chemistry of these compounds.

Experimental Section

Synthesis of Zinc (Chloromethyl)phosphonates. $\text{Zn}_2\text{Cl}(\text{O}_3\text{PCH}_2\text{Cl})\cdot(\text{HO}_3\text{PCH}_2\text{Cl})\cdot 3\text{H}_2\text{O}$. In a typical preparation 4.8 g (36.8 mmol) of (chloromethyl)phosphonic acid (Alfa), $\text{H}_2\text{O}_3\text{PCH}_2\text{Cl}$, was dissolved in 20 mL of distilled deionized water (DDI). To this solution was added dropwise with stirring a solution composed of 3.2 g (23.5 mmol) of ZnCl_2 (Mallinckrodt, reagent grade) in 20 mL of DDI water. After the addition was complete the pH was raised to 2.5-3 by addition of 1 M NaOH solution. A white precipitate formed during addition of the base. The stirred mixture was then kept at 60 °C for 16-17 h and cooled slowly to room temperature. This white solid was recovered by filtration, washed several times with water, and then air dried. Crystals suitable for X-ray studies were prepared by dissolving 100 mg of the white solid in dilute aqueous (~0.2 M) HCl and allowing the water to slowly evaporate.

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Table I. Crystallographic Data for the Zinc (Chloromethyl)phosphonates

	empirical formula		
	ZnPCH ₂ ClO ₄	Zn ₂ P ₂ -Cl ₃ C ₂ O ₉ H ₁₁	ZnPC ₂ -N ₂ ClH ₆ O ₄
fw	211.84	478.17	253.88
a (Å)	4.781(2)	19.500(4)	5.040(3)
b (Å)	19.816(8)	17.686(3)	8.522(3)
c (Å)	5.6975(8)	8.198(1)	17.401(2)
α (deg)	90	90	90
β (deg)	91.91(2)	90	89.80(2)
γ (deg)	90	90	90
V (Å ³)	539.5(3)	2827(2)	747.7(7)
Z	4	8	4
space group	P2 ₁ /n (No. 14)	Pbca (No. 61)	P2 ₁ /c (No. 14)
d _{calc} (g/cm ³)	2.608	2.246	2.256
λ (Å)	0.710 69	0.710 69	0.710 69
temp (°C)	23 ± 1	24 ± 1	23 ± 1
abs coeff (cm ⁻¹)	53.72	43.03	39.04
R(F _o) ^a	0.033	0.038	0.040
R _w (F _o) ^b	0.041	0.042	0.053

^a $R(F_o) = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $R_w(F_o) = [\sum (|F_o| - |F_c|)^2 / \sum w(F_o^2)]^{1/2}$; $w = 4F_o^2 / (\sigma(F_o^2))^2$.

Anal. Found: Zn, 25.1; P, 14.32; Cl, 19.6; C, 5.5; H, 1.69. Calcd: Zn, 27.34; P, 12.95; Cl, 22.24; C, 5.02; H, 2.31.

Zn(O₃PCH₂Cl)·H₂O. Zinc acetate dihydrate (4.4 g, 20 mmol) was dissolved in 100 mL of DDI water. A 100-mL volume of a solution 0.4 M in (chloromethyl)phosphonic acid, ClCH₂PO₃H₂, was added dropwise to the stirred zinc acetate solution. The clear solution was kept at 70 °C for 3 days in a flask fitted with a condenser and then left to evaporate slowly at ambient temperature. Clear colorless crystals formed in a few days.

Zinc (Chloromethyl)phosphonate-Urea Complex, Zn(O₃PCH₂Cl)·NH₂COHH₂. In the synthesis of zinc (chloromethyl)phosphonate, it was thought to eliminate the sodium hydroxide addition step by adding urea to the reactant mix. On heating, the urea should hydrolyze to produce ammonia. Thus, it was expected that precipitation of the desired compound would take place automatically at the correct pH. Instead a urea complex was obtained. In a typical reaction 0.10 mol of ZnCl₂ in 50 ml of water was added to 50 mL of 2 M (chloromethyl)phosphonic acid. To this mixture was added 0.2 mol of urea and the solution kept at 60 °C for 7 days. Small, colorless platelike crystals were obtained. Anal. Found: C, 9.43; H, 2.14; N, 10.92; P, 12.34. Calcd: C, 9.45; N, 2.38; H, 11.02; P, 12.20.

Materials and Methods. All chemicals used were of reagent grade or highest purity available and used without further purification. X-ray powder diffraction patterns were obtained on a Seifert-Scintag PAD-V diffractometer at 50 kV and 40 mA using Ni-filtered Cu Kα radiation (λ = 1.5418 Å). Thermogravimetric analysis (TGA) was carried out with a DuPont Model No. 951 thermal analysis unit at a rate of 10 °C/min under a flow of N₂ unless otherwise specified. Infrared spectra were recorded on a Digilab Model FTS-40 FTIR spectrometer by the KBr disk method.

X-ray Structure Analysis. Zinc (Chloromethyl)phosphonate monohydrate. A colorless platelike crystal of approximate dimensions 0.23 × 0.21 × 0.04 mm³ was cut from a large tabloid crystal of Zn(PO₃CH₂Cl)·H₂O. The crystal fragment was mounted on a glass fiber, and all crystallographic measurements were carried out on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) and a 12-kW rotating anode generator. Cell parameters for data collection were obtained from least-squares refinement of 25 carefully centered reflections chosen from the 15–30° 2θ shell immediately preceding data collection. The unit cell was found to be monoclinic with cell parameters a = 4.781(2) Å, b = 19.816(8) Å, c = 5.6975(8) Å, and β = 91.91(2)°. Intensity data were collected at 23° ± 1 °C using the ω–2θ scan method in shells to a maximum value of 60.1° in 2θ. Standards were chosen automatically on the basis of both intensity and spatial distribution and measured every 150 reflections. Ω scans of several intense reflections, made with a take-off angle of 6.0° prior to data collection, had an average width at half-height of 0.26°. Scans of (1.63 + 0.3 tan θ)° were made at a speed of 16.0°/min (in ω). The weak reflections (I < 10.0σ(I)) were rescanned (maximum of 2 rescans) and the counts were accumulated to ensure good counting statistics. Of the 1800 reflections which were collected, 1635 were unique (R_{int} = 0.117) and equivalent reflections were merged. A total of 1215 reflections were observed with I > 3σ(I).

Table II. Positional Parameters and B(eq) Values (Å²) for Zn(O₃PCH₂Cl)·H₂O

atom	x	y	z	B(eq) ^a
Zn	0.20230(9)	0.23700(2)	0.08703(7)	1.19(2)
Cl	0.1947(3)	0.02964(7)	0.7820(2)	3.72(6)
P	0.2533(2)	0.16807(5)	0.5918(2)	0.96(3)
O1	0.3957(5)	0.2023(2)	0.3841(4)	1.3(1)
O2	0.4407(5)	0.3231(1)	0.0870(4)	1.2(1)
O3	-0.0980(6)	0.1602(2)	0.0986(5)	1.7(1)
O4	0.3992(5)	0.1952(2)	0.8162(4)	1.3(1)
C	0.3384(9)	0.0806(2)	0.5591(7)	1.8(2)
H1	0.5252	0.0741	0.5712	2.1
H2	0.2711	0.0679	0.4267	2.1
H3	-0.2136	0.1650	0.2292	1.9
H4	-0.2178	0.1654	0.0011	1.9

^a $B_{eq} = \frac{1}{3} \sum_i \beta_{ij} A_i A_j$.

Table III. Intramolecular Distances (Å) and Angles (deg) for Zn(O₃PCH₂Cl)·H₂O^a

Distances			
Zn–O1	2.002(3)	Cl–C	1.779(4)
Zn–O1A*	2.195(3)	P–O1	1.542(3)
Zn–O2	2.052(3)	P–O2A†	1.504(3)
Zn–O3	2.094(3)	P–O4	1.533(3)
Zn–O4A**	2.013(3)	P–C	1.791(5)
Zn–O4B*	2.113(3)		
Angles			
O1–Zn–O1A*	154.9(1)	O1–P–O4	106.6(2)
O1–Zn–O2	92.5(1)	O1–P–C	103.8(2)
O1–Zn–O3	91.2(1)	O2A†–P–O4	113.5(1)
O1–Zn–O4A**	106.8(1)	O2A†–P–C	109.9(2)
O1A*–Zn–O2	84.6(1)	O4–P–C	109.1(2)
O1A*–Zn–O3	88.2(1)	Zn–O1A*–ZnA*	122.2(1)
O1A*–Zn–O4A**	98.2(1)	Zn–O1–P	126.2(1)
O2–Zn–O3	170.2(1)	Zn–O1A*–P†	98.1(1)
O2–Zn–O4A**	93.9(1)	Zn–O2–P††	130.4(2)
O3–Zn–O4A**	93.6(1)	Zn–O4A**–P**	124.9(1)
O1–P–O2A†	113.5(1)	Cl–C–P	112.4(2)

^a Key for symmetry codes: (*) $x - 1/2, 1/2 - y, z - 1/2$; (**) $x, y, z - 1$; (†) $x - 1/2, 1/2 - y, z + 1/2$; (††) $1/2 + x, 1/2 - y, 1/2 + z$.

The data were corrected for Lorentz and polarization effects. On the basis of the systematic absences of $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) and the successful solution and refinement of the structure, the space group was determined to be P2₁/n (No. 14). Pertinent crystallographic data are collected in Table I.

Structure Solution and Refinement. The location of the zinc atoms was obtained by deconvolution of the Patterson function with the aid of program PHASE.¹⁴ Other non-hydrogen atoms were found by DIRDIF,¹⁴ a direct method applicable to partially known structures. All of the non-hydrogen atom positions were refined anisotropically following which the hydrogen atom positions were abstracted from a difference Fourier map. They were then assigned fixed temperature factors and included in the last least-squares cycle. An empirical absorption correction, DIFABS,¹⁴ was applied which resulted in transmission factors ranging from 0.572 to 1.00. The linear adsorption coefficient for Mo Kα is 53.72 cm⁻¹. The final cycle of full-matrix least-squares refinement was based on 1215 observed reflections ($I > 3\sigma(I)$) and 163 variable parameters and converged with the largest parameter shift 0.01 times its esd. The standard deviation of an observation of unit weight was 1.432. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.70 and -0.57 e⁻/Å³, respectively. Neutral-atom scattering factors were taken from Cromer and Waber.¹⁵ Anomalous dispersion effects were included in F_o; the values for Δf' and Δf'' were those of Cromer.¹⁶

Final positional and anisotropic thermal parameters are given in Table II; important bond distances and angles in Table III. The molecular unit together with the atom-numbering scheme is given in Figure 1, the

(14) TEXSAN. TEXRAY Structural Analysis Program, Molecular Structure Corp., The Woodlands, TX, 1987 (revised).

(15) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A (Present distributors, Kluwer Publishers: Dordrecht, The Netherlands).

(16) Cromer, D. T. Reference 30, Table 2.3.1.

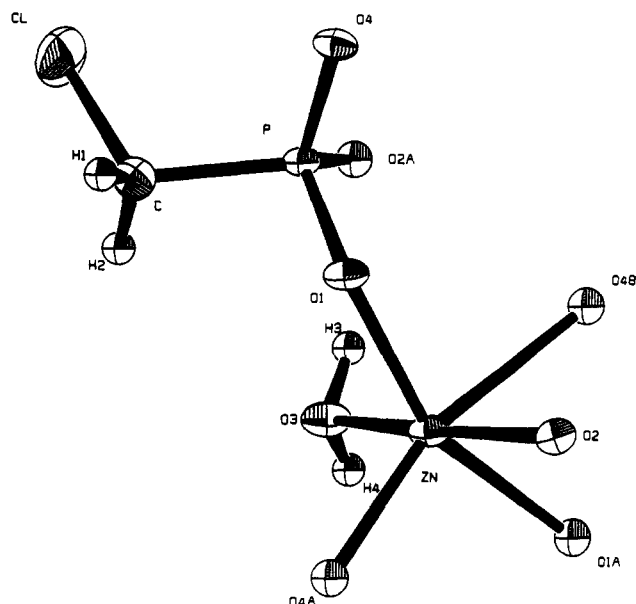


Figure 1. Molecular representation and atom-numbering scheme for zinc (chloromethyl)phosphonate monohydrate.

Table IV. Hydrogen Bond Distances (Å) and Angles (deg) in the Several Zinc Phosphonate Structures

1. Zn(O ₃ PCH ₂ Cl)·H ₂ O					
atom(1)	atom(2)	atom(3)	dist(1-2)	dist(1-2)	dist(1-3) angle
O3	H4	O4C**	0.946	2.931(4)	163.3(2)
O3A*	H3A	O2	0.791	2.802(4)	124.3(2)

* Symmetry position $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$.

**Symmetry position $x - 1, \frac{1}{2}, z - 1$.

2. Zn ₂ Cl(O ₃ PCH ₂ Cl)(HO ₃ PCH ₂ Cl)·3H ₂ O					
atom(1)	atom(2)	atom(3)	dist(1-2)	dist(1-2)	dist(1-3) angle
O1	H2	O8A*	0.948	2.86(1)	92.5(2)
O2	H6	O6A**	0.956	2.748(9)	157.0(3)
O9	H7	O5	0.956	2.57(1)	85.0(2)

* Symmetry code $x, y, z - 1$.

**Symmetry code $\frac{1}{2} - x, \bar{y}, z - \frac{1}{2}$.

3. Zinc chloromethyl phosphonate-urea complex		
Hydrogen Bonds	Distance	Angle
N1C# - H1A# --- O1	3.245(7) Å	112.7(2)°
N1A* - H1B* --- O2	3.045(7) Å	146.9(3)°
N1B** - H2C** --- O4	3.277(8) Å	164.8(3)°
N1B** - H2C** --- O2	3.200(8) Å	121.6(2)°

Symmetrical position $x, 1 + y, z$

*Symmetrical position $-x, -y, 1 - z$

**Symmetrical position $1 - x, -y, 1 - z$

structure of the layers is shown in Figure 2, and the orientation of the layers relative to each other is shown in Figure 3.

Zn₂Cl(O₃PCH₂Cl)(HO₃PCH₂Cl)·3H₂O. A colorless platelike crystal of dimensions $0.15 \times 0.15 \times 0.05$ mm³ was cut from a larger tabloid crystal and mounted on a glass fiber. Unit cell dimensions for data collection were obtained from least-squares refinement of the setting angles of 25 carefully centered reflections in the 20–34° angular range. The unit cell was found to be orthorhombic with cell parameters $a = 19.500(4)$ Å, $b = 17.686(3)$ Å, and $c = 8.198(1)$ Å. Data were collected by the ω -2 θ scan method out to 50° as described for the previous structure. A total of 2875 reflections were collected of which 1446 were observed with $I > 3\sigma(I)$. On the basis of the systematic absences of $0kl$ ($k \neq 2n$), $h0l$ ($l \neq 2n$), and $hk0$ ($h \neq 2n$) and the successful solution and refinement of the structure, the space group was determined to be *Pbca*.

Structure Solution and Refinement. The structure was solved in a manner analogous to that of Zn(O₃PCH₂Cl)·H₂O. Positions of the hydrogen atoms were calculated after anisotropic refinement of all the non-hydrogen atoms. Application of an empirical absorption correction using program DIFABS¹⁴ yielded transmission factors ranging from 0.567

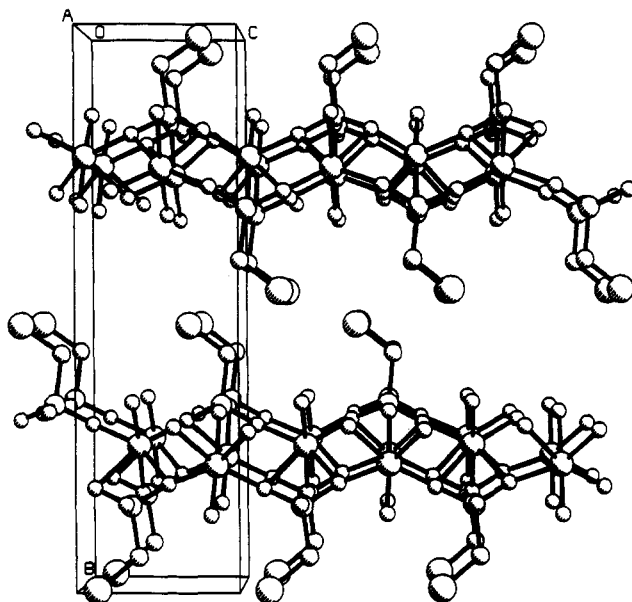


Figure 2. Layer arrangement in Zn(OP₃CH₂Cl)·H₂O as viewed down the *b*-axis.

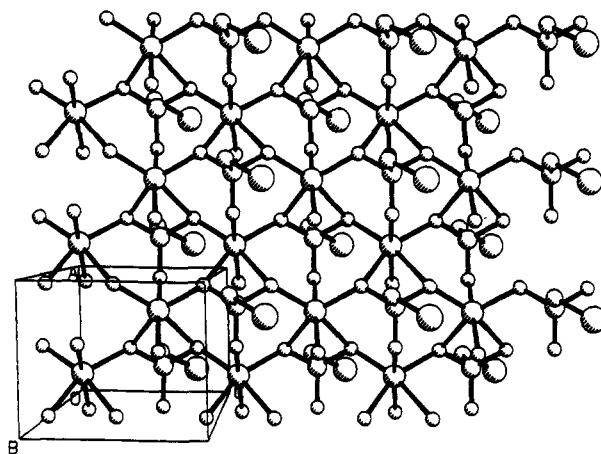


Figure 3. Portion of the structure of Zn(O₃PCH₂Cl)·H₂O, showing the arrangement of atoms in a single layer.

to 1.00. The final cycle of least-squares refinement was based on 1446 observed reflections with $I > 3\sigma(I)$ and 163 variable parameters and converged with the largest parameter shift of 0.01 times its esd. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.45 and -0.53 e/Å³, respectively, and the standard deviation of an observation of unit weight was 1.314. The positional and isotropic thermal parameters are given in Table V.

Zn(O₃PCH₂Cl)(H₂NCONH₂). A clear, colorless crystal of approximate dimensions $0.46 \times 0.23 \times 0.12$ mm³ was mounted on a glass fiber held by the goniometer head. Unit cell dimensions for data collection were obtained from least-squares refinement of 25 carefully centered reflections chosen in the angular range 16–30°. The unit cell was found to be monoclinic with unit cell dimensions of $a = 5.040(3)$ Å, $b = 8.522(3)$ Å, $c = 17.401(2)$ Å and $\beta = 89.80(2)^\circ$. Other pertinent crystallographic data are given in Table I. Data were collected by the ω -2 θ scan method out to an angular value of 55.1°. Of the 1907 reflections collected 1853 were unique ($R_{int} = 0.025$). On the basis of the systematic absences of $h0l$ ($h \neq 2n$) and $0k0$ ($k \neq 2n$) and the successful solution and structure refinement, the space group was determined to be *P2₁/c*. The structure solution and refinement were exactly similar to that described for Zn(O₃PCH₂Cl)·H₂O. However, the hydrogen atom positions were calculated and assigned fixed temperature factors. An empirical absorption correction was applied with the aid of program DIFABS,¹⁴ which resulted in transmission factors of 0.95 to 1.06. The final full-matrix least-squares refinement was based on 1329 observed reflections with $I > 3\sigma(I)$ and 101 variable parameters. The standard deviation of an observation of unit weight was 1.680, and the maximum and minimum peaks on the final difference map corresponded to 0.81 and -0.85 e/Å³.

Table V. Positional Parameters and $B(\text{eq})$ Values for $\text{Zn}_2\text{Cl}(\text{O}_3\text{PCH}_2\text{Cl})(\text{HO}_3\text{PCH}_2\text{Cl})\cdot 3\text{H}_2\text{O}$

atom	x	y	z	$B(\text{eq})^a$
Zn1	0.07174(5)	0.00928(7)	0.0984(1)	1.89(5)
Zn2	0.19798(6)	0.06766(7)	0.05458(1)	1.98(5)
Cl1	0.1457(2)	-0.1652(2)	0.6139(4)	4.9(2)
Cl2	0.022(2)	-0.2274(2)	0.1499(5)	5.2(2)
Cl3	0.1791(1)	0.1683(2)	0.3919(4)	3.5(1)
P1	0.1826(1)	-0.0749(2)	0.3234(3)	1.8(1)
P2	-0.0569(1)	-0.0850(1)	0.2610(3)	1.8(1)
O1	0.1145(3)	-0.0701(4)	-0.0622(8)	22.5(3)
O2	0.1553(3)	0.0805(4)	0.0663(8)	2.5(3)
O3	0.0254(3)	0.0938(4)	0.2304(9)	3.1(4)
O4	-0.0218(3)	-0.0504(4)	0.1161(8)	1.7(3)
O5	0.1105(3)	-0.0433(4)	0.3004(8)	2.0(3)
O6	0.2247(3)	-0.0259(4)	0.4360(8)	2.1(3)
O7	0.2169(3)	-0.0882(4)	0.1605(8)	2.4(3)
O8	0.1235(3)	0.0463(4)	0.6966(8)	2.5(3)
O9	-0.0077(3)	-0.0824(4)	0.4096(7)	2.6(3)
C1	0.1770(5)	-0.1684(6)	0.412(1)	2.9(5)
C2	-0.0730(5)	-0.1828(6)	0.222(1)	2.9(5)
H1	0.0884	-0.1141	-0.0950	2.9
H2	0.1598	-0.0646	-0.1029	2.9
H3	0.0277	0.0960	0.3465	3.7
H4	0.0004	0.1344	0.1756	3.7
H5	0.1574	0.1289	0.1215	2.9
H6	0.1923	0.0676	-0.0046	2.9
H7	0.0233	-0.0810	0.5019	3.1
H8	0.2214	-0.1895	0.4105	3.4
H9	0.1470	-0.1972	0.3459	3.4
H10	-0.1081	-0.1866	0.1431	3.3
H11	-0.0871	-0.2060	0.3208	3.3

^a See Table II for the definition of $B(\text{eq})$.

Results

Three separate layered compounds were obtained in the zinc (chloromethyl)phosphonate system: $\text{Zn}(\text{O}_3\text{PCH}_2\text{Cl})\cdot\text{H}_2\text{O}$, which is the analogue of the previously obtained alkyl- and arylphosphonates,²⁻⁶ the acid form $\text{Zn}_2\text{Cl}(\text{O}_3\text{PCH}_2\text{Cl})(\text{HO}_3\text{PCH}_2\text{Cl})\cdot 3\text{H}_2\text{O}$, and a urea complex, $\text{Zn}(\text{O}_3\text{PCH}_2\text{Cl})\cdot\text{NH}_2\text{CONH}_2$.

$\text{Zn}(\text{O}_3\text{PCH}_2\text{Cl})\cdot\text{H}_2\text{O}$. This compound was prepared using zinc acetate as the source of metal atoms as opposed to ZnCl_2 used in the preparation of $\text{Zn}_2\text{Cl}(\text{O}_3\text{PCH}_2\text{Cl})(\text{HO}_3\text{PCH}_2\text{Cl})\cdot 3\text{H}_2\text{O}$. Our experience has shown¹⁷ that zinc has a tendency to coordinate to chloride ion preventing the formation of a layered structure. By avoidance of the presence of Cl^- , a simple layered structure formed. Each zinc atom is six coordinate (Figure 1). This high coordination number is achieved with only 4 oxygen atoms through chelation of the metal atoms by oxygens O1 and O4. At the same time these oxygens donate an electron pair to adjacent zinc atoms in a direction parallel to the c -axis (Figure 3). The third phosphonate oxygen, O2, bridges to a zinc atom in the a -axis direction, and the sixth coordination site is occupied by a water molecule. As seen in Figure 2 the chloromethyl groups occupy the interlayer space positioning adjacent chlorine atoms 3.366(3) Å apart. Only van der Waals forces exist between layers. The Zn-O distances are quite normal ranging from 2.013(3) to 2.195(3) Å. However, the octahedral coordination is slightly distorted. The two longest Zn-O bonds are those that form the chelate ring, and the two shortest are those formed by the same oxygens donating to adjacent zinc atoms. The same situation holds for the zinc phenylphosphonate.¹ Hydrogen bond distances and, where known, angles are given in Table IV. Hydrogen atoms of the water molecule are in positions to form hydrogen bonds with near-neighbor oxygens O2, which is 2-coordinate, and O4, which is 3-coordinate.

$\text{Zn}_2\text{Cl}(\text{O}_3\text{PCH}_2\text{Cl})(\text{HO}_3\text{PCH}_2\text{Cl})\cdot 3\text{H}_2\text{O}$. This compound contains zinc in both octahedral and tetrahedral coordination as seen in Figure 4. The octahedrally coordinated zinc atoms (Zn1) occur in clusters of two, joined together by phosphonate oxygens

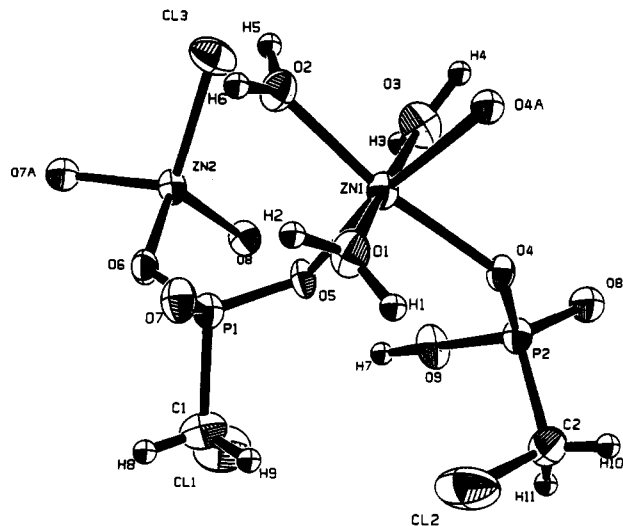


Figure 4. ORTEP and atom-numbering scheme for $\text{Zn}_2\text{Cl}(\text{O}_3\text{PCH}_2\text{Cl})(\text{HO}_3\text{PCH}_2\text{Cl})\cdot 3\text{H}_2\text{O}$, showing zinc with both octahedral and tetrahedral coordination.

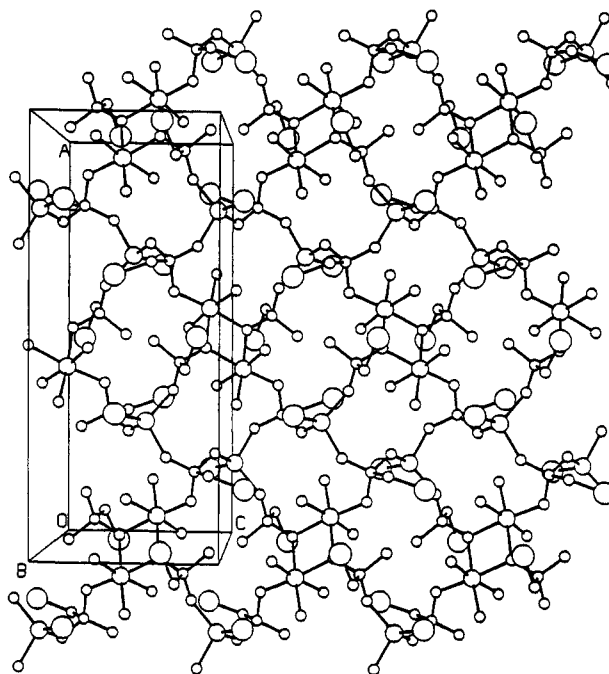


Figure 5. Packing arrangement of atoms in a single layer of $\text{Zn}_2\text{Cl}(\text{O}_3\text{PCH}_2\text{Cl})(\text{HO}_3\text{PCH}_2\text{Cl})\cdot\text{H}_2\text{O}$ as viewed down the c -axis. Note the four-membered rings formed by zinc and oxygen atoms.

O4 and O4A to form four-membered rings (Figure 5). Each of these zinc atoms is then linked to a tetrahedrally coordinated Zn2 atom through a phosphonate group Zn1-O5-P1-O6-Zn2 . The coordination sphere of Zn1 is completed by three water oxygens O1, O2, and O3. The phosphonate groups which form the four-membered rings also contain the P-OH group. The third oxygen of this phosphonate, O8, participates in forming a bridge of the type Zn1-O4-P2-O8A-Zn2 , roughly perpendicular to the O5-P1-O6 bridge. These groupings form 14-membered rings which alternate with the 4-membered rings along the c -axis direction. Such rows of alternating large and small rings are centered very nearly at $b = 0$ and $1/2$.

A second large ring structure (12-membered ring, 12-MR) is formed by one octahedral Zn1 and two tetrahedral Zn2 linked as follows: $\text{Zn1-O5-P1-O6-Zn2-O7-P1-O6'-Zn2-O8-P2-O4-Zn1}$. The sequence within the layer along the a -axis direction is 14-MR, 12-MR, 4-MR, 12-MR, 14-MR, etc. A view of the structure perpendicular to the c -axis showing the orientation of the layers is given in Figure 6. We note that the Cl1 atoms in adjacent layers are within van der Waals distance (3.396 Å) of

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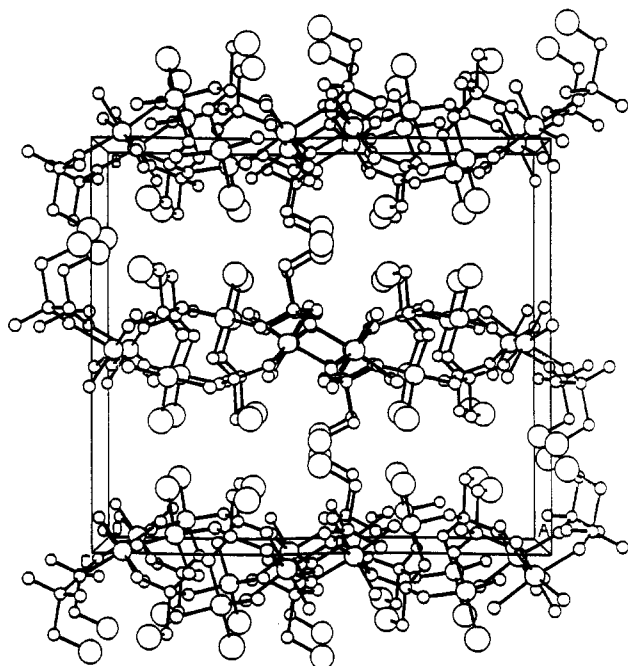


Figure 6. Layer arrangement in the structure of $Zn_2Cl(O_3PCH_2Cl)(HO_3PCH_2Cl) \cdot 3H_2O$ as viewed down the c -axis.

Table VI. Intramolecular Distances (Å) Involving the Non-Hydrogen Atoms for $Zn_2Cl(O_3PCH_2Cl)(HO_3PCH_2Cl) \cdot 3H_2O$

Zn1–O1	2.097(6)	Cl1–C1	1.76(1)
Zn1–O2	2.076(6)	Cl2–C2	1.76(1)
Zn1–O3	2.055(7)	P1–O5	1.524(6)
Zn1–O4	2.113(6)	P1–O6	1.509(7)
Zn1–O4A ^a	2.137(6)	P1–O7	1.512(7)
Zn1–O5	2.045(6)	P1–C1	1.81(1)
Zn2–Cl3	2.215(3)	P2–O4	1.501(6)
Zn2–O6	1.953(6)	P2–O8A ^a	1.509(7)
Zn2–O7A ^b	1.942(6)	P2–O9	1.551(6)
Zn2–O8	1.943(6)	P2–C2	1.79(1)

^a In symmetry position $-x, -y, -z$. ^b In symmetry position $1/2 - x, y, 1/2 + z$.

Table VII. Positional Parameters and $B(eq)$ Values for $Zn(O_3PCH_2Cl) \cdot (NH_2CONH_2)$

atom	x	y	z	$B(eq)^a$
Zn	0.1898(1)	0.33561(9)	0.44968(4)	1.49(3)
Cl	0.6667(6)	0.7136(3)	0.2554(1)	4.6(1)
O1	0.3938(8)	0.4881(5)	0.3935(2)	1.24(6)
O2	0.2105(9)	0.3564(5)	0.5614(3)	1.8(2)
O3	-0.1745(8)	0.3517(5)	0.4158(3)	1.8(2)
O4	0.294(1)	0.1167(5)	0.4391(3)	2.2(2)
N1	0.271(1)	-0.1428(6)	0.4220(4)	2.7(3)
N2	-0.081(1)	0.0114(7)	0.3893(4)	2.6(3)
C1	0.796(1)	0.5385(8)	0.2946(4)	2.1(3)
C2	0.162(1)	-0.0013(7)	0.4185(4)	1.6(2)
H1	0.1480	-0.2264	0.4083	3.3
H2	0.4116	-0.1486	0.4545	3.3
H3	-0.1479	-0.0847	0.3706	3.0
H4	-0.1324	0.1074	0.3770	3.0
H7	0.9502	0.5149	0.2785	2.5
H8	0.7452	0.4523	0.2582	2.5

^a See Table II for the definition of $B(eq)$.

those (Cl2) in an adjacent layer. This creates gaps between the layers as the other chlorine atoms do not extend as far into the interlayer space.

Bond distances are given in Table VI, and the bond angles are available as supplementary data. The Zn–O octahedral bond distances range from 2.045(7) to 2.137(6) Å. The two largest distances are those which form the 4-MR, Zn1–O4. Bond angles in the 4-MR are Zn–O4–Zn = 99.6(3)° and O4–Zn1–O4A = 80.4(3)°. Bond angles in the octahedron are fairly regular with the smallest angle being the 80.4(3)° mentioned above. Other

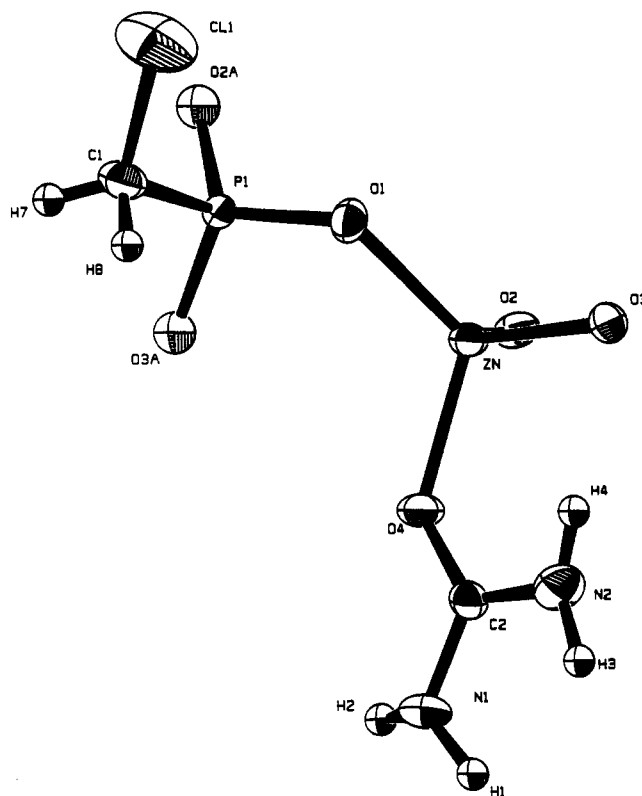


Figure 7. Coordination about the Zn atom and atom-numbering scheme for $Zn(O_3PCH_2Cl) \cdot NH_2CONH_2$.

Table VIII. Intramolecular Distances (Å) and Angles (deg) Involving the Non-Hydrogen Atoms for $Zn(O_3PCH_2Cl) \cdot NH_2CONH_2$

Distances			
Zn–O1	1.922(4)	P–O2	1.515(4)
Zn–O2	1.956(5)	P–O3	1.518(4)
Zn–O3	1.935(4)	P–C1	1.805(7)
Zn–O4	1.947(5)	O4–C2	1.258(8)
Cl–C1	1.766(7)	N1–C2	1.325(8)
P–O1	1.511(4)	N2–C2	1.335(8)
Angles			
O1–Zn–O2	114.4(2)	O2–P–C1	106.2(3)
O1–Zn–O3	107.7(2)	O3–P–C1	105.3(3)
O1–Zn–O4	117.1(2)	Zn–O1–P	126.7(3)
O2–Zn–O3	110.5(2)	Zn–O2–P	128.0(3)
O2–Zn–O4	99.5(2)	Zn–O3–P	124.3(3)
O3–Zn–O4	107.2(2)	Zn–O4–C2	130.6(4)
O1–P–O2	112.9(3)	Cl–C1–P	113.3(4)
O1–P–O3	111.1(3)	O4–C2–N1	119.8(6)
O1–P–C1	108.0(3)	O4–C2–N2	122.0(6)
O2–P–O3	112.7(3)	N1–C2–N2	118.1(6)

angles range from 83.8(2)° (O1–Zn1–O4A) to 95.1° (O2–Zn1–O5). Bond distances in the zinc tetrahedron are about 0.13 Å shorter on average than those in the octahedron, ranging from 1.942(6) to 1.953(6) Å. There are surprisingly few hydrogen bonds in this structure (Table IV) considering the presence of three water molecules and a hydroxyl group. These H–bonds are all intralayer as the layers are too far apart (8.84-Å interlayer distance) for interlayer bonding. However, there is an interlayer C12–C12' close contact (4.176 Å) and an intralayer Cl1–Cl2 contact of 3.396(5) Å.

$Zn(O_3PCH_2Cl) \cdot NH_2CONH_2$. The zinc atom in this structure is tetrahedrally coordinated (Figure 7), being bonded to three phosphonate oxygen atoms and the oxygen atom of a urea molecule. Bond distances and angles, given in Table VIII, are all quite regular. All the phosphonate oxygen atoms are two-coordinate forming O–P–O bridges which link the metal atoms together. Two zinc atoms combine with two phosphonate groups through O1 and O2 to form eight-membered noncoplanar rings. These rings are centered at 0,0,0 and $0, 1/2, 1/2$. The third

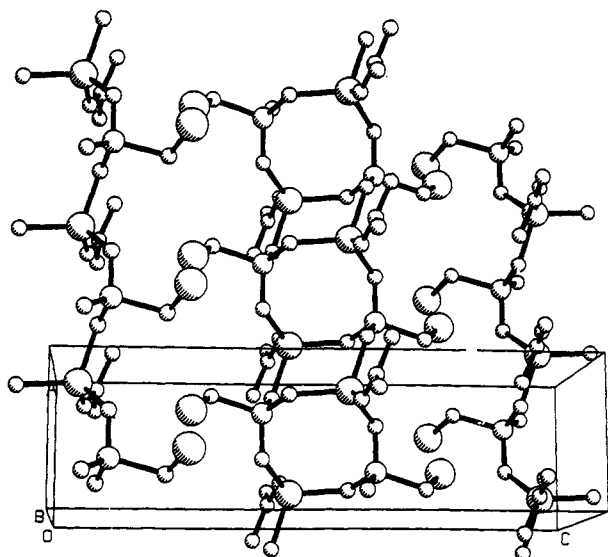


Figure 8. Layer arrangement in $\text{Zn}(\text{O}_3\text{PCH}_2\text{Cl})(\text{NH}_2\text{CONH}_2)$ viewed down the b -axis.

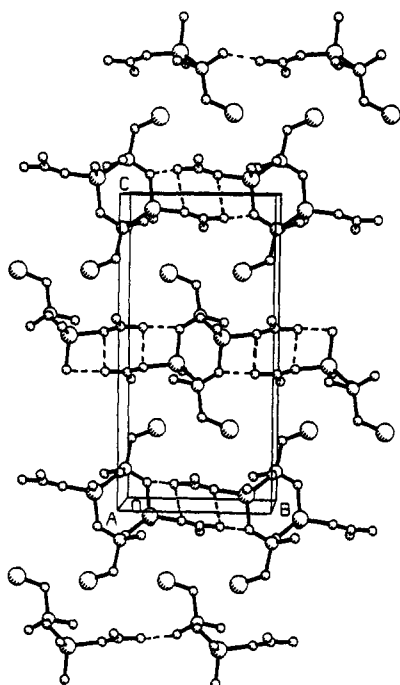


Figure 9. Representation of $\text{Zn}(\text{O}_3\text{PCH}_2\text{Cl})(\text{NH}_2\text{CONH}_2)$ layer as seen perpendicular to the a -axis. The broken lines represent hydrogen bonds between the chains which run parallel to the a -axis.

phosphonate oxygen, O3, points roughly perpendicular to the rings and connects them, by bonding to zinc, into chains running parallel to the a -axis (Figure 8). The chains are then hydrogen bonded to each other through the urea molecules to form layers which are parallel to the ab plane. The hydrogen bonding scheme is shown in Figure 9, and the distances and angles are in Table IV. The (chloromethyl)phosphonate-urea complex is stable to 250 °C, which is quite surprising given the weak nature of the hydrogen bonds. The chloromethyl group decomposes at ~ 400 °C.

The infrared pattern of the urea complex contains two very strong bands at 3453 and 3337 cm^{-1} and two medium-intensity bands at 3249 and 3148 cm^{-1} attributable to the N-H stretching vibrations. The CH stretching vibrations are at 2939 and 3000 cm^{-1} , which is within 5 wavenumbers of these stretching bands

for the other (chloromethyl)phosphonates. The carbonyl stretching band is at 1642 cm^{-1} , while the N-H bend is at 1590 cm^{-1} .

Intercalation of Amines. Both the monohydrate and the trihydrate are able to intercalate amines. This reaction is facilitated by removal of the coordinated water molecules but is not a prerequisite. Butylamine will displace a water molecule from the trihydrate with expansion of the interlayer distance by 4.29 Å. The infrared pattern clearly shows the presence of the C-N stretch at 1520, 1554 cm^{-1} and N-H at 1639, 3391 cm^{-1} and other bands characteristic of the amine. A full report on these reactions will be presented in a subsequent paper.

Discussion

A variety of divalent metal phosphonates have now been synthesized. The methylphosphonates of Zn, Co, and Mg all crystallize in the orthorhombic system with space group $Pmn2_1$.¹⁸ This space group requires the metal atom, the phosphorus atom, and the organic group to lie in a mirror plane which is perpendicular to the layer. Only symmetrical organic groups such as methyl and phenyl groups can satisfy this requirement without imposing strained or energy unfavorable conformations. $\text{Zn}(\text{O}_3\text{PCH}_2\text{Cl})\cdot\text{H}_2\text{O}$ described in this work crystallizes in the monoclinic space group $P2_1/n$. The coordination about the zinc atoms is almost identical to that in the divalent metal methylphosphonates, and the unit cell differs only in the size of the b -axis. However, it is the positioning of the Cl atom that destroys the mirror symmetry required by space group $Pmn2_1$. Thus, it crystallizes in the more common space group $P2_1/n$.

Another example¹⁹ is provided by the recent determination of the structure of $\text{Fe}(\text{O}_3\text{PC}_2\text{H}_5)\cdot\text{H}_2\text{O}$. It crystallizes in space group Pn with cell dimensions $a = 4.856(1)$ Å, $b = 10.33(2)$ Å, $c = 5.744(2)$ Å, and $\beta = 91.0(1)^\circ$. These cell dimensions are very similar to those of $\text{Zn}(\text{O}_3\text{PCH}_2\text{Cl})\cdot\text{H}_2\text{O}$ except that the b -axis is halved because of the absence of the 2_1 axis. Once again the layer structure and Fe(II) coordination sphere is essentially identical to those of the other divalent methylphosphonates. However, the ethyl group cannot satisfy the requirements of the pseudo mirror plane perpendicular to the layer.

New structures are generated in the phosphonate system when other complexing agents are present. For example, in the presence of chloride ion Zn tends to form a tetrahedral species with chlorine bonded directly to the metal as illustrated by the present compound $\text{Zn}_2\text{Cl}(\text{O}_3\text{PCH}_2\text{Cl})(\text{HO}_3\text{PCH}_2\text{Cl})\cdot 3\text{H}_2\text{O}$ and $\text{ZnCl}_2(\text{O}_3\text{PCH}_2\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_3)$.¹⁷ In the latter compound zinc is bonded to two chloride ions and two oxygens of the phosphonate group to form chains of Zn atoms bridged by phosphonate oxygens. Strong hydrogen bonds between the amino groups and the third phosphonate oxygen and Cl^- ions create a three-dimensional structure. Similarly, the urea complex described here also limits the Zn to tetrahedral coordination through bonding by the carbonyl group while hydrogen bonding through amino groups creates a layered structure.

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Supplementary Material Available: Anisotropic thermal parameters for non-hydrogen atoms (Table S1) for all three structures (3 pages). Ordering information is given on any current masthead page. A tabulation of observed and calculated structure factors for all three structures (Tables IX–XI) is available upon request from A.C. for up to 1 year from the date of publication.

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