Pillared Layered Metal Phosphonates. Syntheses and X-ray Powder Structures of Copper and Zinc Alkylenebis(phosphonates)

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Abstract: Covalently pillared layered metal phosphonate compounds were prepared by the reaction of divalent metal salts with alkylenebis(phosphonic acids). Cu(II) yields compounds $Cu_2[(O_3PC_2H_4PO_3)(H_2O)_2]$ (**1**) and $Cu_2[(O_3-PC_3H_6PO_3)(H_2O)_2] \cdot H_2O$ (**2**) when copper sulfate was reacted with ethylenebis(phosphonic acid) and propylenebis-(phosphonic acid), respectively. The corresponding bis(phosphonates) obtained for the reaction with zinc chloride are $Zn_2[(O_3PC_2H_4PO_3)(H_2O)_2]$ (**3**) and $Zn_2[(O_3PC_3H_6PO_3)]$ (**4**). The structures of these four compounds were determined *ab initio* from their X-ray powder diffraction data and refined by Rietveld methods. Crystal data for compound **1**: space group $P2_1/c$, $a = 8.0756(1)$ Å, $b = 7.5872(1)$ Å, $c = 7.4100(1)$ Å, $\beta = 116.319(1)°$, $Z = 2$. Crystal data for compound **2**: space group $Pnc2$, $a = 4.3276(2)$ Å, $b = 17.3181(8)$ Å $c = 6.7624(3)$ Å, $Z = 2$. Crystal data for compound **3**: space group $P2_1/n$, $a = 5.6861(8)$ Å, $b = 15.230(2)$ Å, $c = 4.7923(6)$ Å, $\beta = 91.936(2)°$. Crystal data for compound **4**: space group $Pna2_1$, $a = 8.4886(6)$ Å, $b = 5.2720(4)$ Å, $c = 18.865(1)$ Å, $Z = 4$. The metal−oxygen bridging interactions form two-dimensional layers in all four compounds. The layers are connected to each other by the alkylene groups leading to three-dimensional structures. In the copper compounds the metal atoms are five coordinate where four of the binding sites are from the phosphonate oxygens and one from the water oxygen. The coordination geometry of the copper atoms in compounds **1** and **2** may be described as distorted square-pyramidal, but the distortion is severe in the case of compound **2**. The zinc atoms in zinc ethylenebis-(phosphonate) have distorted octahedral geometry. The phosphonate oxygens provide five binding sites for the metal through chelation and bridging while the water oxygen occupies the sixth coordination site. The metal atoms in compound **4**, on the other hand, are tetrahedrally coordinated by the phosphonate oxygens. Unlike compounds **1**−**3**, this compound does not contain any water molecules. The interlamellar separation is 7.2 and 7.6 Å for copper ethylenebis(phosphonate) and zinc ethylenebis(phosphonate), respectively. The difference in the layer separation, however, is significant in the propylenebis(phosphonates). For copper and zinc compounds the values are 8.65 and 9.4 Å, respectively. The layer-connecting alkyl chains create open spaces whose sizes are determined by the length of the chain. Thus, a new class of pillared materials with definable cavity sizes may be prepared.

Introduction

Layered metal phosphonates are polymeric species that contain alternating hydrophilic and hydrophobic regions.[1] In these compounds the oxygen bridged metal atoms form the central two-dimensional layers which are separated on either side by the organic moities of the phosphonate group. One of the areas of research interest on these compounds is their use as hosts for intercalation reactions. In the case of tetravalent metal phosphonates all the metal coordination sites are occupied by the phosphonate oxygens and therefore molecules can be absorbed only into the interlayer space.[2] On the other hand, most of the phosphonates of the 3d series of metal ions contain water molecules in the metal coordination sphere.[3,4] These water molecules can be thermally removed thus creating vacant

sites for coordination intercalation.[5] Recently, we have demonstrated this type of reaction for the coordination intercalation of primary amines in zinc phenylphosphonate.[6] The host compound, $Zn(O_3PC_6H_5)(H_2O)$, on dehydration, reacts with molar amounts of alkylamines to form compounds of the type $Zn(O_3PC_6H_5)(RNH_2)$ with change in the Zn coordination and layer structure. Johnson et al.[7] have shown similar reactions for the intercalation of various primary alcohols into the vacant coordination site of the vanadium atom in $VO(O_3PR) \cdot H_2O \cdot C_6H_5-CH_2OH$ that was created by the removal of benzyl alcohol. Another interesting aspect of these compounds is the inclusion of functional groups to the organic portion.[8] By introducing

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specific groups one can prepare materials for studies in areas such as catalysis, ion exchange, and sorption.[9]

By utilizing diphosphonic acids, in the place of monophosphonic acids, an interesting series of new compounds with three-dimensional structures was obtained.[10,11] In these compounds the adjacent metal$-O_3PC$ layers are covalently linked by the organic groups of the phosphonate. Structurally these metal bisphosphonate compounds may be described as pillared compounds that contain pores of definite shape and size in the interlayer space. A variety of phosphonic acids, both in terms of the length and nature of the organic group, could be utilized in preparing compounds that open up a new area for extensive research activities. The organic pillars in most of these compounds are closely packed and therefore it is difficult to absorb any guest molecules into the interlayer space. However, by introducing spacers such as phosphites or phosphates between the bisphosphonates in the cross-linked structures, it is possible to create pores in these compounds. Several research groups[10−13] have prepared such porous compounds by using proper spacer groups and bisphosphonic acids. These compounds are structurally microporous, and the fact that the pillars can readily be functionalized, as described above, makes them interesting compounds to design materials for specific functions.[9]

One of our interests in this research area is to understand the properties of the compounds on the basis of their structures. However, due to the very weak interlayer forces, many of the layered metal phosphonates generally yield only polycrystalline samples. Hence the use of X-ray powder diffraction techniques has played a key role in deriving the structural information for this class of compounds that can be obtained only in the polycrystalline form.[2,6,13−16] Earlier structural studies have shown that the monophosphonates of tetravalent metal ions,[2] Cu ions,[3] and other divalent metal ions[4] like Mn, Ni, and Zn form classes of layered compounds that are different in structure from one another. Thus it is necessary to derive structural models for the bis(phosphonates), at least, for the representative member for each of these classes to establish structural relationships among the mono- and bisphosphonates. While the structural information is available for a good number of metal monophosphonates, such data are rare for the metal bis-

(phosphonate) compounds. Recently we reported the X-ray powder structures of Cu[15] and Zn[16] arylenebis(phosphonates). The pheneylenebis(phosphonates) of both Cu and Zn were found to be isostructural with their respective monophosphonate analogues. On the other hand, the compounds of biphenylene-bis(phosphonates), prepared at nearly the same conditions, were shown to have structures different from those of monophosphonates. Related studies as applied to vanadium compounds have been carried out by Soghomonian et al.[17] In many of these studies templates were utilized to produce a variety of porous and unusual compounds.[17b,18] In this paper we report the synthesis and X-ray powder structures of alkylenebis(phosphonates) of copper and zinc.

Experimental Section

Materials and Methods. All reagents were of analytical grade (Aldrich) and were used without further purification. Thermogravimetric analysis was carried out with a TA 4000 unit, at a heating rate of 10 °C/min under a nitrogen atmosphere. The IR spectrum was recorded on a Perkin-Elmer 1720-X FTIR unit by the KBr disk method.

Synthesis of $Cu_2[(O_3PC_2H_4PO_3)(H_2O)_2]$ (1). A 0.475 g (2.5 mmol) amount of 1, 2-ethylenebis(phosphonic acid) was mixed with 1.25 g of $CuSO_4 \cdot 5H_2O$ (5 mmol) in 50 mL of deionized distilled water and the mixture was heated at 60 °C for 4 days. The blue precipitate was filtered, washed with distilled water, and air dried (yield = 1.0 g). Anal. Calcd for $Cu_2[(O_3PC_2H_4PO_3)(H_2O)_2]$: C, 6.88; H, 2.30; H_2O, 10.31. Found: C, 6.67; H, 2.23; H_2O (TGA, 152−290 °C), 12.10.

Synthesis of $Cu_2[(O_3PC_3H_6PO_3)(H_2O)_2] \cdot H_2O$ (2). A 1.25 g amount of $CuSO_4 \cdot 5H_2O$ (5 mmol) and 0.51 g (2.5 mmol) of 1,3-propylenebis-(phosphonic acid) were dissolved in 20 mL of deionized distilled water. The reaction was carried out at 60 °C. Since no precipitate was observed after 24 h, an additional 1.25 g of $CuSO_4 \cdot 5H_2O$ was added to the reaction mixture. The precipitation then started and the reaction was allowed to go to completion over a 6-day period. The blue solid was filtered, washed, and air dried (yield = 0.4 g). Anal. Calcd for $Cu_2[(O_3PC_3H_6PO_3)(H_2O)_2] \cdot H_2O$: C, 9.45; H, 3.15; H_2O, 14.17. Found: C, 9.22; H, 2.79; H_2O (TGA, 85−219 °C), 13.64.

Synthesis of $Zn_2[(O_3PC_2H_4PO_3)(H_2O)_2]$ (3). The compound was prepared by the reaction of 0.475 g (2.5 mmol) of 1,2-ethylenebis-(phosphonic acid) with 0.68 g (5 mmol) of $ZnCl_2$ in 50 mL of deionized distilled water. The reaction mixture was kept at 60 °C, and the compound started to precipitate after about 1 day. The product was filtered off after standing for 1 month and washed with water. The white powder (0.2 g) was dried at room temperature. Anal. Calcd for $Zn_2[(O_3PC_2H_4PO_3)(H_2O)_2]$: C, 8.03; H, 3.35; H_2O, 10.21. Found: C, 6.77; H, 2.23; H_2O(TGA, 131−279 °C), 9.54.

Synthesis of $Zn_2[(O_3PC_3H_6PO_3)]$ (4). A 0.63 g amount of $ZnCl_2$ (4.6 mmol) was mixed with 0.51 g of 1,3-propylenebis(phosphonic acid) in 20 mL of deionized distilled water. The mixture was transferred to a plastic bottle, which was then placed in a drying oven at 60 °C. No precipitate was observed even after 1 week. Addition of an extra 1.23 g of $ZnCl_2$ and urea (0.60 g, 10 mmol) to the reaction mixture resulted in precipitation after several days. The product was filtered after 1 month and washed with distilled water. The white powder (0.95 g) was then dried at room temperature. The X-ray diffraction pattern of this compound (used for structural work and elemental analysis) contained a broad amorphous peak at around 13° in 2θ. The compound shows no weight loss up to 490 °C. The burning of the organic starts at around 500 °C. Anal. Calcd for $Zn_2[(O_3PC_3H_6PO_3)]$: C, 10.88; H, 1.81. Found: C, 8.68; H, 1.07.

The same compound without the impurity phase was obtained by increasing the pH with NaOH. The pH of the reaction mixture

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Table 1. Crystallographic Data

	$Cu_2[(O_3PC_2H_4PO_3)(H_2O)_2]$ (**1**)	$Cu_2[(O_3PC_3H_6PO_3)(H_2O)_2]\cdot H_2O$ (**2**)	$Zn_2[(O_3PC_2H_4PO_3)(H_2O)_2]$ (**3**)	$Zn_2[O_3PC_2H_4PO_3]$ (**4**)
formula	$C_2H_8O_8P_2Cu_2$	$C_3H_{12}O_9P_2Cu_2$	$C_2H_8O_8P_2Zn_2$	$C_3H_6O_6P_2Zn_2$
fw	349.1	381.2	352.8	330.8
space group	$P2_1/c$ (No. 14)	$Pnc2$ (No. 30)	$P2_{1/n}$(No. 14)	$Pna2_1$ (No. 33)
a (Å)	8.0756(1)	4.3276(2)	5.6861(8)	8.4886(6)
b (Å)	7.5872(1)	17.3181(8)	15.230(2)	5.2720(4)
c (Å)	7.4100(1)	6.7624(3)	4.7923(6)	18.865(1)
β (deg)	116.319(1)		91.936(2)	
V (Å³)	406.96(1)	506.8(1)	414.8(2)	844.2(2)
Z	2	2	2	4
d_{calcd} (g/cm³)	2.85	2.49	2.82	2.60
μ (cm⁻¹)	104.89	85.73	112.77	106.34
pattern range, 2θ (deg)	16−85	12.5−105	15−100	16−100
no. of unique reflcns	288	323	423	467
no. of structural params	28	31	28	51
R_{wp}	0.031	0.044	0.072	0.104
R_p	0.020	0.03	0.055	0.075
R_F	0.050	0.121	0.088	0.067

containing $ZnCl_2$ (5 mmol) and 1,3-propylenebis(phosphonic acid) (2.5 mmol) was raised to 2.5 by 1 N NaOH. On stirring for 2 min the compound $Zn_2[(O_3PC_3H_6PO_3)]$ precipitated (yield = 0.02 g). The precipitate was filtered off, and the filtrate was transferred to a plastic bottle and kept in an oven at 60 °C. The contents in the bottle turned into a gel in about an hour, and on continuing the reaction overnight a crystalline powder sample precipitated (yield = 0.25 g). TGA, IR, and X-ray powder diffraction data showed that this compound is different from compound **4**. X-ray powder structure analysis showed that this compound is $Zn_3[(HO_3PC_3H_6PO_3)(H_2O)]_2$ (see Discussion section).

Compounds **3** and **4** contain significant amounts of amorphous phases. This feature is clearly seen as large background in their X-ray powder diffraction patterns (see Figures 3 and 4 below). Because of this amorphous background the elemental analysis data obtained for these two compounds show large deviations from their expected values.

X-ray Data Collection. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite monochromated radiation. X-ray powder data for the samples were collected with a Rigaku computer automated diffractometer. The samples for the data collection were prepared by using an aerosol suspension chamber[19] to reduce the influence of preferred orientation effects. In this method the finely ground sample particles were dispersed into an aerosol through the action of a fluidized bed of spherical beads. The aerosol is then carried up through a column and is collected by a filter paper mounted on a casette by the action of a vacuum pump. The procedure yields random orientation of the particles within the pores of the filter paper. Room temperature data were collected with a step size of 0.01° and a count time of 10 s per step for compounds **1** and **3**, respectively. The fixed time count for compounds **2** and **4** was 7 s per step. The data were collected up to 85°, 107°, 110°, and 107° (in 2θ) for compounds **1**, **2**, **3**, and **4**, respectively. The powder patterns were indexed by Ito methods,[20] and space groups were derived from systematic absences.

Structure Solution and Refinement. The structure factor amplitudes, for compound **1**, were extracted from the profile with decomposition methods.[21] This procedure yielded 63 single indexed reflections over the range $10 < 2\theta < 65°$. This data set was converted into a single crystal type data set (F_{hkl}, σ_{hkl}) and input to a "direct method programs", MITHRIL,[22] in the TEXAN[23] series of programs. An E-map calculated for a solution with the best figure of merit (Resid = 13.4) revealed the positions of Cu, P, and all the oxygen atoms of the phosphonate group. The carbon atoms and the water oxygen atom were located in subsequent difference Fourier maps.

The X-ray powder patterns for compounds **2**−**4** were decomposed by the Le Bail method[24] with the program EXTRA.[25] The profile R-factors for the Le Bail extraction were 0.16, 0.087, and 0.156 for compounds **2**, **3**, and **4**, respectively. The extracted intensities were input to SIRPOW,[26] a direct methods program applied to powder data for the solution of crystal structures. For copper propylenebis-(phosphonate) the extraction procedure produced 117 independent observations. An E-map computed for a solution with the best figure of merit (CFOM = 0.38) revealed the positions of all the atoms in the structure except one carbon atom of the propylene chain (final R = 19%). In the case of compound **3**, 161 independent reflections were input to SIRPOW. A phase set with CFOM of 0.86 was used to calculate an E-map. The map contained the postions of all the atoms in the structure for which the final R-factor was 20.7%. The structure of zinc propylenebis(phosphonate) was also solved by SIRPOW. The intensities of 196 independent reflections were used and an E-map was computed by using a phase set with a CFOM of 0.3. Out of 13 independent atoms in the asymmetric unit, nine atoms (final R = 15.8%) were located from the E-map. The remaining atoms (2 oxygens and 2 carbon) in this structure and in compound **2** were located from difference Fourier maps calculated after initial Rietveld refinement (see below).

The structural models as obtained above were used for Rietveld refinement of the full pattern in GSAS.[27] After the initial refinement of scale, background function, unit cell parameters, and profile parameters, the atomic positions were refined with soft constraints only for the phosphonate groups. Difference Fourier maps were then calculated which allowed the positioning of the remaining atoms in the structures of compounds **2** and **4**. The full structures were then refined with the above mentioned soft constraints. In the final stages of refinement the weights of these constraints were reduced and kept at a value necessary to maintain a satisfactory geometry for the alkylkene groups of the phosphonates. The preferred orientation factors were refined to a value very close to 1.0, indicating the advantage of the sample preparation method in eliminating the preferred orientaion effects. All the atoms were refined isotropically. Neutral atomic scattering factors, as stored in GSAS, were used for all atoms. No corrections were made for anomalous dispersion, or absorption.

Crystallographic and experimental parameters are given in Table 1 and bond parameters in Tables 2−5. The final Rietveld refinement difference plots are shown in Figures 1−4.

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Table 2. Bond Lengths (Å) and Bond Angles (deg) for $Cu_2[(O_3PC_2H_4PO_3)(H_2O)_2]$

Cu1−O1	2.002(5)	Cu1−O2	1.949(4)
Cu1−O2[a]	2.381(4)	Cu1−O3	1.950(4)
Cu1−O4	2.021(4)	P1−O1	1.573(4)
P1−O2	1.486(4)	P1−O3	1.549(3)
P1−C1	1.841(4)	C1−C1′	1.521(5)
O1−Cu1−O2	164.4(2)	O1−Cu1−O2[a]	107.0(2)
O1−Cu1−O3	95.9(2)	O1−Cu1−O4	91.3(2)
O2−Cu1−O2[a]	88.1(2)	O2−Cu1−O3	88.8(2)
O2−Cu1−O4	86.5(2)	O2[a]−Cu1−O3	86.4(2)
O2[a]−Cu1−O4	83.3(2)	O3−Cu1−O4	168.8(2)
O1−P1−O2	113.7(3)	O1−P1−O3	109.5(3)
O1−P1−C1	106.5(3)	O2−P1−O3	112.5(3)
O2−P1−C1	110.4(3)	O3−P1−C1	103.7(2)
P1−C1−C1′	110.4(4)		

[a] Position of the O(2) atom corresponding to the longer Cu−O bond.

Table 3. Bond Lengths (Å) and Bond Angles (deg) for $Cu_2[(O_3PC_3H_6PO_3)(H_2O)_2]\cdot H_2O$

Cu1−O1	1.863(6)	Cu1−O2	2.171(8)
Cu1−O2	1.958(9)	Cu1−O3	1.927(9)
Cu1−O4	2.671(13)	P1−O1	1.532(8)
P1−O2	1.615(7)	P1−O3	1.483(9)
P1−C1	1.860(7)	C1−C2	1.471(5)
O1−Cu1−O2	90.6(5)	O1−Cu1−O2	131.8(5)
O1−Cu1−O3	92.8(5)	O1−Cu1−O4	144.8(5)
O2−Cu1−O2	121.0(5)	O2−Cu1−O3	140.4(5)
O2−Cu1−O4	74.0(4)	O2−Cu1−O3	84.4(6)
O2−Cu1−O4	82.3(4)	O3−Cu1−O4	80.9(5)
O1−P1−O2	105.2(6)	O1−P1−O3	119.0(7)
O1−P1−C1	105.5(6)	O2−P1−O3	109.1(7)
O2−P1−C1	104.2(6)	O3−P1−C1	112.6(6)
P1−C1−C2	114.9(5)	C1−C2−C1′	114.8(7)

Table 4. Bond Lengths (Å) and Bond Angles (deg) for $Zn_2[(O_3PC_2H_4PO_3)(H_2O)_2]$

Zn1−O1	1.973(6)	Zn1−O1[a]	2.468(7)
Zn1−O2	2.145(7)	Zn1−O3	2.026(6)
Zn1−O3[a]	2.207(6)	Zn1−O4	2.112(6)
P1−O1	1.509(5)	P1−O2	1.503(4)
P1−O3	1.479(5)	P1−C1	1.882(5)
C1−C1′	1.539(7)		
O1−Zn1−O1[a]	161.7(3)	O1−Zn1−O2	94.4(2)
O1−Zn1−O3	108.5(3)	O1−Zn1−O3[a]	98.7(3)
O1−Zn1−O4	90.6(3)	O1[a]−Zn1−O2	84.7(3)
O1a−Zn1−O3	89.8(3)	O1[a]−Zn1−O3[a]	63.0(2)
O1[a]−Zn1−O4	87.3(3)	O2−Zn1−O3	95.3(3)
O2−Zn1−O3[a]	83.7(3)	O2−Zn1−O4	168.3(3)
O3−Zn1−O3[a]	152.8(3)	O3−Zn1−O4	93.1(3)
O3[a]−Zn1−O4	85.2(3)	O1−P1−O2	113.2(4)
O1−P1−O3	110.3(4)	O1−P1−C1	107.0(4)
O2−P1−O3	111.1(4)	O2−P1−C1	106.8(4)
O3−P1−C1	108.1(4)	P1−C1−C1′	107.4(4)

[a] Positions corresponding to the longer Zn−O bond.

Results

The IR spectrum of the Copper ethylenebis(phosphonate) is essentially identical to that of Copper phenylenebis(phosphonate).[15] These compounds show a single strong peak at 3456 cm^{-1} corresponding to the coordinated water. Similarly the zinc ethylenebis(phosphonate) has an IR spectrum similar to that of zinc pheneylenebis(phosphonate).[16] In the case of the Zn compounds the IR spectra show two peaks (3305 and 3041 cm^{-1}) for the OH-stretching vibration. The IR spectrum of copper propylenebis(phosphonate) contains two peaks due to water, a sharp peak at 3514 cm^{-1} and a broad peak at 3254 cm^{-1}. This result indicates a different type of water arrangement in this compound as compared to copper etheylenebis(phos-

Table 5. Bond Lengths (Å) and Bond Angles (deg) for $Zn_2[(O_3PC_3H_6PO_3)]$

Zn1−O2	1.99(2)	Zn1−O4	2.10(2)
Zn1−O5	1.93(2)	Zn1−O6	1.77(2)
Zn2−O1	2.04(2)	Zn2−O2	1.92(2)
Zn2−O3	2.02(2)	Zn2−O4	1.87(2)
P1−O1	1.54(1)	P1−O2	1.57(1)
P1−O3	1.53(1)	P1−C1	1.80(1)
P2−O4	1.57(1)	P2−O5	1.50(1)
P2−O6	1.53(1)	P2−C3	1.83(1)
C1−C2	1.51(1)	C2−C3	1.50(1)
O2−Zn1−O4	106.0(7)	O2−Zn1−O5	104.2(7)
O2−Zn1−O6	111.9(9)	O4−Zn1−O5	113.1(7)
O4−Zn1−O6	106.8(11)	O5−Zn1−O6	115.3(9)
O1−Zn2−O2	103.3(9)	O1−Zn2−O3	111.2(8)
O1−Zn2−O4	111.6(8)	O2−Zn2−O3	115.3(7)
O2−Zn2−O4	111.6(8)	O3−Zn2−O4	104.2(7)
O1−P1−O2	108.8(7)	O1−P1−O3	110.3(8)
O1−P1−C1	109.7(7)	O2−P1−O3	107.8(7)
O2−P1−C1	109.3(7)	O3−P1−C1	110.7(7)
O4−P2−O5	108.5(7)	O4−P2−O6	109.0(7)
O4−P2−C3	107.0(7)	O5−P2−O6	113.1(7)
O5−P2−C3	110.6(7)	O6−P2−C3	108.4(7)
P1−C1−C2	114.1(8)	C1−C2−C3	111.1(8)
C2−C3−P2	112.7(8)		

phonate). The zinc propylenebis(phosphonate), on the other hand, contains no water and accordingly shows no peaks due to water absorption. The IR spectra of these compounds also contain characteristic frequencies due to the phosphate and organic groups.

Structure of $Cu_2[(O_3PC_2H_4PO_3)(H_2O)_2]$. The structure consists of two dimensional layers of −Cu−O$_3$P− groups in the *bc*-plane. The Cu atoms are located almost in this plane at $x = \pm0.055$. The Cu atoms are five coordinate, and their geometries can be described as distorted square pyramidal. Phosphonate oxygens provide four binding sites to the metal while the remaining site is filled with the water oxygen, O4. One of the phosphonate oxygens, O2 is involved in bridging two Cu atoms, which results in four-membered rings (Cu1b−O2−Cu1c−O2c) as shown in Figure 5. The Cu- - -Cu distance in this ring is 3.126 (3) Å. One of the Cu−O2 bond lengths is long (2.381 (4) Å) while the other is similar to the Cu−O bond lengths involving oxygen atoms, O1, O3, and O4 (range 1.949(4)−2.2021(4) Å). The O2 position that makes a long Cu−O bond occupies the axial position of the metal polyhedron. Oxygen atoms O1 and O3 bridge the Cu atoms approximately along the *b*-axis direction, which in turn are linked by O2 atoms along the *c*-axis direction. The layers thus formed are covalently cross-linked by the −C$_2$H$_4$− groups along the *a*-axis direction leading to a three-dimensional structure. The phosphate groups of the bis(phosphonate) are related by a center of symmetry located at the center of the ethyl chain. The coordinated water oxygen (O4) is also involved in intramolecular hydrogen bonding with the phosphonate oxygens, O1 (2.57(1) Å) and O3 (2.75(1) Å).

Structure of $Cu_2[(O_3PC_3H_6PO_3)(H_2O)_2]\cdot H_2O$. In this compound the metal−O$_3$P− layers are located in the *ac*-plane with the Cu atoms positioned at $y = \pm0.25$. The coordination of the metal atoms along with their connections to form a two-dimensional layer is shown in Figure 6. The Cu atoms in this plane are arranged at the corners of a rectangle and are separated by 4.33 Å along the *a*-axis direction and 3.39 Å along the *c*-axis direction. The P atoms are shifted by about 1.7 Å on either side of the mean plane of the Cu atoms. In Figure 6, it may be seen that the P atom is located nearly at the center of the copper rectangles. Its oxygens, O1 and O2 (O1d and O2c) and their symmetrically related positions are utilized in bridging the unit
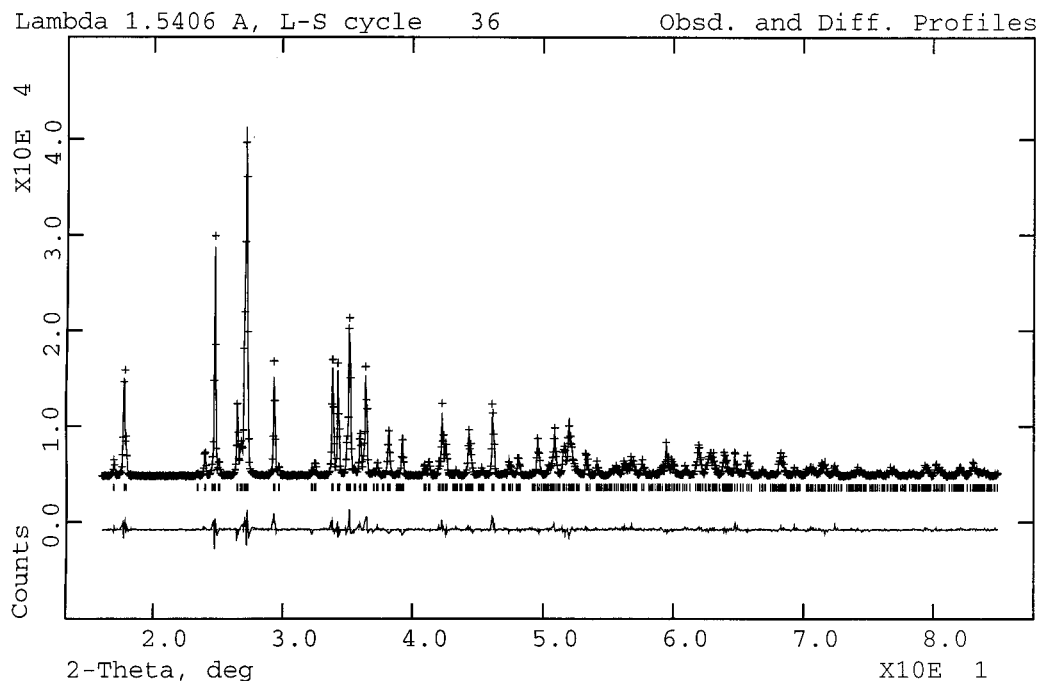
Figure 1. Observed ($+$) and calculated ($-$) profiles for the Rietveld refinement for $Cu_2[(O_3PC_2H_4PO_3)(H_2O)_2]$. The bottom curve is the difference plot on the same intensity scale.
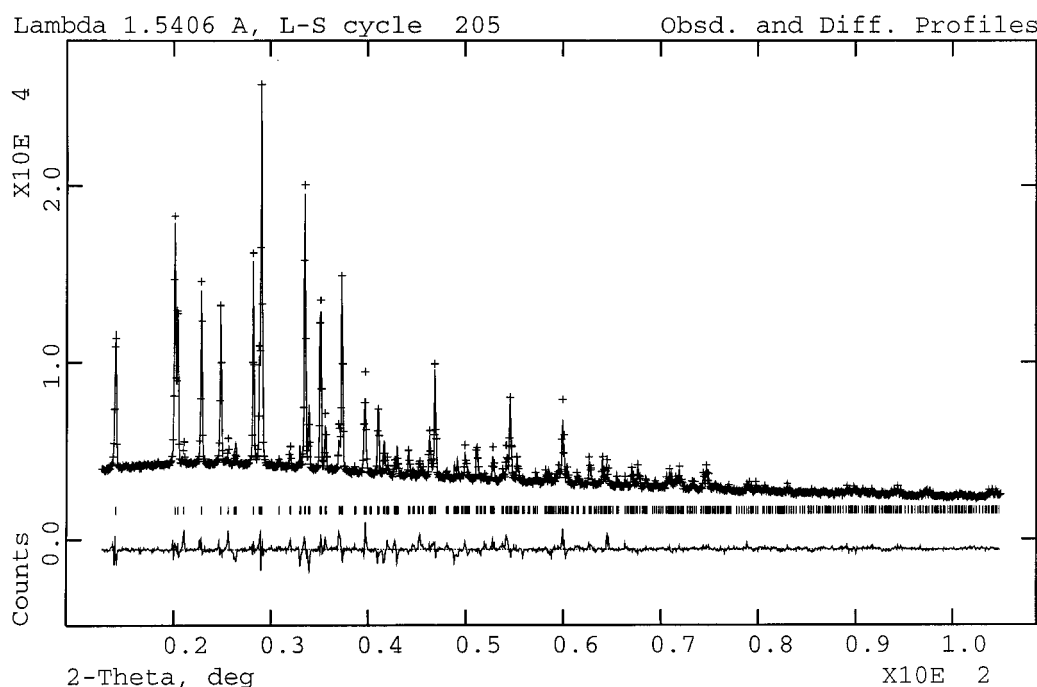
Figure 2. Rietveld difference plot for $Cu_2[(O_3PC_3H_6PO_3)(H_2O)_2] \cdot H_2O$.

cell translated Cu atoms along the *a*-axis direction. Oxygen, O2 at the same time, bridges these rows of Cu atoms to a symmetry related row along the *c*-axis. These bridges are represented by $-Cu1a-O2c-Cu1-$ in Figure 6. These rows (along the *c*-axis) are also linked by the oxygens O3 and O1, and together these interactions form six-membered rings such as $-Cu1a-O1b-P1b-O3c-Cu1-O2c-$. The structure may also be described as linear chains of Cu atoms along the *c*-axis direction (Cu- - -Cu = 3.3891(4) Å) that are directly bridged by O2 and indirectly bridged by O1 and O3 through phosphorus producing a layered connectivity. The Cu atoms are five coordinated, and as described above four of the binding sites (O1c, O2, O2c, O3c) are provided by the phosphonate oxygens. The fifth site is occupied by the water oxygen, O4. The Cu−O

bond lengths involving the phosphonate oxygens are in the range of 1.86(1)−2.17(1) Å. The Cu−O4 bond length, however, is significantly longer (2.67(1) Å) than the other bonds. The coordination polyhedron may be described as a highly distorted square pyramid where the bridging oxygen, O2 with a short Cu−O bond (1.96(1) Å), occupies the axial position. The two trans bond angles in the basal plane are 140(1)° and 144° while the corresponding cis angles are in the range of 74−93°. The axial bond is also bent away from the normal to the basal plane as shown by the corresponding bond angles that cover a wide range of values (82−132°).

Figure 7 shows the cross-linking of inorganic layers by the alkylene chain. The unit cell translated (*c*-axis) propylene carbon atoms (C2) are separated by 6.76 Å. The lattice water
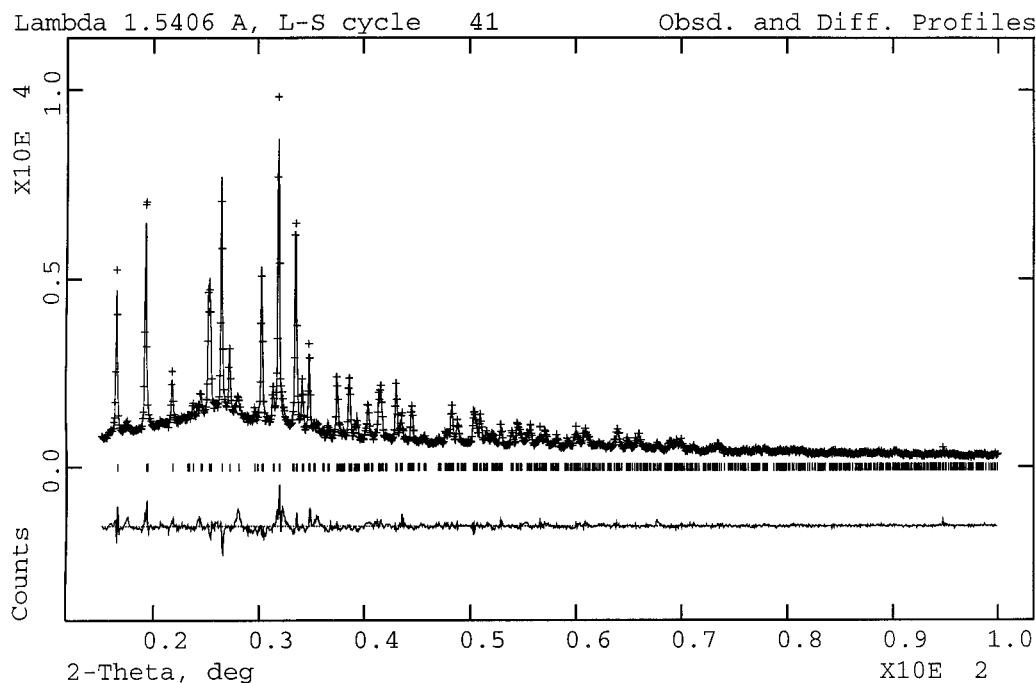
Figure 3. Rietveld difference plot for $Zn_2[(O_3PC_2H_4PO_3)(H_2O)_2]$.

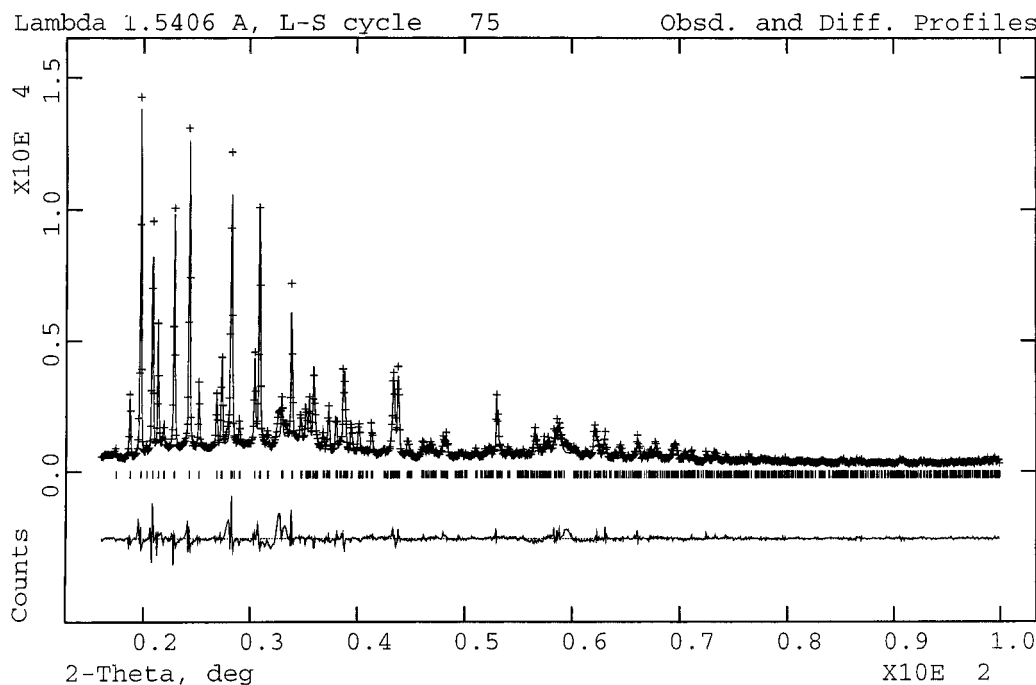**Figure 4.** Rietveld difference plot for $Zn_2[(O_3PC_3H_6PO_3)]$.

molecules (O5) are located in between the propylene groups in such a way that the C2 and O5 atoms are exactly at the centers of the mean planes of the inorganic layers. These atoms, however, are shifted from each other by $^1/_2$ along the projection axis (*a*-axis). All the contacts involving the lattice water with the carbon atoms are above 3.3 Å. Both the coordinated and lattice water molecules are involved in hydrogen bonding interactions. Coordinated water oxygen, O4, donates a hydrogen to an adjacent phosphonate oxygen, O3 (O4- - -O3 = 2.52(2) Å), and also is involved in bonding with the lattice water (shown in Figure 7). The latter interactions, O4- - -O5- - -O4 (O4- - - O5 = 2.61(1) Å), are significant as they also link the adjacent inorganic layers in addition to cross links by the organic moieties. The particular way in which the propylene bis-

(phosphonate) groups bridge the layers creates unidimensional cavities as shown in Figure 7.

Structure of $Zn_2[(O_3PC_2H_4PO_3)(H_2O)_2]$. All the atoms in the structure occupy general positions. The center of the C−C bond of the ethylene group coincides with a center of symmetry. The ethylene groups cross-link the inorganic layers whose mean planes are located in the *ac*-plane at y ∼ 0.25 and 0.75. All the phosphonate oxygens take part in metal binding, and among them two oxygens are involved both in chelation and bridging. Oxygens O1 and O3 chelate the metal and at the same time bridge the unit cell translated Zn atoms along the *a*-axis direction (Figure 8). Along the *c*-axis, the metal atoms are linked by the third oxygen of the phosphonate, O2. Thus the phosphonate provides five binding sites (2 × O1, 2 × O3, and O2) to the
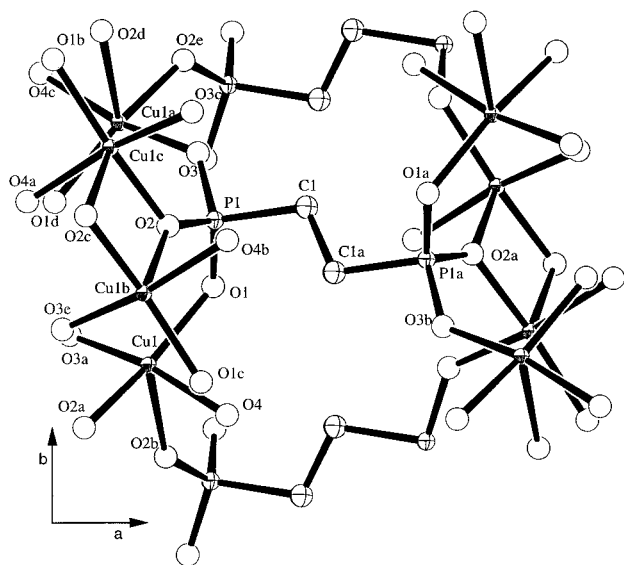
Figure 5. Atom labeling and phosphonate bridging interactions in $Cu_2[(O_3PC_2H_4PO_3)(H_2O)_2]\cdot H_2O$.
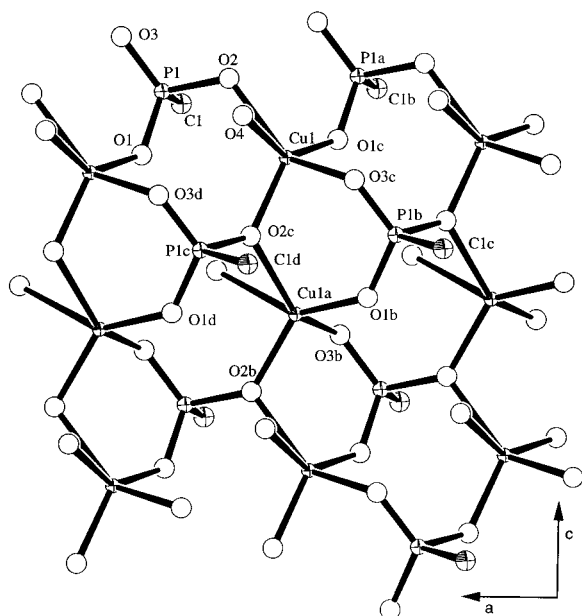
Figure 6. Layer arrangement in the structure of $Cu_2[(O_3PC_3H_6PO_3)-(H_2O)_2]\cdot H_2O$. O4 represents the oxygen atom of the coordinated water.

Figure 7. Structure of $Cu_2[(O_3PC_3H_6PO_3)(H_2O)_2]$ as viewed down the *a*-axis showing the one-dimensional pores. The lattice water molecules (not shown here) occupy the center of these pores and hydrogen bond to the coordinated water molecules which are also projected into the pores.

Figure 8. Metal phosphonate interactions in the structure of $Zn_2[(O_3PC_2H_4PO_3)(H_2O)_2]$. Note both chelation and bridging type of interactions of two of the phosphonate oxygens, O1 and O3.

metal atom while the remaining sixth coordination site is occupied by the oxygen atom (O4) of the water molecule. The coordination geometry is a distorted octahedron. The Zn–O bond lengths within the chelate ring are longer (Zn1–O1 = 2.47(1) Å, Zn1–O3 = 2.21(1) Å) than the bond lengths corresponding to the same oxygens involved in the bridging interaction (Zn1–O1 = 1.97(1) Å, Zn1–O3 = 2.03(1) Å). The Zn1–O2 and Zn–O4 bond lengths are 2.15(1) and 2.11(1) Å, respectively. Most of the bond angles for the octahedron deviate by about 10° from their ideal value, but those involving the chelation mode of binding show higher deviation. The angle in the chelation ring, O1–Zn1–O3, is 63.0(2)°. The phosphonate groups display regular bond parameters. The organic groups are well-separated along both the *a*- and *c*-axis directions, being spaced at intervals of about 5.7 and 4.8 Å, respectively.

Structure of $Zn_2[(O_3PC_3H_6PO_3)]$. The asymmetric unit, in this case, consists of two Zn atoms and a 1,3-propylenebis-(phosphonate) group where all the atoms occupy general positions. Therefore, unlike the previous three compounds, the
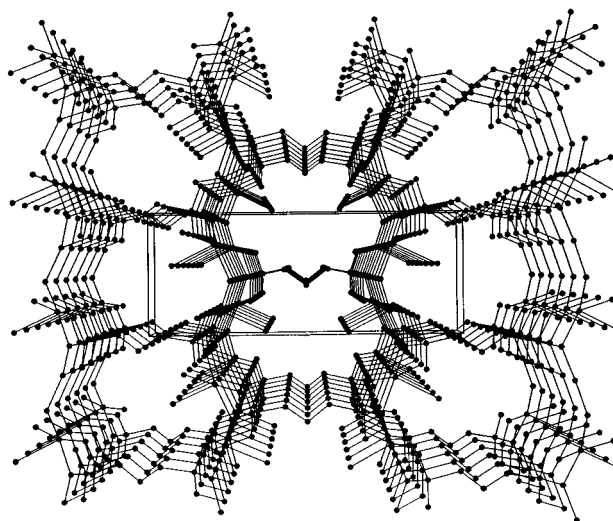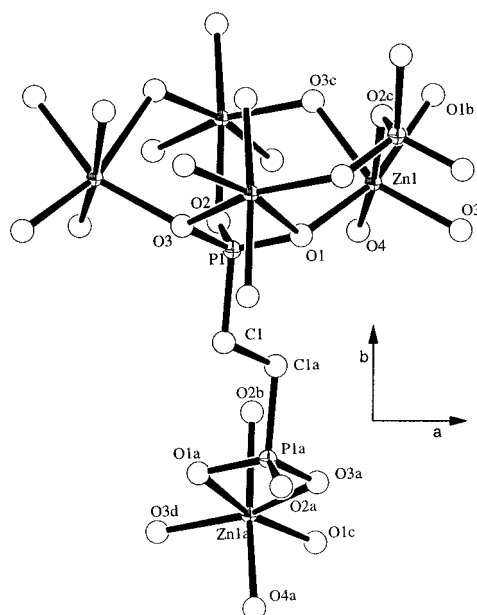
phosphonate groups of the bisphosphonate in this case are not symmetry related. Both the Zn atoms in the structure are tetrahedrally coordinated. Three of the Zn1 coordination sites are occupied by three oxygens (O4a, O5a, and O6) from three different P2-phosphonates while the fourth site is filled by an oxygen, O2, from a P1-phosphonate. Similarly Zn2 is coordinated by three oxygens (O1a, O2a, and O3) from three P1-type phosphonate groups and one oxygen (O4) from a P2-phosphonate. As can be seen in Figure 9, oxygens O2 and O4 are also involved in bridging adjacent Zn atoms that are separated by about 3.3 Å along the *b*-axis direction. This leads to a zigzag chain of Zn atoms along the *b*-axis, such as −O2a−Zn2−O4−Zn1a−O2− in Figure 9. These chains are connected by Zn1−O6−P2 and Zn2−O1−P1 bridges along the *a*-axis direction forming a two-dimensional layer in the *ab*-plane. The mean planes of the Zn atoms in the layer are located at $z = 0.19$ and 0.69. The Zn atoms alternate by about 1 Å on either side of
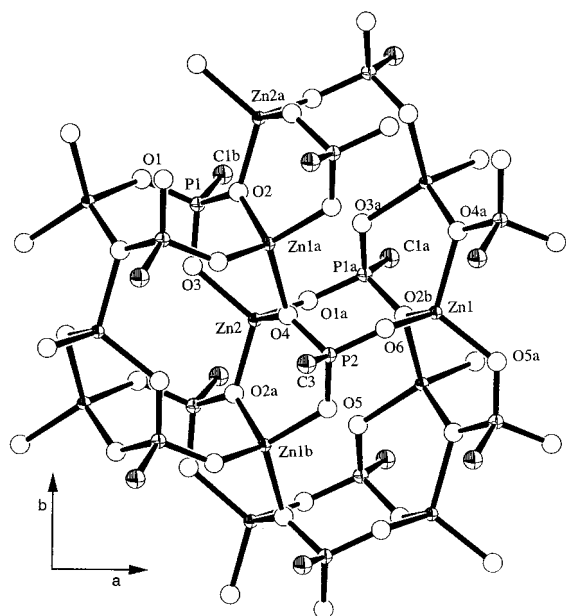
Figure 9. Layer structure of $Zn_2[(O_3PC_3H_6PO_3)]$. The Zn atoms are coordinated only by the phosphonate oxygens.

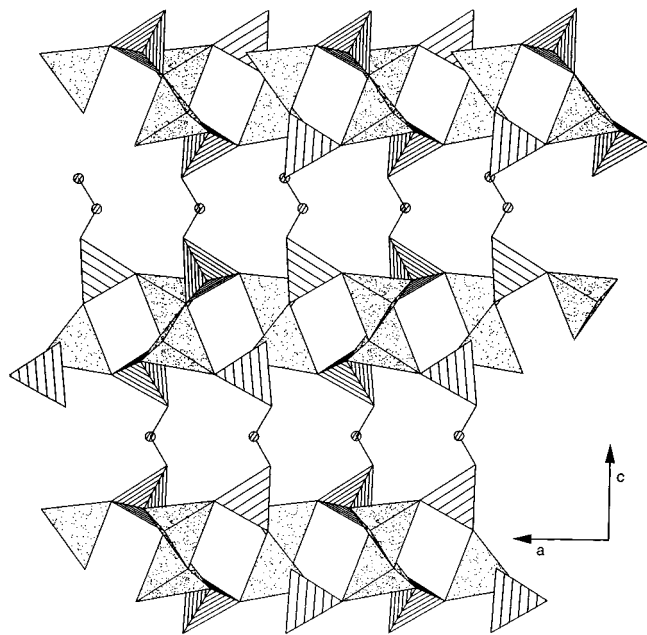**Figure 10.** Polyhedral representation of the structure of $Zn_2[(O_3PC_3H_6-PO_3)]$ down the *b*-axis. The adjacent alkyl groups as seen in this projection are shifted $^1/_2$ along the *b*-axis. The zinc tetrahedra are stippled and the phosphonate groups are striped.

the mean plane. Similarly, the P atoms are located above and below the metal mean planes, but their location is about 1.9 Å from the mean layer plane. A polyhedral representation of the structure depicting the cross-linking of the layers is shown in Figure 10. The central carbon atoms of the propylene groups form rows (along the *a*-axis) in between the adjacent inorganic layers. The central carbon atoms in adjacent rows are shifted by $^1/_2$ along the projection axis (*b*-axis) to each other, placing them about 5 Å apart.

Discussion

The structures of the ethylenebis(phosphonates) of the Cu and Zn compounds described here are similar, in their layer arrangement, to those found for their phenylenebis(phosphonate) analogues. The copper phenylenebis(phosphonate),[15] $Cu_2[(O_3-$

$PC_6H_5PO_3)(H_2O)_2]$, belongs to the space group $C2/c$ with $a = 18.8892(4)$ Å, $b = 7.6222(2)$ Å, $c = 7.4641(2)$ Å, $\beta = 90.402°$, and $Z = 4$. The in-layer dimensions (*b* and *c*) are very close to the values found for the copper ethylenebis(bisphosphonate), but the interlayer separations in these compounds are different due to the size of the cross-linking group. It may be noted that the layer separation in the phenyl compound corresponds to $^1/_2$ of the *a*-axis dimension. The zinc phenylenebis(phosphonate),[16] $Zn_2[(O_3PC_6H_5PO_3)(H_2O)_2]$, also contains very similar metal−O_3PC layers as described for the zinc ethylenebis(phosphonate). The phenylene compound, however, crystallizes in a different space group symmetry (*Pnnm*, $a = 19.2988(6)$ Å, $b = 4.8229-$ (2) Å, $c = 5.6544(2)$ Å, $Z = 2$) and the *c*- and *b*-dimensions in this case correspond to *a*- and *c*-dimensions, respectively, in the present ethylene compound. The arrangements of the layer structures in the above-mentioned Cu and Zn compounds are also similar to those in the corresponding monophosphonate compounds.[3,4] The difference in these two sets of compounds is in their molecular formula and in their interlayer separations. In the case of monophosphonates,[4] the compounds have the general formula $M(O_3PR)(H_2O)(M = Cu, Zn, Mn, Cd; R = $ methyl, ethyl, phenyl). As can be seen, the metal to organic group (R) ratio in the case of monophosphonates is 1 while it is $^1/_2$ for the bis(phosphonates), although the metal to P ratio is the same in all these compounds. The organic groups are connected to the layers in a similar manner both in the mono- and bis(phosphonates), but in the latter case they are also linked to the adjacent layers. On the other hand, the organic groups in the case of monophosphonates project away into the interlayer space from either side of the layers that create an organic bilayer. The groups in these bilayers are held together only by van der Waals forces. Thus the structures of the monophosphonates are separable two-dimensional layers while those of the bis-(phosphonates) are ideally three-dimensional layers.

This type of structural relationship among different phosphonate compounds, however, does not hold for the compounds formed by the reaction of Cu and Zn salts with 4, 4′-biphenylenebis(phosphonic acid) prepared under similar conditions. The compounds formed in this system are Cu-$[HO_3P(C_6H_4)_2PO_3H]$[15] and $Zn[HO_3P(C_6H_4)_2PO_3H]$[16] for Cu and Zn, respectively. In both cases an oxygen of each phosphonate group is protonated. The Cu atoms in this structure are arranged in the form of linear chains that are bridged by phosphonate groups. The hydroxyl groups form very weak axial bonds with the copper of the adjacent chains. In addition, these adjacent chains are linked through hydrogen bonds involving the hydroxyl groups. The structure of the Zn compound consists of double chains with alternating Zn and P atoms connected to each other by phosphonate bridges. These double chains are cross-linked by the biphenylene groups which leads to a new type of two-dimensional sheet. The hydrogen bonds involving the hydroxyl groups then connect the sheets forming a loosely held three-dimensional structure.

It appears that the chain-like structures formed for the Cu[15] and Zn[16] biphenylenebis(phosphonates) are due to the protonation of the phosphonate groups that makes it difficult for them to bridge the metal ions to form two-dimensional layers. To understand this, we have prepared the compounds at slightly higher pH (4−5) either by using less acid metal salts like acetates or by the addition of base to the reaction mixture. In this condition, both Cu and Zn lead to new phases with biphenylenebis(phosphonic acid) that are different from those mentioned above. However, because of the poor quality powder data the pattern of the Cu compound could not be indexed so far, but it appears that the compound contains two-dimensional

layers similar to that obtained for the protonated phosphonate compounds. In the case of Zn, the powder pattern could be indexed and the structure was solved and refined with use of the Rietveld method. The compound $Zn_2[(O_3PC_{12}H_8PO_3)-(H_2O)_2]$ crystallizes in the space group *Pnn*2 with $a = 27.904-(1)$ Å, $b = 4.8273(3)$ Å, and $c = 5.6450(2)$ Å. The final agreement factors for the Rietveld refinement (2θ range $10-70°$) are $R_{wp} = 0.135$, $R_p = 0.107$, and $R_F = 0.024$ for 191 independent reflections. The layer dimensions, b and c here, are very close to those found for the zinc phenylenebis-(phosphonate) compound.[16] Accordingly the structures of these two compounds are similar except for the fact that the layers are expanded in the biphenylene compound along the *a*-axis direction due to the additional phenylene group. Also the biphenylene compound was refined in a noncentric space group to remove the constraints of the mirror symmetry on the atoms. Details will be presented later.

The copper and zinc propylenebis(phosphonate) structures are new although they contain two-dimensional metal$-O_3PC$ layers similar to those found for other metal phosphonate compounds. The phosphonate groups are deprotonated, and all their oxygens take part in metal binding. As described in the Results section, the metal$-$phosphonate bridging interactions in these compounds are different from their respective ethyl-enebis(phosphonate) analogues. This feature is also reflected in the coordination geometries of the metal atoms. In the case of copper propylenebis(phosphonate), the coordination geometry is highly distorted and the Cu$-$water interaction is very weak. In addition, this compound contains a lattice water molecule that is located in between adjacent alkylene groups. To the best of our knowledge, this represents the first example of a metal$-$phosphonate compound containing lattice water molecules in the hydrophobic region of the compound. The zinc propylenebis(phosphonate) is especially different from the zinc ethylenebis(phosphonate) and other zinc phosphonates. The propylene compound does not contain any water molecules either in the metal coordination sphere or in the lattice. Yet, the compound contains two-dimensional layers formed by the bridging of oxygen atoms. The metal atoms are tetrahedrally coordinated as opposed to octahedral coordination in the ethylenebis(phosphonate) compound and other zinc monophos-phonate compounds. The other zinc phosphonate compounds where the Zn atoms are tetrahedrally coordinated are Zn-$[HO_3P(C_6H_4)_2PO_3H]$,[16] the primary amine intercalates of zinc phenylphosphonate[6] and $Zn(O_3PC_2H_4NH_2)$.[28] All these com-pounds have a very similar layer structure; however, in $Zn(O_3-PC_2H_4NH_2)$ the inorganic layers are cross-linked by the phosphonate oxygens on one side and by the nitrogen on the other side.

The two zinc compounds and the copper ethylenebis-(phosphonate) described here are three-dimensional pillared solids but they do not possess any significant open spaces as the organic groups are positioned at van der Waals contact distances. In the copper propylenebis(phosphonate), on the other hand, the organic groups are spaced further apart (6.8 Å) as a result of the presence of these lattice water molecules in between them. Also, the coordinated water oxygen binds weakly to the Cu atoms and this oxygen is strongly involved in hydrogen bonding with the lattice water. If these two water molecules were removed from the structure without disturbing the overall framework, a cavity of diameter about $6-7$ Å would be created in the interlayer space of the compound. Reference to Figure 7 shows that this open space is uniform in the crystal and it has

an opening along the *a*-axis direction. The TGA curve for the compound shows that the weight loss due to the release of water molecules takes place in a single step starting at 85 °C and the process is complete at around 220 °C. On the basis of these TGA data, the compound was dehydrated in several steps starting at 80 °C. The XRD patterns of the heated sample, in the beginning ($80-120$ °C), show peaks corresponding to both the hydrated and the dehydrated phases. On increasing the temperature (above 120 °C) and the duration of dehydration, the peaks due to the hydrated phase decrease in intensity while those corresponding to the dehydrated phase increase. Complete removal of water could be achieved at a temperature of about 200 °C. The heated sample does not pick up water readily on exposure to the atmosphere. However, on adding water the phase reverts to the starting hydrated phase as shown by its powder diffraction pattern. This result shows that the compound retains its structural integrity on removing the water molecules. The interlayer separation is about 9.4 Å for the dehydrated phase, and that is about 0.7 Å longer than that in the hydrated phase. Incidentally, the d-spacing observed for this dehydrated phase is about the same as that seen for the zinc propylenebis-(phosphonate). This increase in interlayer separation may be due to the rearrangement of inorganic layers following the coordination change of Cu. In fact, an even larger (about 1 Å) increase in the layer separation on dehydration was observed for the un-cross-linked copper monophosphonate compounds.[5a,29] Studies are underway to measure the pore size in this dehydrated compound and to examine the sorption characteristics of this compound. It would be interesting to see whether bis-(phosphonic acids) with longer alkyl chains containing an odd number of carbon atoms, 5, 7, or more, could form structures similar to the copper propylenebis(phosphonate). In these cases, the increased interlayer spacings would allow large molecules to diffuse and possibly coordinate the metal ions.

The type of product obtained from the reaction of Zn salts with propylenebis(phosphonic acid) depends on the reaction conditions, particularly the pH. In a highly acidic condition (pH ∼1.5), Zn^{2+} ions replace only one proton from each of the phosphonate groups of the propylenebis(phosphonate) to yield the compound $Zn(HO_3PC_3H_6PO_3H)$. The crystals of this compound are monoclinic, with space group $P2_1/n$, $a = 18.167-(3)$ Å, $b = 5.0829(8)$ Å, $c = 8.658(1)$ Å, and $\beta = 93.630(2)°$. Structure solution by using the powder diffraction data shows that this compound contains double chains similar to that observed earlier for $Zn(HO_3PC_{12}H_{10}PO_3H)$.[16] As mentioned in the Experimental Section, the reaction of a Zn salt with propylenebis(phosphonate) at pH 2.5 resulted in a crystalline product that was found to be $Zn_3[(HO_3PC_3H_6PO_3)(H_2O)]_2$. This compound crystallizes in the monoclinic space group $C2/c$, with $a = 20.5803(5)$ Å, $b = 5.0461(1)$ Å, $c = 18.0070(3)$ Å, $\beta = 97.255(1)°$. Its structure was solved by using the powder diffraction data, and the details concerning the above two structures will be presented in a subsequent publication. The structure of $Zn_3[(HO_3PC_3H_6PO_3)(H_2O)]_2$ is layered but consists of a new and highly open metal$-O_3PC$ framework linked by organic groups to form a 3-dimensional structure. In the case of $Zn(HO_3PC_{12}H_8PO_3H)$ both phosphonate groups are singly protonated while in $Zn_3[(HO_3PC_3H_6PO_3)(H_2O)]_2$ one of the phosphonate protons is exchanged for Zn atoms. The remaining proton is exposed to a fairly large opening in the interlayer space and it is possible to exchange it for other ions. The structure also contains a second cavity in the interlayer space to which coordinated water oxygens are exposed. This is a large elliptical open space through which the coordinated water molecules may

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be removed on heating. This dehydration provides spaces into which small and medium sized molecules may be incorporated. While the body of this region is hydrophobic, the Zn atoms have open coordination sites that may serve as catalytic centers. The same is true for the copper propylenebis(phosphonate) but only one type of cavity is present. Furthermore, it may be possible to prepare open spaces of controlled sizes by varying the size of the alkyl chains in the bis(phosphonate). Additionally, the chains may be functionalized with oxo, amino, or carboxyl groups so as to change the character of these pores.[30] We are pursuing these options.

Supporting Information Available: Tables providing a complete listing of atomic parameters and isotropic thermal displacement parameters for compounds **1**−**4** (4 pages). See any current masthead page for ordering and Internet access instructions.

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