Chem. Mater. **1995,** *7,* 1095–1102

Articles

Synthesis, Characterization, and Amine Intercalation Behavior of Zinc Phosphite Phenylphosphonate Mixed Derivatives

K. J. Scott, Y. Zhang, Ren-Chain Wang, and A. Clearfield*

Department of Chemistry Texas A&M University, College Station, Texas 77843

Received July 22, 1994. Revised Manuscript Received April 7, 1995[⊗]

Layered compounds of general formula $Zn(O_3PH)_x(O_3PC_6H_5)_{1-x}\cdot yH_2O$ (where x varies between 0.26 and 0.60) have been synthesized and characterized by X-ray powder diffraction, IR, TGA, and ^{31}P MAS NMR. The mixed derivatives consist of single-phase solid solutions in which the overall structure type is maintained while the ratio of phosphite to phenylphosphonate incorporated into the product varies. The interlayer distance of the mixed derivatives is maintained at 14 Å, equivalent to the phenyl–phenyl interlayer abutment, even at 60% phosphite loading. The intercalation behavior of two representative mixed derivatives, $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}\cdot H_2O$ and $Zn(O_3PH)_{0.60}(O_3PC_6H_5)_{0.40}\cdot 1.2H_2O$ toward normal and branched chain alkylamines was also studied.

Introduction

Since the discovery of α-zirconium bis(monohydrogen orthophosphate) monohydrate, α-ZrP, in 1964 by Clearfield and Stynes,[1] α-ZrP has become the most well-known and most studied insoluble α-layered acid salt of tetravalent metal ions. The literature is replete with comprehensive studies on the properties and reactivities of α-ZrP.[2-7] In 1978,[8] it was discovered that compounds of the type $Zr(O_3PR)_2$ and $Zr(O_3POR)_2$ (where R is an organic radical) can be synthesized by simply replacing phosphoric acid with the acids H_2O_3PR or H_2O_3POR in the synthesis of α-ZrP by the HF method. The $Zr(O_3PR)_2$ and $Zr(O_3POR)_2$ derivatives represent a new class of inorganic/organic hybrids that adopt the α-ZrP structure type in which the layered structure is maintained but the tetrahedral P–OH groups that point between the layers are replaced by tetrahedral P–R or P–OR moieties.

Researchers have since synthesized many analogous organophosphonate layered metal salts of trivalent and divalent metal ions.[9-15] Through these numerous examples it was discovered that the structure-directing properties of phosphonic, phosphorous, and phosphoric acids toward transition-metal ions to form layered compounds in which the metal centers are linked together through tetrahedral phosphate groups is general. Functionalizing the organic groups can result in structures that have highly reactive sites both on the surface of the compound and in the interlayer region. The strong covalent bonding of the organic moiety to the stable inorganic support as well as the ability to change the nature of the R group could be exploited through many applications in fields such as chromatography, photochemistry, ion exchange, sorbants, and catalysis.[3,16-18] Therefore, provided that the vast internal surfaces of these layered hybrids can be made accessible to external species, highly selective and reactive sites can be built into the interlayer region of these compounds.

A number of research groups[8,18-22] have conceptualized that porosity can be built into inorganic/organic

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1995.

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Table 1. Interlayer Spacings and Carbon Content for Mixed Derivative Samples as a Function of the Stoichiometric Ratio of Phosphorus Acid to Phenylphosphonic Acid Used in the Reaction Procedure

derived formula	interlayer dist (Å)	starting ratio PH/Pϕ	% C (found)	% C (expected)[a]
$Zn(O_3PH)_{0.60}(O_3P\phi)_{0.40}\cdot 1.1H_2O$	13.4	2.5/1.0	14.83	14.74
$Zn(O_3PH)_{0.50}(O_3P\phi)_{0.50}\cdot 0.92H_2O$	14.3	1.0/1.0	17.69	18.02
$Zn(O_3PH)_{0.44}(O_3P\phi)_{0.56}\cdot 1H_2O$	14.6	1.0/1.0	21.66	19.59
$Zn(O_3PH)_{0.43}(O_3P\phi)_{0.57}\cdot 0.95H_2O$	14.5	1.0/1.5	20.04	19.96
$Zn(O_3PH)_{0.26}(O_3P\phi)_{0.74}\cdot 0.89H_2O$	13.7	1.0/2.3	24.40	24.49

[a] Based on proposed formula.

metal phosphonates by replacing some of the organic R groups with smaller groups such as $-H$, $-OH$, and $-CH_3$. The large organic groups would act like a pillar to hold the layers apart while the smaller groups would provide space so that pores may be built into the interlayer region. The first reports of the synthesis of mixed derivative compounds, where there are two types of groups that point into the interlayer region, began to appear around 1982–1983.[16,23] Early studies[24] indicated that the surface areas of these mixed derivatives were quite high, presumably due to the inclusion of the sorbent species into the interlayer region by way of intercalative diffusion. These findings sparked an interest in synthesizing these mixed derivative compounds.

Although there are a number of layered mixed derivatives of zirconium and other tetravalent metal ions reported in the literature,[7,16,19–23,25–29] the analogous layered metal salts of trivalent and divalent metal phosphonates have not received attention.

The objective of this research was to synthesize mixed derivative single-phase solid solutions of the divalent metal ion, Zn, using phenylphosphonic and phosphorous acids. To fully characterize the products, a variety of analytical techniques were utilized to demonstrate that the product is a single-phase solid solution mixed derivative rather than a staged structure or a simple physical mixture of the pure phases. The synthesis and characterization of the layered compounds, $Zn(O_3PH)_x(O_3PC_6H_5)_{1-x}\cdot yH_2O$ (where x varies between 0.26 and 0.60) and the intercalation behavior of two representative mixed derivatives, $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}\cdot H_2O$ and $Zn(O_3PH)_{0.60}(O_3PC_6H_5)_{0.40}\cdot 1.1H_2O$ toward alkylamines are herein reported.

Experimental Section

Materials and Methods. Reagents and solvents used were obtained from Aldrich and were used without further purification. Deionized water used in all experiments was purified to a resistivity of 17.6 MΩ cm with a Barnstead Nanopure II system. X-ray powder diffraction (XRD) patterns were acquired with a Seifert-Scintag PAD V diffractometer (no internal standard) using nickel-filtered Cu Kα radiation. With the sample in the form of a KBr disk, infrared spectra (IR) were recorded with a BIO-RAD FTS-40 spectrometer. A duPont thermal analyst 950 unit was used for thermogravimetric analyses (TGA) at a typical heating rate of 10 °C/min under a flow-by of nitrogen, unless specified otherwise. All solid-state ^{31}P NMR spectra were recorded on a Bruker MSL-300. Surface area studies were performed on a Quantachrome Autosorb 6 unit. C, H chemical analysis was determined by Desert Analytical and P analysis by ICP at the Texas A&M Horticulture Laboratories unless specified otherwise.

Synthesis of $Zn(O_3PH)_x(O_3PC_6H_5)_{1-x}\cdot yH_2O$. Typically a mixed ligand solution was made by dissolving a stoichiometric amount of phenylphosphonic acid and phosphorous acid in approximately 40 mL of deionized H_2O. Dilute NaOH was added to the mixed ligand solution until the pH reached 11. $ZnCl_2$ (2.0 g) was dissolved in about 20 mL of deionized H_2O (mole ratio ligand:metal = 1:1). The $ZnCl_2$ solution was added dropwise to the basic mixed ligand solution. After stirring at room temperature the product was filtered, washed with ethanol, and allowed to air dry. Subsequently the product was refluxed for 2 days in deionized H_2O. After filtering the C, H, P composition was determined. Analytical results calculated for $Zn(O_3PH)_{0.50}(O_3PC_6H_5)_{0.50}\cdot 0.92H_2O$ (FW = 200): C, 18.00%; H, 2.42%; P, 15.48%. Found: C, 17.69%; H, 2.07%; P, 15.46%. The yield was generally ≈80–90%.

Dehydration and Intercalation of $Zn(O_3PH)_x(O_3PC_6H_5)_{1-x}\cdot yH_2O$. The dehydration of $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}\cdot H_2O$ and $Zn(O_3PH)_{0.60}(O_3PC_6H_5)_{0.40}\cdot 1.1H_2O$ was carried out by heating the monohydrate in a vacuum oven at 120 °C overnight. Typically, 0.20 g of the dehydrated sample was placed in a small glass screw top vial. To this was added about 5–10 mL of neat alkylamine. The vial was sealed and allowed to stir at room temperature for three to five days. The sample was then filtered and allowed to air dry. All of the amine intercalated samples (aside from propylamine) were placed in an oven at 70 °C overnight for further drying.

Results and Discussion

Following the synthetic procedure outlined above, mixed derivatives of general formula $Zn(O_3PH)_x(O_3PC_6H_5)_{1-x}\cdot yH_2O$ can be readily synthesized. Furthermore, considerable control over the ratio of phosphite to phenylphosphonate in the final material can be attained by varying the mole ratios of the phosphorous acid and the phenylphosphonic acid of the starting mixed ligand solution. Examination of Table 1 shows that control over the amount of phosphite incorporated into the final product was attained by varying the ratio of phosphite to phenylphosphonate in the starting mixed ligand solution. The ratio of phosphite to phenylphosphonate in the final product was determined based on the percentage of carbon contained in the final product. As emphasized in Table 1, the percentage of carbon found in the final product was in good agreement with the derived formula and the ratio of ligands in the products roughly paralleled their ratio in the starting solutions.

The formation of zinc phosphite phenylphosphonate mixed derivatives required coprecipitation of the metal ion with the phosphite and phenylphosphonate ligands under rapid reaction rates. Only at high pH (see Experimental Section) did the reaction proceed quickly

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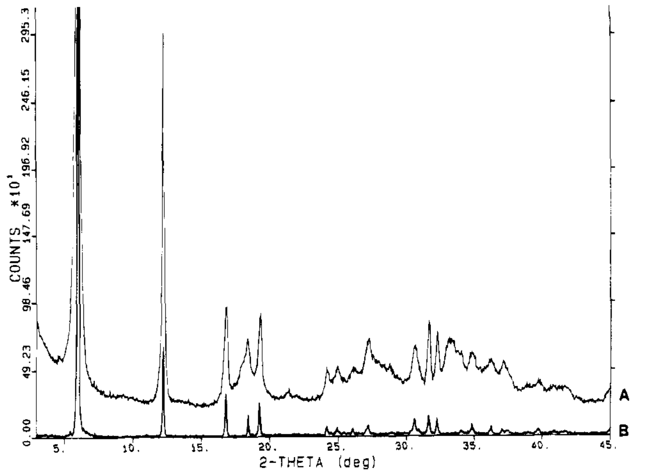

Figure 1. XRD powder pattern of $Zn(O_3PH)_{0.6}(O_3PC_6H_5)_{0.4}\cdot 1.1H_2O$ (A) compared with the XRD powder pattern of $Zn(O_3PC_6H_5)\cdot H_2O$ (B).

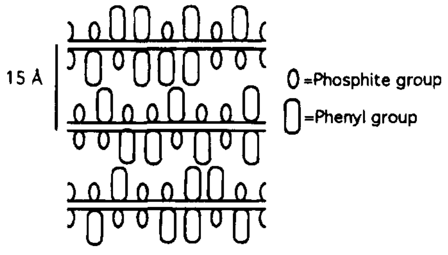

Figure 2. Schematic representation of the most likely interlayer arrangement of $Zn(O_3PH)_{1-x}(O_3PC_6H_5)_x{\cdot}yH_2O$ compounds showing the random dispersion of PH and PC_6H_5 groups throughout the layer as well as the phenyl−phenyl abutments between the layers.

enough to ensure simultaneous reaction of both acids with the metal salt. The addition of the ligand solution and high pH at ambient temperatures leads to immediate precipitation, indicating that the metal−oxygen network that makes up the layer forms very rapidly. Such rapid structural formation is needed to bring about simultaneous inclusion of both phosphite and phenylphosphonate groups into the metal−oxygen framework. Although these conditions promote the formation of amorphous products, it was found that the crystallinity of the mixed derivatives can be improved by refluxing the samples in water overnight. The parent zinc phenylphosphonate is soluble in acid solutions, allowing for resolution and growth of single crystals.[30] Refluxing the initial poorly crystalline precipitate in near neutral media resulted in semicrystalline products as shown in Figure 1A, probably by a similar mechanism of resolution and precipitation. However, at this pH, the solubility is still quite low, so that the ligand ratio in the product remains unchanged.

In Figure 1, we compare the X-ray powder patterns of the crystalline zinc phenylphosphonate monohydrate with one of the mixed ligand derivatives which has nearly the same interlayer spacing as the parent compound. It is seen that the two X-ray patterns have many features in common, but many of the reflections of the mixed derivative are broadened. The first, second, and fourth reflections are 010, 020, and 030, while the third reflection is 110. Thus the powder patterns of zinc phosphite phenylphosphonate mixed derivatives are characteristic of layered compounds and all displayed an interlayer d spacing of about 14 Å (Table 1), together with multiple orders of this reflection. The interlayer distances of the mixed derivatives are in good agreement with the interlayer distance (14.6 Å) of the pure parent compound $Zn(O_3PC_6H_5)\cdot H_2O$[30] and indicate that the phenyl rings protrude into the interlamellar region beyond that of the phosphite group on both sides of the layer with enough phenyl−phenyl abutments to hold the layers apart at the distance found for $Zn(O_3PC_6H_5)\cdot H_2O$. Such an arrangement is most consistent with a structure in which the PH and P−phenyl groups are randomly distributed throughout the layer as shown in Figure 2. There was no evidence of peaks in the XRD powder patterns of the zinc mixed derivatives that suggest a structural organization of staged disposition. In addition, since no layered zinc phosphite phases have been reported, the possibility of a staged structure made up of pure phosphite layers interspersed with pure phenyl layers is unlikely. Furthermore the zinc phosphite phase that predominantly forms upon contacting the metal salt with a solution of HPO_3^{2-} in water at high pH is the three-dimensional product, $Zn_2(HPO_3)_2(H_2O)_4\cdot H_2O$.[31] This phosphite phase is quickly identified in the XRD powder pattern by a sharp doublet at 7.65 and 7.54 Å. These peaks are not present in the XRD powder pattern of the mixed derivatives and supports the formation of a single-phase product as opposed to a simple physical mixture of zinc phosphite and zinc phenylphosphonate. Furthermore, there appears to be a fairly consistent correspondence of Bragg reflections in the XRD patterns of the mixed derivatives with $Zn(O_3PC_6H_5)\cdot H_2O$. However, peaks for the mixed derivatives are broadened due to the randomness of the phosphite−phosphonate arrangement. Consequently, the schematic in Figure 2, displaying a random mixture of PH and P−phenyl groups on both sides of the layer is the most probable contender for the interlamellar arrangement of phosphite and phenylphosphonate groups in the zinc mixed derivatives listed in Table 1.

Although tetravalent mixed derivatives were found to form staged compounds or to form separate phases upon varying the ratio of the two pendant groups incorporated into the structure,[25] the zinc phosphite phenylphosphonate compounds as already indicated did not segregate into separate phases. The $Zn(O_3PH)_{1-x}(O_3PC_6H_5)_x{\cdot}yH_2O$ mixed derivatives form part of a continuous series where the interlayer distance remains virtually unchanged upon varying the amount of PH to P−phenyl. The literature[25,29] reported tetravalent mixed derivatives predominantly formed staged structures. However, they were synthesized under hydrothermal conditions or by slow coprecipitation of the reactants over a period of days. In contrast, the recently reported $Zr(O_3P(CH_2)_3NH_2)_x(O_3PCH_3)_{2-x}{\cdot}yH_2O$ series, synthesized by dropwise addition of the metal salt to a solution containing both acids, formed a single-phase solid solution with a d spacing of 10.4 Å, equivalent to the propylamine−methyl abutment.[28] These literature reports together with information uncovered through the

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course of this research suggest that a kinetic product (randomly dispersed PH and P−phenyl groups) is usually synthesized only under conditions of rapid coprecipitation. The thermodynamically controlled reactions (hydrothermal treatment or slow crystallization) promote an ordering of the inorganic/organic layers as found in staged compounds or separate phases. The formation of ordered structures appears to be influenced by the increase in enthalpy that results from the more effective packing that occurs between two layers of like groups.[29] Therefore under slow reaction conditions the compounds form in such a way that the packing arrangement of the collateral layers influences the organization of the metal−oxygen network so that the more favorable packing order (layers of like groups) dictates the layer formation. Contrastingly, under accelerated reaction conditions the metal−oxygen network forms very rapidly, and the resultant individual layers of randomly dispersed groups then pack together in the most favorable arrangement.

Infrared spectroscopy (IR) was utilized to identify the functional groups that have been incorporated into the mixed derivative, specifically, P−H stretching bands at 2430−2280 cm^{-1} and the phenyl C=C band at 1450−1425 cm^{-1} and out-of-plane bands at 695 and 745 cm^{-1}. Although no absolute structural conclusions can be drawn based solely on the IR spectra of the mixed derivatives, many of the band assignments can be rationalized through comparison with assignments determined on known structures.[33] Furthermore, IR also helps to distinguish the product from a simple two-phase physical mixture of the two parent compounds or a one-phase product that has incorporated both phosphite and phosphonate groups. A simple physical mixture would give an IR spectrum displaying features of both parent compounds as an overlapping spectra sequence, whereas a single-phase mixed derivative may exhibit new or shifted bands relative to the pure parent compounds. For example, Figure 3 contrasts the IR spectra of pure zinc phenylphosphonate (A) and pure zinc phosphite (C) with a sample that contains a mixture of pure zinc phosphite and zinc phenylphosphonate, shown in B. Spectrum B is clearly an overlay of both the parent spectra (A and C). The sharp P−H doublet at 2375 and 2383 cm^{-1} in B, as well as the bands at 1167 and 793 cm^{-1}, are all bands that are found in the pure phosphite spectrum (C). The remaining bands can be found in the parent zinc phenylphosphonate (A). The only obscure band present is that of the weak shoulder at 2412 cm^{-1}, near the P−H stretches. The spectrum of the mixed derivative, $Zn(O_3PH)_{0.6}(O_3PC_6H_5)_{0.4}\cdot 1.1H_2O$, shown in Figure 4B, is more closely related to that of the pure zinc phenylphosphonate (A) than the zinc phosphite in C. It is obvious, however, that the spectrum of $Zn(O_3PH)_{0.6}(O_3PC_6H_5)_{0.4}\cdot 1.1H_2O$ is not a simple overlay of spectrum A and C. In particular the sharp doublet that occurs around 2380 cm^{-1} in the phosphite is transformed into a broadened, less intense absorbance centered at a higher wavenumber, 2403 cm^{-1}, and the bands at 1167 and 793 cm^{-1} are not present in spectrum B. This change in P−H stretching frequency is a good indicator that the PH groups in the mixed derivatives are both chemically and geometrically distinct from those of the pure zinc phosphite, thereby maintaining that the product is not a simple physical mixture of the pure-phase parent compounds. Furthermore, aside from differences in relative intensities of the PH and phenyl bands, the spectra of the mixed derivatives, $Zn(O_3PH)_{1-x}(O_3PC_6H_5)_x\cdot yH_2O$, are all virtually superimposable with that shown in Figure 4B.

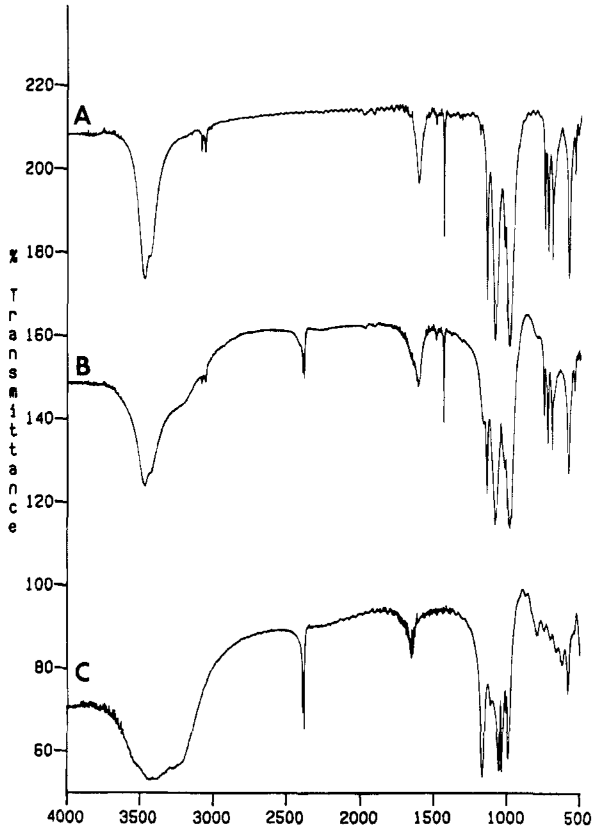

Figure 3. Infrared spectra of $Zn(O_3PC_6H_5)\cdot H_2O$ (A) and $Zn_2(HPO_3)_2(H_2O)_4\cdot H_2O$ (C) compared with a sample that was found to be a physical mixture of both the compounds shown in A and C.

The contention that the zinc phosphite phenylphosphonate mixed derivatives are single-phase products as opposed to physical mixtures is also supported by ^{31}P MAS NMR data. The ^{31}P NMR spectrum of $Zn(O_3PC_6H_5)\cdot H_2O$ contained a very sharp doublet of almost equal intensity at 22.6 and 23.9 ppm (Figure 5C), whereas the pure phosphite compound, $Zn_2(HPO_3)_2(H_2O)_4\cdot H_2O$, exhibited a single broad resonance centered at 3.2 ppm (Figure 5A). The ^{31}P NMR data of the mixed derivative $Zn(O_3PH)_{0.43}(O_3PC_6H_5)_{0.57}\cdot H_2O$ showed the intense ^{31}P resonance of the phenylphosphonate group at 23.3 ppm, as well as a ^{31}P shift at 5.9 ppm (Figure 5B). The resonance at 5.9 ppm is attributed to the phosphite ^{31}P atom since it increased in intensity during a proton-decoupled ^{31}P NMR experiment while the other resonances remain unchanged. The similarity of the chemical shift value of the ^{31}P of the phenylphosphonate groups in the mixed derivatives to the ^{31}P shift value found for the phenylphosphonate groups in $Zn(O_3PC_6H_5)\cdot H_2O$ supports the supposition that the oxygen-bonding modes of the phenylphosphonate tetrahedra, in both compounds, are very much alike. The observed change in the chemical shift attributed to the PH group of the mixed derivative relative to that found for $Zn_2(HPO_3)_2(H_2O)_4\cdot H_2O$ and the broadening of the peaks

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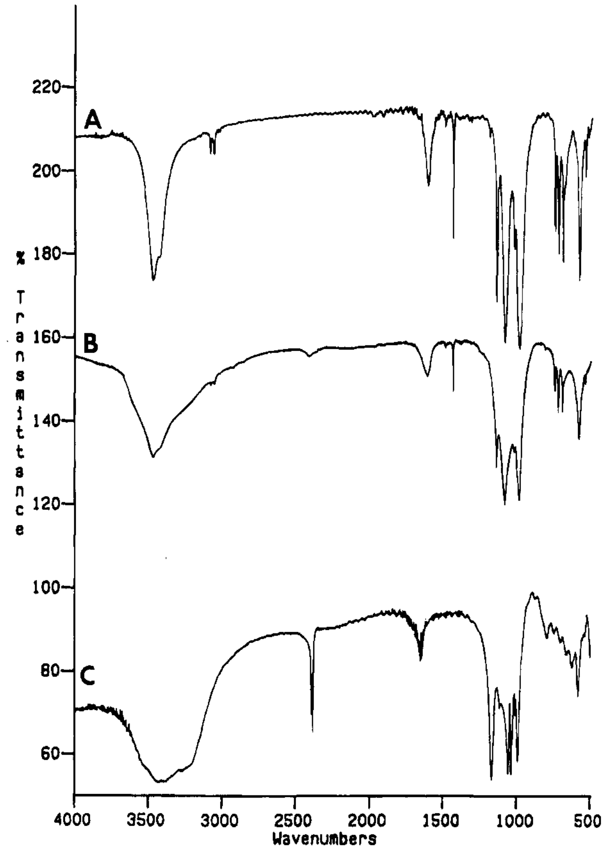

Figure 4. Infrared spectra of $Zn(O_3PC_6H_5){\cdot}H_2O$ (A) and $Zn_2(HPO_3)_2(H_2O)_4{\cdot}H_2O$ (C) compared with a mixed derivative sample, $Zn(O_3PH)_{0.6}(O_3P\phi)_{0.4}1.1H_2O$, shown in B.

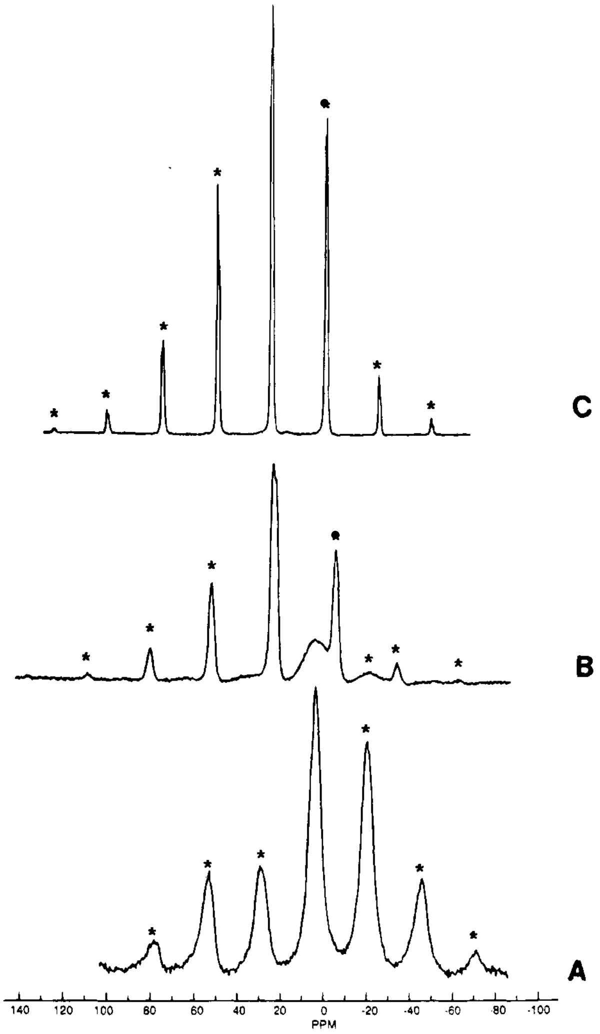

Figure 5. Solid-state MAS ^{31}P NMR spectra for (A) $Zn(O_3PC_6H_5){\cdot}H_2O$ and (B) the mixed derivative $Zn(O_3PH)_{0.43}(O_3PC_6H_5)_{0.57}{\cdot}H_2O$ and (C) $Zn_2(O_3PH)_2{\cdot}H_2O$. The asterisks denote spinning sidebands.

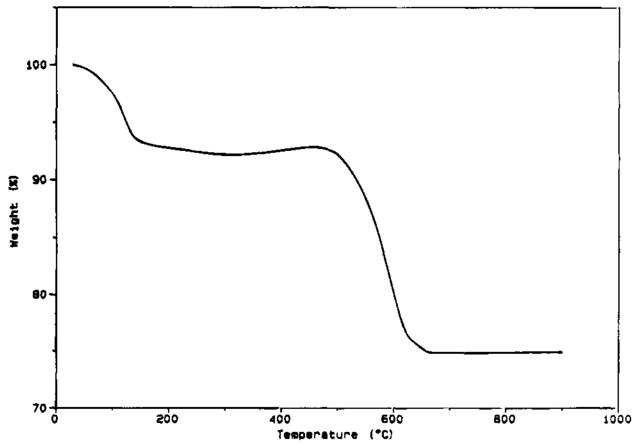

Figure 6. TGA trace of $Zn(O_3PH)_{0.43}(O_3PC_6H_5)_{0.57}{\cdot}0.95H_2O$. The TGA experiment was run in a N_2 atmosphere at a heating rate of 10 °C/min.

argues against the possibility that the product is a simple physical mixture of the two parent compounds.

Thermogravimetric analyses of the mixed derivatives yielded two major weight loss regions. The representative TGA trace shown in Figure 6 is of $Zn(O_3PH)_{0.43}(O_3PC_6H_5)_{0.57}{\cdot}0.95\ H_2O$. The first region involves dehydration of the coordinated water molecule which occurs between 50 and 150 °C and accounts for about 8.0% of the mass (calculated 8.3%). Following dehydration, the compounds decompose with loss of the organic portion at temperatures between 450 and 625 °C. Decomposition of the C_6H_5 group gave a weight loss of 18% for $Zn(O_3PH)_{0.43}(O_3PC_6H_5)_{0.57}{\cdot}0.95\ H_2O$ compared to a calculated value of 17.67% on the assumption that the final product is $Zn_2P_2O_7$. The weight gain shown in the TGA observed between 400 and 500 °C is presumably due to oxidation of phosphite to phosphate. Unfortunately, obtaining direct proof of the oxidation reaction was rendered difficult due to decomposition of the organic group which occurred in the same temperature range.

Perhaps the most important experimental data in favor of the formation of a single-phase solid solution of zinc phosphite phenylphosphonate comes from the intercalation studies of the representative mixed derivatives, $Zn(O_3PH)_{0.43}(O_3PC_6H_5)_{0.57}{\cdot}0.95H_2O$ and $Zn(O_3PH)_{0.60}(O_3PC_6H_5)_{0.40}{\cdot}1.1H_2O$, toward alkylamines. Alkylamines intercalated into the dehydrated zinc mixed derivative phases bind at Lewis acid sites created at the metal center by loss of water molecules that served to satisfy the coordination sphere of otherwise unsaturated zinc centers.[34] Table 2 shows that the interlayer distances of intercalated $Zn(O_3PH)_{0.43}(O_3PC_6H_5)_{0.57}{\cdot}0.95H_2O$ agree remarkably well with the analogous intercalated $Zn(O_3PC_6H_5)$. Notice that the interlayer spacing of the intercalated mixed derivatives are almost the same as the distances found for the analogous intercalated pure phenylphosphonates.

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Table 2. Interlayer Distances As Determined by XRD Powder Diffraction of $Zn(O_3PH)_{0.43}(O_3PC_6H_5)_{0.57}\cdot RnH_2$ and $Zn(O_3PC_6H_5)\cdot RNH_2$ together with the Percent Amine Intercalated into the Mixed Derivative According to TGA Results[a]

	interlayer distance (Å) of		TGA % RNH_2 intercalated	
RNH_2	$Zn(O_3PC_6H_5)\cdot RNH_2$	$Zn(O_3PH)_{0.43}(O_3PC_6H_5)_{0.57}\cdot RNH_2$	obsd	calcd
n-$C_3H_7NH_2$	13.7	13.8	24	24
n-$C_4H_9NH_2$	14.4	14.6	28	28
n-$C_5H_{11}NH_2$	15.7	16.3	30	32
n-$C_6H_{13}NH_2$	16.8	17.0	37	35
n-$C_7H_{15}NH_2$	18.5	19.0	35	38
n-$C_8H_{27}NH_2$	19.2	19.4	37	41

[a] Desorbed from $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}\cdot C_nH_{2n+1}NH_2$ together with the calculated value required for intercalation of 1 mole/formula weight.

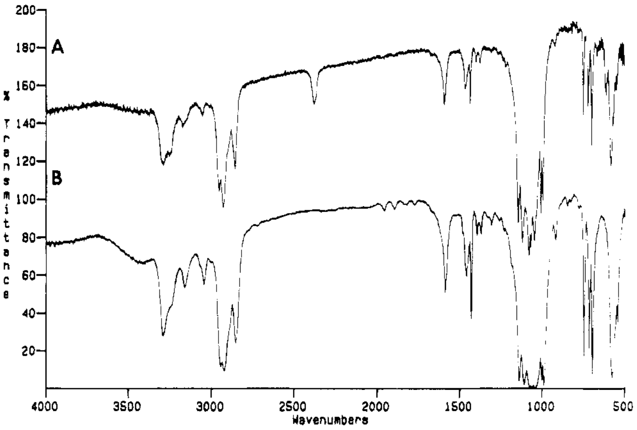

Figure 7. Infrared spectrum of $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}\cdot C_7H_{15}NH_2$ shown in A together with the analogous IR spectrum of $Zn(O_3PC_6H_5)\cdot C_7H_{15}NH_2$ in B.

The remarkable similarity in interlayer distance of the intercalated mixed derivatives versus the intercalated pure phenylphosphonate suggests that the alkylamines pack into the interlayer region in the same way for both compounds. As a matter of fact, the slope of the line of the interlayer distance versus the number of carbon atoms is almost identical for both compounds, 1.24 Å/CH_2 for $Zn(O_3PC_6H_5)\cdot RNH_2$ and 1.23 Å/CH_2 for $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}\cdot RNH_2$. The slope of both lines is smaller than 1.27 Å/CH_2 which is the maximum value for a monolayer of fully extended all-trans oriented alkylamines. This indicates that the alkyl chains of the amine in the interlayer region of both compounds are most likely packed in an interdigitated monolayer fashion with a tilt angle of 78° for the pure phenyl compound and a tilt angle of 76° for the mixed derivative.

Further evidence for intercalation of primary amines into the mixed derivative comes from the infrared spectra of the $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}\cdot RNH_2$ products. Figure 7 compares the IR spectra of heptylamine intercalated into the mixed derivative (A) and into pure zinc phenylphosphonate (B). Clearly, the OH bands at 3400 and 1600 cm^{-1}, in the original zinc phenylphosphonate monohydrate (Figure 3A) are replaced by three sharp bands at 3283, 3246, and 3168 cm^{-1}, which correspond to the N–H stretching bands, and one near 1597 cm^{-1} that is due to the N–H bending mode. The N–H modes as well as the C–H and methylene bands of both the intercalated mixed derivative (A) and the intercalated zinc phenylphosphonate (B) appear at almost identical wavenumbers in both spectra. The IR spectra of the mixed derivative intercalates are virtually identical to one another with the intensity of the methylene bands increasing when proceeding up the series from propyl- to octylamine. Notice, however, that the P–H stretching band near 2377 cm^{-1} has resolved into a much sharper, more intense band from that present in the hydrate phase (Figure 4B). This is most likely attributed to a decrease in hydrogen bonding following intercalation. The O–H stretching region of the hydrated mixed ligand phase (Figure 4B) is broad and extends toward lower frequency, consistent with the presence of a significant amount of hydrogen bonding. The intercalated mixed derivatives contain hydrophobic alkyl groups that decrease the extent of hydrogen bonding. Consequently, the hydrogen bonding associated with the phosphite group is also diminished, allowing the P–H band to become more intense and well defined. The IR spectra of the intercalated series $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}\cdot C_nH_{2n+1}NH_2$ where n ranges from 3 to 8 all display a sharpened P–H band relative to the hydrated phase. This behavior strongly supports the contention that the mixed derivatives are a single-phase solid solution as opposed to a physical mixture. If the mixed derivative were a simple physical mixture of pure zinc phenylphosphonate and zinc phosphite, a change in the appearance of the P–H band would not be expected.

Thermogravimetric analysis was used to determine the quantity of primary amine intercalated in the $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}\cdot C_nH_{2n+1}NH_2$ products. In all cases 1 mol of primary amine was found to be intercalated in place of the 1 mol of water that was lost. The TGA results are in excellent agreement (±2%) with the calculated values, with the exception of octylamine which was found to contain slightly less amine. Octylamine may be approaching the limit of the number of carbon atoms for intercalation of primary amines, or perhaps the reaction was stopped before the optimum amount of alkylamine was absorbed. Table 2 lists the TGA results of the thermal desorption of the alkylamine from $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}\cdot C_nH_{2n+1}NH_2$ together with the calculated values. Two representative TGA curves are shown in Figure 8. The loss of amine does not occur until around 200 °C as was found for the analogous intercalated zinc phenylphosphonate compounds. Not surprisingly, the drop in weight percent between 200 and 400 °C in Figure 8A (heptylamine) is much greater than the weight loss of the propylamine intercalate shown in Figure 8B. Since the amine is a stronger Lewis base than water, the amine groups are not replaced by water molecules on exposure to moisture. The fact that the mixed derivative intercalated a full mole of amine for the alkylamines tested is perhaps the strongest piece of information in support of a single-phase solid solution as opposed to a physical mixture. Because the pure zinc phosphite, $Zn(HPO_3)_2(H_2O)_4\cdot H_2O$, does not intercalate amines and the $Zn(O_3PC_6H_5)\cdot H_2O$ does, the mixed derivative product $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}$ would be expected to intercalate only about 0.56 mol of amine if it were a simple physical mixture of the two parent compounds rather than the full mole observed.

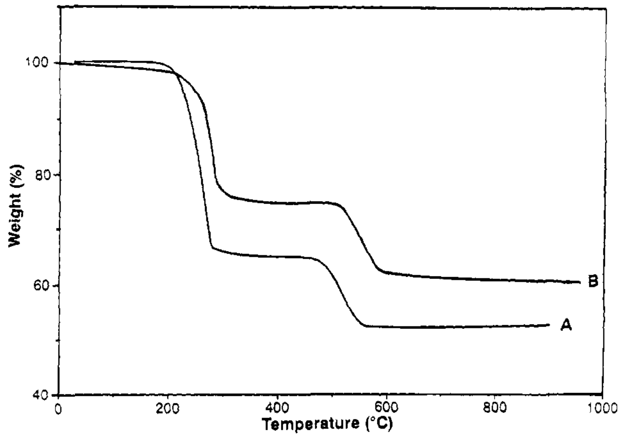

Figure 8. TGA trace of (A) $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}{\cdot}C_7H_{15}NH_2$ and (B) $Zn(O_3PH)_{0.44}(O_3PC_6H_5)_{0.56}{\cdot}C_3H_7NH_2$.

The intercalation behavior of a variety of layered organophosphonates toward alkylamines has recently received considerable attention.[34-39] Particularly, the intercalation chemistry of many of the divalent organophosphonates has been closely studied[34,37,39] and shown to selectively intercalate primary alkylamines. Cao and co-workers[37] examined the reversible dehydration and intercalation behavior of $M(O_3PCH_3){\cdot}H_2O$, where M = Mg, Zn, and Co, and found that the structural environment of the space created by loss of the water molecule is such that a pocket is created following dehydration. The pocket is surrounded by four methyl groups. Two of the groups are about 2.8 Å on either side of the pocket and the other two are about 2.4 Å from the site. Cao et al.[37] found that only primary *n*-alkylamines are able to approach the metal center, and we have shown that only NH_3 could be intercalated into zinc phenylphosphonate from the gas phase.[38] However, a later study[34] revealed that *n*-alkyl primary amines do intercalate as neat liquids. Apparently in the liquid state the amines are able to diffuse into the pockets left by the arrangement of the phenyl rings.

The data in Table 2 show that the interlayer spacing of both zinc phenylphosphonate and the mixed phosphonate–phosphites does not increase for propyl and butylamine. In fact, the interlayer spacing for the propylamine intercalate decreases. The explanation for this behavior is rooted in the structure of the layers which have a zigzag shape.[30] The phenyl rings are attached to the layers at the crests, and the water molecules are in the valleys. Intercalation occurs by displacement of the water molecule and coordination through the nitrogen lone pairs to zinc. Thus, the 6-fold coordination of the zinc atoms is maintained without disrupting the layer structure. Fully extended butylamine in the trans–trans conformation would extend $\approx$7.4 Å from the zinc atom to the methyl protons when oriented perpendicular to the layers or 7.2 Å when oriented at a 76° angle. The phenyl groups, by the same calculation, would extend outward 7.2 and 7.0 Å, respectively. However, because of their respective locations, the phenyl rings extend out farther into the interlayer space than the butylamine groups. The addition of another carbon atom in pentylamine lengthens the chain sufficiently so that it extends beyond the phenyl rings and now determines the interlayer spacing. In zinc phenylphosphonate, the layers are staggered such that the phenyl groups in one layer are midway between those in the adjacent layer. Thus, the alkyl chains, when extending beyond the phenyl rings into the interlamellar space, would abut against the phenyl rings in the adjacent layer. This arrangement amounts to an interdigitation of the alkyl chains, even though they are surrounded by phenyl groups. In fact, in the case of propylamine, there would be empty space between the phenyl ring in one layer and the methyl group of the amine. The increased van der Waals forces resulting from the presence of the alkyl chains would then tend to close this gap by reducing the interlayer spacing as is actually observed.

Similar studies of the intercalation behavior of the mixed derivatives toward α-branched and β-branched alkylamines indicates that there are some subtle differences in the intercalation behavior of the zinc phosphite phenylphosphonate mixed derivatives relative to that of zinc phenylphosphonate. For example, both $Zn(O_3PH)_{0.60}(O_3PC_6H_5)_{0.40}$ and $Zn(O_3PC_6H_5)$ were able to intercalate 2-aminoheptane (α-branched amine) by contacting the dehydrated layered compounds with neat 2-aminoheptane. However, $Zn(O_3PC_6H_5)$ intercalated a full mole of amine, whereas $Zn(O_3PH)_{0.60}(O_3PC_6H_5)_{0.40}$ only intercalated 0.6 mol of amine. Contacting the mixed derivative with pure liquid 2-methylbutylamine (β-branching) gave up to only 0.57 mol of intercalated amine. Contacting zinc phenylphosphonate with a dilute ethanolic liquid solution of 2-methylbutylamine also resulted in uptake of a full mole of amine. It was expected that the phosphite phenylphosphonate mixed derivatives would have more void space (Figure 2) in the interlayer region than in zinc phenylphosphonate and thus be more capable of accommodating branched chain amines. Since the mixed derivatives were able to intercalate a full mole of primary chain alkylamines the behavior toward branched chain amines appears to be a result of steric restrictions as opposed to electronic effects. Perhaps the replacement of phenylphosphonate tetrahedra with phosphite tetrahedra has resulted in a compression of the basal area associated with the zinc center, thereby restricting the intercalation of branched chain amines at metal centers closely associated with phenyl groups. There appears to be a direct correlation between the quantity of branched chain amine intercalated and the amount of phosphite groups incorporated into the metal–oxygen network of the mixed derivative. This in turn implies that intercalation of amines with branching in the α-position can approach only empty Zn coordination sites associated with phosphite groups.

The BET surface areas of the zinc mixed derivatives were lower than expected for microporous solids. Table 3 lists the surface areas determined for representative mixed derivative samples as well as the parent compound, $Zn(O_3PC_6H_5){\cdot}H_2O$. The analyses clearly reveal that the BET surface areas of the mixed derivatives are

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Table 3. BET Surface Area Data of Zinc Mixed Derivatives versus the Parent Zinc Phenylphosphonate

compound	5-point BET surface are (m^2/g)	langmuir SA (m^2/g)	*C*	total pore vol (cm^3/g)	micropore vol (cm^3/g)
$Zn(O_3PC_6H_5)\cdot H_2O$	9.7		82.1		
$Zn(PH)_{0.43}(P\phi)_{0.57}\cdot 0.95H_2O$	46.3	686	107.7	0.292	0.0223
$Zn(PH)_{0.44}(P\phi)_{0.56}\cdot 1H_2O$	29.1	343	63.3	0.304	0.0165
$Zn(PH)_{0.50}(P\phi)_{0.50}\cdot 0.92H_2O$	28.4	454	85.4	0.157	0.0163
$Zn(PH)_{0.60}(P\phi)_{0.40}\cdot 1.1H_2O$	39.1	788	84.3	0.279	0.0176

only slightly larger than their parent compounds. Furthermore, the isotherms were all type II isotherms[40] frequently encountered for nonporous powders. The small increase in surface area is likely attributable to a decrease in particle size since few micropores have been introduced as indicated by the isotherms and the measured micropore volumes. Although the phenyl groups appear to be good candidates for holding the layers apart at 14 Å, the phenyl mixed derivatives consistently give mesoporous products. However, the data in Table 3 shows that a small amount of microporosity exists. Whenever a phenyl ring is opposite a phosphite group, the free space between them is about 4.1 Å. Only where phosphite groups are opposite each other in the layers would there be enough room for a monolayer of N_2 on all the surfaces. Therefore, the BET method underestimates the surface area. However, because an outer surface containing a high level of pockets created by a random distribution of phenyl and phosphite groups would be expected to have many strongly sorbed layers of N_2, the Langmuir method greatly overestimates the surface area. The true surface area must lie somewhere in between. However, the presence of a small amount of micropore volume would favor the notion that pores of the type shown in Figure 2 are present but that access to many of the pores in the interior is blocked.

Both phosphite and phenylphosphonate ligands have been shown to adopt a variety of different bonding modes. For example there are two major types of phosphite groups in the layered compound, $Co(HPO_3)\cdot H_2O$.[41] One type of phosphite group has oxygen atoms that are all three coordinate and link metal centers together. The other phosphite group has two oxygens that are three coordinate with the third not involved in bridging to a metal center. The octahedral Zn atoms in $Zn(O_3PC_6H_5)\cdot H_2O$ are linked together with a combination of two-coordinate and three-coordinate phosphonate oxygen atoms.[30] Furthermore, any unsaturated metal centers will satisfy their octahedral coordination sphere by binding water molecules at the empty coordination site. Since the phosphite and phenylphosphonate oxygen atoms have been shown to adopt three-coordinate, two-coordinate, and even one-coordinate bonding modes, both phosphite and phenylphosphonate tetrahedra are capable of coexisting indiscriminately in relation to one another throughout the metal–oxygen network that makes up the layer. The proven flexibility of the phosphonate and phosphite oxygen atoms to adopt a variety of different bonding modes coupled with the ability of the zinc center to satisfy its coordination sphere with water molecules whenever necessary has been exploited to synthesize zinc phosphite phenylphosphonate mixed derivatives.

Synthetically, the ability to make single phase mixed derivatives of general formula, $Zn(O_3PH)_{1-x}(HO_3PC_6H_5)_x\cdot yH_2O$, relied heavily on being able to control the reaction rate of the two acids so that the probability of forming a mixed derivative was optimized. The relatively consistent interlayer distance strongly implies that the mixed derivatives form a continuous series in which the general structure remains the same with only the percentage of phosphite incorporated into the compound being varied. The ability to synthesize mixed derivatives as part of a continuous series appears to be dependent on the initial reaction rate. Instantaneous reaction of the starting materials favored the formation of an initial kinetic product in which there is a random dispersion of phosphite and phenylphosphonate groups throughout the layer. Once the initial zinc phosphite phenylphosphonate compound is formed, the crystallinity was improved by refluxing in water. Investigations are underway to improve the formation of well-defined pores by synthesizing mixed derivatives in which the "pillarlike" group is a bisphosphonic acid that actually anchors the layers together. Dispersing these types of ligands with smaller groups may yield products with high surface areas such as those reported for $Zr(O_3POH)_{0.764}(O_3PC_6H_4C_6H_4PO_3)_{0.618}\cdot 1.59H_2O$.[27]

Acknowledgment. This work was supported by the Robert A. Welch Foundation under Grant No. A-673 for which grateful acknowledgment is made.

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