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Synthesis and X-ray Powder Structures of Covalently Pillared Lamellar Zinc Bis(phosphonates)

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Two new lamellar metal phosphonates, zinc phenylenebis(phosphonate), $Zn_2[(O_3PC_6H_4PO_3)(H_2O)_2]$ (**1**), and zinc biphenylylenebis(phosphonate), $Zn[HO_3P(C_6H_4)_2PO_3H]$ (**2**), have been synthesized. The structures of these compounds were solved *ab initio* from X-ray powder diffraction data and refined by Rietveld methods. Compound **1** is orthorhombic: space group *Pnnm*, $a = 19.2991(6)$ Å, $b = 4.8232(2)$ Å, $c = 5.6545(2)$ Å, and $Z = 2$. The structure is layered, and its layer arrangement is similar to that in zinc phenylphosphonate. The zinc atoms are octahedrally coordinated. Two of the oxygens of the phosphonate group are involved in chelation and bridging the metal atoms. The third oxygen binds to only one metal atom. The sixth coordination site is occupied by a water molecule. The adjacent layers are bridged by the phenylene group of the bis(phosphonate). Compound **2** is triclinic: space group $P\bar{1}$, $a = 9.5097(3)$ Å, $b = 5.0074(2)$ Å, $c = 14.2109(4)$ Å, $\alpha = 92.797(3)°$, $\beta = 99.725(3)°$, $\gamma = 92.003(3)°$, and $Z = 2$. In this case the metal atoms are tetrahedrally coordinated by four oxygens, two from each of the phosphonate groups of the bis(phosphonate). The third oxygen of the phosphonate group is protonated and is not involved in metal binding. The structure consists of double chains with alternating Zn and P atoms connected to each other by phosphonate bridges. These double chains run along the *b* axis and are linked to similar chains along the *a* direction through hydrogen bonds involving P−OH groups. This arrangement leads to loosely bound metal−CPO_3 networks in the *ab* plane which are bridged by the biphenylylene groups along the *c* axis. Thus in a broad sense this compound may also be considered as layered.

Introduction

Early work on metal phosphonate chemistry was centered on the layered compounds of group 4 and 14 elements largely because of their similarity to the inorganic phosphates of these metals and their great stability.[1,2] Tetravalent metal phosphonates $M(O_3PR)_2$, have octahedrally coordinated metal atoms, where all the coordination sites are occupied by the phosphonate oxygens. The metal phosphate networks, which constitute the layers, are separated by the organic portion of the phosphonate group.[1−4] Studies from this and other groups have now shown that a variety of other metal ions can form similar layered compounds.[5−7] In addition, some of these compounds have been shown to form a variety of new structural types,[6−9] including porous structures.[10−13] The metal phosphonate compounds have attracted substantial research interest primarily because of their potential application in the areas of sorption and ion exchange,[14] catalysis,[15,16] sensors,[5,17] and nonlinear optics.[3,5,18]

Dines et al.[16,19] conceived of the idea of creating pillared or cross-linked compounds by using a bis(phosphonic acid). A

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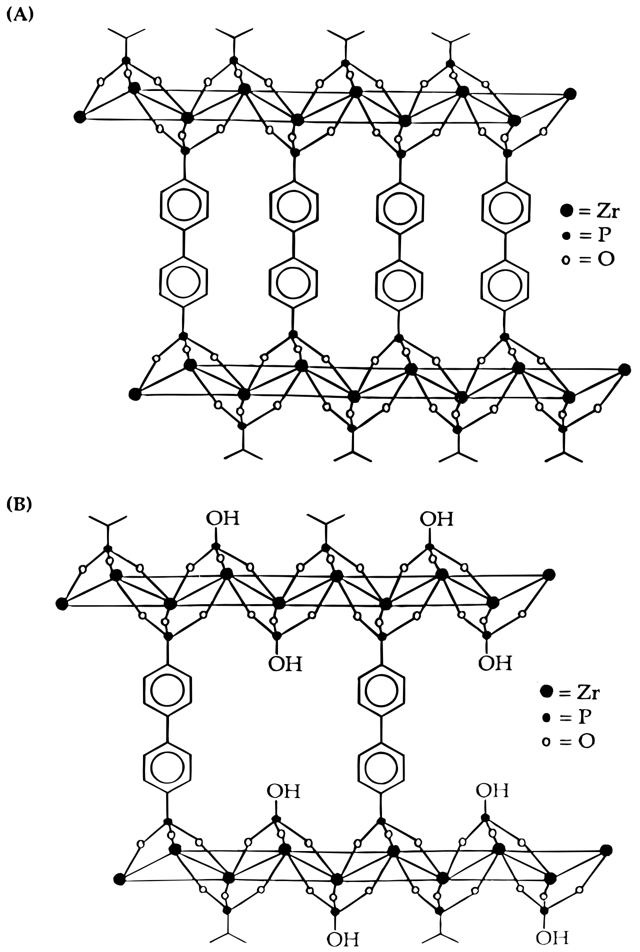

Figure 1. Schematic representation of (A) $Zr(O_3P-C_6H_4-C_6H_4-PO_3)$ and (B) $Zr(O_3P-C_6H_4-C_6H_4-PO_3)_{0.5}(HPO_4)$ based on the α-zirconium phosphate layer structure. Reflection positions are marked.

schematic illustration of such a derivative is shown in Figure 1A. In order to introduce micropores, they prepared mixed derivatives in which the cross-links were spaced by smaller phosphate or phosphite groups as illustrated in Figure 1B. These compounds exhibited high surface areas[16] but with a broad distribution of pore sizes.[20] A possible reason for the nonuniformity of pores is the clustering or segregation of pillars and spacers. Indirect evidence that this hypothesis has a certain validity was provided by Alberti et al.[10c] They used 3,3′,5,5′-tetramethylbiphenylylenebis(phosphonic acid) as cross-linking agent. The bulkiness of the methyl groups prevented the pillars from occupying adjacent positions on the layer. Thus, the phosphite spacer groups must occupy all the positions adjacent to each pillar. This arrangement created uniform micropores of 5−6 Å as predicted. Recently, pillared layered phosphonates of other metal ions were reported which include a zinc compound[21] containing a functionalized phosphonic acid ((2-aminoethyl)phosphonic acid) and vanadium compounds of bis(phosphonates).[22]

The difficulty in characterizing the porous pillared materials lies in their amorphous or weakly crystalline nature. The X-ray patterns yield broad spacings of 9.8 Å for the monophenylene and 13.8 Å for the biphenylylene derivatives in accord with the model shown in Figure 1, but no direct structural evidence is available to confirm the model. Since it is possible to vary the length of the pillaring group at will by using alkylene, arylene, and mixed alkylene−arylene cross-linking agents, it may be possible to create a family of molecular sieve like compounds. Thus direct structural information is a key ingredient required to understand the behavior of such a class of compounds.

Divalent metal phosphonates are much more soluble than those based on 4-valent species. Thus, in many cases it is possible to crystallize them and determine their crystal structures by conventional single-crystal X-ray diffraction methods. In this regard the structures of the layered Zn,[7a] Cu,[7b] and Mn[5] phenylphosphonates have been solved. More recently we were able to solve the structures of amine intercalates of zinc phenylphosphonate from their powder patterns.[7d] These results were sufficiently encouraging for us to extend our studies to the synthesis of divalent bis(phosphonates). Accordingly, we were able to prepare zinc bis(phosphonate) compounds with reasonable crystallinity. In this paper, we report the X-ray powder structures of zinc phenylenebis(phosphonate) and zinc biphenylylenebis(phosphonate) compounds and compare some salient features to those of their monophosphonate analogues.

Experimental Section

Materials and Methods. Chemicals used were of reagent grade quality and were obtained from commercial sources without further purification. Thermogravimetric analyses (TGA) were carried out with a Du Pont Model 951 unit, at a rate of 10 °C/min under an oxygen atmosphere. Infrared spectra were recorded on a Digilab Model FTS-40 FTIR unit by the KBr disk method. ^{31}P NMR spectra were obtained on a Bruker MSL-300 solid-state NMR spectrometer where proton and phosphorus nuclei resonate at 300.1 and 121.5 MHz, respectively. The ^{31}P chemical shifts were referenced to 85% H_3PO_4 (aqueous solution).

Synthesis Procedures. The phenylenebis(phosphonic acid) and biphenylylbis(phosphonic acid) were prepared according to the reported procedure.[23] Zinc 1,4-phenylenebis(phosphonate) hydrate was prepared by mixing 10 mmol (1.36 g) of $ZnCl_2$ (Mallinckrodt, reagent grade) and 5 mmol (1.19 g) of 1,4-phenylenebis(phosphonic acid) in water at 60 °C. After about 7 days, a white precipitate was formed, which was filtered off, washed, and dried at room temperature (yield 1.41 g; 70.3%). Anal. Found: C, 18.88; H, 1.95; H_2O (TGA), 8.6. Calcd for $Zn_2[(O_3PC_6H_4PO_3)(H_2O)_2]$: C, 17.97; H, 2.0; H_2O, 8.98.

Zinc 4,4′-biphenylylenebis(phosphonate), $Zn[HO_3P(C_6H_4)_2PO_3H]$, was prepared by mixing 1.0 g (3.18 mmol) of 4,4′-biphenylylenebis(phosphonic acid) and 0.44 g (3.55 mmol) of $ZnCl_2$ in 10 mL of water (pH = 1.61). The resulting white thick slurry was heated at 90 °C for 7 days. The white precipitate formed was filtered off, washed, and dried at 50 °C (yield 1.1 g; 82%). The same compound was also prepared by using a Zn:P ratio of 1:1 in which 3.18 mmol of 4,4′-biphenylylenebis(phosphonic acid) and 7.01 mmol of zinc chloride were treated as before (yield 1.16 g; 86% based on phosphonic acid). However, a higher crystallinity product was obtained in the former case. Anal. Found: C, 38.14; H, 2.68; H_2O (TGA), 4.23. Calcd for $Zn[HO_3P(C_6H_4)_2PO_3H]$: C, 38.16; H, 2.65; H_2O, 4.77.

The deprotonated form of zinc 4,4′-biphenylylenebis(phosphonate), $Zn_2[O_3P(C_6H_4)_2PO_3]$, was prepared by mixing 3.18 mmol of 4,4′-biphenylylenebis(phosphonic acid) with 7.01 mmol of zinc chloride. The pH of the solution was raised slowly to 6.7 with 1 N NaOH. The reaction mixture was then heated at 94 °C for 7 days. The product was filtered off, washed with water, and air-dried. The yield was 1.334

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g (95% based upon phosphonic acid). Anal. Found: C, 32.98; H, 2.10. Calcd for $Zn_2[O_3P(C_6H_4)_2PO_3]$: C, 32.69; H, 1.83.

X-ray Data Collection. Step-scanned X-ray powder data for the samples (side-loaded into a flat aluminum sample holder) were collected on the finely ground sample by means of a Rigaku computer-automated diffractometer. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite-monochromated radiation. Data for compound **1** were collected between 6 and 85° in 2θ with a step size of 0.01° and a count time of 12 s/step. For compound **2** the same step size was used, but the 2θ range was 3−80° and the time constant was 12 s/step. Data were mathematically stripped of the $K\alpha_2$ contribution, and peak picking was conducted by a modification of the double-derivative method.[24] The powder pattern was indexed by Ito methods[25] on the basis of the first 20 observed lines. The best solution (FOM = 87) which indexed all the peaks of the compound **1**, indicated an orthorhombic cell with lattice parameters $a = 19.32$ Å, $b = 4.83$ Å, and $c = 5.66$ Å. The systematic absences were consistent with the space group *Pnnm* or *Pnn*2. In the case of compound **2** the best solution (FOM = 41) corresponded to a triclinic cell with $a = 9.51$ Å, $b = 5.0$ Å, $c = 14.2$ Å, $\alpha = 92.8°$, $\beta = 99.8°$, and $\gamma = 92.1°$. The initial selection of the centric space group, $P\bar{1}$ was found to be correct from the successful solution and refinement of the structure.

Structure Solution and Refinement of $Zn_2[(O_3PC_6H_4PO_3)(H_2O)_2]$. Integrated intensities for compound **1** were extracted from the profile over the range $6° < 2\theta < 80°$ by decomposition methods as described earlier.[26] This procedure produced 31 single indexed reflections and 16 peaks with two or three contributors. The intensities of the latter set of peaks were divided equally between the number of contributing reflections and added to the starting data set. A Patterson map was computed using this data set in the TEXSAN[27] series of single-crystal programs. The positions of the Zn atom and that of the P atom were derived from this Patterson map. Constrained refinements and subsequent difference Fourier maps revealed the approximate positions of the oxygen atoms of the phosphonate and the water molecule. These oxygen atoms complete a distorted octahedral geometry about the Zn atoms.

The carbon atom of the phenylene group bonded to the phosphorus atom was placed at a calculated position to complete the P tetrahedra. The raw powder data were transferred to the GSAS[28a] program package for full-pattern refinement. For this purpose, the data from both $K\alpha_1$ and $K\alpha_2$ were used. After the refinement of scale, background, and unit cell constants, the atomic positions were refined with soft constraints. As indicated earlier, the coordination about the Zn atom in compound **1** is a distorted octahedron. Therefore, no constraints were applied to the O−O nonbonded distances about the Zn polyhedra. However, in the initial stages of refinement, the Zn−O distances were constrained to a value of 2.12 Å, which is the average of Zn−O bond distances obtained for the isostructural compound zinc phenylphosphonate as determined from a single-crystal study.[7a] The P−O and P−C bond distances were held at 1.53(1) and 1.80(1) Å, respectively. The tetrahedral geometry about the P atom was obtained by constraining the O---O and O---C nonbonded distances to 2.55(1) and 2.73(1) Å, respectively. A difference Fourier map computed at this stage revealed the position of the remaining carbon atoms of the phenylene group. Constrained refinement of the phenylene group was carried out by assigning a value of 1.39(1) Å for the C−C bonds. The distance between two carbon atoms bonded to a carbon atom whose angle was to be constrained to 120° was held to a value of 2.39(1) Å. As the refinement neared convergence, the constraints on zinc polyhedra were removed but those relating to the phosphonate group could not be lifted without reducing the stability of refinement. Neutral atomic scattering factors were used for all atoms. A correction was made for the preferred orientation effect by using the March−Dollase method[28b] in the GSAS suite of programs. The diffraction vector in the present case is along the a^* axis. The refined parameter was the ratio (0.823) of the effect along this axis to that along the perpendicular plane. No corrections were made for anomalous dispersion and absorption effects. A final Rietveld refinement plot is given in Figure 2A.

Structure Solution and Refinement of $Zn[HO_3P(C_6H_4)_2PO_3H]$. The decomposition method yielded 45 single indexed reflections up to a 2θ limit of 53°. An equal number of peaks with two or three contributors were also included in the single-crystal-type data set by the method as described above. The positions of the Zn atom and the two P atoms of the bis(phosphonate) were derived from the Patterson map. Subsequent difference Fourier maps calculated with the same data set revealed the positions of the oxygen atoms of both phosphonate groups. Four of these oxygens, two from each of the phosphonate groups, were also bonded to the zinc atom in a tetrahedral manner. The positions of the Zn, P, and O atoms thus obtained were used as a starting model for full-pattern refinement.

Refinement of the profile was carried out using the program GSAS with the partial structural model obtained above. Initially, the parameters like zero-point error, scale factor, lattice parameters, terms for background, and peak shape functions were refined. The positional parameters were then refined with soft constraints. No constraints were applied to either Zn−O bonds or O---O nonbonded distances in the zinc polyhedron. The phosphonate groups were constrained to the tetrahedral geometry as described above. A series of difference Fourier maps computed at this stage revealed the positions of all the carbon atoms of the biphenylylene group. The refinement of the phenylene groups was carried out with constraints for C−C bond lengths and C---C nonbonded distances as in the case of compound **1**. The C−C bond connecting the two phenylene groups was held at a distance of 1.47(1) Å. As the refinement progressed, the weights for the soft constraints were reduced, but they could not be removed without distorting the structure, particularly the geometry of the organic group. All the atoms were refined isotropically. Corrections were made for preferred orientation effects as described above. The diffraction vector in the present case is along the c^* axis (ratio = 0.899). A final difference Rietveld plot is given in Figure 2B.

Results

TGA and Spectral Properties of the Compounds. The zinc phenylenebis(phosphonate), $Zn_2[(O_3PC_6H_4PO_3)(H_2O)_2]$ begins to lose its coordinated water around 110 °C. The observed weight loss of 8.6%, corresponding to this process, is in good agreement with the calculated value of 8.98% for the removal of two water molecules. The water loss is complete around 200 °C, and no additional weight loss occurs until about 525 °C. The removal of the phenylene group takes place in a single step starting at 570 °C (Figure 3A). The calculated and observed weight losses (up to 1000 °C) for the removal of the organic group are 18.96% and 16.5%, respectively. The difference may be due to slow burning of the organic groups in the structure. The biphenylylenebis(phosphonate), $Zn[HO_3P(C_6H_4)_2PO_3H]$, on the other hand, showed no weight loss up to 300 °C, indicating the absence of water molecules in the structure (Figure 3B). The weight loss due to the condensation of the hydroxyl groups of the phosphonate begins around 318 °C and continues to 411 °C with a weight loss of 4.23%. The process continues at a much lower rate up to about 500 °C, releasing an additional 0.2% of the weight, thus accounting for a total weight loss of 4.43% corresponding to the release of one water molecule per formula unit (calculated value is 4.77%). The removal of the organic group appears to start around 550 °C. Most of the organic group is lost by 650 °C, and the compound then slowly loses some additional weight as the temperature is increased. The total weight loss due to the burning of the organic group up to 1000 °C is 37.9%, while the calculated weight loss for this process is 40.3%. The compound $Zn_2[O_3P(C_6H_4)_2PO_3]$ does not show any weight loss corresponding either to the removal of coordinated water or to condensation of the hydroxyl groups

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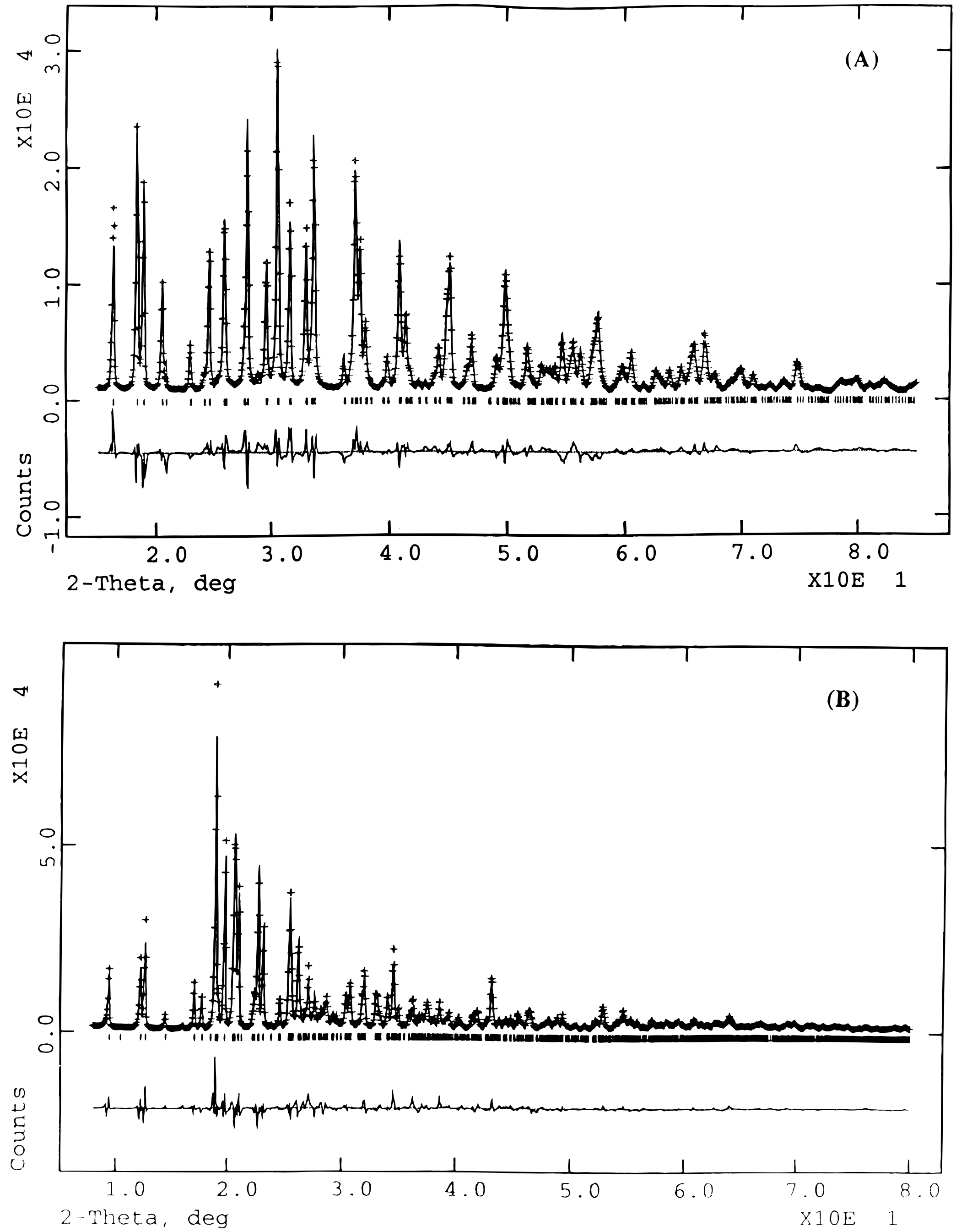

Figure 2. Observed (+) and calculated (−) profiles for the Rietveld refinement of (A) zinc phenylenebis(phosphonate) and (B) zinc biphenylylenebis-(phosphonates). The difference plot is on the same intensity scale.

(Figure 3C), in agreement with the formula. The observed weight loss of about 1% up to 120 °C is due to surface water. The burning of the organic group starts around 485 °C accompanied by a weight loss of 31% in a single step around 600 °C. The total weight loss up to 1000 °C due to the release of the biphenylylene group is approximately 33%, which is close to 34.5% calculated for this process.

The IR spectrum shows that compound **1** contains water molecules (Figure 4A). The O−H stretching bands (3460, 3430 cm^{-1}) and the deformation band (1610 cm^{-1}) are prominently seen in the spectrum. These bands are clearly absent for compound **2** (Figure 4B) and for $Zn_2[O_3P(C_6H_4)_2PO_3]$ (Figure 4C), as they do not contain either coordinated or lattice water molecules. The spectrum of **2**, however, contains a broad band centered at 3000 cm^{-1}, which is characteristic of strongly hydrogen bonded hydroxyl groups (Figure 4B). For the compound $Zn_2[O_3P(C_6H_4)_2PO_3]$ this band is absent, since the phosphonate groups are deprotonated. The spectra of all the compounds contain characteristic C−C stretching frequencies of the phenylene group in the range 1380−1386 cm^{-1} and $-PO_3$ vibration frequencies at 1000−1150 cm^{-1}. Sharp bands at 835 cm^{-1} for compound **1**, at 815 cm^{-1} for compound **2**, at and 817 cm^{-1} for $Zn_2[O_3P(C_6H_4)_2PO_3]$ are attributed to the out-of-plane vibrations for para-substituted phenylene rings.

The ^{31}P NMR spectrum of compound **1** indicates a single phosphorus site (chemical shift 22.9 ppm) in the structure. Compound **2** shows closely spaced resonances centered at 17 ppm. These results are consistent with those obtained from the crystal structure determinations.

Structure of $Zn_2[(O_3PC_6H_4PO_3)(H_2O)_2]$. Crystallographic data are given in Table 1, positional and thermal parameters are listed in Table 2, and selected bond parameters are presented

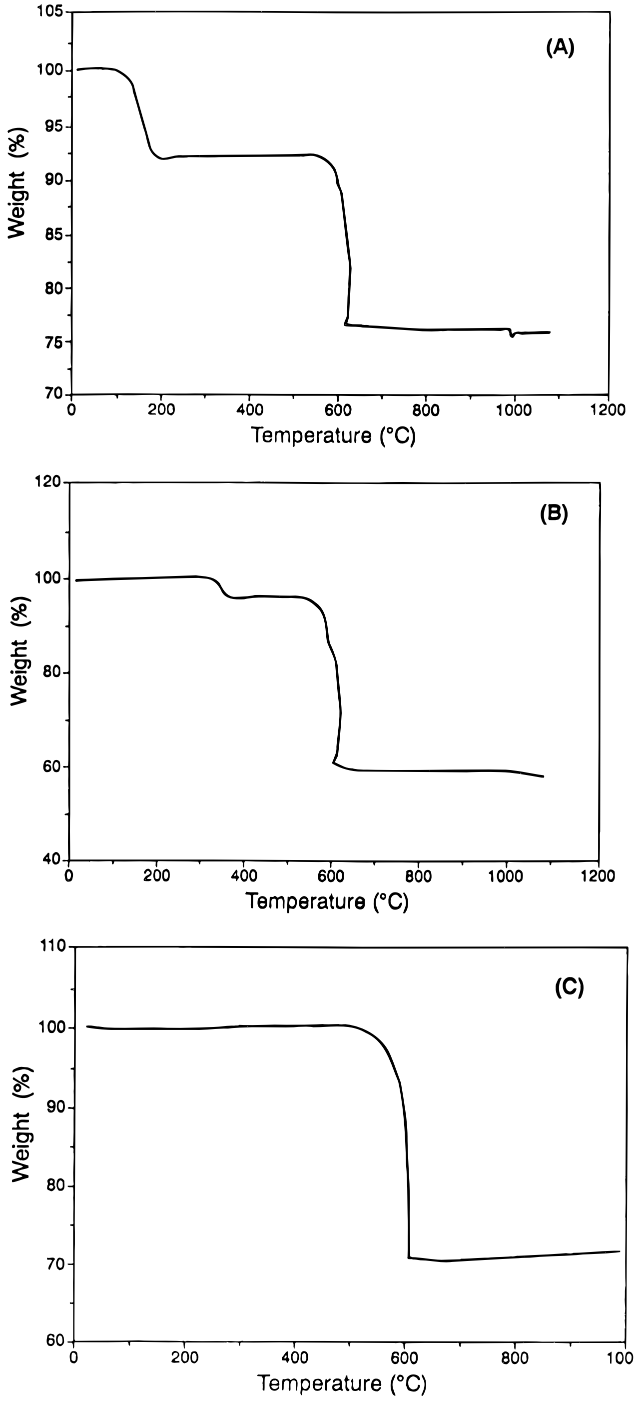

Figure 3. TGA curves for (A) zinc phenylenebis(phosphonate), (B) zinc biphenylylenebis(phosphonate), and (C) deprotontated zinc biphenylylenebis(phosphonate).

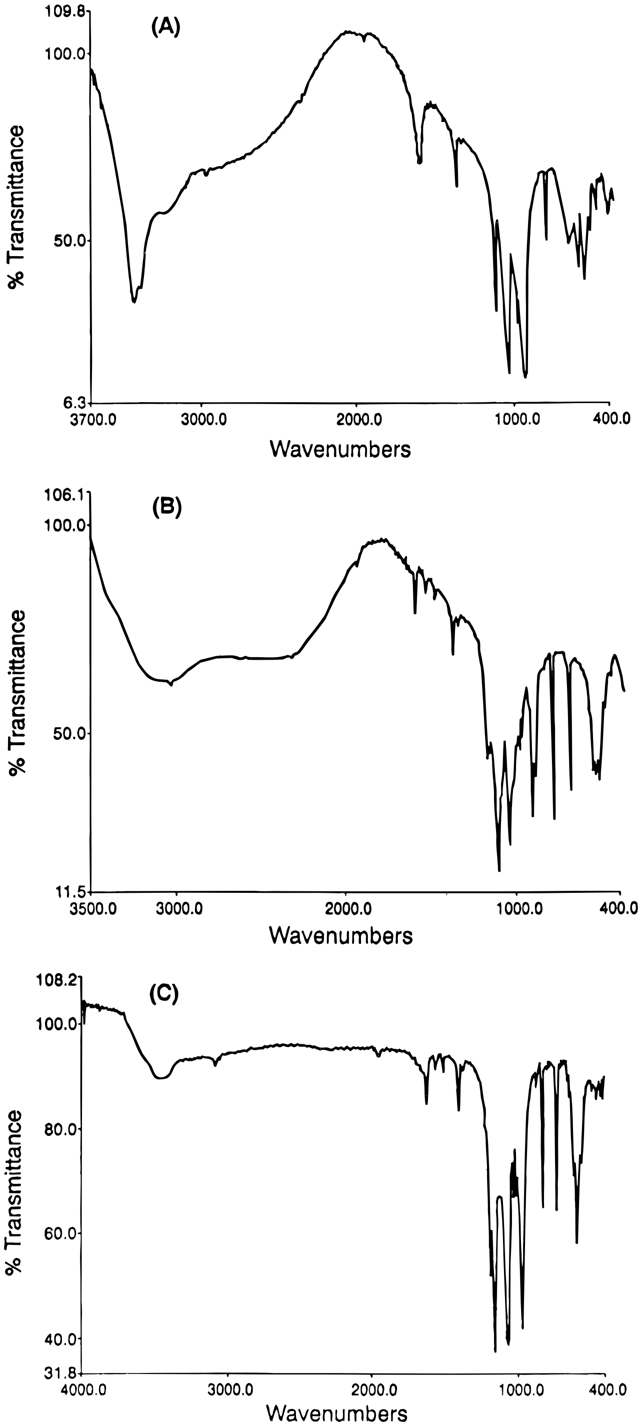

Figure 4. IR spectra for (A) zinc phenylenebis(phosphonate), (B) zinc biphenylylenebis(phosphonate), and (C) deprotontated zinc biphenylylenebis(phosphonate).

in Table 4. The layer arrangement is shown in Figure 5, and the projection of the structure down the *b* axis is presented in Figure 6.

All the atoms except O1 and C2 are located on mirror planes at $z = 0.0$ and 0.5. The center of the phenyl group coincides with 2/*m* symmetry, which results in a centrosymmetric relationship between the two PO_3 groups of the bis(phosphonate). Due to this symmetry, the phenyl group has only two independent carbon atom positions, C1 and C2. The C1 atom lies on a mirror plane, while C2 is in a general position. The phenyl groups are located in the *ac* plane primarily due to the small *b* axis dimension (Figure 6).

The zinc atoms have a distorted octahedral geometry. Four of the coordination sites are occupied by the symmetry-related positions of oxygen atom O1. The mirror-related atoms O1 and O1a chelate the metal, Zn, as shown in Figure 5. At the same time, these two oxygens bridge unit cell translated zinc atoms Zn1b and Zn1c, respectively, along the *c* axis direction. The zinc atoms along the *b* axis are linked by the remaining oxygen atom of the phosphonate, O2, thus resulting in a metal−phosphate layer in the *bc* plane. The sixth coordination site is occupied by the oxygen atom (O3) of the water molecule. There are two types of Zn−O1 bond lengths. The shorter bonds (2.009(3) Å) correspond to the bridging mode of binding, such as Zn1b−O1 in Figure 5. Due to chelate effect, the Zn−O bonds in the chelate ring are longer (2.339(4) Å). The Zn−O2 bond distance is normal, while the bond involving the water

Table 1. Crystallographic Data

	1	**2**
formula	$C_6H_8O_8P_2Zn_2$	$C_{12}H_{10}O_6P_2Zn$
fw	400.8	377.5
space group	*Pnnm* (No. 58)	$P\bar{1}$ (No. 2)
a (Å)	19.2991(6)	9.5097(3)
b (Å)	4.8232(2)	5.0074(2)
c (Å)	5.6545(2)	14.2109(4)
α (deg)		92.797(3)
β (deg)		99.725(3)
γ (deg)		92.033(3)
V (Å^3)	526.34(4)	665.53(2)
Z	2	2
d_{calcd} (g/cm^3)	2.53	1.88
μ (cm^{-1})	90.15	51.64
pattern range, 2*θ* (deg)	15−85	8−80
no. of independent reflns	213	800
no. of geometric observations	12	50
R_{wp}[a]	0.108	0.111
R_p[a]	0.082	0.084
R_F[a]	0.035	0.032

[a] See ref 28 for definitions.

Table 2. Positional Parameters and U_{iso} Values (Å^2) for Compound **1**

atom	*x*	*y*	*z*	U_{iso}
Zn1	0.2365(1)	0.6400(3)	0.5	0.022(3)
P1	0.3352(1)	1.0828(5)	0.5	0.017(3)
O1	0.3060(2)	0.9358(8)	0.2738(6)	0.025(4)
O2	0.3242(2)	0.4070(11)	0.5	0.039(3)
O(W)	0.1568(2)	0.9628(9)	0.5	0.038(4)
C1	0.4284(2)	1.0188(13)	0.5	0.042(5)
C2	0.4682(2)	1.0774(19)	0.2970(6)	0.045(5)

[a] $U_{iso} = B_{iso}/8\pi^2$.

Table 3. Positional Parameters and U_{iso} (Å^2) Values for Compound **2**

atom	*x*	*y*	*z*	U_{iso}
Zn1	0.1830(4)	0.112(1)	−0.0523(2)	0.006(1)
P1	0.3281(6)	0.579(1)	−0.1297(3)	0.008(3)
P2	−0.1595(7)	0.118(1)	−0.1462(3)	0.022(3)
O1	0.4856(10)	0.757(2)	−0.1025(7)	0.008(5)
O2	0.3350(11)	0.376(2)	−0.0537(6)	0.008
O3	0.2137(10)	0.771(2)	−0.1144(7)	0.008
O4	−0.2524(11)	0.384(2)	−0.1339(6)	0.008
O5	−0.1869(12)	−0.103(2)	−0.0875(6)	0.008
O6	−0.0039(9)	0.239(2)	−0.1203(6)	0.008
C1	0.2963(10)	0.464(2)	−0.2529(3)	0.044(7)
C2	0.1833(11)	0.560(3)	−0.3158(4)	0.044
C3	0.1847(15)	0.526(3)	−0.4132(4)	0.044
C4	0.2705(14)	0.338(2)	−0.4458(4)	0.044
C5	0.3445(14)	0.172(2)	−0.3811(5)	0.044
C6	0.3685(!4)	0.252(3)	−0.2849(5)	0.044
C7	−0.1950(7)	0.009(2)	−0.2708(5)	0.044
C8	−0.3302(7)	−0.098(3)	−0.3105(5)	0.044
C9	−0.3579(10)	−0.160(3)	−0.4082(5)	0.044
C10	−0.2452(13)	−0.218(3)	−0.4544(5)	0.044
C11	−0.1066(11)	−0.175(3)	−0.4065(5)	0.044
C12	−0.0825(8)	−0.029(3)	−0.3196(6)	0.044

Table 4. Bond Lengths (Å) and Bond Angles (deg) for Compound **1**

Zn1−O1	2.339(4)	2×	Zn1−O1	2.009(3)	2×
Zn1−O2	2.032(5)		Zn1−O(W)	2.188(4)	
P1−O1	1.568(3)	2×	P1−O2	1.578(4)	
P1−C1	1.825(4)		C1−C2	1.409(5)	4×
C2−C2	1.437(7)	2×			

O1−Zn1−O1	162.6(2)	2×	O1−Zn1−O1	96.4(1)	2×
O1−Zn1−O1	66.3(2)		O1−Zn1−O1	100.8(2)	
O1−Zn1−O2	81.9(1)	2×	O1−Zn1−O2	93.9(2)	2×
O1−Zn1−O(W)	88.2(1)	2×	O1−Zn1−O(W)	93.6(1)	2×
O2−Zn1−O(W)	168.2(2)		O1−P1−O1	109.4(3)	
O1−P1−O2	113.5(2)	2×	O1−P1−C1	106.2(2)	2×
O2−P1−C1	107.5(3)		P1−C1−C2	120.2(2)	2×
C2−C1−C2	109.0(6)	2×	C1−C2−C2	111.2(6)	4×

Table 5. Bond Lengths (Å) and Bond Angles (deg) for Compound **2**

Zn1−O2	1.93(1)	Zn1−O3	1.94(1)
Zn1−O5	1.98(1)	Zn1−O6	2.01(1)
P1−O1	1.69(1)	P1−O2	1.511(1)
P1−O3	1.51(1)	P1−C1	1.79(1)
P2−O4	1.64(1)	P2−O5	1.46(1)
P2−O6	1.56(1)	P2−C7	1.80(1)
C1−C2	1.395(3)	C1−C6	1.381(3)
C2−C3	1.388(3)	C3−C4	1.380(3)
C4−C5	1.388(3)	C5−C6	1.384(3)
C4−C10	1.491(3)	C10−C9	1.380(3)
C9−C8	1.385(3)	C8−C7	1.391(3)
C7−C12	1.383(3)	C12−C11	1.384(3)
C11−C10	1.381(3)		

O2−Zn1−O3	113.2(5)	O3−Zn1−O5	99.9(4)
O2−Zn1−O6	110.7(4)	O3−Zn1−O5	114.4(5)
O3−Zn1−O6	106.9(5)	O5−Zn1−O6	111.8(5)
O1−P1−O2	104.5(5)	O1−P1−O3	106.2(6)
O1−P1−C1	110.4(6)	O2−P1−O3	107.7(7)
O2−P1−C1	119.2(6)	O3−P1−C1	108.1(5)
O4−P2−O5	115.6(7)	O4−P2−O6	101.4(7)
O4−P2−C7	107.2(5)	O5−P2−O6	112.8(6)
O5−P2−C7	110.2(6)	O6−P2−C7	109.1(5)
C2−C1−C6	118.2(3)	C1−C6−C5	119.8(2)
C6−C5−C4	118.7(3)	C5−C4−C3	118.9(3)
C4−C3−C2	119.6(2)	C3−C2−C1	118.0(4)
C3−C4−C10	123.5(1)	C5−C4−C10	112.5(1)
C4−C10−C9	119.2(1)	C4−C10−C9	121.0(1)
C10−C11−C12	119.0(3)	C11−C12−C7	119.3(2)
C12−C7−C8	119.3(2)	C7−C8−C9	117.7(4)
C8−C9−C10	118.8(3)	C9−C10−C11	119.8(2)

oxygen is slightly longer (2.188(4) Å). The cis bond angles are close to their expected values (maximum deviation 11°) except the one in the chelation ring, which is 66.3(2)°. Due to this chelate effect, the trans angles, involving the O1 atoms, are also significantly reduced from 180° (162.6°).

The coordination geometry described here is similar to that observed for zinc phenylphosphonate, whose structure was determined earlier by single-crystal methods.[7a] In zinc phenylphosphonate the Zn−O distances corresponding to the bridging and chelating modes of binding are 2.04(1) and 2.28(1) Å, respectively. The bond distance involving the water oxygen is 2.12(3) Å, and that involving the oxygen atom which bridges the metal atoms along the shortest axis (correspondingto O2 in the present case) is 2.05(2) Å. The bond angle in the chelating ring is 64.5(5)°, very close to the value observed in compound **1**.

The metal−phosphate network forms two-dimensional layers in the *bc* plane, as described above, whose mean planes are located at *x* ∼ 0.25 and 0.75. These layers have a basal spacing of 9.65 Å. The layers viewed end-on have a zigzag appearance, with the P atoms above and below the plane of the layer at the crests and the water molecule at the troughs. These layers are bridged by the organic groups of the phosphonate (Figure 6). The phenylene groups are parallel to the *ac* plane. These rings are separated by 5.65 Å along the *c* axis, and since the plane of these rings is separated by 4.8 Å along the *b* axis, the arrangement leads to severe nonbonded hydrogen interactions. In the structure, the phenylene rings are constrained by the 2/*m* symmetry which forces them to align parallel to the *ac* plane. It is possible that the group may have an out-of-plane rotation about the P−C1 bond to overcome these contacts. This possibility was tested by changing the crystal symmetry to the noncentric space group *Pnn*2. In *Pnn*2, the phenylene groups are not constrained by the mirror symmetry and hence are free to rotate about the P−C bond. However the refinement in this space group did not converge. It is also possible that one or both of the layer dimensions are doubled, which would then

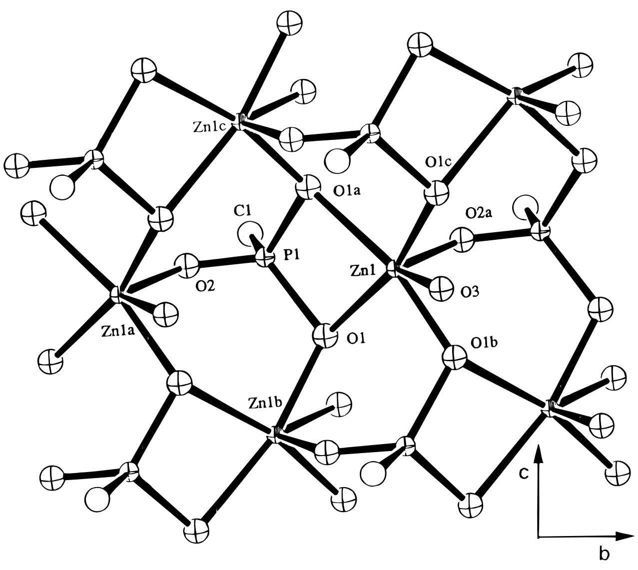

Figure 5. Layer arrangement in the structure of zinc phenylenebis(phosphonate) showing the in-layer connectivity.

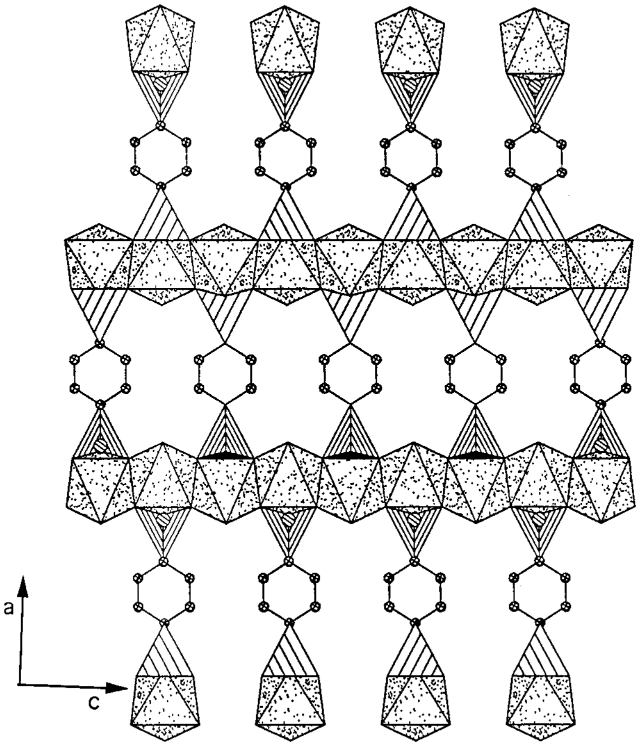

Figure 6. Projection of the structure of zinc phenylenebis(phosphonate) down the *b* axis showing the bridging nature of the diphosphate.

allow the positioning of groups in two orientions canted to each other. This latter possibility seems to be highly likely on the basis of the results obtained earlier for the isostructural zinc[7a] and manganese[6] phenylphosphonates of general formula M[(O_3-PC_6H_5)(H_2O)], in which it was shown that the rings are canted to each other. The carbon atoms of the phenylmonophosphonate groups in these compounds show elongated thermal ellipsoids perpendicular to the plane of the phenyl rings. Careful examination of their diffraction patterns showed weak spots along the layer dimensions corresponding to the doubling of the unit cell dimensions, but the refinement of their structures in the larger cell proved difficult. However, the canted arrangement of phenyl rings that one would expect in the superlattice structure was found in lanthanum phenylphosphonate.[7c]

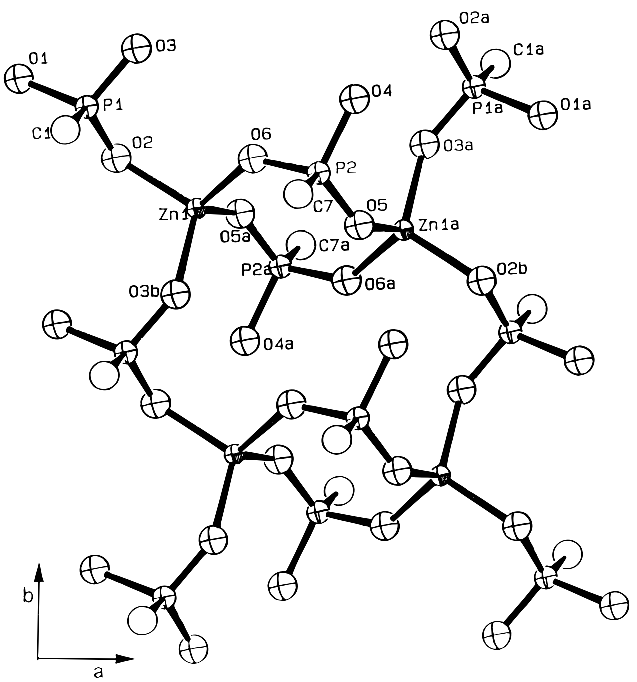

Figure 7. Diagram showing the metal coordination and the bridging of phosphate groups to form double chains.

Structure of Zn[$HO_3P(C_6H_4)_2PO_3H$]. Positional and thermal parameters are given in Table 3, and bond distances and angles, in Table 5. Metal coordination along with the bridging nature of the phosphonate groups in the double chain is shown in Figure 7. A packing diagram of the molecules down the *b* axis is given in Figure 8.

Unlike that of compound **1**, the metal to P ratio in this case is 1:2. The two PO_3 groups of the bis(phosphonate) are structurally independent. One of the oxygens of each phosphonate group is protonated, rendering overall charge balance to the compound. Oxygen atoms O1 of P1 and O4 of P2 phosphonate groups are bonded to protons, and they are not involved in metal coordination. The zinc atoms are tetrahedrally coordinated. The coordination sites are occupied by four oxygen atoms: O2, O3, O5, and O6. Unlike those in compound **1**, these oxygens are not involved in bridging or chelation; instead, they bind only to a single metal atom. As shown in Figure 7, O2 and O3 belong to the P1 phosphonate while O4 and O5 belong to the P2 phosphonate group. The Zn−O bond lengths are normal for 4-coordination, and they are in the range 1.93(1)−2.01(1) Å. The bond angles are very close to their tetrahedral value, and they are in the range 100−114°.

The structure is not layered in the traditional sense. It may be better described as a double-chain structure consisting of alternating Zn and P atoms in each of the chains. These chains are centrosymmetrically related, and they run along the *b* axis (5.0 Å) direction. The unit cell translated Zn atoms along the *b* axis in a chain are bridged by the P1 phosphonate group through oxygen atoms O3 and O2 as shown in Figure 7. These chains are connected to each other by the other phosphonate group (P2) of the bis(phosphonate) through oxygens O5 and O6. The connections involve the centrosymmetrically related Zn atoms (Zn1 and Zn1a) and similarly related phoshonate groups (P2 and P2a). The arrangement thus leads to alternating 8-membered (Zn1−O6−P2−O5−Zn1a−O6a−P2a−O5a−Zn1) and 16-membered (−O3−P1−O2−Zn1−O6−P2−O5−Zn1a−O3a−P1a−O2a-- etc. in Figure 7) rings along the *b* axis direction. In other words, one end of the bis(phosphonate) is located on the outer periphery of the double chain and bridges the unit cell translated Zn atoms, while the other end lies at the

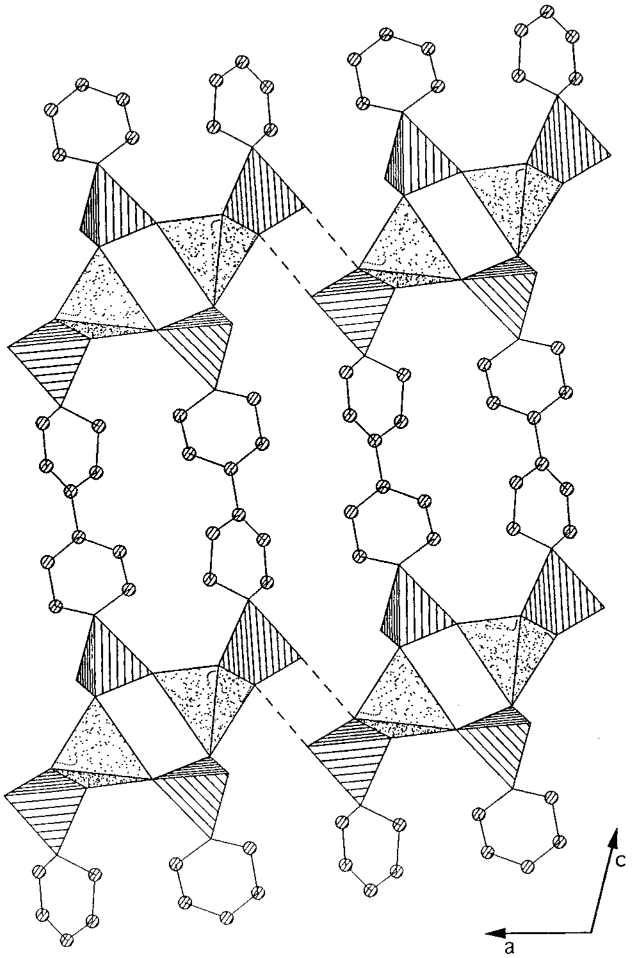

Figure 8. Plot of the structure of zinc biphenylylenebis(phosphonate) as viewed down the *b* axis. Hydrogen bonding between the double chains are shown by dotted lines.

center of double chain and links the centrosymmetrically related Zn atoms. Thus, the two metal-binding oxygens of the phosphonate at one end are roughly trans to two such oxygens of the phosphonate at the other end. This feature is also clearly seen in Figure 8.

The mean plane of the double chains is located approximately at $z = 0.0$ and 1.0. These double-linked chains propagate infinitely along the *b* axis. They are in turn linked to each other in the *c* axis direction by the biphenylylene groups, as shown in Figure 8, creating a true layer or slab whose thickness extends over two biphenylylenebis(phosphonate) groups. The mean planes of the two phenylene groups are not parallel; instead they are inclined to each other by about 52° about the C4−C10 bond. As a result, the neighboring phenylene groups in the adjacent chains are also inclined by the same amount (Figure 8). The organic groups in the chains are separated by the length of the *b* axis along that direction and by about 5.5 Å along the *a* direction. The adjacent layers or slabs are, in turn, connected to each other along the *a* axis direction through hydrogen bonds as shown by dotted lines in Figure 8. This interaction involves the protonated oxygen atom, O1, and the oxygen atom, O2, of the same phosphonate in the centrosymmetrically related group (O1---O2 = 2.69(1) Å). The other hydroxyl group (O4) is not involved in hydrogen bonding between such double chains (closest contact: O1---O4 = 3.24(1) Å), as it is pointing toward the center of the double chains. It, however, forms a strong hydrogen bond with oxygen atom O5 (O4---O5 = 2.64(1) Å), which is translated one unit cell along the *b* axis. The hydrogen bonds between neighboring layers make it a loosely formed three-dimensional structure. In such an arrangement, the layers are in the (011) plane and the mean plane of the double chains of Figure 7 is located at $z = 0$ and 1.0. It is interesting to point out that the dimensions (9.5, 5.0 Å) in the *ab* plane are very similar to those in the layered α-zirconium phosphate or phosphonate[4a] systems and both of these compounds have metal to phosphorus ratios of 1:2. The inability of the present Zn compound to form a layer structure similar to that of α-zirconium phosphate may be due to the protonation of the phosphonate groups, which makes them unsuitable for metal binding in the more usual manner (Figure 1) that requires utilization of all three phosphonate oxygens in bridging type connectivity.

Discussion

The layer arrangement observed in the structure of the zinc phenylenebis(phosphonate) is strikingly similar to that in zinc phenylphosphonate, $Zn(O_3PC_6H_5)\cdot H_2O$,[7a] and its isomorphous compounds of Mn,[6] Co, and Cd.[29] The crystals of the the zinc phenylphosphonate are orthorhombic: space group $Pna2_1$ with $a = 5.634(2)$ Å, $b = 14.339(5)$ Å, $c = 4.833(1)$ Å. The layer dimensions, *a* and *c*, in this compound are essentially identical to the *c* and *b* dimensions in the monophenylenebis(phosphonate compound **1**. The basal spacings are different, however, being 14.339 Å in the zinc phenylphosphonate and 19.2988 Å in the monophenylenebis(phosphonate) with the distance between adjacent layers being half this value (9.649 Å). The larger separation in the phenylphosphonate is due to the bilayer arrangement of the phenyl groups in the interlayer space. The layers in the present case are connected to each other by the bis(phosphonate) groups. In order to align the adjacent layers to achieve this bridging, the symmetry changes from $Pna2_1$ to *Pnnm*. As in the present case, the zinc atoms in the phenylphosphonate have a distorted octahedral coordination and the phosphonate oxygens are involved in both bridging and chelation. The coordination polyhedra also contain a water molecule. Recently we also solved the structures of copper monophenylenebis(phosphonate), $Cu_2[(O_3PC_6H_4PO_3)(H_2O)]$,[30] and barium monophenylenebis(phosphonate), $Ba(HO_3PC_6H_4PO_3H)$,[31] from their powder diffraction data. As in the case of zinc, the copper and barium monophenylenebis(phosphonates) retained the layer structures of their respective phenylmonophosphonate analogs. Since zinc phenylphosphonate is isostructural with Mn, Co, Ni, and Cd analogs, the results presented here on zinc phenylenebis(phosphonate), together with those found for copper and barium phenylphosphonates[7b,7f] and phenylenebis(phosphonates),[30,31] indicate that the layer structures of the metal monophosphonates can be cross-linked by bis(phosphonates), at least in the monophenyl case, with only minimal layer rearrangement.

The above conclusion that the layer arrangements in both the cross-linked metal monophenylenebis(phosphonate) and the respective non-cross-linked phenylphosphonate are entirely similar lends credence to the formation of the cross-linked zirconium phenylenebis(phosphonates) as shown in Figure 1. Recent electron diffraction data[32] on $Zr(O_3PC_6H_4PO_3)$ fixed the space group as $C2/c$, which is the same space group as that of $Zr(O_3PC_6H_5)_2$. However, in the latter compound the phenyl rings are inclined at 30° to the layer perpendicular so that a similar inclination for the cross-linked compounds may hold. The basal spacing of 9.8 Å is closer to that expected for the

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(29) Cao, G.; Lynch,V. M.; Yacullo, L. N. *Chem. Mater.* **1993**, *5*, 1000.
(30) Poojary, D. M.; Zhang, B.; Bellinghausen, P.; Clearfield, A. *Inorg. Chem.*, in press.
(31) Poojary, D. M.; Zhang, B.; Clearfield, A. Under preparation.
(32) Bellinghausen, P. M. S. Thesis, Texas A&M University, Dec 1995.

perpendicular than to the inclined arrangement of the pillars. In addition, self-assembled monolayers prepared from bis(phosphonic acids) are built up into multilayer films by successive contact with Zr and acid.[5] The increase in film thickness can be explained on the basis of an α-zirconium phosphonate structure in which the pendent groups would be perpendicular to the layers as in α-zirconium phosphate.[33]

It was hoped that the preparation of the biphenylylene cross-linked zinc compound would shed further light on the situation. The zinc compound (**2**), prepared at low pH, on the other hand yielded a double-chain layered structure rather than the expected layer type structure of compound **1** although the conditions of preparation were similar. We note that the bonding in compound **1** is highly structured; each phosphonate group chelates one zinc atom, while the chelating oxygens also bridge to adjacent Zn atoms, forming chains. These chains are then linked to each other by the remaining phosphonate oxygens, forming the layer. The requirement that both phosphonate groups of the bis(phosphonate) bond in the same way constrains the Zn atom and the phosphonate group to lie on mirror planes. Rotation of the rings of the biphenylylenebis(phosphonate) breaks this confinement and destroys the mirror symmetry. This allows a simpler form of bonding in which connectivity is through simple phosphonate bridging of the metal atoms. The bridging to form chains rather than layers, together with a lower coordination number, 4 instead of 6, leaves one oxygen of each phosphonate group free to bond to protons. Since the preparations were carried out in acid solutions, protonation occurred naturally.

A similar situation has been observed in the case of copper arylenebis(phosphonates). As in the case of the zinc compounds, the copper phenylenebis(phosphonate) is isostructural with the copper phenylmonophosphonate. However, the compound prepared with biphenylylenebis(diphosphonic acid) at low pH consists of linear chains and not the regular layer structure of the copper phenylphosphonate. The inability of zinc and copper biphenylylenebis(phosphonates) to form layer structures is mainly due to the presence of a proton on one of the phosphonate oxygens, which leaves only two oxygens available for metal binding. In order to form a layered compound, it is necessary that all the three phosphonate oxygens take part in metal binding. Among the many layered divalent transition metal phosphonate compounds thus far characterized, there is not even a single example of a P−OH group involved in metal bonding. The M−O distances in these layered compounds is about 2.0 Å, and the resulting O---O nonbonded distances about the metal polyhedra are of the order of 2.9 Å. Since the metal polyhedra are periodically positioned along both of the layer dimensions, the presence of a proton on any of the phosphonate oxygens would result in unfavorable proton−metal interactions. However, if the metal−oxygen bonds are longer and the metal has a larger coordination sphere compared to that normally exhibited by 3d transition metal ions, the P−OH groups can take part in metal binding. This situation has been observed in barium and lead phenylphosphonate compounds, $M(HO_3PC_6H_5)_2$ (M = Ba, Pb).[7f] In these compounds, all phosphonate oxygens including those of the OH groups are involved in metal binding, leading to layer structures. The Ba−O and Pb−O distances are in the range 2.64−2.84 Å, and the metal atoms are 8-coordinated. For the same reason, contrary to the case of the zinc compounds, the barium compounds of both phenylenebis(phosphonic acid) and biphenylylenebis(phosphonic acid) retained the layer structure of barium phenylphosphonate. These results indicate that in favorable cases both phenylene and biphenylylene groups can be used to cross-link the metal−O_3-PC layers regardless of the presence of protons on the phosphonate groups.

In an attempt to understand the role of phosphonate protons in metal−biphenylylenebis(phosphonate) compounds, we have prepared a compound at near-neutral pH. Chemical analyses indicate that the compound formed under these conditions is $Zn_2(O_3PC_{12}H_8PO_3)$. The compound shows no weight loss to 485 °C in the TGA curve, indicating the absence of both coordinated water and hydroxyl groups. The IR data are also consistent with this formula. The X-ray powder pattern shows basal peaks with *d* spacings of about 14 Å, similar to that observed for compound **2**. However, the positions of the other peaks indicate that the structure of this phase of zinc biphenylylenebis(phosphonate) obtained at near-neutral pH is of a different type. It is likely that this compound is layered but with a mode of phosphonate binding different from that observed for compound **1**. Similar results were obtained for the copper biphenylylenebis(phosphonate).[30] As indicated above, at low pH the compound formed is $Cu(HO_3PC_{12}H_8PO_3H)$ and it contains linear chains. Upon an increase in the pH to 4.5, the reaction mixture led to the compound $Cu_2(O_3PC_{12}H_8PO_3)$, as in the case of Zn. Since these higher pH compounds of zinc and copper contain no water oxygens for metal binding, only the three phosphonate oxygens are required to provide all the coordination sites for the metal atoms. This could be achieved by the bridging interactions of either two or three oxygen atoms. These compounds at the moment are not sufficiently crystalline to permit solution of their structures.

However, it is still not clear why the zinc and copper biphenylylenebis(phosphonates), prepared at low pH, do not contain coordinated water molecules as was found for their phenylenebis(phosphonate) analogs. It may be noted that the biphenylylenebis(phosphonic acid) is less insoluble in water than the monophenylenebis(phosphonic acid). It may be possible that the increased hydrophobic environment created by the biphenylylene group as compared to phenylene group is responsible for the exclusion of water molecules in the biphenylylenebis(phosphonate) compounds. Additional experiments are, however, needed to shed more light to this problem.

As indicated in the Introduction, one of the main purposes of using bis(phosphonic acids), $H_2O_3P-R-PO_3H_2$, is to synthesize covalently pillared layered metal compounds. These compounds either as synthesized or as post-synthesis modifications could provide channel structures similar to those of zeolites. The wide choice of organic groups with diverse functionality that can be utilized to prepare the metal phosphonates suggests the possibility of designing structures for highly specific applications. In the zinc phenylenebis(phosphonate), the phenylene groups are closely packed, and hence no guest molecules can be introduced into the interlayer space. However, with use of a mixture of phosphorous and phenylphosphonic acids, it was observed[34] that some of the phenylphosphonate groups in the structure can be replaced by the phosphite groups. We have also been able to substitute phosphate groups for one in every three bis(phosphonate) groups in structure **1**. The X-ray powder diffraction pattern of the mixed compound indicates that it has unit cell dimensions similar to those of the unsubstituted bis(phosphonate) compound. However, the crystallinity of the mixed compound is poor. Efforts are underway to increase the amount of phosphate groups in the structure while retaining the layer arrangement and to obtain better crystallinity. These

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results will be presented in a subsequent publication. In this context, it is interesting to mention two other porous, layered metal diphosphates obtained by using similar methods. Alberti et al.[10] have used a mixture of phosphite and methyl-substituted biphenylylenebis(phosphonate) groups to obtain microporous zirconium layered compounds. Substitution of phosphite groups for bulky 3,3′,5,5′-tetramethylbiphenylylenebis(phosphonate) creates free open space within the interlayer space. Recently a covalently pillared metal phosphonate compound having a new type of layer structure was obtained by utilizing a mixture of phosphoric acid and viologenbis(phosphonic acid).[35]

The double-chain structure obtained for the biphenylylenebis(phosphonate) is new and arises, as described above, because only half the protons of the acid groups are displaced by Zn atoms. Thus the compound utilizes only two of the phosphonate oxygens for binding, which leads to a favorable tetrahedral coordination for the Zn atoms. The phosphonate oxygens bind to only one metal atom, and the metal centers are well separated, since only bridging bonds are present. The double-chain arrangements also lead to a favorable packing of organic groups in the crystal without any packing constraints as observed for compound **1** and its phenylmonophosphonate analogue. Additional stabilization of the structure arises from interlayer hydrogen bonds involving the hydroxyl protons. These hydroxyl protons may be exchanged for metal ions and molecular species. Under favorable conditions, by eliminating the hydrogen-bonding interaction between the double chains, it is possible to obtain individual inorganic−organic sheets. We are also carrying out amine intercalation reactions with this compound. Preliminary results show that amines can be intercalated between the double chains without disturbing the structure apparently topotactically. A full report on these reactions will be published in a subsequent paper. It is instructive here to compare the present structure to some related double-chain structures. Molybdenum phenylphosphonate[7e] and a zirconium viologenphosphonate compound[4d] form similar types of structures. However, the latter two compounds have metal to P ratios of 1:1 and the phosphonate oxygens are not protonated. In the case of the molybdenum compound, the structure consists of bent MoO_2 groups coordinated by three phosphonate oxygens and a water molecule. Two of the phosphonate oxygens bridge unit cell translated molybdenyl groups along the *a* axis, leading to a linear chain arrangement. These chains are in turn bridged by the third oxygen atom of the phosphonate to a similar chain, thus forming a double-chain arrangement. These double chains are separated by the bilayers of the organic groups on one side, while they are held together by hydrogen-bonded water molecules on the other. The zirconium viologenphosphonate, a photochemically active compound,[36] consists of a bis(phosphonate) similar to that of the title compound. The zirconium atoms in this case are octahedrally coordinated by three phosphonate oxygens and three F ions. The bridging of metal ions by the phosphonates to form double chains is similar to that in molybdenyl compounds.[4d] In the zirconium compound the double chains are connected to similar double chains on either side by the viologenbis(phosphonate). The arrangement thus forms metal−phosphonate sheets which are separated by the lattice water molecules.

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