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Coordinative Intercalation of Alkylamines into Layered Zinc Phenylphosphonate. Crystal Structures from X-ray Powder Diffraction Data

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Abstract: Zinc phenylphosphonate monohydrate takes up 1 mol of amine when contacted with liquid primary alkylamines. The mechanism of intercalation involves replacement of the coordinated water molecule by the amine molecules. Although the composition of the intercalate $Zn(O_3PC_6H_5)(RNH_2)$ is consistent with the analytical and spectroscopic data, there exist discrepancies in the observed interlayer *d* spacings of the intercalate with respect to that in the host compound. The *d* spacing for the propylamine intercalate is in fact smaller than that in zinc phenylphosphonate itself. In order to understand this feature specifically and to explain the mechanism of amine intercalation in metal phosphonates in general, we have determined the structures of the intercalates. The structures of $Zn(O_3PC_6H_5)(RNH_2)$, R = $-C_3H_9$ (**1**), $-C_4H_{11}$ (**2**), $-C_5H_{13}$ (**3**), were solved *ab initio* from X-ray powder diffraction data and refined by Rietveld methods. All the compounds are isostructural, and they crystallize in the monoclinic space group $P2_1/c$ with $a = 13.978(3)$ Å, $b = 8.791(2)$ Å, $c = 9.691(2)$ Å, and $\beta = 102.08(1)°$ for **1**, $a = 14.698(4)$ Å, $b = 8.957(3)$ Å, $c = 9.712(3)$ Å, and $\beta = 102.465(3)°$ for **2**, and $a = 16.267(3)$ Å, $b = 8.935(2)$ Å, $c = 9.695(2)$ Å, and $\beta = 102.32(1)°$ for **3**. The structures of these intercalates are new and are different from that of the host compound although all of them are layered. In the intercalate the zinc atoms are tetrahedrally coordinated as opposed to octahedral coordination in the host compound.

Introduction

Metal phosphonate chemistry is expanding at a rapid rate.[1] Previous studies were centered on tetravalent metals largely dominated by examination of zirconium compounds.[1–3] Tetravalent metal phosphonates $M(O_3PR)_2$ have octahedrally coordinated metal atoms, where all the coordination sites are occupied by the phosphonate oxygens. Many of these compounds are layered, containing a $-PO_3MO_3P-$ inorganic core separated by the organic portion of the phosphonate residing in the interlamellar region.[4,5] A rich chemistry has been developed because of the ease with which functional groups can be introduced via the phosphonate ligands.[4,5] Much recent work has centered on producing porous materials[6–8] and self-assembled monolayers on multilayered materials[2] for use as sensors, nonlinear optical materials,[9] ion exchangers, and sorbents.[10]

Recent attention has focused on synthesizing metal phosphonates of other than tetravalent metals. A variety of new-structure types have been uncovered[11–14] including self-assembled porous compounds.[7,8] However, in this study we are concerned with the layered compounds of the divalent first-row transition metals[11,12a,14] and particularly the zinc phosphonates. The phenylphosphonates of Mn, Co, and Zn are isostructural of composition $M(O_3PR)\cdot H_2O$.[11a,15] The metal atoms are six-coordinate, being chelated to two phosphonate oxygens that in turn are bonded also to adjacent metal atoms through electron pair donation. This arrangement forms linear chains that are bridged by the third phosphonate oxygens to form layers. The sixth coordination site is occupied by the water

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molecule. The layers are corrugated, with the organic groups located at the crests of the undulations and the water molecules at the troughs. The water molecules are readily removed thermally, leaving an open coordination site on the metal for possible intercalation or catalytic reactions.[16,17] In several cases the water was shown to be removed topotactically and in some favorable cases to have the same space group symmetry as the corresponding hydrated phase. These dehydrated phases exhibit shape selectivity in amine intercalation.[16]

A recent example of such shape selectivity was provided by Johnson et al.[18] with the compound $VO(O_3PR)\cdot H_2O\cdot C_6H_5CH_2OH$. The benzyl alcohol is lost on heating, creating a vacant coordination site at the vanadium atom. A variety of primary alcohols can bind at these sites, while secondary and tertiary alcohols are excluded.[16] Similarly it was found that anhydrous cobalt and zinc methylphosphonates $M(O_3PCH_3)$ react with NH_3 and primary amines to form $M(O_3PCH_3)\cdot RNH_2$, R = H to n-C_8H_{17}. The intercalation reaction is shape selective in that amines with branching at the α-carbon are excluded. In contrast it was found that zinc and cobalt phenylphosphonates reacted only with ammonia but not with any amine vapors.[17] However, both the hydrated and anhydrous zinc phenylphosphonates did react with primary amines in the liquid or solution state to yield monoamine intercalates[19] $Zn(O_3PC_6H_5)\cdot RNH_2$, R = H to n-C_8H_{17}. Since computer simulation models[17] indicated that intercalation of molecules larger than ammonia would result in overlap of van der Waals surfaces between the bulky phenyl groups and the alkyl chains, it was of interest to explore the nature of the intercalation reaction further. Our results are reported here in the form of crystal structure determinations for the propyl-, butyl-, and pentylamine intercalates.

Experimental Section

Materials and Methods. The 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 No. 951 unit, at a rate of 10 °C/min. Infrared spectra were recorded on a Digilab Model FTS-40 FTIR unit by the KBr disk method. X-ray powder patterns were taken with Cu Kα radiation on a Rigaku RU-200 automated powder diffractometer (rotating anode).

Synthesis Procedures. Zinc phenylphosphonate monohydrate was prepared according to the published procedure using $ZnCl_2$ (Mallinckrodt, reagent grade) and phenylphosphonic acid (Alfa) at about 60 °C.[11a,15] This compound can be dehydrated by keeping the sample in vacuo at 200 °C overnight. The amine intercalates were prepared by contacting solid, well-ground $Zn(O_3PC_6H_5)(H_2O)$ with liquid amines at room temperature for about 3–4 days. Intercalation takes place in a shorter time when dehydrated zinc phenylphosphonate is used. The intercalate was separated by filtration and dried.

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 were collected between 3° and 80° in 2θ with a step size of 0.01° and a count time of 15 s per step. Data were mathematically stripped of the Kα2 contribution, and peak picking was conducted by a modification of the double-derivative method.[20] The powder pattern was indexed by Ito methods[21] on the basis of the first 20 observed lines. The indexed cell (symmetry and unit cell dimensions) is different from that of the host zinc phenylphosphonate. The crystals of the intercalates have monoclinic symmetry with systematic absences consistent with the space group $P2_1/c$.

Table 1. TGA Data and Interlayer Distances in Zinc Phenylphosphonate and Its Intercalates

	weight loss (%)		
	obsd	calcd	interlayer distance (Å)
H_2O	7.82	7.52	14.34[a]
n-$C_3H_7NH_2$	20.9	21.1	13.67
n-$C_4H_9NH_2$	24.7	24.8	14.35
n-$C_5H_{11}NH_2$	27.5	28.6	15.89
n-$C_6H_{13}NH_2$	30.2	31.4	17.1[b]
n-$C_7H_{15}NH_2$	33.3	34.2	18.5[b]
n-$C_8H_{17}NH_2$	37.2	36.9	19.2[b]
n-$C_9H_{19}NH_2$	39.8	39.3	20.5[b]

[a] From ref 15. [b] From ref 19.

Structure Solution. Integrated intensities for the propylamine intercalate were extracted from the profile over the range $3° < 2\theta < 50°$ by decomposition methods as described earlier.[22] This procedure produced 30 single indexed reflections and 21 peaks with 2 or 3 contributors. The intensities of the latter set of peaks were divided equally among the number of contributing reflections and added to the starting data set. A Patterson map was computed using this data set in the TEXSAN[23] series of single-crystal programs. The position of the Zn atom and that of the P atom were derived from this Patterson map. Constrained refinements and subsequent difference Fourier maps allowed the positioning of four atoms coordinated to the zinc atom, three of which were also bonded to the P atom. The remaining coordinating atom therefore should be the nitrogen atom of the amine. These phosphonate oxygens are involved only in binding to a single metal atom but not in bridging or chelation. Since there exist only three phosphonate oxygens and only one nitrogen of the amine for metal binding, the coordination of the metal atom is four and should be either square-planar or tetrahedral. From the positions of the atoms derived from this limited number of low-angle powder data, it was difficult to distinguish the correct geometry of the metal coordination sphere at this stage. These atoms were however sufficient for Rietveld refinement and structure completion using the full pattern.

The carbon atom of the phenyl group bonded to the P atom was placed at a calculated position to complete the P tetrahedron. The raw powder data were transferred to the GSAS[24a] program package for full-pattern refinement. In this case, the data from both Kα1 and Kα2 were used. After the initial refinement of the scale, background, and unit cell constants, the atomic positions were refined with soft constraints for Zn and P polyhedra. The refinement at this stage indicated a tetrahedral geometry about the zinc atom. From the difference Fourier maps and model building the positions of the carbon atoms of the phenyl group were derived, which were then included in the structural model. The agreement between the observed and calculated powder profiles improved significantly, and a series of subsequent difference Fourier maps allowed the positioning of all the carbon atoms of the propylamine. Final refinement was carried out with soft constraints for all the atoms (Table 2). The carbon–carbon distances in the phenyl rings were constrained to a distance of 1.39(1) Å and those in the alkyl chains to a distance of 1.54(1) Å. To obtain similar constraints on the bond angle, the distances between the two atoms bonded to the carbon atom whose angle is to be constrained were held to values of 2.39(1) Å for the aryl groups and 2.51(1) Å for the alkyl carbon atoms. The weight of these constraints was reduced as the refinement progressed, but the constraints could not be removed completely without reducing the stability of the refinement. All the atoms were refined isotropically. In the final cycles of refinement the shifts in all the parameters were less than their estimated standard

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Table 2. Crystallographic Data

	1	2	3
formula	$C_9H_{14}NO_3PZn$	$C_{10}H_{16}NO_3PZn$	$C_{11}H_{18}NO_3PZn$
formula weight	280.6	294.6	308.6
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	13.978(3)	14.698(4)	16.267(3)
b (Å)	8.791(2)	8.957(3)	8.935(2)
c (Å)	9.691(2)	9.712(3)	9.695(2)
β (deg)	102.08(1)	102.465(3)	102.32(1)
V (Å^3)	1164(1)	1248(1)	1377(1)
Z	4	4	4
λ (Å)	1.5406, 1.5444	1.5406, 1.5444	1.5406, 1.5444
T (K)	296	296	296
d_{calcd} (g/cm^3)	1.598	1.567	1.489
μ (cm^{-1})	42.1	39.5	36.1
pattern range (2θ)	10.5−80	10−80	10−80
step size (2θ)	0.01	0.01	0.01
step scan time (s)	15	15	15
radiation source	rotating anode	rotating anode	rotating anode
no. of geometric observations	36	38	40
Zn−O and Zn−N distances (Å)	1.95(1)	1.95(1)	1.95(1)
O−O distance for the Zn tetrahedron (Å)	3.18(1)	3.18(1)	3.18(1)
P−O distance (Å)	1.53(1)	1.53(1)	1.53(1)
O−O distance for the P tetrahedron (Å)	2.55(1)	2.55(1)	2.55(1)
C−C distance for the phenyl group (Å)	1.38(1)	1.38(1)	1.38(1)
C−C distance for the amines (Å)	1.47(1)	1.47(1)	1.47(1)
R_{wp}[a]	0.091	0.103	0.116
R_p[a]	0.065	0.074	0.082
R_F[a]	0.049	0.044	0.06

[a] See ref 24 for definitions.

deviations. Neutral atomic scattering factors were used for all atoms. A correction was made for the preferred orientation effect by using the March−Dollase method[24b] in the GSAS suite of programs. The diffraction vector in the present case is along the a^* axis. The refined parameter was the ratio of the effect along this axis to that along the perpendicular plane. No corrections were made for anomalous dispersion and absorption effects.

Refined atomic positions of the propylamine intercalate were then used as starting models for the structure solution and refinement of butylamine (**2**) and pentylamine (**3**) intercalates. Additional carbon atoms of these amines were found by difference Fourier maps. The structures were refined as described above.

Results

TGA and IR Spectral Properties of the Intercalates. These results were discussed in depth in earlier papers.[17,19] The zinc phenylphosphonate begins to lose its coordinated water at around 80 °C. The hydrate and anhydrous phase are layered, and in fact they are isomorphous. These phases whether hydrated or anhydrous take up 1 mol of primary alkylamines to form compounds of composition $Zn(O_3PC_6H_5)(RNH_2)$. Unlike the water loss, the deamination process does not occur until about 200 °C as shown by the TGA results, indicating high stability of the amine intercalates. Some pertinent data are given in Table 1. These compounds undergo another weight loss at around 500 °C corresponding to the removal of the phenyl groups.

The IR spectra clearly show that the water molecule is completely replaced by the amine molecules. The O−H stretching bands (3469, 3430 cm^{-1}) and deformation band (1646 cm^{-1}) are absent in the intercalates. Instead the spectra of the intercalates contain specific frequencies due to the $-NH_2$ group (3288, 3242, 3158, 1606 cm^{-1}). The characteristic stretching frequencies of the phenyl group remain unchanged in the intercalates. Additional bands due to the CH groups of the methyl and methylene carbons can also be seen prominantly in the spectra. The IR spectra of the different intercalates are qualitatively superimposable although their relative intensities show some differences.[19]

Table 3. Bond Lengths (Å) and Bond Angles (deg) for **1**

Zn1−O1	1.924(6)	Zn1−O2	1.913(5)
Zn1−O3	1.885(6)	Zn1−N1	2.039(7)
P1−O1	1.550(6)	P1−O2	1.538(6)
P1−O3	1.607(6)	P1−C1	1.854(5)
C1−C2	1.373(7)	C1−C6	1.412(7)
C2−C3	1.393(7)	C3−C4	1.390(7)
C4−C5	1.402(7)	C5−C6	1.368(7)
N1−C7	1.54(1)	C7−C8	1.49(1)
C8−C9	1.41(1)		
O1−Zn1−O2	110.9(3)	O1−Zn1−O3	110.5(3)
O1−Zn1−N1	109.6(3)	O2−Zn1−O3	94.8(3)
O2−Zn1−N1	112.3(4)	O3−Zn1−N1	118.1(4)
O1−P1−O2	110.8(5)	O1−P1−O3	109.1(5)
O1−P1−C1	108.4(5)	O2−P1−O3	109.0(5)
O2−P1−C1	112.1(5)	O3−P1−C1	107.3(6)
P1−C1−C2	121.4(6)	P1−C1−C6	119.0(6)
C1−C2−C3	121.3(5)	C2−C3−C4	118.5(5)
C3−C4−C5	120.4(5)	C4−C5−C6	120.2(5)
C5−C6−C1	119.7(5)	C6−C1−C2	119.2(5)
N1−C7−C8	107.3(9)	C7−C8−C9	115.4(9)
Zn1−N1−C7	126.6(8)		

Structure of the Intercalates. Crystallographic data for the subject compounds are given in Table 2. Selected bond parameters are presented in Tables 3−5. Observed and calculated powder patterns are shown in Figure 1; the projections of the structure down the a, b, and c axes are given in Figures 2−4, respectively.

In all three intercalates the zinc atom exhibits a slightly distorted tetrahedral geometry. The coordination sites are occupied by three oxygen atoms from three different phosphonate groups and a nitrogen atom of the amine. The average Zn−O and Zn−N bond distances in these compounds are 1.91(1) and 2.01(1) Å, respectively. Among the six bond angles about the metal atom, four have normal tetrahedral values while one is larger and the other is smaller by about 10−15°. The angle O2−Zn−O3 is notably small, 94.8(3)° in **1**, 98.2(5)° in **2**, and 93.4(4)° in **3**, whereas the angle O3−Zn−N has expanded (118.1(4)° in **1**, 115.0(4)° in **2**, and 121.5(4)° in **3**) possibly due to the spacial requirements for the positioning of the amine

Table 4. Bond Lengths (Å) and Bond Angles (deg) for **2**

Zn1−O1	1.939(6)	Zn1−O2	1.904(7)
Zn1−O3	1.902(7)	Zn1−N1	1.993(9)
P1−O1	1.537(7)	P1−O2	1.526(7)
P1−O3	1.594(7)	P1−C1	1.790(6)
C1−C2	1.374(8)	C1−C6	1.380(8)
C2−C3	1.385(7)	C3−C4	1.385(8)
C4−C5	1.392(9)	C5−C6	1.380(8)
N1−C7	1.45(1)	C7−C8	1.41(1)
C8−C9	1.55(1)	C9−C10	1.53(1)
O1−Zn1−O2	111.2(3)	O1−Zn1−O3	113.2(5)
O1−Zn1−N1	107.5(4)	O2−Zn1−O3	98.2(5)
O2−Zn1−N1	111.6(5)	O3−Zn1−N1	115.0(4)
O1−P1−O2	112.9(6)	O1−P1−O3	111.0(6)
O1−P1−C1	108.0(6)	O2−P1−O3	110.4(7)
O2−P1−C1	110.6(6)	O3−P1−C1	103.5(8)
P1−C1−C2	120.7(7)	P1−C1−C6	118.2(7)
C1−C2−C3	120.1(5)	C2−C3−C4	118.1(6)
C3−C4−C5	119.2(8)	C4−C5−C6	118.4(8)
C5−C6−C1	118.8(6)	C6−C1−C2	120.9(5)
N1−C7−C8	119(1)	C7−C8−C9	114(1)
C8−C9−C10	105(2)	Zn1−N1−C7	132(1)

Table 5. Bond Lengths (Å) and Bond Angles (deg) for **3**

Zn1−O1	1.903(7)	Zn1−O2	1.907(7)
Zn1−O3	1.918(7)	Zn1−N1	1.999(9)
P1−O1	1.544(7)	P1−O2	1.576(7)
P1−O3	1.569(7)	P1−C1	1.838(7)
C1−C2	1.387(9)	C1−C6	1.401(9)
C2−C3	1.390(9)	C3−C4	1.384(9)
C4−C5	1.391(9)	C5−C6	1.359(9)
N1−C7	1.45(1)	C7−C8	1.50(1)
C8−C9	1.53(1)	C9−C10	1.47(2)
C10−C11	1.52(1)		
O1−Zn1−O2	114.3(4)	O1−Zn1−O3	112.1(4)
O1−Zn1−N1	103.7(4)	O2−Zn1−O3	93.4(4)
O2−Zn1−N1	112.1(5)	O3−Zn1−N1	121.5(4)
O1−P1−O2	109.5(5)	O1−P1−O3	110.0(5)
O1−P1−C1	104.0(6)	O2−P1−O3	113.9(6)
O2−P1−C1	111.0(7)	O3−P1−C1	108.1(8)
P1−C1−C6	119.3(8)	P1−C1−C6	119.8(8)
C1−C2−C3	120.2(7)	C2−C3−C4	116.1(7)
C3−C4−C5	122.0(7)	C4−C5−C6	119.4(7)
C5−C6−C1	119.1(6)	C6−C1−C2	119(1)
N1−C7−C8	113(1)	C7−C8−C9	109(1)
C8−C9−C10	108(1)	C9−C10−C11	106(1)
Zn1−N1−C7	131(1)		

group. It may be noted that the distortion in the bond angles is less for the butylamine compound as compared to the other two intercalates. The phosphonate tetrahedron and the phenyl group show very regular bond parameters in all three compounds. The bond parameters involving the carbon atoms of the amine are also normal although the values have larger errors and these errors increase as the number of carbon atoms in the chain increases. The N−C−C and C−C−C angles vary between 105° and 122° in these compounds. The larger errors in these cases may be attributed to their thermal motion and also to the difficulties involved in defining their geometries with reasonable bond constraints which is essential in refining the structure against the X-ray powder data.

In the structure, the inorganic framework forms a two-dimensional layer (Figure 2) whose mean plane is located in the *bc* plane at $x = 0.0$ and 1.0. These layers have basal spacings of 13.67, 14.35, and 15.89 Å in **1**, **2**, and **3**, respectively. The metal atoms are situated almost in the mean plane, and the P atoms are alternatively above and below the mean plane by 1.5−1.6 Å (Figure 3). As shown in Figure 2, the metal atoms are linked to each other in an interesting manner to form alternating sixteen- and eight-membered rings in the *bc* plane. The centers of these rings coincide with the centers of symmetry in the crystal. The eight-membered rings (Zn−O1−P−O3−Zn−O1−P−O3) are formed by bridging the zinc atom, Zn1, to its centrosymmetrically related (at 0, 0, 0) position (Zn1A) through oxygen atoms O1 and O3. The third oxygen atom, O2, of the phosphonate bridges across a glide-related Zn atom. The oxygen atoms O3 and O2 of a single phosphonate group then bridge this glide-related zinc atom to another centrosymmetrically related atom which in this case is the translated position of Zn1A (one unit cell along the *b* axis). The symmetry brings the linkages back to the starting metal atom, Zn1, and thus creates sixteen-membered rings (Zn−O1−P−O2−P−O3−P−O2−Zn−O1−P−O2−P−O3−P−O2) whose centers are located at (0, 1/2, 0) and (0, 0, 1/2). The relationship of this layer arrangement to that in the zinc phenylphosphonate will be described in the Discussion section.

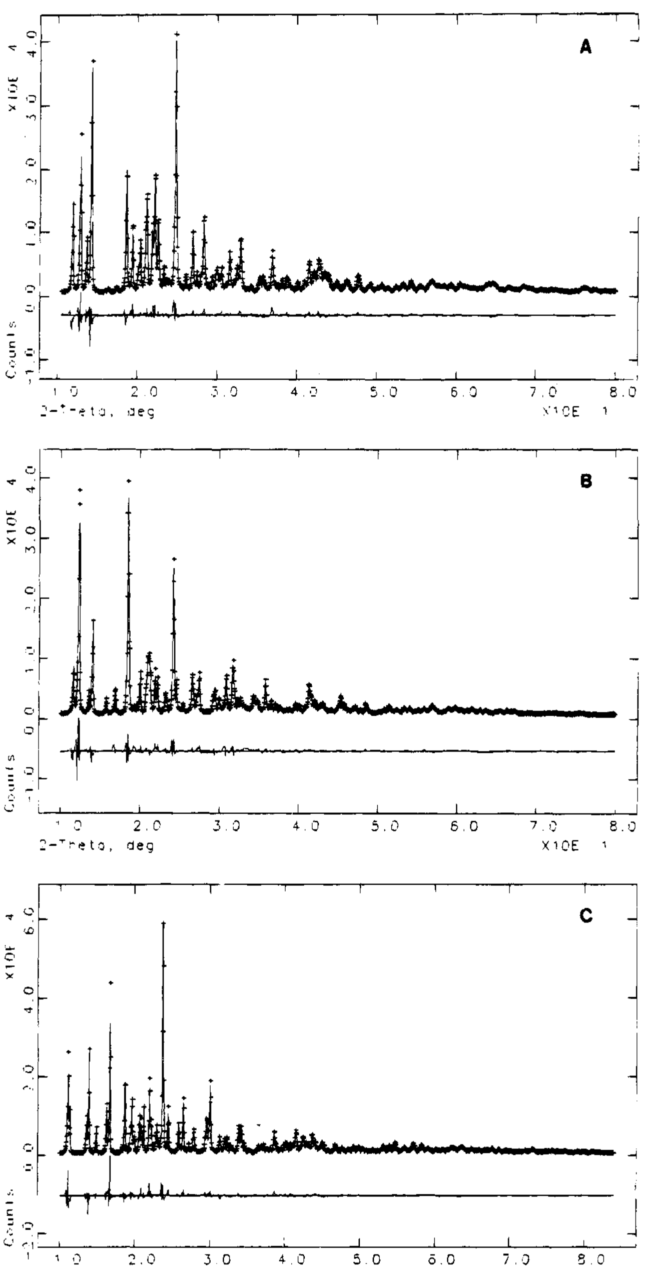

Figure 1. Observed (+) and calculated (−) profiles for the Rietveld refinement for (A) propylamine, (B) butylamine, and (C) pentylamine intercalates. The bottom curve is the difference plot on the same intensity scale.

The phenyl groups and the alkyl chain of the amines are projected toward the interlayer space. The phenyl groups are nearly planar and they are diagonally oriented both to the *ab*

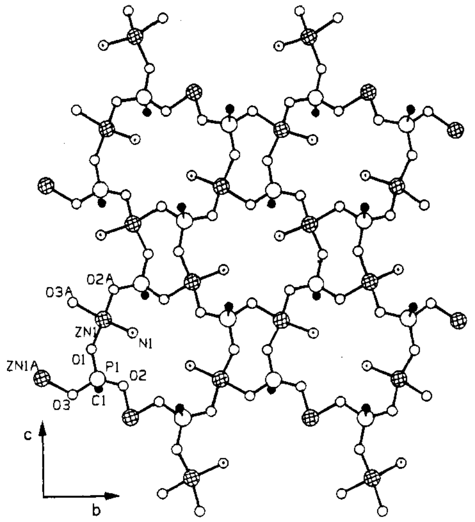

Figure 2. Arrangement of the inorganic framework in the layers of the intercalates. The carbon atom bonded to the P atom is represented by a filled circle. Other atoms of the phenyl and carbon atoms of the amine groups are omitted for clarity.

and *ac* planes (Figure 4 and 3, respectively). Along the *b* direction the phenyl groups are well separated by the length of the *b* cell dimension. The grouping of two phenyl rings and two amine chains as seen in the projection diagram down the *c* axis direction (Figure 4) arises due to the *c* glide symmetry along the projection axis. Another way of viewing the structure is to note that the layer is built up of zigzag chains running in the direction of the *c* axis (P1−O1−Zn1−O2A−P, etc. in Figure 2). All the phenyl rings in this chain are pointing down while the amine chains are pointing in the opposite direction. The adjacent zigzag chain in the *c* direction (Figure 2) is centrosymmetrically related to the first chain. Thus, all the phenyl rings in this chain point in the up direction (positive *a* direction) and all the amine chains point in the negative *a* direction. This structure as viewed along or parallel to the *c* axis (Figure 3) shows the alternating up−down sequence, but because of the center of symmetry both the phenyl rings and the amine alkyl chains are oriented in the same direction down the *b* axis direction. This is seen clearly in Figure 3 in which the view is down the *b* axis. The tilt of both groups away from the perpendicular to the mean plane is also evident. On the other hand, looking down the *c* axis (Figure 4), we see all the phenyl rings in one row either down or up, with the zigzag nature of the chains within the layer lining the rings up in two positions. The amino groups are oriented in the opposite direction to the phenyl rings as illustrated in Figure 4. The groups are well separated. The closest approach of the phenyl groups to each other is 5.4 Å while the closest approach of the amino nitrogen to C1 is across the eight-membered ring, 4.8 Å. This distance increases to 5.4 Å across the sixteen-membered ring.

The alkyl chains are nearly in a trans conformation. The average distance between C_n (and N) and C_{n+2} (N1···C8 and C7···C9 in **1**, N1···C8, C7···C9, and C8···C10 in **2**, and N1···C8, C7···C9, C8···C10, and C9···C11 in **3**) is 2.44 Å (see Figures 3 and 4). Similarly the distance between C_n (and N) and C_{n+3} averages to 3.75 Å in these compounds. In the case of compounds **2** and **3** the average distance between C_n (and N) and C_{n+4} is 4.87 Å, and in **3** the amine nitrogen is 6.1 Å away from the terminal carbon atom. An inspection of the projection plots (Figure 3) suggests that the zinc phenylphosphonate layers in these intercalates can accommodate the propylamine molecule without any further expansion of the layers. In fact the wider spacing of the phenyl rings in the present case allows a closer approach of the layers than in the parent zinc phenylphosphonate. The terminal carbon atom of this amine does not even extend up to the end carbon atom of the phenyl group. The length of the butylamine chain extends just below the phenyl group. However, increased layer−layer repulsion due to the methyl protons requires a small increase (0.7 Å) in the interlayer separation from the propylamine to the butylamine intercalate. In **3**, the interlayer distance increases by about 1.55 Å from that in **2** due to the additional methylene group in the alkyl chain which is clearly seen in Figure 4.

Since all the metal atoms are located nearly in the *bc* plane, the angle between this plane and the vector along the different atoms in the amine group would give the conformation of the amine molecules in the crystal lattice. The alkyl chains are oriented to different extents along the two layer axes *b* and *c*. The Zn−N bond along the *b* axis is inclined by 36−39° to the plane of the layers in these compounds. The angle between the mean plane of the layer and the Zn to C vector then increases with an increase in the number of carbon atoms (averages for the first and second carbon atoms are 55° and 62°) and reaches a steady value of about 70° for the end carbon atoms (Figure 3) in all three compounds. Along the *c* direction, the Zn−N bond is inclined by about 65° to the layer mean plane. In this direction this angle increases to about 71° (average) for the first carbon and reaches a near orthogonal value of about 95° for the second carbon atom (Figure 4). The angle then remains steady for the rest of the carbon atoms of the alkyl chain. Thus, the alkyl chains are almost perpendicular to the mean plane of the layer when viewed along the *c* axis and are slightly inclined (about 70°) in the *b* axis projection. The steady increase in the interlayer spacings for the alkyl chains (Table 1) suggests that the higher alkylamines containing six or more carbon atoms adopt a similar conformation in the crystal.

Reversibility of Intercalation. Treatment of the amine-intercalated zinc phenylphosphonates with dilute (0.02 M) HCl removes the amine. At the same time the remaining zinc phenylphosponate reverts to the structure it had before intercalation of the amine as shown by its X-ray powder pattern. Thus, the intercalation reaction is perfectly reversible. The amine intercalation of the zinc phenylphosphonate takes place in the solid state since the host compound does not dissolve during this process. Similarly, the intercalate releases its amine without being dissolved in the dilute acid solution. Thus, these reversible reactions may be considered as topotactic and not topochemical.

Discussion

The structure of the host zinc phenylphosphonate $Zn(O_3PC_6H_5)\cdot H_2O$ was solved by single-crystal methods.[15] The crystals are orthorhombic with $a = 5.634(2)$ Å, $b = 14.339(5)$ Å, and $c = 4.833(1)$ Å. A portion of the layer is shown schematically in Figure 5. The zinc has a distorted octahedral coordination. Two of the oxygens of the phosphonate group chelate a metal atom. These chelating oxygens also bridge adjacent metal atoms along the *a* direction. The third oxygen binds to only one metal atom along the *c* axis, creating four- and six-membered rings in the layer. The sixth coordination site is occupied by a water molecule. The layers viewed end on have a zigzag appearance, with the phenyl groups above and below the plane of the layer at the crests and the water molecules at the troughs. The phenyl groups are 4.8 Å apart along the *c* direction, and they show elongated thermal ellipsoids perpendicular to the plane of the phenyl ring. These rings are 5.63 Å apart in the *a* direction, and since the plane of these rings is almost parallel to the *a* axis, the arrangement leads to

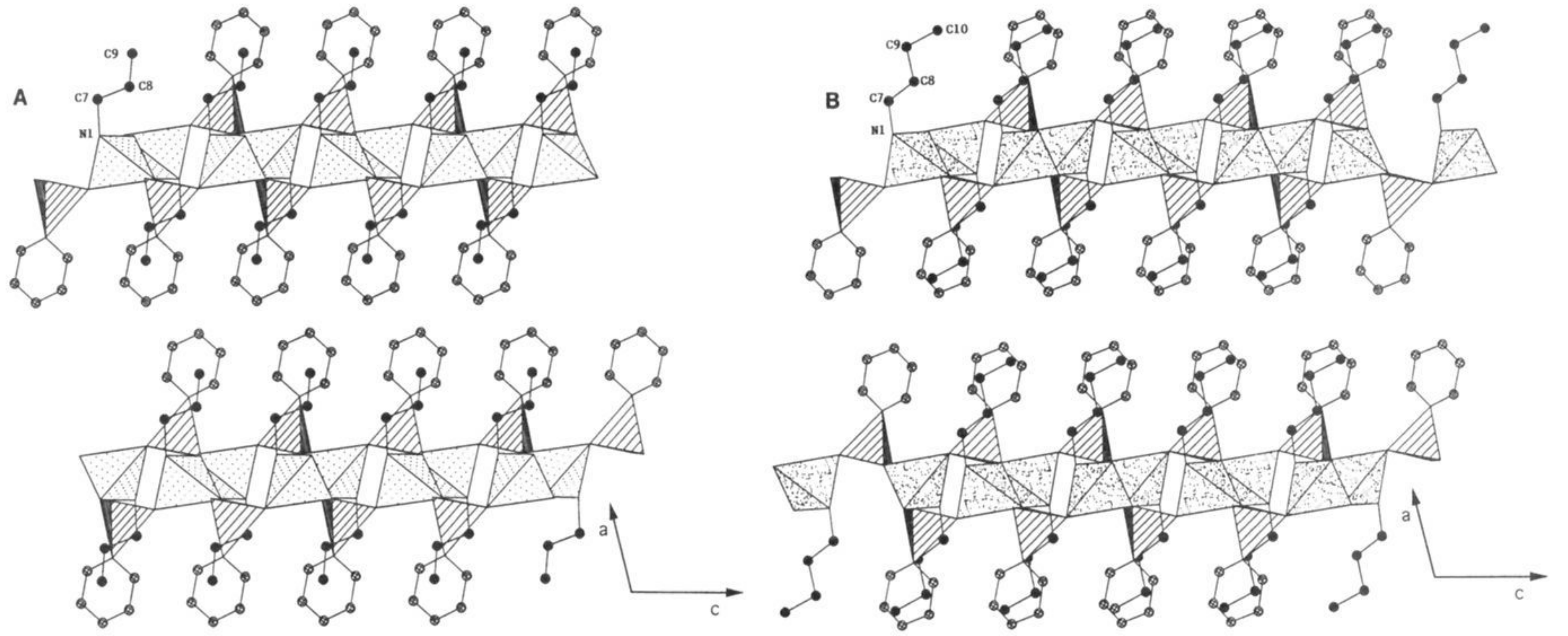

Figure 3. Projection of the intercalate structure down the *b* axis for (A) propylamine and (B) butylamine intercalates. The carbon atoms of the amines are shown by filled circles. The amine molecules are shifted along the projection axis. Molecular arrangement in **3** is similar to that shown here.

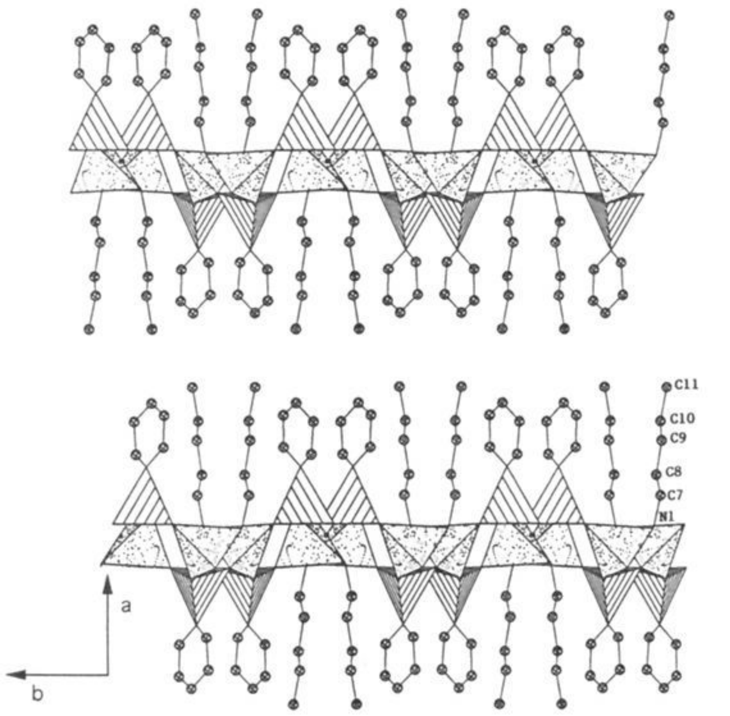

Figure 4. Structure of **3** as viewed down the *c* axis showing the arrangement of amine chains between the phenyl groups. In this projection there are two orientations for the amine and the phenyl groups on either side of the layer due to the screw axis along *b*. The groups with similar orientation repeat by the length of the *b* axis.

severe nonbonded interactions. It is likely that one of the axes is doubled in the crystal, which would then allow the positioning of the groups in two orientations canted to each other. The hyphothesis is supported by indirect evidence. In the zinc and isomorphous cadmium[26] and manganese[11a] structures the same disorder of the phenyl rings was observed. Weak diffraction spots were found along either the *a* or *c* axis or both, indicating that a doubling of the cell in one or both directions was necessary. However, refinement in the larger cell proved difficult. The type of canted arrangement that might be expected was found in lanthanum phenylphosphonate[12b] and copper(II) phenylphosphonate.[12a]

Because of the close proximity of the phenyl rings in the Zn and presumably in the isomorphous Mn, Co, and Cd compounds, amine vapors do not intercalate into the dehydrated phase for lack of space. In contrast NH_3 does find a position on the open coordination site[17] because of its small size and electron pair donor capability. Liquid amines as shown in this study are able to intercalate by virtue of a structural rearrangement that produces a more open structure. The amine chains in the rearranged lattice are 4.8−5.4 Å from the phenyl rings. Upon removal of the amine, the structure reverts to its original one.

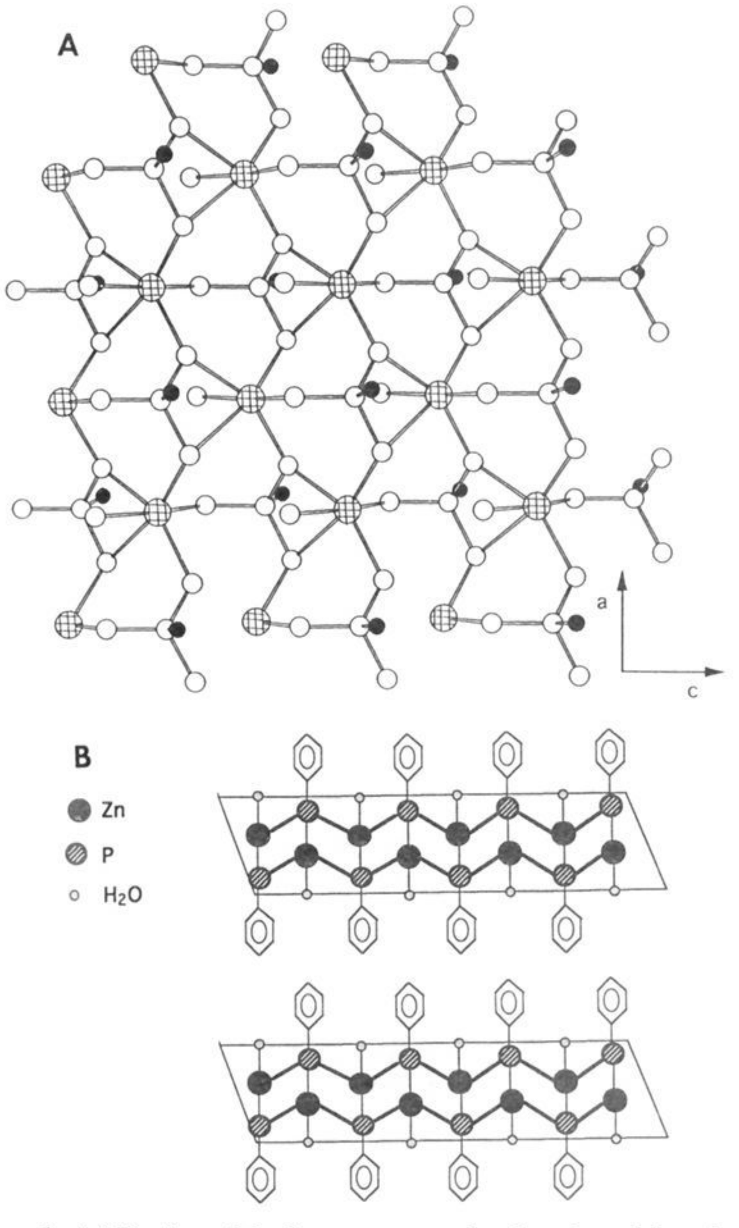

Figure 5. (a) Portion of the layer structure in zinc phenylphosphonate showing the chelation and bridging connections of the Zn atoms by the phosphonate groups. (b) A schematic view of the zinc phenylphosphonate layers (with oxygens omitted) emphasizing the pleated nature of the sheet as opposed to the flat arrangement in the intercalates (Figures 3 and 4).

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The anhydrous zinc phenylphosphonate is isomorphous with the hydrated phase as shown by their X-ray powder patterns, indicating that the dehydration only results in reducing the metal coordination number to five but not in changes in the layer arrangements.[16,17] The rearrangement is keyed by contact with the amine, with the driving force being the shift from an unfavorable coordination to a more favorable one. This is accomplished by opening of the chelate rings such that the three-coordinate oxygens, in fact all the phosphonate oxygens, become two-coordinate. Since there are only three oxygens and one nitrogen for bonding, the Zn atoms are constrained to be four-coordinate. This leads to the formation of the larger open rings containing four zinc atoms. In the course of the rearrangement, two bonds per zinc atom must break, and the freedom thus created allows a rotation of the phosphonate groups to form the observed ring structures. In the process the puckered layers flatten out. The energy required for these structural changes is supplied by coordination of the amine to the zinc and probably the relaxation of the layers into a more planar shape.

Zinc and cobalt methylphosphonates have been shown to exhibit shape selectivity in amine intercalation.[16] Primary amines readily intercalate into the anhydrous phases, but those with branching at the α-carbon atom do not. The methylphosphonates also are orthorhombic and have the same space group, $Pmn2_1$, as their phenylphosphonate counterparts. Their unit cell dimensions are $a = 5.68$ Å, $b = 8.73$ Å, and $c = 4.78$ Å for the zinc methylphosphonate and $a = 5.66$ Å, $b = 8.69$ Å, and $c = 4.79$ Å for the cobalt analogue. These unit cell dimensions are similar to those in zinc phenylphosphonate except for the smaller b dimension which results from the size difference between the larger phenyl group and the methyl group. The powder patterns of the dehydrated phases of the methylphosphonates also belong to the same symmetry but with reduced values for the b axis and increased size of the c axis ($a = 5.42$ Å, $b = 6.94$ Å, and $c = 5.22$ Å for the Zn compound and $a = 5.44$ Å, $b = 6.85$ Å, and $c = 5.24$ Å for the Co compound). Unlike the phenylphosphonates, the anhydrous salts of the methylphosphonates show less affinity for water, and in fact the zinc compound is unreactive even when contacted with liquid water. The substantial shrinkage in the b axis on dehydration was attributed to a shift of the layers so that the methyl groups of one layer nestle in the space vacated by loss of the water molecules. Cao and Mallouk[16] assumed that the layer structure remains essentially intact during intercalation and interpreted the observed basal spacings on a combination of interdigitated and/or bilayer structures. The increased c axis dimension and the decreased bulkiness of the methyl as opposed to the phenyl group may allow such an arrangement rather than the rearrangement exhibited by the phenylphosphonate, but resolution of the problem must await additional structural studies. However, our recent studies[2] with zinc phosphite phenylphosphonates of composition $Zn(O_3PH)_x(O_3PC_6H_5)_{1-x}$ indicate the same layer-type rearrangement as with the parent phenylphosphonate. A full analysis has not been done but the interlayer spacings of the mixed derivatives are very close to those of the parent phenylphosphonate.

An interesting feature observed in the intercalation of primary amines into copper phosphonates[28] is that different amounts of amines are absorbed depending upon the type of organic substituent on the phosphonate. The methylphosphonate and phenylphosphonate have a similar layer structure, and in both cases the metal atom is in a distorted tetragonal pyramidal coordination.[12a] The dehydrated copper methylphosphonate reacts with 1 mol of primary amine while the phenylphosphonate takes up 2 mol. The additional mole of amine apparently occupies the sixth coordination site of the copper atom which then may adopt a distorted octahedral coordination. It is difficult to visualize this effect on steric grounds since phenyl groups are bulkier than the methyl groups. It is therefore possible that these two phosphonates adopt slightly different layer structures on amine coordination.

Finally it should be noted that the present study and the resolution of the structural problems described here are made possible by the advances in powder X-ray diffractometry.[20–22,24,25,29,30] While the Rietveld method[30] has played a seminal role in these advances, the missing link was the application of direct methods as well as known Patterson methods to obtain the model structure to enable routine structure solutions to become a reality.[12c,d,31–34]

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Supporting Information Available: Tables providing a complete listing of atomic parameters and isotropic thermal displacement parameters for compounds **1**, **2**, and **3** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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