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Synthesis and Stability of Mixed Ligand Zirconium Phosphonate Layered Compounds

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The synthesis of layered phosphonates of zirconium was carried out using ligands which were combinations of phenylphosphonic acid and either phosphoric or phosphorus acid. At high ratios of phosphate to phenylphosphonic acid in the presence of HF a staged or interstratified product was obtained in which layers of pure phosphate alternated with those of phenyl pendant groups. At lower ratios of phosphate to phosphonate both ligands are randomly dispersed on the layers with compositions $Zr(O_3PC_6H_5)_x(HPO_4)_{2-x}$, where $x = 0.7–1$. When the second ligand was phosphite, a greater variety of products were obtained. In the case where both ligands were randomly dispersed on the layers, the interlayer distances ranged from 15.5 Å (almost all phenylphosphonate) to 10.4 Å (mostly phosphite). This latter spacing arises from each phenyl group in one layer lying opposite a phosphite group in the adjacent layers. Interstratified phosphonate phosphites were also obtained. The behavior of these mixed derivatives on sulfonation under fuming sulfuric acid is also described.

INTRODUCTION

Electron-transfer (ET) reactions are key steps in a variety of chemical, physical, and biological processes (1–5). Probably the most impressive example of an ET process occurs in photosynthesis, where nature solved the problem of converting solar energy into chemical energy by using photoinduced ET to efficiently separate charge. Studies of natural and model systems have shown that a fundamental step necessary for artificial photosynthesis is charge separation via vectorial electron transport in a compartmentalized system (1–6). Such compartmentalization allows electron transfer across phase boundaries while suppressing energy-releasing back reactions.

One of the goals of materials chemists is to mimic nature by creating similar compartmentalized or otherwise organized structures to effect reactions under mild conditions. Our research has been concerned with manipulation of layered compounds to produce organized structures such as interlayered or staged compounds and structures containing more than one functional group. Our concern here is whether the organized assemblies so produced can be considered stable or metastable. Such considerations are important because the systems are required to carry out their functions when cycled over many iterations of the process.

Our work has involved the use of layered zirconium phosphate and derivatized organic phosphonates. Layered compounds such as clay (7–9) and zirconium phosphate (10) have been used to encapsulate photoactive molecules and the latter compounds have been found to be greatly affected by the microenvironment of the layered compound. Therefore in our initial study (11a) $Ru(bpy)_3^{2+}$ (bpy, 2,2′-bipyridine) was encapsulated between the layers of zirconium phosphate sulfophenylphosphonate (ZrPS) of approximate composition $Zr(O_3PC_6H_4SO_3H)(HPO_4)$ and used as a probe of the chemical microenvironment. In this case, the observed spectral shifts were found to result from interactions of the probe molecule with the phenyl rings of the host. Subsequently, both $Ru(bpy)_3^{2+}$ and methylviologen were incorporated within the ZrPS layers and the photoinduced electron transfer reaction was examined (11b). The microenvironment within ZrPS was found to restrict the movement of ions through the interlayer space, probably because of the high concentration of sulfophenyl groups in the interlayer space. However, diffusion leading to dynamic quenching reactions did occur and these were accounted for by a model combining diffusional quenching and sphere of action quenching of $Ru(bpy)_3^{2+}$ by the methylviologen.

Since those initial studies we have attempted to synthesize new derivatives of ZrPS in which the distance between the phenyl rings is systematically increased. This larger space should increase the mobility of the ions between the ZrPS layers. In addition, we are attempting to produce staged layered compounds in such a way that the electron donor would reside in one layer and the acceptor in an adjacent layer. The present report focuses

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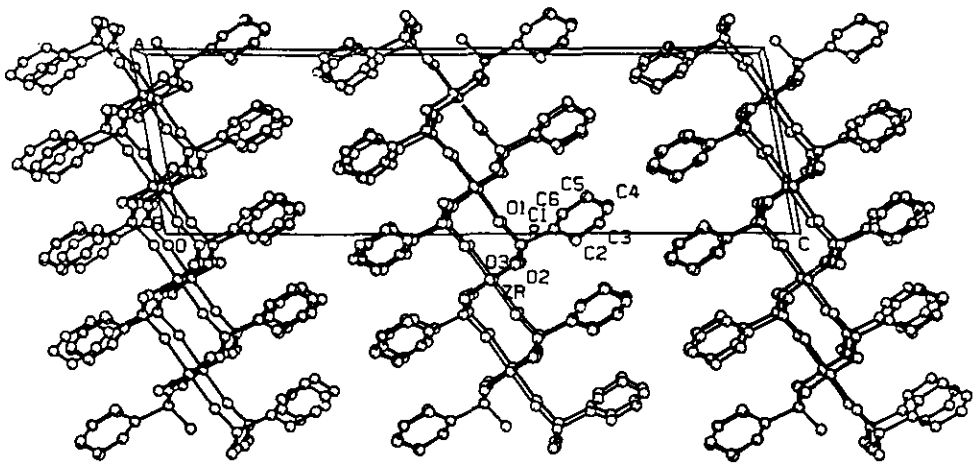

FIG. 1. Projection of the structure of zirconium phenylphosphonate viewed down the *b*-axis. The overlapping phenyl rings along the projection axis are separated by the *b*-distance (5.42 Å) (from Ref. (14)).

on results for some staged compounds and otherwise organized layers and their intercalation chemistry. These results build on earlier studies in which two different functional groups were incorporated into the zirconium phosphate layers (12).

The first types of compounds to be discussed are based on zirconium phenylphosphonate. The compound was first prepared by Alberti *et al.* (13). The structure of the phenylphosphonate (ZrPP) was solved (14) from X-ray powder data and a schematic drawing of the structure is shown in Fig. 1. The layers of ZrPP are very similar to those of α-zirconium phosphate (α-ZrP), $Zr(HPO_4)_2 \cdot H_2O$ (15a, 15b). The essential difference in the two compounds is that in α-ZrP the symmetry ($P2_1/c$) allows the Zr atoms to alternate slightly above and below the mean planes of the layers. This has the effect of placing the P–OH groups very nearly perpendicular to the plane of the layers. In ZrPP the symmetry (C^2/c) requires the metal atoms to lie directly in the plane, which in turn tilts the phosphonate groups about 30° from the perpendicular.

Two types of mixed derivatives will be described: those in which the phenyl groups are functionalized by sulfonation and those in which two different ligands occur in the same compound. Using the slow decomposition of $[ZrF_6]^{2-}$ in the presence of a mixture of two phosphonic acids, Alberti *et al.* (16) prepared zirconium phosphonates containing both organic groups in the same compound. Three types of derivatives were obtained: (1) $Zr(O_3PR)_{2-x}(O_3POH)_x$ with $1 \leq x \leq 1.3$; (ii) $Zr(O_3PR)_{2-x}(O_3PR')_x$ with $x = 1.25$; (iii) $Zr(O_3PR)_{2-x}(O_3PH)_x$ with $0.8 \leq x \leq 1$. When R was phenyl in case (i), a compound with $x = 1.15$ was obtained. Its interlayer spacing as observed by X-ray diffraction was 24.9 Å. This interlayer spacing indicates an interstratified structure in which one layer contains only phosphate groups with some phenyl groups randomly dispersed on the layers and the other layer is mainly composed of phenyl pendant groups with some replacement by phosphate groups (Fig. 2). In the case of $Zr(O_3POH)(O_3PH)$, zirconium phosphate–phosphite, it was shown from X-ray powder data that the compound is also interstratified, with alternating phosphate and phosphite layers (17).

We note that in the three types of mixed ligand compounds described by Alberti *et al.* (16) that the composition ranges are close to a ratio of 1:1 for the two ligands. In fact, solid solutions were also obtained in which one ligand predominated and small amounts ($x = \sim 0.1$) of the other ligand were randomly dispersed on the layers. However, when the ratio is close to 1:2 a model was suggested in which one of the ligands predominated in one layer and the other ligand predominated in an adjacent layer (Fig. 2).

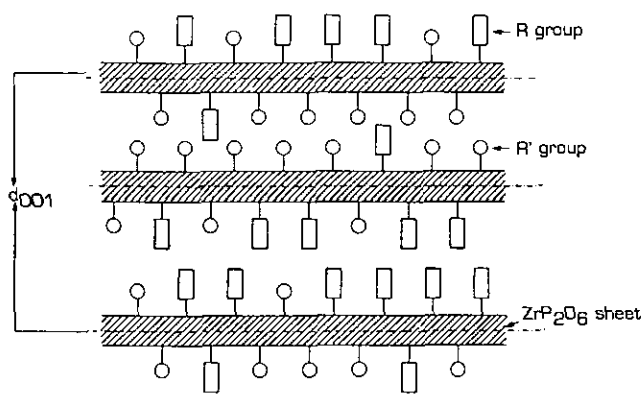

FIG. 2. Suggested arrangement of RPO_3 and $R'PO_3$ groups in a mixed organic derivative of α-zirconium phosphate (from Ref. (16), with permission).

Dines *et al.* (18, 19) claimed to have produced a broader range of derivatives by exerting kinetic control. This control was mainly obtained by avoiding long gestation times in HF. Hydrofluoric acid forms a complex ion, ZrF_6^{2-}, which prevents the zirconium from reacting with the added phosphorus-containing ligands. However, at elevated temperatures the equilibrium

$$ZrF_6^{2-} \rightleftharpoons Zr^{4+} + 6F^-$$

comes into play, allowing slow precipitation of the mixed ligand product. This procedure leads to the interstratified derivatives (12, 16). However, rapid precipitation in the absence of HF yields mainly amorphous products with a broader distribution of the two ligands in the same layer. We set forth our findings in terms of their relationship to the chemical stability of these complexes in the study described herein.

EXPERIMENTAL

Preparation of zirconium phenylphosphonate phosphates. Two types of reactions were run in the presence of HF: one leading to the mixed derivative 14.8 Å phase and the other leading to staged compounds. A mixture of phosphorus acids was prepared by dissolving 2.16 g (13.7 mmole) of phenylphosphonic acid in 20 ml of distilled deionized water (DDI) and adding 9.4 ml of concentrated H_3PO_4 (136.6 mmole). In a plastic beaker 5.42 g (16.8 mmole) of $ZrOCl_2 \cdot 8H_2O$ was dissolved in 20 ml of DDI water. To this solution was added 13.4 ml of concentrated HF (382 mmole). This represents a F : Zr ratio of 22. The phosphorus acid solution was added to the Zr(IV) solution dropwise with stirring and rinsed with 20 ml of DDI water. The whole was then placed into an oil bath and kept at 70°C for 24 hr. During this time the volume was reduced to less than half of the original volume and a white precipitate formed. This solid was collected by filtration but during washing some peptidization occurred with loss of solid through the filter. The recovered yield of solid was 2.32 g (Exp. 13A). The filtrate and colloidal dispersion of solid were combined and reheated for 24 hr to yield 3.04 g of solid (Exp. 13B). This latter solid was found by X-ray diffraction to be mainly α-zirconium phosphate together with small amounts of the 14.8-Å phase and the staged compound with a 23.3-Å basal spacing. The initial precipitate was the 14.8-Å phase, as shown by the X-ray powder pattern of Fig. 3A.

Preparation of staged zirconium phenylphosphonate phosphate. The general procedure was the same as given in the previous preparation but the amount of phosphoric acid added was increased. In the description below the ratio of H_3PO_4 to $C_6H_5PO_3H_2$ was 90 : 1. A ZrF_6^{2-} solution was prepared by first dissolving 5.43 g

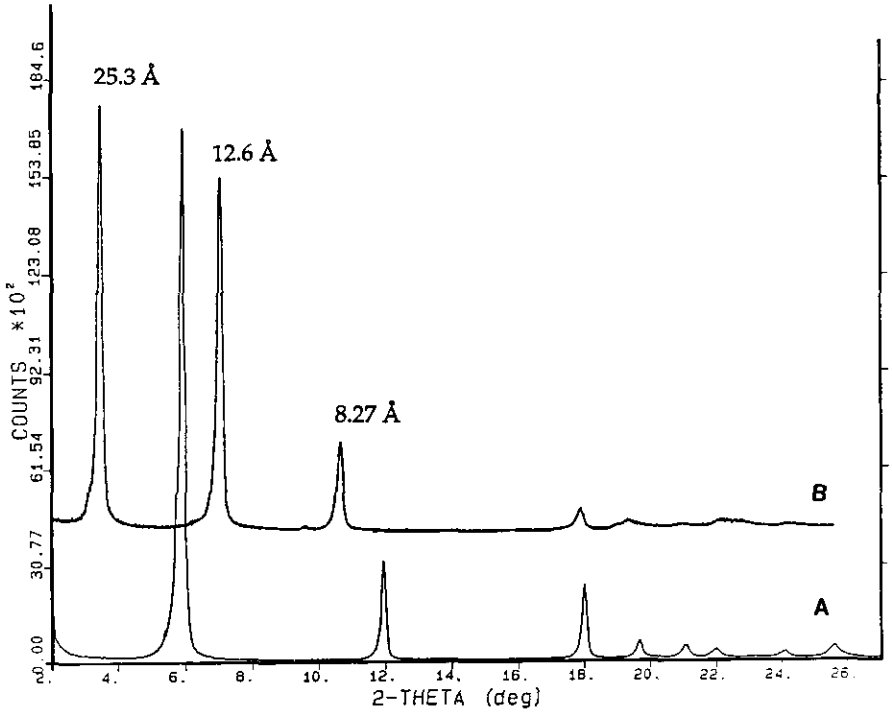

FIG. 3. X-ray diffraction pattern of (A) the 14.8-Å phase $Zr(O_3PC_6H_5)_x(HPO_4)_{2-x}$ where $x > 1$ and (B) the fully hydrated crystalline staged compound ($d_{001} \cong 25.3$ Å).

TABLE 1
Composition and Type of Zirconium Phenylphosphonate Phosphate Formed in HF Media

Exp. No.	Reactant $ZrOCl_2 \cdot 8H_2O$ (mmole)	Composition[a] Ratio $\frac{C_6H_5PO_3H_2}{Zr}$	Ratio $\frac{H_3PO_4}{\phi PO_3H_2}$	Product formula	d-spacing (Å)
YT-IV-98A	8.36	0.82	98.6	$Zr(C_6H_5PO_3)_{0.71}(HPO_4)_{1.29} \cdot 0.95H_2O$	25.2
JDW-II-69	4.16	0.82	98.6	$Zr(C_6H_5PO_3)_{0.77}(HPO_4)_{1.23} \cdot 1.2H_2O$	25.5
JDW-II-70A	4.16	0.82	98.6	$Zr(C_6H_5PO_3)_{0.8}(HPO_4)_{1.2} \cdot 0.5H_2O$	22.7
JDW-II-70B	4.26	0.83	98.6	$Zr(C_6H_5PO_3)_{0.91}(HPO_4)_{1.19} \cdot H_2O$[b]	25.0
YT-V-08	4.20	1.62	49.3	$Zr(C_6H_5PO_3)_{0.95}(HPO_4)_{1.05} \cdot 0.4H_2O$	22.5
YT-V-10	8.36	0.82	10.1		14.8
YT-V-11	8.36	0.82	20.	$Zr(C_6H_5PO_3)_{1.38}(HPO_4)_{0.62} \cdot 0.5H_2O$	14.8
YT-V-12	8.36	0.82	32.5		22.5 + 14.8
YT-V-13A	8.36	0.82	10.1	$Zr(C_6H_5PO_3)_{1.4}(HPO_4)_{0.6} \cdot 0.3H_2O$	14.8
YT-V-14	8.36	0.82	20.0		14.8
YT-V-15	8.36	0.82	40	$Zr(C_6H_5PO_3)_{1.36}(HPO_4)_{0.64} \cdot 0.6H_2O$	25 + 14.8
YT-V-16A	8.36	0.82	50		14.8
YT-V-16B[c]					
YT-V-17	8.36	0.82	99		25
YT-V-18	33.5	1.0	80.5		24.3

[a] HF/Zr = 23.
[b] By elemental analysis.
[c] 16B represents a second crop of crystals obtained by evaporating the filtrate from 16A to a smaller volume.

(16.8 mmole) of zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$, in 30 ml of distilled water in a plastic beaker and then adding 12.4 ml of 48% hydrofluoric acid. A second solution was prepared by dissolving 2.16 g (13.7 mmole) of phenylphosphonic acid, $C_6H_5PO_3H_2$, in 45 ml of water and adding 84.6 ml of concentrated H_3PO_4 (1.24 mole). The zirconyl fluoride solution was then added slowly at room temperature to the phosphorus-containing solution and then the container was rinsed with 28 ml of water, which was added to the mix. The combined volume was then approximately 200 ml. This mixture was heated in an oil bath at 60–70°C for several days to gradually reduce the volume, whereupon a precipitate began to form. The reaction was stopped after 24 hr of additional heating. The yield was 3.6 g, or 60% based upon recovered zirconium (Exp. 26). Additional reactions are summarized in Table 1.

Hydrothermal preparation of the staged zirconium phenylphosphonate phosphate. In order to improve the yield and reduce the amount of H_3PO_4 required, we turned to the use of hydrothermal reactions. In a typical run the staged compound was prepared in a Teflon-lined high-pressure reaction vessel at temperatures of 150 to 200°C. A mixture of 6.2 mmole of $ZrOCl_2 \cdot 8H_2O$ was dissolved in 20 ml of water and added dropwise to a solution of 0.98 g of $C_6H_5PO_3H_2$ (6.2 mmole) and 4.2 ml of concentrated H_3PO_4 (62 mmole). The white precipitate which formed was stirred for 1 hr and then rotovapped to dryness at 50°C. The product gave the X-ray pattern shown in Fig. 3B. The reflections match those for the staged compound with a 25-Å interlayer spacing. The solid was transferred to a Teflon-lined pressure vessel and covered with 15 ml of water containing 1 ml of concentrated H_3PO_4. The mixture was sonicated for $\frac{1}{2}$ hr and then kept at 150°C for 24 hr. The X-ray diffraction pattern of the product showed that the solid was only slightly better crystallized but remained in the staged condition.

Synthesis of zirconium phenylphosphonate phosphite in the presence of HF. $ZrOCl_2 \cdot 8H_2O$ (2.76 g) (8.54 mmoles) was dissolved in 20 ml of water and added to 6.4 ml of concentrated HF held in a polyethylene beaker. In a separate beaker 2.34 g (14.8 mmole) of phenylphosphonic acid was dissolved in 100 ml of water and 48 g (585 mmole) of phosphorous acid was added. This mixed acid solution was then added to the zirconyl chloride solution and the beaker rinsed with 40 ml of water. This rinse was also added to the reaction mixture in the polyethylene container and the whole was diluted to 200 ml. The beaker was then placed in an oil bath and kept at 60–70°C for 7 days. This procedure reduced the volume by half and yielded 1.54 g of product or 55%, based on the formula $Zr(O_3PC_6H_5)(HPO_3)$. This preparation is essentially that described by Alberti *et al.* (16) in which P/Zr = 70, the mole fraction $C_6H_5PO_3H_2$/total P = 0.024, F/Zr ≅ 20, and the total phosphorus concentration is 3 *M*.

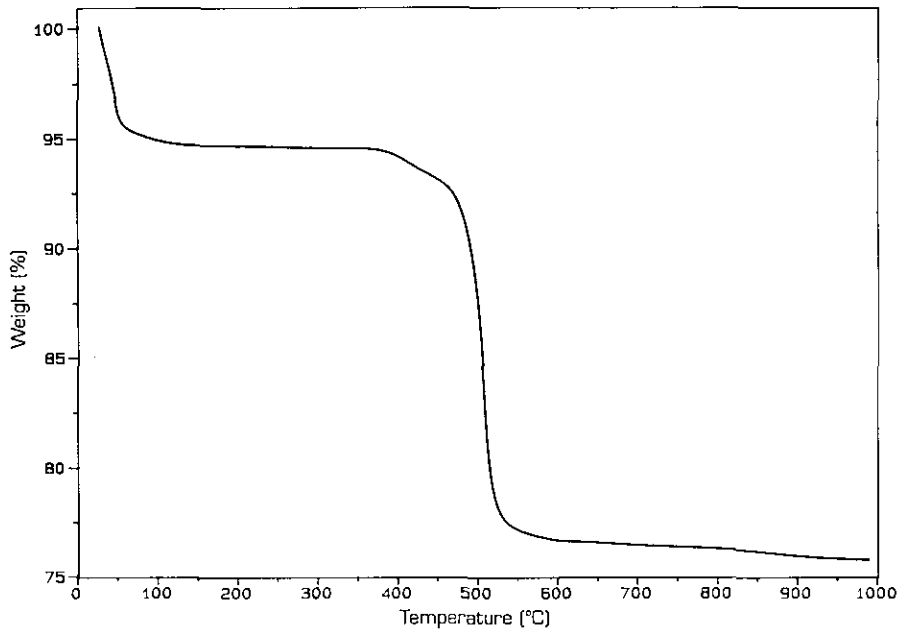

FIG. 4. Thermogravimetric analysis curve for the crystalline staged compound, $Zr(C_6H_5PO_3)_{0.81}(HPO_4)_{1.19} \cdot H_2O$.

Several variants of this procedure were tried, of which only one is described. Four grams (12.4 mmole) of zirconyl chloride was dissolved in 20 ml of water and 9 ml of concentrated HF added in a polyethylene beaker. A second solution was prepared containing 1.06 g (6.7 mmole) of phenylphosphonic acid and 26.8 g (32.7 mmole) H_3PO_3 in 50 ml of water. The zirconyl chloride hydrofluoric acid solution was added to the mixed acid solution and the beaker rinsed with 14 ml of water and combined with the reactant solution. The beaker was held in an oil bath kept at 60–70°C until 24 hr after the first appearance of solid. Yield, 2.6 g, 65%.

Zirconium phenylphosphonatephosphites prepared without addition of HF: atmospheric pressure reactions. One gram (6.33 mmole) of phenylphosphonic acid and 1.04 g (12.7 mmole) of phosphorous acid were dissolved in 20 ml of water. To this solution was added 2.04 g of $ZrOCl_2 \cdot 8H_2O$ dissolved in 5 ml of water. The mixture was then heated at 90°C or under reflux for 1–2 days and the solid was recovered, washed with water, and air dried. Several variations in mole ratios of the reactants were tried and the results are presented in Table 2.

Hydrothermal reactions. These reactions were typically carried out in a Teflon-lined high-pressure reaction vessel placed in a constant-temperature furnace. After addition of the zirconyl chloride to the mixed acid solution, the mixture was evaporated to dryness with a rotary evaporator. The solid was then transferred to the Teflon-lined steel bomb of 40 ml capacity and covered with 7–12 ml of water. The contents were heated in the sealed bomb at temperatures of 100 to 200°C for 1 to 7 days. After that the solid was recovered by filtration, washed, and dried in air. The results of all the phosphite phenylphosphonate reactions are summarized in Table 2.

Sulfonation of the mixed layered derivatives. Sulfonation of the phenyl rings was carried out by use of fuming sulfuric acid (20). In a typical example, 2 g of zirconium phenylphosphonate phosphite was added to 12 ml of fuming sulfuric acid and kept at 60°C with stirring for 15 min. An apparently homogenized solution was obtained. The excess SO_3 was then expelled at 75°C and the mixture cooled in an ice bath. Water was slowly added until precipitation occurred. The solid was then centrifuged off, washed until free of sulfate ion, and air dried. Found: C, 15.3%; H, 2.28%; S, 9%; LOI, ≈35%. Calculated for $Zr(O_3PC_6H_4SO_3H)_{0.9}(HPO_4)_{1.1} \cdot H_2O$: C, 15.2%; H, 1.78%; S, 6.78%; LOI, 37.6%. Apparently the phosphite group had been oxidized to phosphate during the sulfonation reaction.

Instrumental procedures and other experimental details have been presented previously (12).

RESULTS

Zirconium phenylphosphonate phosphates. In carrying out the reactions in HF two main products were obtained, either the staged derivatives with basal spacings

between 22.5 and 25.4 Å, depending on the water content, or the phase with interlayer spacing of 14.8 Å. Which product is obtained depends mainly upon the amount of phosphoric acid used as provided in Table 1. When the ratio $H_3PO_4 : C_6H_5PO_3H$ is less than 20 and the $Zr/C_6H_5PO_3H$ is close to 1, the precipitate was the pure 14.8-Å phase. When this ratio was greater than 70, the initial product was staged. X-ray patterns for the two types are given in Fig. 3. Analysis of the products was carried out by means of thermogravimetric weight loss under an oxygen atmosphere. A typical curve is shown in Fig. 4. The end product of the thermal reaction is ZrP_2O_7 (Formula Weight = 266.2). The initial weight loss is due to interlayer water and the major weight loss at higher temperature converts the complex to the pyrophosphate

$$Zr(C_6H_5PO_3)_x(HPO_4)_{2-x} \xrightarrow{O_2} ZrP_2O_7 + 6xCO_2 + (4x + 2)H_2O.$$

To calculate the composition we use

$$\frac{[92.2^2 + 158x + 96(2 - x) - 266.2] \times 100}{\text{Formula Weight of Complex}} = \% \text{ weight loss above 400°C.} \quad [1]$$

Analysis of this TGA curve yields a composition of $Zr(C_6H_5PO_3)_{0.81}(HPO_4)_{1.19} \cdot H_2O$. In the previous study (12) elemental analysis for the sample whose X-ray pattern is given in Fig. 3B yielded the formula $Zr(C_6H_5PO_3)_{0.8}(HPO_4)_{1.2} \cdot 0.5H_2O$. A sample prepared with the highest ratio of phosphoric acid to phenylphosphonic acid (98.6) gave a product with 0.71 phosphonate (YT-IV-98). Likewise a sample prepared at the low range of phosphoric acid (ratio of 49.3) gave a composition with almost equal moles of each ligand; $Zr(C_6H_5PO_3)_{0.95}(HPO_4)_{1.05} \cdot 0.4H_2O$. The fact that the amount of HPO_4^{2-} always exceeded one indicates that the phosphate layer is always 100% phosphate but the phosphonate layer may contain up to 30% phosphate. An idealized depiction of the staged product with equal amounts of phosphate and phosphonate is shown in Fig. 5.

Intercalation of butylamine into the phosphate layer increased the interlayer spacing to 34.7 Å, which is somewhat larger than expected (18.6 Å for $Zr(HPO_4)_2(C_4H_9NH_2)_2$ (15) + 14.8 Å for ZrPP). This increase is due mainly to the uptake of excess water in the amine layer. Butylamine forms a bilayer in the phosphate layer only, increasing that basal spacing to 18.6 Å (21), with some additional expansion from water uptake (Fig. 6A). By the same token, only half a mole of ethylenediamine should be taken up with formation of a monolayer and an increase in the basal spacing of 3.5 Å. In the actual result only ¼ of a mole of ethylenediamine was taken up by the staged product and the increase amounted to 2.9 Å. However, it has been shown (21) that ethylenediamine also forms an intermediate phase when intercalated into α-ZrP with a 10.4-Å basal spacing. Hence the observed 2.9-Å overall increase in interlayer spacing is reasonable and indicative of the formation of a tilted monolayer in the phosphate layer. The solid state ^{31}P MAS NMR of the interstratified compound shows that there are two major resonances present: one at −5.3 ppm and the other at −20.2 ppm (12). A spectrum for pure zirconium phenylphosphonate exhibited a single resonance peak at −5.3 ppm and Clayden (22) has shown that $Zr(HPO_4)_2 \cdot H_2O$ yields a single resonance at −18.7 ppm. Thus the spectrum reveals that the two phosphorus-containing groups retain almost the same environment in the interstratified compound as they possessed in their pure zirconium salts. An NMR spectrum of the butylamine intercalate was consistent with the proposed structure that the amine was intercalated into the phosphate layer. Again two peaks were observed: one at −18.7 ppm and the other at −5.3 ppm. Thus, the phosphonate phosphorus peak had remained unchanged both in position and shape whereas the ^{31}P phosphate peak was shifted downfield from −20.3 to −18.7 ppm and broadened. Amine intercalation in α-ZrP has been shown to shift the ^{31}P resonance downfield (23).

The range of H_3PO_4 used, in terms of the ratio $H_3PO_4 : C_6H_5PO_3H_2$ to obtain the pure staged product, was 70–120. Above a ratio of 120, some α-ZrP appears in the first crop of crystals. We have seen that ratios

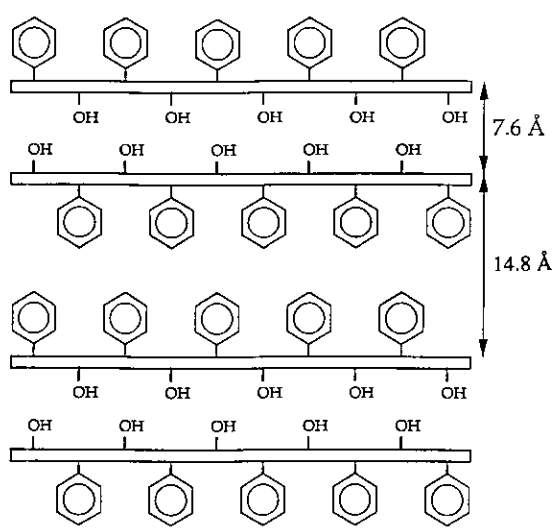

FIG. 5. Idealized depiction of staged zirconium phenylphosphonate phosphate.

[2] Takes into account the presence of 2% Hf in zirconium compounds.

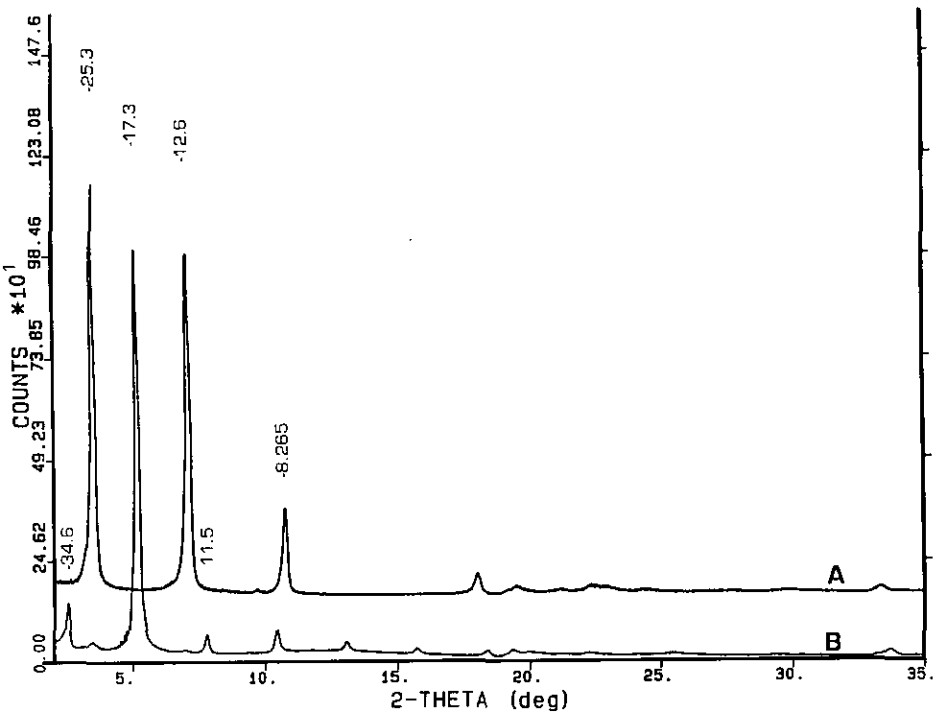

FIG. 6. (A) X-ray diffraction pattern of staged zirconium phenylphosphonate phosphate as in Fig. 3 and (B) X-ray powder pattern of its butylamine intercalate.

between 10 and 20 yield the 14.8-Å phase and the results in Table 1 show that for this phase the ratio of phenyl to phosphate is greater than one. Thus, it is essentially zirconium phenylphosphonate with phosphate groups randomly dispersed on the layers. In the 30–60 composition region both the 14.8 Å and staged products are obtained as mixtures. Caution should be applied to these limits. By changing other variables such as temperature, concentration, and amount of Zr relative to the acids, there may be a corresponding shift in the product mix.

The staged compound of composition close to $Zr(O_3PC_6H_5)(HPO_4)$ was clearly the compound we sought for our photochemical studies. By sulfonating the phenyl rings it was felt that sufficient swelling of the sulfonic acid layers would take place so that if $Ru(bipy)_3^{2+}$ was fixed in the sulfonate layers, the amine would then go into the phosphate layers. The sulfonation was carried out under 30% fuming H_2SO_4. Instead of obtaining the expected staged compound in sulfonated form, the product was identical to that obtained by sulfonation of the 14.8-Å phase (see below). Apparently the staged compound is not stable in the sulfuric acid medium and reverts to the more stable 14.8-Å phase, which then sulfonates in the usual way.

Hydrothermally prepared staged compound. The outcome of the hydrothermal reaction was a staged compound with an interlayer spacing of ~23 Å. In fact, three orders of (*00l*) reflections were present in the X-ray pattern. Upon treatment with butylamine the basal spacing increased to 35.3 Å and six orders of (*00l*) were present. Thus, in both the original staged compound and the amine-intercalated derivative the basal spacing was increased by about 1 Å over the product prepared in HF at 60–70°C. This difference was again traced to the water content of the staged product. The product with the larger basal spacing contained 1 mole of water while the one with the 22.3-Å spacing contained ½ mole of interlayer water. It could be shown by partially dehydrating the 24-Å phase that two solid phases are present, one with a 24-Å basal spacing and the other with a basal spacing of 22.3 Å. The hydrothermal method has the advantage of avoiding use of a large excess of H_3PO_4 and the use of HF. However, the crystallinity of the product is much lower.

Characterization of zirconium phenylphosphonate phosphite. In the first reaction containing phosphite, with HF added to complex the zirconium, the product gave an X-ray pattern revealing the presence of several phases. The most abundant phase (~60%) had a *d*-spacing of 25.5 Å (*00l*) and higher-order reflections out to the sixth order. In addition, the second most abundant phase (~25%) had a basal spacing of 10.3 Å with higher orders (*002*) and (*003*). The third phase exhibited an interlayer

spacing of 14.7 Å and is arguably of the type $Zr(C_6H_5PO_3)_{2-x}(HPO_3)_x$, where x is 0.1 or less. It will be shown that the 10.3-Å phase has an approximate composition approaching $Zr(C_6H_5PO_3)_{0.5}(HPO_3)_{1.5}$ and may be thought of as having a structure with both phenyl groups and phosphite groups in the same layer. Because of the high proportion of phosphite groups, the probability is great that each phenyl group in a layer lies opposite a phosphite group and therefore the interlayer spacing is half the sum of the pure zirconium phosphite (5.6 Å) plus the zirconium phenylphosphonate (14.8 Å) interlayer distance.

According to Alberti *et al.* (16) the staged phosphite phenylphosphonates should have a basal spacing of 14.7 + 5.6 or 20.3 Å. They obtained a product with a value of 21.1 Å. The 25.5-Å phase that we obtained as a part of the mixture or in the pure state had a full mole of water present in the phosphite layer, which would increase the spacing by 2.5 Å. Once this mole of water was removed by slow dehydration, the layer distance decreased to ~21 Å and the compound did not rehydrate, owing to the hydrophobic nature of the interlayer groups. The presence of phenylphosphonate and phosphite groups were reconfirmed by ^{31}P NMR.

In a second experiment, all the conditions were kept the same except the ratio F/Zr was now 30. This increased the time required for precipitation to 21 days and yielded as the major product zirconium phosphite (5.6-Å basal spacing), zirconium phenylphosphonate containing a small amount of phosphite (14.7-Å basal spacing), and a phase with an interlayer spacing of 30.4 Å. This latter spacing may be explained on the basis of more highly staged products. For example, two phosphite layers plus one phenylphosphonate layer in the anhydrous condition should yield a basal spacing of 25.9 Å, while three phosphite layers plus a phenylphosphonate layer would lead to an (*001*) reflection of 31.5 Å. Thus, approaching equilibrium very slowly as in this experiment yields mainly a pure phosphite phase together with more highly staged products.

In order to isolate single phases of the various products, a large number of variations in the preparative procedure were tried out. The conditions and results of some of these experiments are summarized in Tables 2 and 3. The reactions can be classified into two types: thermal and hydrothermal. The thermal reactions were carried out at ambient pressure at 90°C or under reflux. The hydrothermal reactions were carried out in Teflon-lined steel bombs at temperatures ranging from 100 to 200°C.

Thermal reactions. As soon as the zirconyl chloride was added to the mixture of phosphorous and phenylphosphonic acids, a white precipitate formed and remained suspended in the water. An X-ray pattern of the solid separated at this stage showed it to be poorly crystalline but with a broad peak at ~15 Å representing the interlayer spacing. This solid is apparently a mixed phosphite phosphonate derivative with sufficient phenyl groups in the interlamellar space to require the larger d-spacing in which phenyl groups in adjacent layers are separated by slightly greater than the van der Waals distance. The increased (over 14.8 Å) layer spacing must arise from the disorder of the poorly crystalline product. When this solid was heated in its mother liquor at 90–100°C (thermal reaction), the kind of product obtained depends upon the ratio of phosphite to phosphonate in the reactant mix. This ratio in turn determines the relative amounts of these ligands incorporated. Thus, when the phosphorous to phenylphosphonic acid ratio was 1 : 1, the product had an ~15-Å interlayer spacing (Fig. 7A). Analysis of one of the products (YT-IV-56A) gave 20.36% C, 2.62% H, and a total weight loss of 29.9% with 12.6% being water. This yields an empirical formula of $Zr(C_6H_5PO_3)_{1.03}$

TABLE 2
Zirconium Phenylphosphonate Phosphites Prepared at Ambient Pressure and 90–100°C

Exp. No.	Reactants: Zr (mmole)	Reactants: $\frac{\phi PO_3H_2}{Zr}$	Reactants: $\frac{H_3PO_3}{\phi PO_3H_2}$	Time (days)	d-Space (Å)	Formula
JD-II-47A	15.5	1.02	2.89	2	11.8	$Zr(C_6H_5PO_3)(HPO_3)\cdot 0.2H_2O$
JD-II-48	6.3	1	1	1	11.0	$Zr(C_6H_5PO_3)_{0.99}(HPO_3)_{1.01}\cdot 0.22H_2O$
JD-II-49	6.3	1	1	1	15.1	$Zr(C_6H_5PO_3)_{1.01}(HPO_3)_{0.99}\cdot 0.96H_2O$
JD-II-50	6.3	1	6	2	10.8	$Zr(C_6H_5PO_3)_{0.97}(HPO_3)_{1.03}\cdot 0.25H_2O$
YT-IV-56A	6.3	1	1	2	15.2	$Zr(C_6H_5PO_3)_{1.04}(HPO_3)_{0.96}\cdot 2.7H_2O$
YT-IV-57A	6.3	1	2	2	11.8	$Zr(C_6H_5PO_3)_{1.01}(HPO_3)_{0.99}\cdot 5.4H_2O$
YT-IV-81	6.3	1	4.8	1	10.8	
YT-IV-83	6.3	1	9.6	1	10.6	$Zr(C_6H_5PO_3)_{0.83}(HPO_3)_{1.17}\cdot 0.1H_2O$
YT-IV-85	6.3	1	14.4	1		
YT-IV-86	15.5	0.5	9.7		10.8	

TABLE 3
Hydrothermally Synthesized Zirconium Phenylphosphonate Phosphites

Exp. No.	Reactants: Zr (mmole)	Reactants: $\frac{\phi PO_3H_2}{Zr}$	Reactants: $\frac{H_3PO_3}{\phi PO_3H_2}$	Time (days)	Temp (°C)	d-Spacing (Å)	Formula
JD-II-39A	3.9	1	3.17	7	150	21.3 + 15.1	$Zr(C_6H_5PO_3)_{1.1}(HPO_3)_{0.9}\cdot 0.1H_2O$
JD-II-41	7.74	1	3.17	7	200	24.5 15.5 (15%)	
JD-II-43A	15.5	1	3.2	1 h	25	14.5	
JD-II-43B	15.5	1	3.2	2 h	50	15.1	Nonhydrothermal
JD-II-43C	15.5	1	3.2	1	200	14.8	
JD-II-43D	15.5	1	3.2	2	200	~15.1	
JD-II-44A	15.5	1	3.2	3	200	24.7+ 15	
JD-II-44B	15.5	1	3.2	5	200	25.0+ 15	
JD-II-46A	15.5	1	3.2	1 h	25	22.5 14.4 10.7	As precipitated at 25°C
JD-II-46B	15.5	1	3.2	5	150	15.0	$Zr(C_6H_5PO_3)_{1.01}(HPO_3)_{0.99}\cdot 0.15H_2O$
JD-II-51A	6.3	1	3	2	100	15	
JD-II-51B	6.3	1	3	4	100	15.1+ 11	
YT-IV-89	6.3	1	4.8	5	200	25.6	
YT-IV-92	6.3	1	4.8	9	200	10.6	$Zr(C_6H_5PO_3)_{0.82}(HPO_3)_{1.18}$
YT-IV-93	6.3	1	9.5	4	200	30	

$(HPO_3)_{0.97}\cdot 2.6H_2O$, which is very close to the composition found from TGA (Table 2). The ^{31}P NMR (−5, −16 ppm) confirms the presence of both phosphorus-containing groups. Therefore, we may conclude that the product is a single phase in which the excess of phenyl groups over phosphite on the layers requires that the interlayer spacing be close to that of the zirconium phenylphosphonate. However, this positioning of the layers leaves void spaces filled by water.

Increasing the ratio $H_3PO_3 : C_6H_5PO_3H_2$ to 2 : 1 causes the interlayer spacing to decrease to 11.8 Å (Fig. 7B and sample YT-IV-57A, Table 2) and the analytical and TGA data indicate a formula of $Zr(C_6H_5PO_3)_{1.01}(HPO_3)_{0.99}\cdot 5.4H_2O$, which is supported by NMR and IR spectra. As the ratio of phosphorous acid to phenylphosphonic acid was increased, the interlayer spacing further decreased to 11 Å [$Zr(C_6H_5PO_3)(HPO_3)$ with no water of crystallization] and finally to a value of 10.6 Å. This last solid has a formula of $Zr(C_6H_5PO_3)_{.51}(HPO_3)_{1.49}$ (TGA weight loss 8.6%). In these solids with smaller interlayer spacings, each phenyl group must be opposite a phosphite group in an adjacent layer. The interlayer spacing should then be half the sum of the basal spacings of $Zr(O_3PC_6H_5)_2$ and $Zr(O_3PH)_2$ or 10.2 Å. The ^{31}P NMR shows the presence of two resonances at −4.85 ppm for the phenylphosphonate group and −16.3 ppm for the phosphite group (12). The different interlayer spacings reflect the composition of the product. In compounds containing both ligands in the same layer the phenyl groups must be able to arrange themselves opposite to phosphite groups in order to lower the interlayer spacing below 15 Å. However, when the ratio of phosphite to phenylphosphonate is 3, the probability is very high that each phenylphosphonate group is opposite a phosphite group so that a low basal spacing close to 10.2 Å is attained. The data in Table 2 show that with a ratio of phenylphosphonate to phosphite of 0.7 the interlayer spacing may reach a value as low as 10.6 Å.

Hydrothermal reactions. At low temperature (100°C) and for a 2–4 day reaction time, mixtures of the 15 and 11-Å phases were obtained (Table 3, 51A and B). Increasing the reaction time and temperature (150°C) yielded a mixed component solid (d = 15 Å), which by C, H analyses is $Zr(C_6H_5PO_3)_{1.08}(HPO_3)_{0.92}$ and by TGA is $Zr(C_6H_5PO_3)_{1.01}(HPO_3)_{0.99}\cdot 0.12H_2O$ (Table 3, 46B). The NMR spectrum for ^{31}P revealed resonances at −5 and −15 ppm, confirming the phosphonate phosphite nature of the compound. Further increase in temperature to 200°C produced a variety of products depending upon the time of reaction. Reaction times of 1–2 days yielded the ~15 Å phase, and a 7-day reaction yielded a mixture of the 25-Å phase and the ~15-Å phase. The ^{31}P NMR spectra of these solids

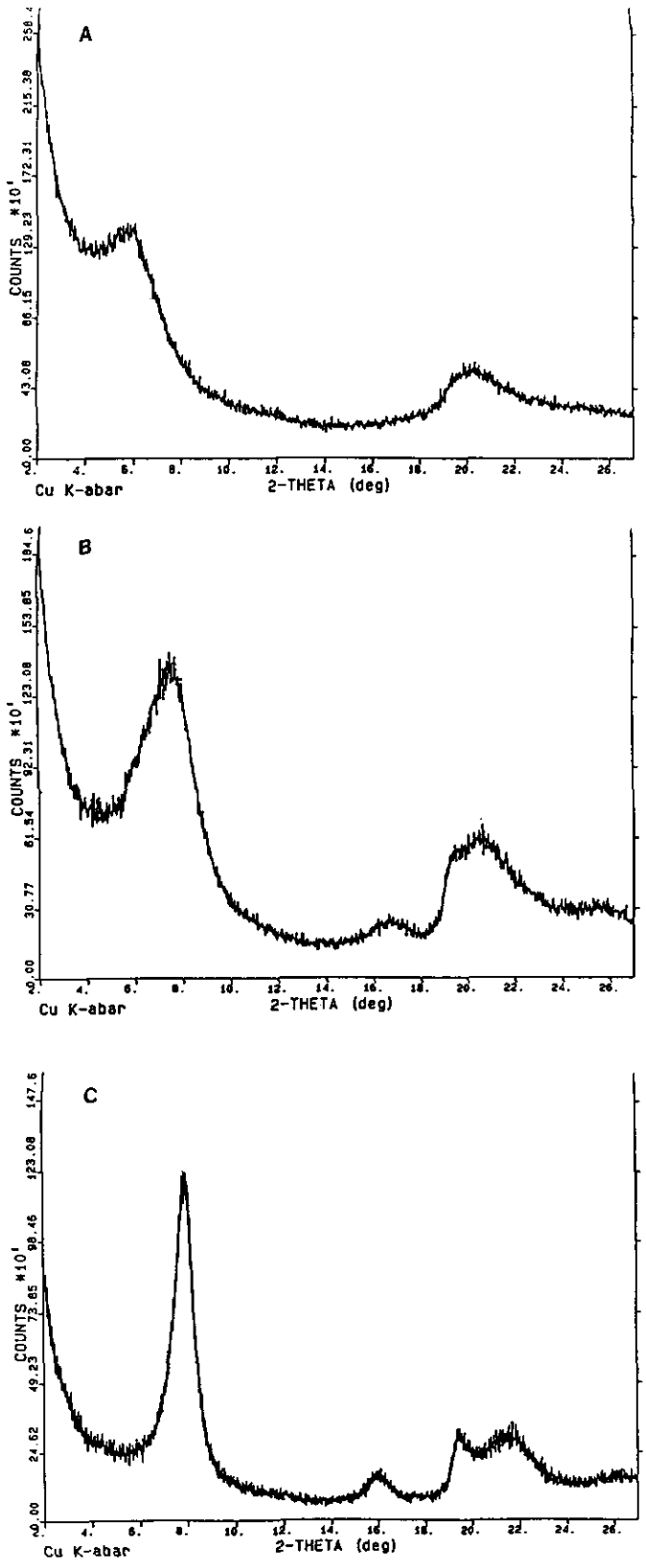

FIG. 7. X-ray diffraction patterns of zirconium phenylphosphonate phosphites: (A) the 15-Å phase formed at 90–100°C reflux; (B) a similar phase to (A) but having an excess of phosphite over phenylphosphonate; and (C) compound (B) heated in concentrated H_2SO_4 at 65°C.

showed the presence of approximately equal amounts of phenylphosphonate and phosphite groups, consistent with elemental analyses and IR characteristics. The IR spectrum showed a P–H phosphite stretch at 2471 cm^{-1} and no P–OH bands, indicating that oxidation of the phosphite groups did not occur.

From the above results we may conclude that when the ratio $H_2O_3PH/C_6H_5PO_3H_2$ is 3, the most stable phase is that having the basal spacing of 10.7 Å. It was also obtained as a single phase on refluxing (in the absence of HF) the mixture at 90–100°C (thermal reactions). It should be remembered that on first adding the acid mixture to zirconyl chloride, the first product was the nearly amorphous 15-Å phase. This phase transformed to the 10.7-Å phase on refluxing or by special hydrothermal reactions. In order to determine the stability of the several phosphite phases, they were treated with concentrated H_2SO_4 at several temperatures up to 100°C. The effect was to sharpen the X-ray patterns, as shown in Fig. 7C. Thus, some recrystallization must take place under such severe conditions. As seen in Fig. 8B the band for the P–H stretch at 2464 cm^{-1} is still present. However, a new band appears at 1334 cm^{-1}. This band is attributed to sulfate bonded to the layer by displacement of phosphite. No evidence of sulfonation is present. Note that in Fig. 8A the original phosphonate–phosphite spectrum clearly shows the phenyl out-of-plane vibrations attributed to monosubstitution at 692 and 750 cm^{-1}. These same vibrations remain unaltered in the sulfate-treated sample (Fig. 8B). However, under fuming sulfuric acid sulfonation occurs as described below.

Sulfonation reactions. Sulfonation of the phenylphosphonate–phosphites results in oxidation of the phosphite group to phosphate so that the same products are formed as are obtained by using the zirconium phosphonate–phosphates. For example, Fig. 9A shows the X-ray diffraction pattern of the 14.8-Å phase of a phosphonate–phosphite made in the presence of HF. This product is much more crystalline than the comparable one made by refluxing in the absence of HF (Fig. 7A). On sulfonation the diffraction pattern is as shown in Fig. 9B. The new interlayer spacing in the anhydrous form is 16.1 Å, but this compound takes up water readily with expansion of the interlayer spacing to ~19.1 Å. An infrared spectrum is shown in Fig. 10. There is now a very large water and O–H stretching band centered at 3455 cm^{-1}. The water bending band is at 1635 cm^{-1}. The out-of-plane bending vibrations for the phenyl ring, indicative of metasubstitution, are present at 686 and 802 cm^{-1}. During sulfonation a change in composition occurs, as shown in Table 4. Apparently some of the phosphonate bonds are cleaved and on the addition of water form P–OH bonds. This reaction bears further examination. Once again the staged phosphonate–phosphites of greater than 20-Å interlayer

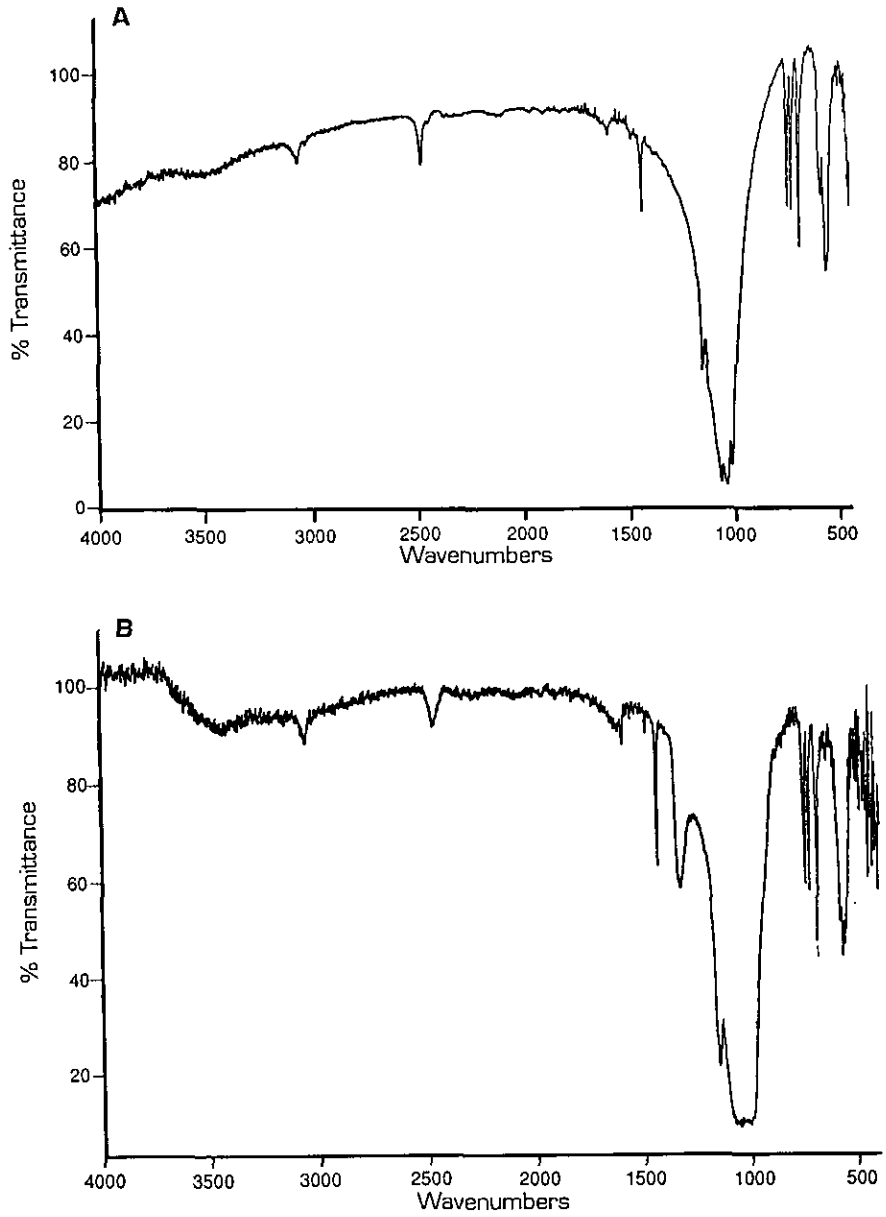

FIG. 8. Infrared spectrum of (A) zirconium phenylphosphonate phosphite and (B) the same compound heated in concentrated H_2SO_4 at 65°C. Note the new band at 1334 cm^{-1}.

TABLE 4
Composition of Zirconium Phenylphosphonates before and after Sulfonation

Compound sulfonated	Sulfonation product	% C	% H	% S	% Weight loss TGA
$Zr(C_6H_5PO_3)_2$ JD-II-47A	$Zr(O_3PC_6H_4SO_3H)_{1.73}(HPO_4)_{0.27} \cdot 4.93H_2O$	20.31	2.94	9.99	56.84
$Zr(C_6H_5PO_3)(HPO_3) \cdot 0.2H_2O$ YT-IV-98A Staged	$Zr(O_3PC_6H_4SO_3H)_{0.78}(HPO_4)_{1.22} \cdot 3.15H_2O$ $Zr(O_3PC_6H_4SO_3)_{0.57}(HPO_4)_{1.43} \cdot 1.67H_2O$	12.46 10.31	2.38 1.82	7.63	40.97 32.57
$Sr(C_6H_5PO_3)_{0.71}(HPO_4)_{1.29} \cdot 0.95H_2O$					

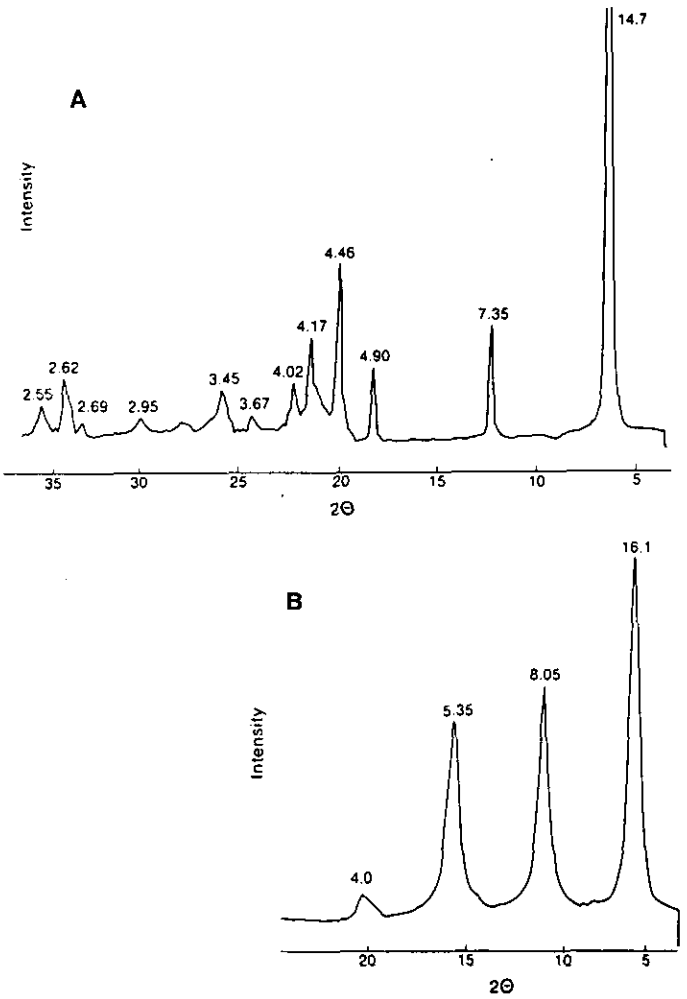

FIG. 9. XRD patterns of (A) zirconium phenylphosphonate phosphite made in HF media and (B) after sulfonation.

spacing were converted to a sulfonated product of the type shown in Fig. 9B.

DISCUSSION

When two different ligands are incorporated into the same layered compound, several different structure types may be visualized. These are pictured in cartoon form in Fig. 11. Two types of preparations can be carried out: those that are under kinetic control and those situations where the reaction is allowed to proceed to equilibrium. Of course additional reactions in which there is a partial approach to equilibrium can also be carried out. Zirconium phosphates and phosphonates are extremely insoluble. Therefore, if a soluble zirconium salt is added to solutions of phosphates or phosphonic acid, rapid precipitation of an amorphous gel takes place. Under such conditions, when two phosphorus based ligands are present, both would be expected to precipitate simultaneously upon addition of Zr(IV). We have reported earlier (12) that carrying out a reaction of this type with H_3PO_4 and $H_2O_3PC_6H_4PO_3H_2$ as a mixed ligand solution leads to compounds of the type $Zr(O_3PC_6H_4PO_3)_{1-\frac{1}{2}x}(HPO_4)_x$, with $x = 0.1$ to 0.9. All of the compounds were amorphous even after refluxing for several days. However, a very broad initial reflection in the X-ray powder pattern revealed an interlayer distance near 10 Å. When the same reactions were carried out in the presence of excess HF and precipitation occurred slowly, much more crystalline samples were obtained but their composition range was restricted in the range $x \cong 0.44$–0.72. This range was maintained up to a ratio of 12 : 1 of added phosphate to phosphonate.

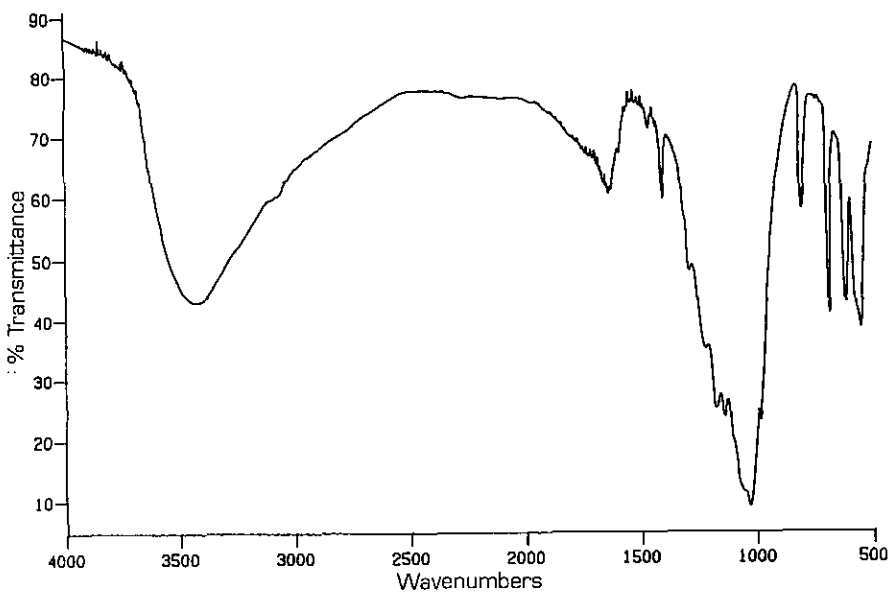

FIG. 10. Infrared spectrum of sulfonated zirconium phenylphosphonate phosphate prepared from the phosphite.

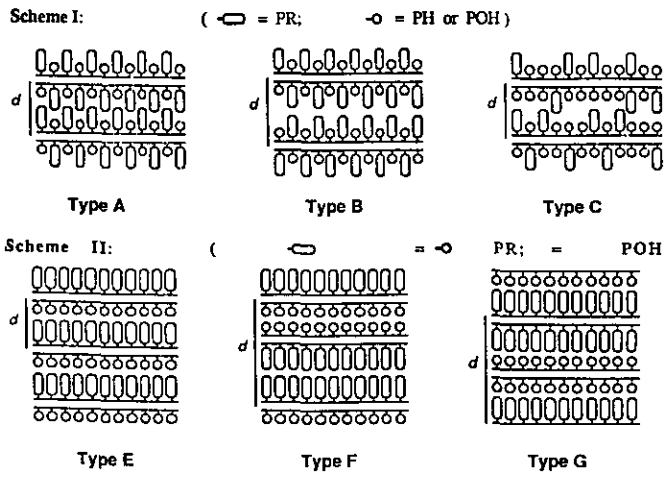

FIG. 11. Cartoon representation of possible structures of layered compounds containing two ligands.

In the case of the phenylphosphonates with phosphate or phosphite as the second ligand, the composition range has been found to be fairly narrow. For example, even when the ratio of phosphite to phenylphosphonate is 6 : 1, the initial amorphous precipitate has a composition in which the mole ratio of the two ligands is close to one. There is a fine distinction here. If the ratio of phenylphosphonate to phosphite exceeds one, even by the slightest margin, the interlayer spacing is ~15 Å. As the amount of phosphite incorporated increases, the interlayer spacing decreased to a level of 10.4 Å. The structure of the 15-Å phase (or 14.8-Å if better crystallized in HF) must be of type B. As the smaller phosphite groups increase in number, the chances that a phenyl group is opposite a phosphite group increases and the structure is of Type C. The closest distance of approach is when every phenyl group is unobstructed and opposite a phosphite group. The interlayer distance should then be half the sum of the distances of the end-member pure phases 10.2 Å, i.e., ½(14.8 + 5.6 Å). The closest we achieved was 10.6 Å in a hydrothermal reaction. These hydrothermal reactions were unpredictable, some yielding a mixture of phases and others giving pure phases, but they could be staged or not. These reactions need further study so as to better control the result. However, what is evident is that kinetic control in this system is limited. Even when an excess of phosphorous acid is present, the initial precipitate has a 15.0-Å basal spacing, indicating a slight excess of phenylphosphonate in the precipitate. This initial precipitate thus must contain an excess of the phenylphosphonate ligand even though it was present in a much lesser amount. One reason put forward by Alberti is that the ligands are size-incompatible, i.e., that because of the large difference in size of the two ligands they do not form a continuous solid solution. This point bears further investigation.

In order to obtain staged compounds the composition must have the phosphate or phosphite to phosphonate ratio ≥1.0. Also, a larger variation in composition is more readily achieved with the smaller ligand predominating. This allows for one layer to be exclusively phosphate while the other layer is a solid solution of phosphate and phenylphosphonate with the organic occupying 70% or more of the layer. All the evidence points to a type F structure as most likely. The other possibility is structure type G. For this structure the intercalation of butylamine would yield the same result as obtained for structure F. However, in structure G, it would be expected that the ethylenediamine would intercalate into both layers and, if in the *trans* conformation, would increase the interlayer distance by twice the amount observed. In addition, we would expect twice the amount of ethylenediamine (or any diamine) to be intercalated into the type G structure as in type F. The amount of ethylenediamine actually intercalated was a quarter of a mole. This result may arise from the greater difficulty in moving the staged layers apart as opposed to pure α-ZrP layers. The staged compounds also cannot have the structure pictured in Fig. 2. The presence of phenyl groups in the predominately phosphate or phosphite layer would expand this layer by 2.6–4.6 Å.

Additional evidence to distinguish structure Type F from Type G is derived from consideration of intensities of powder X-ray reflections. In Type G a mirror plane divides the upper and lower halves of the unique layer. A straightforward calculation that follows shows that the (*001*) reflection should be absent in either the starting material or the intercalates. In structure Type F (*001*) is expected not to be absent, in agreement with observation. α-ZrP crystallizes in the monoclinic space group $P2_1/c$ and therefore the layers are located at $Z = 0$ and 1/2. This arrangement thus produces the *00l* reflections only with $l = 2n$. The X-ray powder pattern of the staged compounds display both the odd and even indices for the *00l* reflections, indicating that the layers are not located at $Z = 0$ and $Z = 1/2$, as in the case of α-ZrP. It is also observed that the intensities of (*001*) and (*002*) reflections in these compounds are different, depending on hydration and/or the type of intercalated amines. In order to understand these observed features purely on a qualitative basis, the relative intensities of the *001* and *002* reflections were calculated on the basis of the layer structure of α-ZrP and the observed *d*-spacings of the *00l* reflections. The positional coordinates of α-ZrP were converted to those in the space group $P\bar{1}$ and the same values for *a*, *b*, and β were assumed. The *Z* coordinates were obtained on the basis of the *d*-spacings observed in the powder pattern. Calculations were done for the hydrated sample having a *d*-spacing of 24.5 Å (Fig. 6) for the (*001*) reflection (Table 5). According to the proposed model II (Type F), the layers should be placed at $Z = 0$ and $Z = 0.6$. In

TABLE 5

Calculation of Relative Intensities of the *00l* Reflections for Staged Zirconium Phenylphosphonate Phosphate

	Relative intensity				
h k l	Case: I	II	III	IV	V
001	0	27	100	100	1
002	100	100	34	10	100

Note. Case I, layers at $z = 0$ and $\frac{1}{2}$; Case II, layers at $z = 0$ and 0.6; Case III, layers at $z = 0$ and 0.65; Case IV, layers at $z = 0$ and 0.7; and Case V, butylamine intercalate.

this hydrated structure the phenylphosphonate layer is 14.8-Å thick and by difference the basal spacing of the phosphate layer is 9.72 Å or $0.4c$. This calculation corresponds to case II in Table 5. The calculations were made only for each layer containing Zr and PO_4 groups. This simplified calculation introduces an error due to neglect of water molecules and phenyl ring carbons. However, these atoms are of low atomic number and not expected to change the order of the (*00l*) intensities. The calculation predicts that the (*002*) reflection should be much more intense than the (*001*) and this is the case. On dehydration of the staged compound, the interlayer (*001*) spacing is ~22 Å and the layers are at 0 and $0.65c$. This calculation shows a reversal in intensities (Type III) and is borne out by the observed X-ray patterns. Finally, when butylamine is intercalated, the basal spacing is 34.6 Å with the layers at $0.425c$ and zero. Again the calculation shows a drastic reduction in the (*001*) reflection relative to the (*002*) Case V and this reversal is also seen on the X-ray powder pattern (Fig. 6).

It should be remarked that in all these calculations we have neglected preferred orientation effects but these appear to be secondary in importance.

In terms of stability we see that the staged products, both with phosphite and phosphate, rearrange when subjected to fuming sulfuric acid. The products obtained are of the type $Zr(O_3PC_6H_4SO_3H))_x(HPO_4)_{2-x} \cdot nH_2O$ with both groups in all the layers. Similar products may be obtained by treating the phosphite and phosphate 14.8-Å phases. The fact that the products from the staged and nonstaged starting materials are the same shows that rearrangement of the layers has occurred for the staged materials. A certain amount of cleavage of the P–C bond takes place during sulfonation and this increases the amount of phosphate relative to phenylphosphonate (Table 4). In fact it presents a means of extending the composition range of the mixed derivatives.

We have observed that the zirconium phosphonates dissolve in 100% H_2SO_4. In the dissolved state the mixed ligand derivatives might be expected to rearrange into the pure α-ZrP or zirconium phosphite and zirconium phenylphosphonate. We found no tendency in this direction. However, with the mixed ligand derivatives of the type $Zr(O_3PC_6H_4PO_3)_x(HPO_4)_{2-2x}$, rearrangement did occur when the amount of HPO_4 on the layers was large. Kinetic and thermodynamic control in that system will be discussed in another paper.

Finally, we may remark on the strange behavior of the phosphate–phenylphosphonate ligands in the presence of HF. The product obtained depended strongly on the ratio of phosphate to phenylphosphonate. Up to a ratio of 20 : 1 the product was the 14.8-Å phase, and this phase did not vary appreciably in composition. Not until the ratio was 70 was a pure staged product obtained. The mechanism by which this is achieved bears further study and we are attempting to isolate any intermediates which may form. The staged phosphate compounds appear easier to make than the analogous phosphite and this may be connected with the greater hydrophilic character of the phosphate. Ligands of similar hydropholicity mix more readily, while segregation tends to occur if these properties diverge in the ligands.

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