

trosopic properties of these macrocycle compounds.

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ment of Energy. J.P.S. received summer support in 1977 from an NSF Undergraduate Research Participation grant (No. SMI 76-03095 A01). Tom Merriam provided the estimate in Figure 5 of the molar extinction coefficient for  $\text{P}^{\text{III}}(\text{Pc})$  and solubility data. Professor Donn G. Shankland of the Air Force Institute of Technology, Dayton, Ohio, kindly provided the numerical analysis of the titration data.

**Registry No.** P(OEP)(OH) $_2$ ClO $_4$ , 62638-18-0; P(MesoDME)(OH) $_2$ PF $_6$ , 75444-55-2; P, 7723-14-0; H $_2$ (Pc), 574-93-6; P(Meso)O(OH), 75431-38-8; P(Meso)O $_2^-$ , 75431-39-9; PBr $_3$ , 7789-60-8.

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## Derivatized Lamellar Phosphates and Phosphonates of M(IV) Ions

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By means of a metathetical precipitation reaction, a broad series of crystalline and semicrystalline layered products which can have various organic groups affixed on the inorganic sheets of zirconium phosphate related structures has been prepared. These compounds are exceedingly thermally stable as shown by TGA measurements, and they are quite chemically stable in nonalkaline media. Crystallinity and particle size were found to depend on the conditions of preparation; the effect of the appended organic group on basal spacing was clearly evident by X-ray diffraction. IR spectra in all cases are consistent with the disposition of the groups as well. Surface area measurements have tended to verify the accessibility of the relatively vast internal surface of the compounds, as have some intercalation reactions.

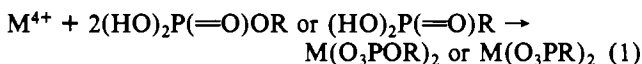
### Introduction

Recent investigations have shown the viability and desirability of "heterogenization" of various solution phase agents onto certain solid supports.<sup>1</sup> The bulk of this work has involved inorganic substrates such as silica<sup>2</sup> or organic polymers based mainly on polystyrene.<sup>3</sup> In the former case, affixation has usually been accomplished by reacting terminal trichloro- or trimethoxysilyl compounds with pendant inorganic hydroxyl groups; in the latter, phenyl rings on the polymer backbone were typically derivatized with appropriate coordinating functions. In both approaches, the strategy was to anchor ligating groups onto the solids prior to incorporation of an active metal site. There are alternative methods of obtaining essentially the same sort of products such as polymerization of the metal-site-containing monomer to get the product in one step<sup>4</sup> or reaction of allyl organometallic compounds directly with hydroxylic surfaces.<sup>5</sup> Generally, the concept has proven to be feasible, but problems of activity loss primarily due to accessibility to sites and attrition have plagued investigators.<sup>6</sup>

Recognizing that both the inorganic and organic supports previously employed have an intrinsically disordered disposition of sites upon or within them, we considered the possibility of using a highly ordered source of handles for subsequent anchoring. One obvious class of candidates possessing an array of planar handles is the inorganic hydroxylic layered compounds, epitomized by certain of the clay minerals such as montmorillonite or hectorite. In fact, these materials have been derivatized with some passive organics,<sup>7</sup> and recently attempts at incorporating active catalysts via ion exchange of interlayer cations have been described.<sup>8</sup> Typically, site-site distances

are on the order of 25 Å, leading to relatively low capacities. Moreover, ion-exchanged groups tend to be labile and/or mobile under most conditions. Nevertheless, the idea of using layered solids for supports is a compelling objective, for the vast potential internal surface could be highly advantageous. If sites situated within the bulk of a suitable layered solid can be prepared and shown to be accessible to exterior species (via intercalation), one might expect enhanced selectivity for certain reactions to result from the two-dimensional nature of the site environment,<sup>9</sup> as well as minimal attrition due to the chelating effect of a bilayered situation of ligands. High site densities would also be expected if intersite distances were considerably smaller than in the clays.

Crystalline layered zirconium phosphate<sup>10</sup> presents an ideal model on which to test the foregoing ideas. It contains on its lamellar surfaces a hexagonal array of hydroxyl groups spaced about 5.3 Å apart (see Figure 1). This leads to an area per site of 24 Å<sup>2</sup>, which is quite suitable as a cross-sectional limit for many affixed substituents. It is known to undergo intercalative ion exchange and inclusion with a broad series of species.<sup>11</sup> Although it was our initial intention to attempt to attach organic functions to the pre-formed phosphate via the pendant hydroxyl group as done by Yamanaka,<sup>12</sup> and also with silicas,<sup>2</sup> we found that a far superior approach involved direct precipitation of the derived phosphate (or phosphonate) with Zr<sup>4+</sup> or other tetravalent metal ions (eq 1).



- (1) For a recent general review, see D. D. Whitehurst, *CHEMTECH*, 44 (1980), and references cited therein.
- (2) F. R. Hartley and P. N. Vezey, *Adv. Organomet. Chem.*, 15, 189 (1977).
- (3) J. I. Crowley and H. Rapoport, *Acc. Chem. Res.*, 9, 135 (1976).
- (4) C. U. Pittman, Jr., *CHEMTECH*, 116 (1971).
- (5) J. P. Candlin and H. Thomas, *Adv. Chem. Ser.*, No. 132, 212 (1974).
- (6) C. U. Pittman, Jr., L. R. Smith, and R. M. Hanes, *J. Am. Chem. Soc.*, 97, 1974 (1975).
- (7) E. V. Kukharskaya and A. D. Fedoseev, *Russ. Chem. Rev. (Engl. Transl.)*, 32, 490 (1963).

- (8) T. J. Pinnavaia, "Catalysis in Organic Synthesis", G. V. Smith, Ed., Academic Press, New York, 1977.
- (9) Such effects have been seen in clays. See T. J. Pinnavaia, R. Raythatha, J. G. Lee, L. J. Halloran, and J. F. Hoffman, *J. Am. Chem. Soc.*, 101, 6891 (1979).
- (10) G. Alberti, *Acc. Chem. Res.*, 11, 163 (1978); A. Clearfield, G. H. Nancollas, and R. H. Blessing, "Ion Exchange and Solvent Extraction", Vol. 5, J. H. Marinsky and Y. Marcus, Eds. Marcel Dekker, New York, 1973.
- (11) D. Behrendt, K. Beneke, and G. Lagaly, *Angew. Chem., Int. Ed. Engl.*, 15, 544 (1976).
- (12) S. Yamanaka, *Inorg. Chem.*, 15, 2811 (1976).

Table I. Representative List of the Compounds Prepared

compd	d spacing, Å	compd	d spacing, Å	compd	d spacing, Å
Zr(O <sub>3</sub> PCH <sub>2</sub> Cl) <sub>2</sub>	10.05	Zr(O <sub>3</sub> PCH <sub>2</sub> CH=CH) <sub>2</sub>	12.6	Th(O <sub>3</sub> PC <sub>18</sub> H <sub>37</sub> ) <sub>2</sub>	42.0
Zr(O <sub>3</sub> PH) <sub>2</sub>	5.61	Zr(O <sub>3</sub> PCH=CH <sub>2</sub> ) <sub>2</sub>	10.6	Ti(O <sub>3</sub> PC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sub>2</sub>	18.4
Zr(O <sub>3</sub> PC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	15.0	Zr(O <sub>3</sub> PCH <sub>2</sub> SCH <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	14.6	Ti(O <sub>3</sub> PCH <sub>2</sub> Cl) <sub>2</sub>	10.4
Zr(O <sub>3</sub> POCH <sub>2</sub> CH <sub>2</sub> CN) <sub>2</sub>	13.2	Zr(O <sub>3</sub> AsC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	14.3	Th(O <sub>3</sub> POC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> ) <sub>2</sub>	16.4
Zr(O <sub>3</sub> PCH <sub>2</sub> COOH) <sub>2</sub>	11.1	Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> SH) <sub>2</sub>	15.5	Ce(O <sub>3</sub> PC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	15.5
Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> COOH) <sub>2</sub>	12.8	Zr(O <sub>3</sub> P(CH <sub>2</sub> ) <sub>10</sub> PO <sub>3</sub> ) <sub>2</sub>	17.3	Th(O <sub>3</sub> PCH <sub>3</sub> ) <sub>2</sub>	8.9
Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> COOH) <sub>2</sub>	14.8	Zr(O <sub>3</sub> AsC <sub>6</sub> H <sub>4</sub> Cl) <sub>2</sub>	17.7	U(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SO <sub>3</sub> H) <sub>2</sub>	29.4
Zr(O <sub>3</sub> P(CH <sub>2</sub> ) <sub>4</sub> COOH) <sub>2</sub>	16.8	Zr(O <sub>3</sub> PCH <sub>2</sub> OC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	19.0	Ti(O <sub>3</sub> PCH=CH <sub>2</sub> ) <sub>2</sub>	10.6
Zr(O <sub>3</sub> P(CH <sub>2</sub> ) <sub>5</sub> COOH) <sub>2</sub>	19.0				

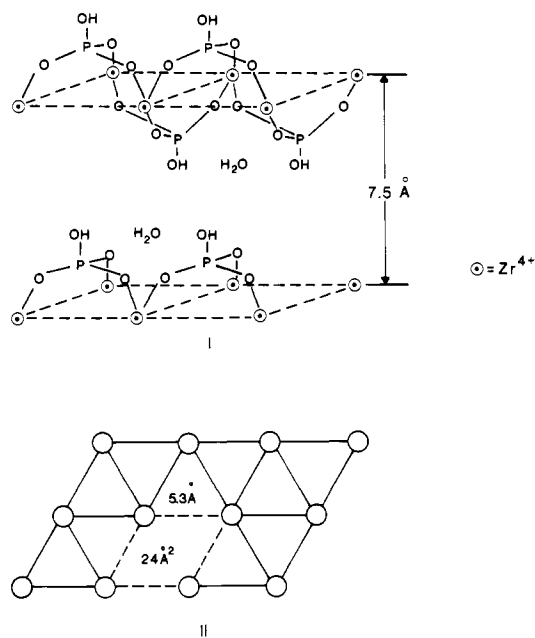


Figure 1. Simplified structure of  $\alpha$ -zirconium phosphate: I, perspective showing layered construction; II, projection of a layer to show site spacing on surfaces.

This reaction is exactly analogous to the formation of zirconium phosphate itself. Typically an amorphous or semi-crystalline solid or a gel is the initial product, and crystallinity is found to be enhanced on extended reflux or by the use of precomplexation agents such as HF.<sup>13</sup> In nearly all of the cases so far encountered, the products gave X-ray powder patterns exhibiting a prominent series of low-angle reflections indicative of a layered compound. Recently, in the course of this investigation, Alberti disclosed the above-mentioned route in the preparation of three such derived compounds.<sup>14-16</sup> In our laboratories the reaction has been considerably extended to encompass several M<sup>4+</sup> ions and numerous pendant groups. In addition, we have characterized these products and report their thermal behavior, spectroscopic properties, and surface area behavior.

### Results and Discussion

**Synthesis.** In many cases, the phosphonic acid or corresponding dialkyl ester was readily available; however, in certain cases we had to prepare it. Usually, a conventional Arbuzov reaction<sup>17</sup> (eq 2) will afford the desired starting material. In

$$P(OC_2H_5)_3 + RX \rightarrow (C_2H_5O)_2P(=O)R + C_2H_5X \quad (2)$$

(13) G. Alberti and E. Torracca, *J. Inorg. Nucl. Chem.*, **30**, 317 (1968).

(14) G. Alberti, U. Costantino, S. Alluli, and N. Tomassini, *J. Inorg. Nucl. Chem.*, **40**, 1113 (1978).

(15) G. Alberti, U. Costantino, and M. L. L. Giovagnotti, *J. Chromatogr.*, **180**, 45 (1979).

(16) Also see L. Maya, *Inorg. Nucl. Chem. Lett.*, **15**, 207 (1979).

(17) R. F. Hudson, "Structure and Mechanism in Organophosphorous Chemistry", Academic Press, New York, 1965, p 135 ff.

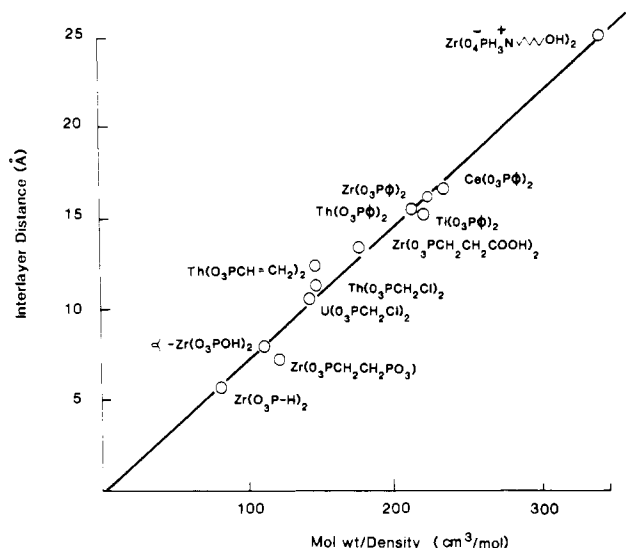
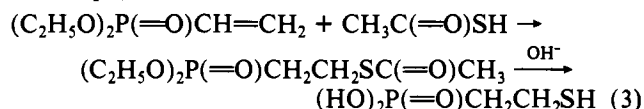


Figure 2. Plot of molecular volume vs. interlayer spacing, illustrating that an isostructural series is likely for the compounds shown. The slope of the line is equivalent to 23 Å<sup>2</sup> per molecule, indicating the site area.

other cases such as for the 2-mercaptoethylphosphonic acid, alternative routes starting with simpler phosphonates must be used (eq 3).



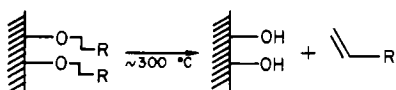
The formation of derivatized layered phosphates and phosphonates of tetravalent metals according to eq 1 is a general result, as shown in Table I. The nature of the terminal group on the bound organic moiety seems to have little effect on the outcome, providing, of course, that its bulk size is within the 24 Å<sup>2</sup> allotted per site by the inorganic sheets. The crystallinity of the products, as assessed by the breadth of the X-ray diffraction reflections, was diminished as the groups approached this limit in cross-sectional area. As mentioned, crystallinity could often be maximized by extensive digestion of the precipitates, by the use of sequestering agents such as HF or by employing relatively large ions such as Th<sup>4+</sup> or M.

**Structure.** The metal phosphites—M(O<sub>3</sub>PH)<sub>2</sub>—can be considered as the first members of the homologous series of derivatized layered phosphonates. Although crystalline metal(IV) phosphites have been previously reported, their apparent layered structure escaped notice.<sup>18</sup> We infer a layered structure on the basis of the fact that the first reflection of the zirconium salt falls at a value corresponding to an interlamellar repeat distance of 5.6 Å (consistent with the value expected on the basis of the published structure of  $\alpha$ -zirconium phosphate);<sup>19</sup> furthermore, it is found that the molecular

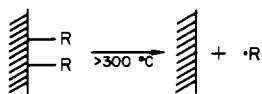
(18) K. A. Avdueva and V. S. Mironova, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **6**, 391 (1970).

## Scheme I. Likely Decomposition Routes for Anchored Solids

phosphates



phosphonates

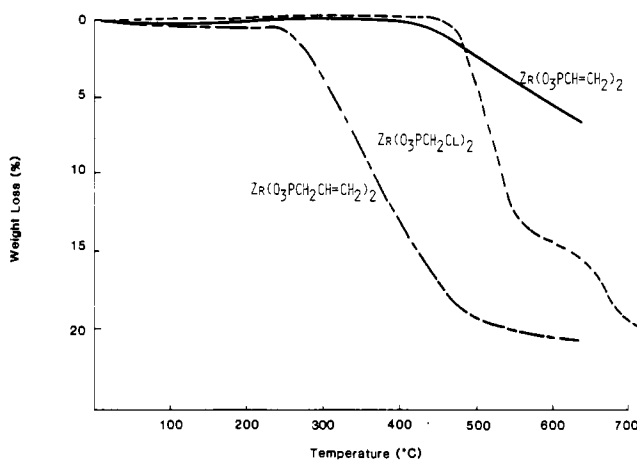


volume vs. basal distance falls exactly on the line of the isostructural series (Figure 2). When the molecular volume (molecular weight/density) is plotted against interlayer distance for the series of compounds reported here, a straight line having a slope corresponding to the common site area ( $24 \text{ \AA}^2$ ) results. This observation is consistent with an isostructural group.

In general, the diffraction patterns exhibited by these compounds could not be indexed to a simple hexagonal structure; rather, it is likely that there are distortions to monoclinic (or lower symmetry) structures, as has been reported for the prototype  $\alpha$ -zirconium phosphate.<sup>19</sup> However, the assignments of the low-angle series of reflections observed to  $00l/n$  planes and hence inferring basal distances from them are considered warranted by the consistent agreement with expected values based on this model. CPK-type space-filling molecular models were also in agreement with this interpretation. Observed values of the basal repeat distances are also given in Table I. In those cases in which relatively nonpolar organics were affixed, there was no interlamellar water present. This was verified by the infrared spectra of the products, as well as thermogravimetric behavior.

**Thermogravimetric Analyses.** On heating a typical derivatized product in nitrogen, we observed essentially no weight change (unless interlamellar water was included in the precipitation) below  $300 \text{ }^\circ\text{C}$ , where decomposition of the organic moiety apparently begins. Water was present only in those cases where highly polar substituents such as alcohols or sulfonic acids were affixed. Generally, it seemed that phosphonates survived to higher temperatures than phosphates. This may be attributable to a dissociation pathway for phosphates similar to ester eliminations, whereas phosphonates may decompose via homolytic P-C bond scission (see Scheme I). In Figure 3, the TGA of zirconium chloromethylphosphonate is presented for illustration. This material is exceptionally stable for an organic-inorganic hybrid. In part, this can be due to the effect of separating the organic groups by attachment at sites  $5.3 \text{ \AA}$  apart, thereby inhibiting collisional routes to dissociation.

For a further illustration of the effect of the organic group on the decomposition behavior of the material, the thermogravimetric curves for the allyl- and vinylphosphonates of zirconium are also shown in Figure 3. Homolysis of the phosphorus-carbon bond leads in the first instance to an allyl radical, while in the second case a vinyl radical is formed. Whereas the allyl product begins to decompose at about  $225 \text{ }^\circ\text{C}$  and loses nearly the exact weight calculated for its organic component over a broad temperature range, a marked contrast is seen for the vinyl analogue, which has lost only about one-third of its hydrocarbon content by  $650 \text{ }^\circ\text{C}$ ! The assumption of a simple homolytic mechanism for the decomposition may be an oversimplification of the process, but the principle still holds that, by so affixing organics rigidly on inorganic sites at distances greater than the normal van der Waals contact, remarkably stable products are formed. The



**Figure 3.** Thermogravimetric curves for derivatized phosphonates: solid line,  $\text{Zr}(\text{O}_3\text{PCH}=\text{CH}_2)_2$ ; broken line,  $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}=\text{CH}_2)_2$ ; simple dashed curve,  $\text{Zr}(\text{O}_3\text{PCH}_2\text{Cl})_2$ .

accumulated data indicate that the phosphonates decompose ca.  $100 \text{ }^\circ\text{C}$  higher than their analogous phosphates.

Generally, the substances are quite acid stable, as expected, since they are usually prepared in acidic milieu. In higher pH media they are prone to attack by hydroxide to form hydrated  $\text{ZrO}_2$ , which is, of course, very stable. The products are exceedingly insoluble in water and organic solvents, as was observed for the phosphate. In the presence of high concentrations of other phosphoric or phosphonic acids, a given salt may slowly exchange its anions. The exchange reaction of zirconium 2-hydroxyethyl phosphate with phosphoric acid was reported recently by Yamanaka and co-workers.<sup>20</sup> Such behavior was also observed for zirconium 2-bromoethylphosphonate slurried in solutions of 2-carboxyethylphosphonic acid.

**Particle Size, Crystallinity, and Surface Areas.** In contrast to crystalline zirconium phosphate, which can be obtained as sharply well-formed hexagonal platelets of micron dimensions, the derivatized products are typically afforded as  $10\text{--}100\text{-}\mu\text{m}$  aggregates of crystallites. SEM inspection of some representative products reveals submicron-sized grains which are more blocklike than zirconium phosphate (Figure 4). Control of the reaction conditions, for instance, by using HF as a sequestering agent<sup>13</sup> or exhaustive digestion, does narrow the range of particle size considerably (Figure 5) and elevates the crystallinity (as assessed by X-ray diffraction). As an example, in Figure 6 the powder patterns of two zirconium bis(2-carboxyethylphosphonate) products are shown. The only difference in their preparation was the amount of HF added to slow precipitation.

Surface areas were determined on many of the products, by using a standard one-point BET method with nitrogen as sorbant. In general, the solids exhibited quite high values, as shown in Table II. Certainly, areas in the range of  $50\text{--}200 \text{ m}^2/\text{g}$  are not consistent with particles even on the order of  $0.1 \text{ }\mu\text{m}$  dimension, assuming coverage of external surface only. In fact, using as a model a platelet (density ca.  $2 \text{ g/cm}^3$ ) with aspect ratio 10 and a width of  $0.1 \text{ }\mu\text{m}$  leads to an expected value of about  $2\text{--}5 \text{ m}^2/\text{g}$ . Therefore, we surmise that, to varying extents, our products are incorporating considerable nitrogen into the internal surface presented by the lamella. A limiting value of about  $400\text{--}500 \text{ m}^2/\text{g}$  would be expected for complete monolayer coverage of all of the potential surface in this case. Consistent with this picture of incorporated sorbant is the observation that uptake gradually increased with time allowed for adsorption, i.e., that equilibrium was not

(19) A. Clearfield and G. D. Smith, *Inorg. Chem.*, **8**, 431 (1969).

(20) S. Yamanaka and M. Hattori, *Chem. Lett.*, 1073, (1979).

Table II. Single-Point BET Surface Areas (Using Nitrogen) of Some Tetravalent Metal Phosphonates

compd	surface area, m <sup>2</sup> /g	compd	surface area, m <sup>2</sup> /g	compd	surface area, m <sup>2</sup> /g
Zr(O <sub>3</sub> PC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	180-220 <sup>a</sup>	Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> Cl) <sub>2</sub>	35	Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> PO <sub>3</sub> )	55
Ti(O <sub>3</sub> PC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	160	Th(O <sub>3</sub> PCH <sub>2</sub> Cl) <sub>2</sub>	9.7	Zr(O <sub>3</sub> P(CH <sub>2</sub> ) <sub>10</sub> PO <sub>3</sub> )	109
Th(O <sub>3</sub> PC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	67	Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> COOH) <sub>2</sub>	26	Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> SH) <sub>2</sub>	44
Zr(O <sub>3</sub> PH) <sub>2</sub>	108	Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> CN) <sub>2</sub>	73	Zr(O <sub>3</sub> PCH <sub>3</sub> ) <sub>2</sub>	260-500 <sup>a</sup>
Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	72	Zr(O <sub>3</sub> PCH=CH <sub>2</sub> ) <sub>2</sub>	2	Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	72
Zr(O <sub>3</sub> PCH <sub>2</sub> Cl) <sub>2</sub>	32	Zr(O <sub>3</sub> PCH <sub>2</sub> CH=CH <sub>2</sub> ) <sub>2</sub>	90	Zr(O <sub>3</sub> PCH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> Br) <sub>2</sub>	39

<sup>a</sup> In these cases, a range of surface areas was found, the value depending on the conditions of preparation.

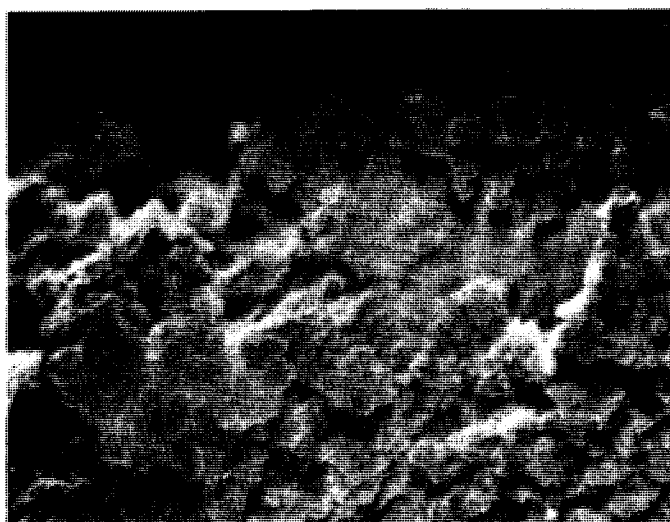
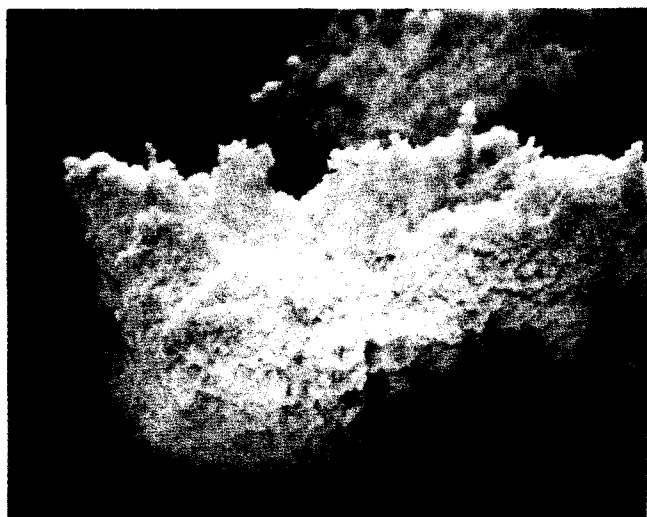


Figure 4. SEM photographs of Zr(O<sub>3</sub>PC<sub>6</sub>H<sub>11</sub>)<sub>2</sub>, illustrating the typical appearance of the agglomerates and composite particles. Magnification of the top image is 2000 times; bottom is 20000 times.

reached even in relatively large (>1 h) time periods. In order to gain a better understanding of the sorptive behavior of such solids, we ran a complete isotherm on two of our products, the titanium and zirconium bis(phenylphosphonates), for both sorption and desorption, and these curves are reproduced in Figure 7. As can be seen, there was definite hysteresis in both cases. Since the hysteresis persisted in both cases below  $p/p_0$  of 0.2, it is unlikely that it derived from capillary condensation in pores of macroscopic size such as might result from external surface texture or from voids in the powder.<sup>21</sup> Although we hypothesize that the hysteresis is a result of microscopic in-

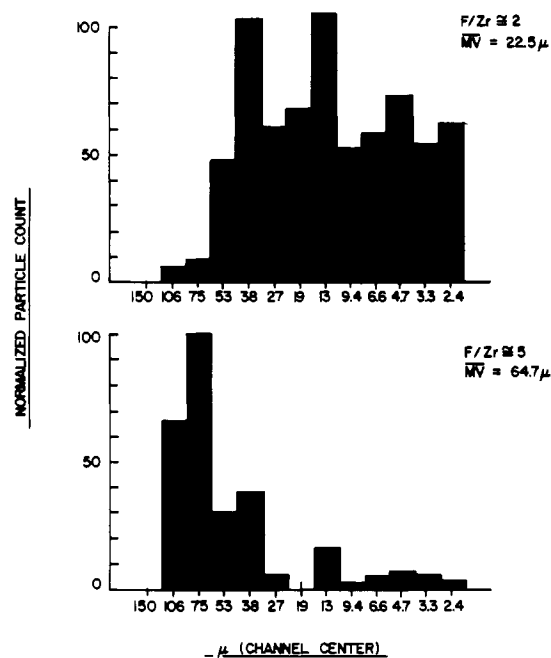


Figure 5. Particle-size histograms of Zr(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>Cl)<sub>2</sub> illustrating the effect of the HF/Zr<sup>4+</sup> ratio in the preparation on the distributions.

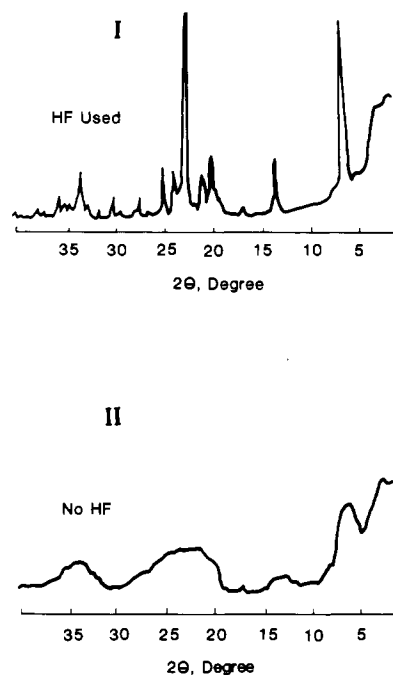
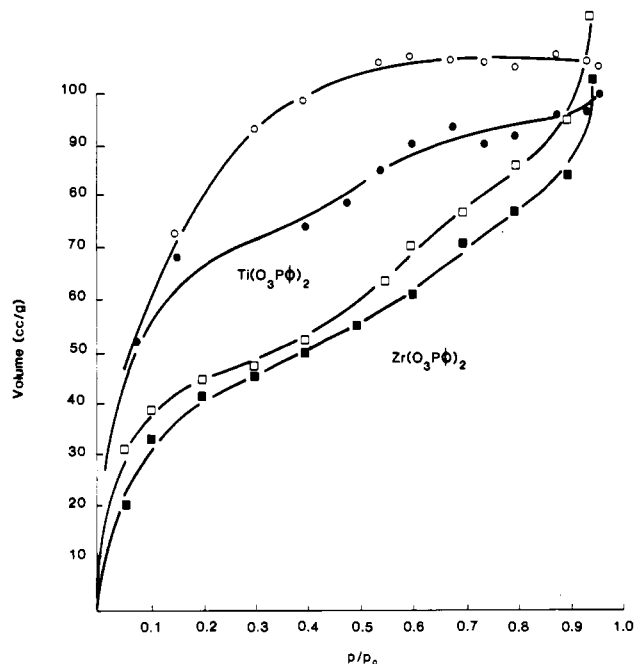


Figure 6. X-ray diffraction powder patterns of Zr(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>COOH)<sub>2</sub> prepared in the presence (I) and absence (II) of HF.

tercalation of the gas, we cannot advance this interpretation with any certainty since the SEM's do not show well-defined and -shaped crystals. Nevertheless, it is interesting to note from the figure that the desorption curve for the titanium

(21) G. D. Parfitt and K. S. W. Sing, "Characterization of Powder Surfaces", Academic Press, London, 1976.



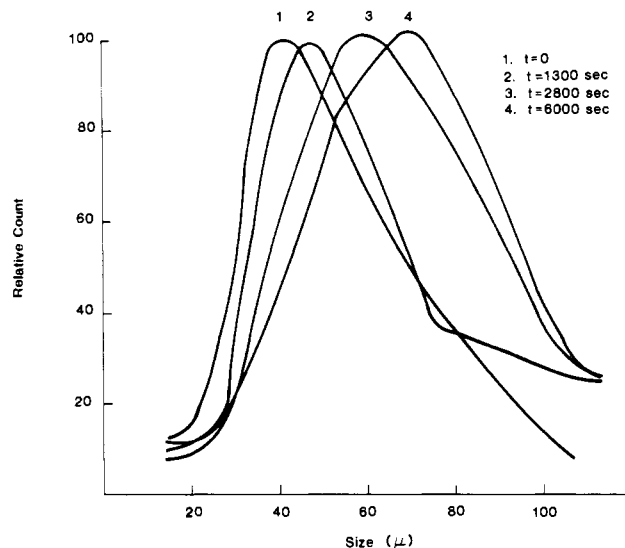
**Figure 7.** Nitrogen isotherms for two phenylphosphonates showing hysteresis behavior. Closed data points are adsorption; open points are for desorption.

compound is level at an uptake value which corresponds quite closely to that calculated for saturation with monolayer occupation of the interlamellar spaces, about 400 m<sup>2</sup>/g. This desorption value quite likely corresponds with the equilibrium uptake limit. A similar value in the one-point BET was found for the zirconium bis(methylphosphonate). As expected, we found that crystallinity plays a significant role in determining the surface area.<sup>22</sup>

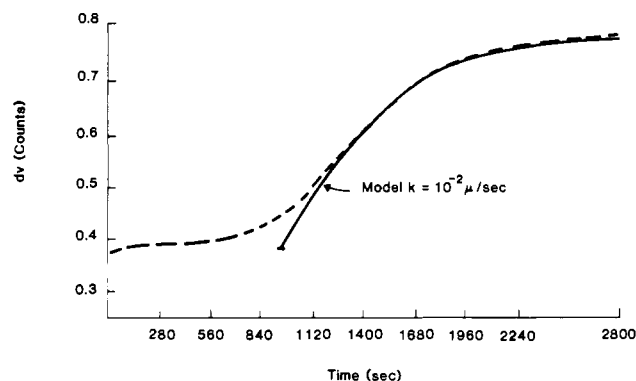
Although we could not show definitely that nitrogen intercalation had indeed occurred, we have found that other nonpolar guests such as benzene or halocarbons do intercalate in similar compounds with consequent changes in the interlayer spacings. Thus, a 20-mm column of Zr(O<sub>3</sub>PCH<sub>2</sub>CH<sub>2</sub>Cl)<sub>2</sub> swells to 25 mm after being in 1,4-dichlorobutane for 1 h.<sup>23</sup>

**Kinetics of Intercalation.** To further understand the behavior of these materials under conditions of intercalation, i.e., topotactic incorporation of species from an external phase, we undertook a study of the evolution of the particle size and volume of a typical anchored carboxylic acid on treatment with an organic amine. Using a particle-size analyzer, we followed the change in both average particle size and volume of zirconium bis(2-carboxymethylphosphonate)—Zr(O<sub>3</sub>PCH<sub>2</sub>COOH)<sub>2</sub>—on addition of 6-aminohexanol (chosen because of its water solubility and size). From the X-ray diffraction patterns of the starting carboxylic acid and the product, the ammonium salt, we expected about a doubling of the interlamellar distance on intercalation; hence each particle should double in volume in the course of reaction.

As is indicated in Figure 8, we started with an average particle size of about 40 μm. Microscopy has revealed that these particles are, in actuality, composites of much smaller crystallites. In the course of the reaction, they appear to maintain their integrity, however growing to a value of approximately 70 μm, at the same time somewhat broadening in the distribution. The change in average particle volume with time afforded a curve which could be fit quite well with a



**Figure 8.** Evolution of the particle-size distribution of Zr(O<sub>3</sub>PCH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub> on treatment with 6-aminohexanol.



**Figure 9.** Change in the average particle volume (arbitrary units) with time for the reaction described in Figure 8. The dashed-line tracks the experimental data; the solid line is based on a model of a front of intercalant moving at a constant rate of 10<sup>-2</sup> μm/s (see text).

simple model of a shrinking core, growing shell sphere. That is, we calculated the volume dependence with time of a spherical particle subjected to a front of intercalation moving from the surface to the center at a constant rate, behind which the volume is doubled. The equation for the volume at time  $t$  is

$$V_t = (n-1)\frac{4}{3}\pi k^3 t^3 - (n-1)4\pi r k^2 t^2 + (n-1)4\pi r^2 k t + \frac{4}{3}\pi r^3 \quad (4)$$

where  $n$  represents the final to initial volume ratio,  $r$  is the starting radius, and  $k$  is the rate constant (in μm/s) of the advancing front. The observed curve was best fit with a value of  $k$  of 10<sup>-2</sup> μm/s (10<sup>-6</sup> cm/s), which is in the normal expected range of such diffusional phenomena. We observed induction periods of varying magnitudes, as is typical of many intercalation reactions for which nucleation of a phase occurs. Figure 9 illustrates the comparison of experimental and model behavior.

### Summary and Conclusions

Providing the starting phosphonic acid can be obtained and the substituent is not overly bulky (that it has a cross-sectional area not in excess of about 24 Å<sup>2</sup>), a broad class of layered tetravalent metal salts are quite easily affordable by the reaction of eq 1. Depending on the conditions of the preparation and the use of sequestering agents, the crystallinity can vary rather broadly from amorphous gels to well-ordered phases

(22) Details of the pore and surface area behavior will be reported on separately.

(23) It was not possible to obtain an X-ray powder diffraction pattern on this product, since it apparently deintercalates in the absence of excess guest.

based upon the zirconium phosphate structure. Such products have pendant organic groups oriented more or less perpendicularly into the interlamellar region and can be used in subsequent intercalation reactions. These compounds are remarkably stable, owing to the placement of the groups at 5.3-Å separated sites upon the planar inorganic backbone. The surface areas are generally quite high, presumably due to the inclusion of sorbents into the bulk of the crystals via intercalative diffusion.

We have conducted extensive investigations into the ion-exchange behavior of certain of the products obtained, which will be reported on separately. Furthermore, we have found that there is considerable latitude in designing and tailoring the nature of the interlayer phases by forming mixed component products, in which two (or more) different groups are present within the interlayers. In addition, we have found that pillaring is possible by the use of terminal bis(phosphonates) of varying length and rigidity. These features will also be described in later reports.

### Experimental Section

All of the preparations were carried out in air with no special precautions taken to eliminate moisture or oxygen. Reagents were usually used as received from suppliers, once it was established by conventional means that they were of reasonable purity. Phosphonic acids were prepared from dialkylphosphonate esters by hydrolysis with  $\text{HBr}^{24}$  when necessary. Tetravalent metal salts of various anions could be used as long as they were water soluble and stable. Since the many preparations were essentially identical in procedure, we will present only a few examples to illustrate the method. In all cases, elemental analyses were obtained and were consistent with the formulated product.

Powder X-ray diffraction patterns were measured on a Phillips diffractometer ( $\text{Cu K}\alpha$  radiation). Thermogravimetry was determined with a Du Pont 990 instrument at a  $20^\circ/\text{min}$  heating rate and with nitrogen as carrier gas. The particle-size experiment was conducted on a Leeds and Northrup Microtrac Analyzer. Surface areas and isotherms were measured with a Quantachrome Quantasorb instrument employing a flow technique, with nitrogen in helium. Densities were obtained on a Quantachrome null pycnometer. Infrared spectra were measured on a Beckman Acculab 10 spectrophotometer (mineral oil or Fluorolube mulls). Gas chromatography was carried out on a Hewlett-Packard 5830A. Routine NMR spectra were run on a Varian EM 360A spectrometer.

The following two procedures describe the preparation of zirconium 2-carboxyethylphosphonate of a low and relatively high crystallinity, as shown by the X-ray diffraction (Figure 6).

**Semicrystalline  $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ .** To a 25-ml three-necked flask fitted with a reflux condenser, stirrer, thermometer, and heating mantle were charged 21.8 mL of aqueous 38% 2-carboxyethylphosphonic acid (11.1 g) and 25 mL of  $\text{H}_2\text{O}$ . Stirring was commenced, and 9.2 g of  $\text{ZrOCl}_2$  in 10 mL of water was added. Immediately a

white precipitate was formed. Water (17 mL) was added to fluidize the slurry, and the temperature was raised to gentle reflux for 15 h. The slurry was cooled to room temperature, and the white solid, isolated by filtration, was washed on the filter with water, acetone, and then ether. The solid product was dried at  $110^\circ\text{C}$  to a constant weight (12.1 g).

**High-Crystalline  $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ .** The procedure is the same as above except that 4 mL of 48% HF was added to the initial mixture and a slow inert-gas purge ( $\text{N}_2$ ) was maintained during the reflux. Anal. Calcd: C, 18.23; H, 2.54; P, 15.7. Found: C, 18.42; H, 2.42; P, 15.5.

The infrared spectra in both cases were identical (run as mineral oil mulls). They showed  $\nu_{\text{CO}}$  at  $1690\text{ cm}^{-1}$  and  $\nu_{\text{PO}_3}$  as a broad envelope centered at  $1045\text{ cm}^{-1}$ .

Infrared spectra were routinely run on all of the products discussed in this paper and proved to be straightforward to interpret, both as a diagnostic for the presence of included water and as an affirmation of the presence of the various functional groups.

**Preparation of  $\text{Zr}(\text{O}_3\text{POCH}_2\text{CH}_2\text{CN})_2$  via the Barium Salt.** To a slurry of 6.28 g of  $\text{BaO}_3\text{POCH}_2\text{CH}_2\text{CN}\cdot 2\text{H}_2\text{O}$  (obtained from Matheson Coleman and Bell Co.) in 50 mL of water was added 2 mL of concentrated HCl. Then the solution was heated to reflux, as 1.10 g of  $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$  was added. A precipitate formed immediately, but the reaction was kept at reflux overnight. The product was filtered and washed with dilute (0.1 N HCl) acid, water, acetone, and ether to yield a white powder. After the product was dried at  $60^\circ\text{C}$ , it weighed 1.39 g, the expected value for  $\text{Zr}(\text{O}_3\text{POCH}_2\text{CH}_2\text{CN})_2\cdot \text{H}_2\text{O}$ . Anal. Calcd: C, 18.17; H, 2.27; N, 7.07. Found: C, 17.60; H, 2.76; N, 6.22. The infrared spectrum of the product, run as a Fluorolube mull, had a sharp absorption at  $2250\text{ cm}^{-1}$  attributable to the nitrile and broad bands at 1660 and  $3400\text{ cm}^{-1}$  arising from interlamellar water.

**Acknowledgment.** We are indebted to Vic Parziale, Peter Griffith, and Ricci Cooksey, without whose very able assistance and input into this effort we would not have been able to undertake this work.

**Registry No.**  $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{CO}_2\text{H})_2$ , 75406-99-4;  $\text{Zr}(\text{O}_3\text{POCH}_2\text{CH}_2\text{CH}_2\text{CN})_2$ , 75422-73-0;  $\text{Zr}(\text{O}_3\text{PCH}_2\text{Cl})_2$ , 75406-90-5;  $\text{Zr}(\text{O}_8\text{PH})_2$ , 28482-76-0;  $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_5)_2$ , 69031-88-5;  $\text{Zr}(\text{O}_3\text{PCH}_2\text{COOH})_2$ , 75431-28-6;  $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{COOH})_2$ , 75406-89-2;  $\text{Zr}(\text{O}_3\text{P}(\text{C}-\text{H}_2)_4\text{COOH})_2$ , 75407-09-9;  $\text{Zr}(\text{O}_3\text{P}(\text{CH}_2)_5\text{COOH})_2$ , 75431-29-7;  $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}=\text{CH}_2)_2$ , 75406-93-8;  $\text{Zr}(\text{O}_3\text{PCH}=\text{CH}_2)_2$ , 75407-05-5;  $\text{Zr}(\text{O}_3\text{PCH}_2\text{SCH}_2\text{CH}_3)_2$ , 75407-11-3;  $\text{Zr}(\text{O}_3\text{AsC}_6\text{H}_5)_2$ , 14658-59-4;  $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{SH})_2$ , 75431-30-0;  $\text{Zr}(\text{O}_3\text{P}(\text{CH}_2)_{10}\text{PO}_3)_2$ , 75349-03-0;  $\text{Zr}(\text{O}_3\text{AsC}_6\text{H}_4\text{Cl})_2$ , 75407-12-4;  $\text{Zr}(\text{O}_3\text{PCH}_2\text{OC}_6\text{H}_5)_2$ , 75407-06-6;  $\text{Th}(\text{O}_3\text{PC}_{18}\text{H}_{37})_2$ , 75406-85-8;  $\text{Ti}(\text{O}_3\text{PC}_6\text{H}_4\text{OCH}_3)_2$ , 75431-31-1;  $\text{Ti}(\text{O}_3\text{PCH}_2\text{Cl})_2$ , 75406-78-9;  $\text{Th}(\text{O}_3\text{POC}_6\text{H}_4\text{NO}_2)_2$ , 75431-32-2;  $\text{Ce}(\text{O}_3\text{PC}_6\text{H}_5)_2$ , 75406-80-3;  $\text{Th}(\text{O}_3\text{PCH}_3)_2$ , 75406-83-6;  $\text{U}(\text{O}_3\text{PCH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{H})_2$ , 75431-33-3;  $\text{Ti}(\text{O}_3\text{PCH}=\text{CH}_2)_2$ , 75406-87-0;  $\text{Ti}(\text{O}_3\text{PC}_6\text{H}_5)_2$ , 75406-75-6;  $\text{Th}(\text{O}_3\text{PC}_6\text{H}_5)_2$ , 75406-79-0;  $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{C}_6\text{H}_5)_2$ , 75431-34-4;  $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{Cl})_2$ , 75406-95-0;  $\text{Th}(\text{O}_3\text{PCH}_2\text{Cl})_2$ , 75431-35-5;  $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{PO}_3)_2$ , 75406-94-9;  $\text{Zr}(\text{O}_3\text{PCH}_3)_2$ , 25588-92-5;  $\text{Zr}(\text{O}_3\text{PCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{Br})_2$ , 75431-36-6;  $\text{Zr}(\text{O}_3\text{PC}_6\text{H}_{11})_2$ , 75431-37-7;  $\text{Th}(\text{O}_3\text{PCH}=\text{CH}_2)_2$ , 75406-88-1;  $\text{U}(\text{O}_3\text{PCH}_2\text{Cl})_2$ , 75406-77-8;  $\text{Zr}(\text{O}_3\text{POH})_2$ , 13772-29-7.

(24) Reference 17, p 265.