Organically Pillared Micro- and Mesoporous Materials

Abraham Clearfield

Department of Chemistry, Texas A&M University, College Station, Texas 77842-3012

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There is currently a great deal of research activity dealing with the synthesis and characterization of inorganic micro- and mesoporous materials. This activity not only stems from their possible use as sorbents, catalysts, molecular sieves, and related applications but also is due to fascination for their varied forms and novel structures. A somewhat promising but less thoroughly investigated topic is that of organically pillared layered compounds where the pillars are covalently bonded to the layers. These compounds are the cross-linked metal phosphonates of the type $M^{z+}{}_{4/z}(O_3P-R-PO_3)$, where R is an alkyl or aryl group. Because of the great variety of R groups containing different functional groups that can be used, these compounds have great potential utility. That this has not been realized is mainly due to the inability to control the pore sizes. The chemistry of this group of compounds will be reviewed and the prognosis for the future indicated.

Introduction

One area of solid-state chemistry that has shown remarkable growth over the past 25 years is that involving the synthesis and applications of porous materials. The classic porous materials include active carbons and oxides, such as silica and alumina. These materials are heterogeneous in the sense that they have a relatively broad pore size distribution.[1−6] A milestone in the field of porous materials was achieved through the development of synthetic zeolites. These crystalline aluminosilicates possess cavities of precisely defined geometries with pores in the range of 3−12 Å.[7,8] The remarkable success of zeolites as catalysts, sorbents, and ion exchangers has fueled an enormous amount of basic and applied research.[9−11]

Aluminophosphate gels combined with amine templates, when treated by synthetic techniques similar to those employed in zeolite synthesis, yielded a family of porous, crystalline aluminophosphates.[12,13] Several of these compounds exhibited pores significantly larger than those in the aluminosilicate system.[14,15] Subsequently, zeolite-like zinc phosphate,[16] gallophosphates,[17] and vanadium phosphate[18] have been prepared. The thermal stability of these compounds is generally much lower than that of the aluminosilicate zeolites and limits their application to lower temperatures.

A significant amount of effort was expended in attempts to prepare nanoporous materials other than zeolites and zeolite-like compounds. The hope was that these new materials would overcome the limitations in the size of the zeolite cavities and entranceways into the cavities. One such group of materials is the pillared clays.[19] These composites were found to contain both micropores and mesopores and to exhibit a diversity of behaviors depending upon the nature of the clay and pillar type.[20−22] Many layered compounds other than clays have been pillared.[23−25] Although few commercial uses of these composites have developed, their uses as catalysts,[22] as sorbents for gas separations,[22,26] and as ion exchangers are being actively investigated.[27]

A breakthrough in the synthesis of mesoporous materials was achieved by researchers at Mobil Oil Corp. with the discovery of the M41S family of compounds.[28] Advances in synthetic procedures and new materials were rapid in coming.[29−31] The key element was the use of surfactant molecules as templates. The pores are uniform in size and can be controlled to pore sizes ranging from small (∼15 Å) to large (>100 Å). The surfactants may be positively charged,[28] negatively charged,[29] or neutral.[31] Removal of the templates produces materials of exceptionally high surface areas.

Concomitant to these developments are the application of sol−gel chemistry[32] and aerosol methods[33] to the synthesis of porous metal oxides. Use of these techniques allows better control of pore size and pore size distribution, surface area, and other textural properties. Impressive advances have also been made in the field of porous carbons. Molecular sieve carbons have pores of molecular dimensions and have been used to separate molecules in the 3−10 Å range.[33] These materials are prepared by carbonization of polymers in the 400−800 °C range. More recently carbon nanotubes have been prepared[34] and intensively studied.[35]

Our fascination with zeolites has led investigators to attempt the preparation of sulfur analogues. Indeed several of them have been synthesized.[36] Finally, we may consider the recent activity in producing microporous solids via self-assembly of metal−organic[37] and organic frameworks.[38,39] A wide variety of such complex structures has been assembled with extended or open frameworks. However, in many cases interpenetrating structures form or large open spaces usually contain guest molecules necessary to provide stability. Removal of the guest leads to collapse of the framework. Nevertheless a host of extremely interesting and in some cases stable structures has been obtained.[37d]

In this paper we describe a group of relatively stable structures based upon phosphonate chemistry. The challenge is to control the pore size and pore homogeneity. The reward is the ability to functionalize the

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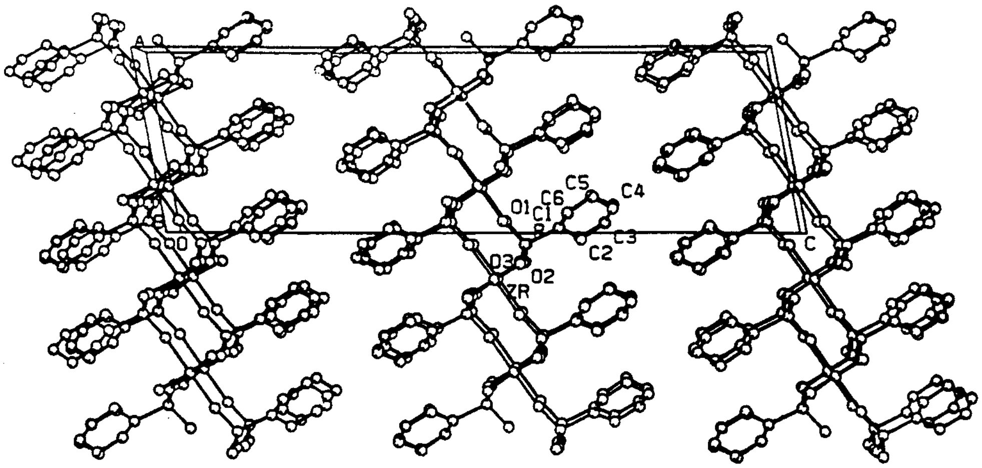


Figure 1. Projection of the structure of zirconium phenylphosphonate as viewed down the short *b*-axis.

Table 1. Interlayer Distances Found for Cross-Linking Groups

compd	d-spacing from XRD (Å)
$Zr(O_3PCH_2CH_2PO_3)$	7.8
$Zr(O_3PCH_2CH_2CH_2PO_3)$	no reflecn obsd
$Zr[O_3P(CH_2)_{10}PO_3]$	17.2
$Zr(O_3PC_6H_4PO_3)$	9.6
$Zr[O_3P(C_6H_4)_2PO_3]$	13.9
$Zr[O_3P(C_6H_4)_3PO_3]$	18.5
$Zr[O_3PCH_2(C_6H_4)CH_2PO_3]$	10.8

organics to produce physical and chemical properties by the choice of metal and functionalized ligand.

Porous Pillared Zirconium Phosphonates

α-Zirconium Phosphonates. One of the first zirconium phosphonates synthesized was the phenylphosphonate,[40a] $Zr(O_3PC_6H_5)_2$. This compound is poorly crystalline, but upon hydrothermal treatment in dilute HF for 30 days it was possible to prepare a more crystalline powder. This sample was supplied by Alberti and Costantino and the crystal structure solved from a limited (35 reflections) powder data set.[40b] A projection of the structure as viewed down the short *b* axis is provided in Figure 1.

Dines et al.[41] conceived of the idea of carrying out the reaction using terminal bisphosphonic acids to cross-link the layers. Both alkyl and aryl bis(phosphonates) were prepared. The interlayer (basal) spacings for these compounds, as reported by Dines, are given in Table 1.

A schematic representation of the zirconium biphenylenebis(phosphonate) is shown in Figure 2. This representation makes it clear that there should be no micropores present because of the closeness of the phenylene pillars (~5.3 Å). Therefore, to create the desired microporosity, mixed-component derivatives were prepared in which a small group such as H, OH, or Me, was interposed between the larger pillaring groups, as illustrated in Figure 3. The lateral pore dimension is dictated by the density of pillars, whereas the pore height is determined by the length of the pillar. It should be pointed out that these observed interlayer spacings are very close to calculated values based upon structures depicted in Figures 2 and 3. Dines et al.[41] prepared a series of phosphite bis(phosphonates) based on the biphenyl pillar. They used surface area measurements based on the one point N_2 Brunauer−Emmet−Teller (BET) method as a means of verifying pillaring. The idea is that there would be very little change in the external surface area from sample to sample. Therefore, any increase in surface area would stem from the increased microporosity. Indeed the particle size was constant (0.06 μm in diameter), and the surface area increased as the amount of phosphite incorporated increased, as shown in Figure 4. For example, at 50 mol % the surface area was 481 $m^2\ g^{-1}$ versus 316 $m^2\ g^{-1}$ for the 100% product. To show that microporosity was indeed responsible for the increase in surface area, the sample containing 30 mol % biphenyl pillars was allowed to sorb nonane, whereupon its measured surface area dropped precipitously. The pore size was estimated to be 8.3 × 5 Å, but no pore size measurements were actually carried out. One of the questions left unanswered by this study was the high surface area of $Zr(O_3PPhPhPO_3)$, 316 $m^2\ g^{-1}$. This compound should have no micropores, and the particle size is too large to create such a large surface area.

In an effort to provide information on several questions left unanswered by the Dines group, additional studies were undertaken in our laboratory.[42] Two types of reactions were carried out, those for which no HF was included and reactions run in the presence of HF. The phosphonic acid employed was 4,4′-biphenylenebis(phosphonic acid), $H_2O_3PC_6H_4C_6H_4PO_3H_2$, either alone or mixed with phosphorous or phosphoric acid and in some cases ethyl phosphate. In each case, the zirconium solution was added to the acid. In the reactions containing no HF, the precipitate that formed initially was refluxed for 18 h. The HF containing reactions were carried out at 60−70 °C in an open container. These products were much more crystalline than those obtained by the reflux method without added HF.[43] The situation as far as surface area and pore size are concerned is complex and depends on the solvent used in the reaction, as detailed below. The X-ray powder patterns of these preparations show a major peak at 13.8 Å with a second order of this reflection at 6.9 Å. These reflections are a clear indication of an interlayer spacing of this magnitude considering the reflections as (001) and (002). A typical X-ray pattern for the HF preparations is given in Figure 5. This spacing is very close to what is expected from the length of the biphenyl group (7.05 Å) and the thickness of the inorganic layer.

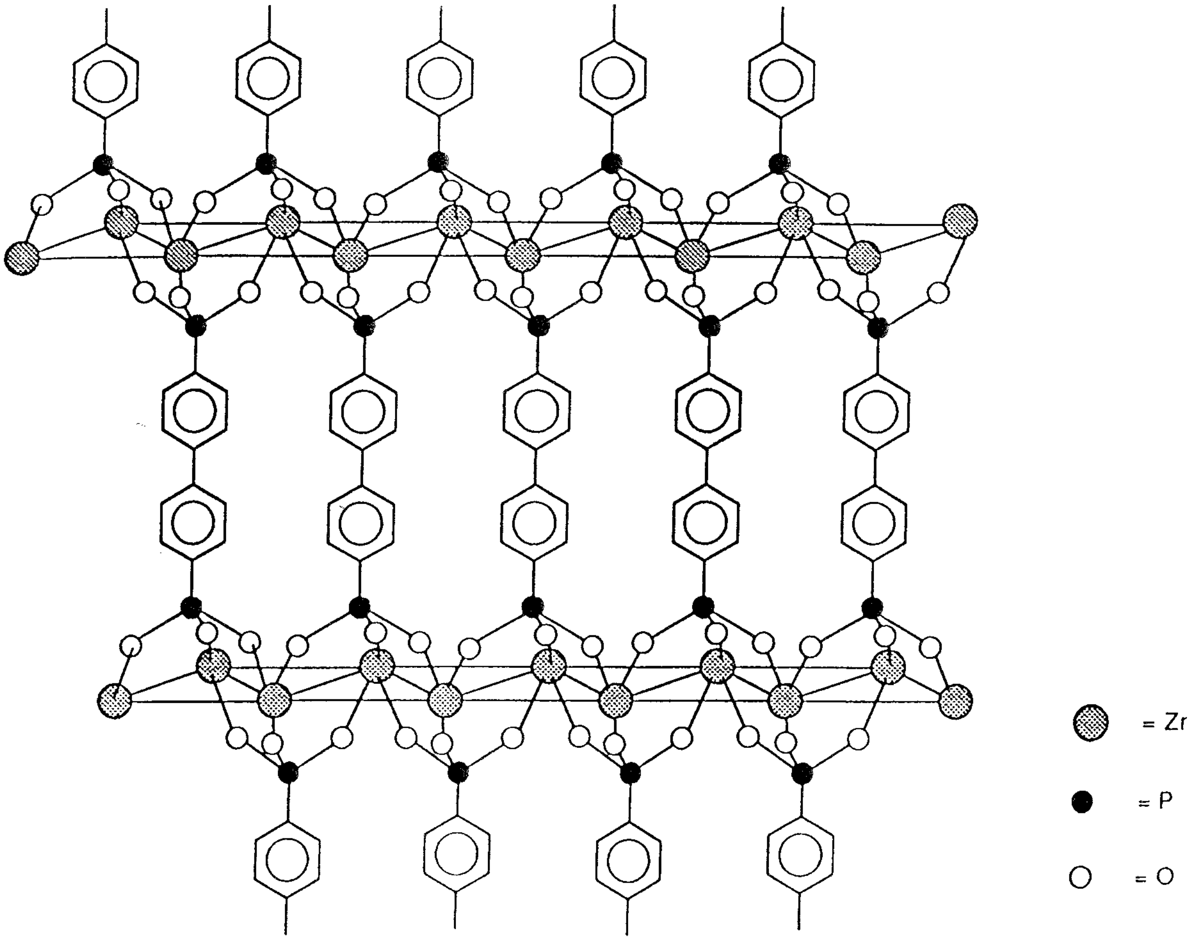


Figure 2. Idealized conception of a portion of the structure of $Zr(O_3PC_6H_4C_6H_4PO_3)$ showing the cross-linking of the layers indicating that no microporosity is to be expected in this compound.

The latter value is derived from the layer thickness of α-ZrP, 6.3 Å,[44] augmented by the difference in bond lengths of P−C (1.80 Å) and P−O (1.55 Å). From this analysis, it would be expected that the surface area would depend on the particle size distribution. However, the surface areas were much larger than could be accounted for on the basis of particle size.[42] The compounds prepared in dimethyl sulfoxide (DMSO) appeared to be grouped into two categories. Those that were prepared in DMSO diluted with benzene had relatively low surface areas (133−213 $m^2\ g^{-1}$) and no micropores. The average pore radius was in the range 48−90 Å. In contrast, when the synthesis was carried out in concentrated DMSO solutions, the surface areas ranged from 270 to 397 $m^2\ g^{-1}$ and there was a significant contribution from micropores (25−50% of the surface area). The average pore size of these products was in the range 11−15 Å. Finally, the products obtained from the alcohol−water mixtures were high in surface area and had intermediate pore sizes (average 24−30 Å). These preparations were carried out in considerably more dilute solutions than any of the DMSO preparations because of the low solubility of the biphosphonic acid in this medium. Yet the textural properties were intermediate to those prepared in diluted and concentrated DMSO solutions. Thus, it appears that the solvent plays a significant role in determining the textural properties of the end product. Typical BET N_2 sorption−desorption curves for two types of these compounds are shown in Figure 6.

The ^{31}P MAS NMR spectrum of the zirconium biphenylenebis(phosphonate) contains a major peak at −4.8 ppm ascribed to the phosphorus atoms that belong to the phosphonate bonded to zirconium. A second weak resonance is also present at +4.2 ppm and is attributed to the unbonded end of a surface located phosphonic acid group. By way of comparison the ^{31}P spectrum for zirconium phenylphosphonate, $Zr(O_3PPh)_2$, contains a single peak at −5.1 ppm. In this compound, all of the phosphonate groups are bonded to zirconium atoms, giving rise to the single resonance. The free acid $PhPO_3H_2$ contains a single peak at +15 ppm and biphenylenebis(phosphonic acid) yields a single resonance at +15.3 ppm (relative to H_3PO_4 at 0 ppm). Thus, the observed weak resonance at +4.8 ppm is not due to free acid but, rather, we believe, to diphosphonate groups, one end of which is bound to zirconium but the other is not.

To account for the high surface area and the pore structure, we proposed a model that is shown schematically in Figure 7. The pores result from the coming together of layers of unequal size. Thus, one layer may terminate, while another bonded to it keeps growing laterally and then binds to other layers leaving a gap. Variations on this procedure are readily envisioned to give pores of different sizes from large mesopores, which may be strictly between particles to micropores and pores of intermediate size. The solvents used and the concentration of reagent in these solvents mediate the type of porous structure obtained. By studying these

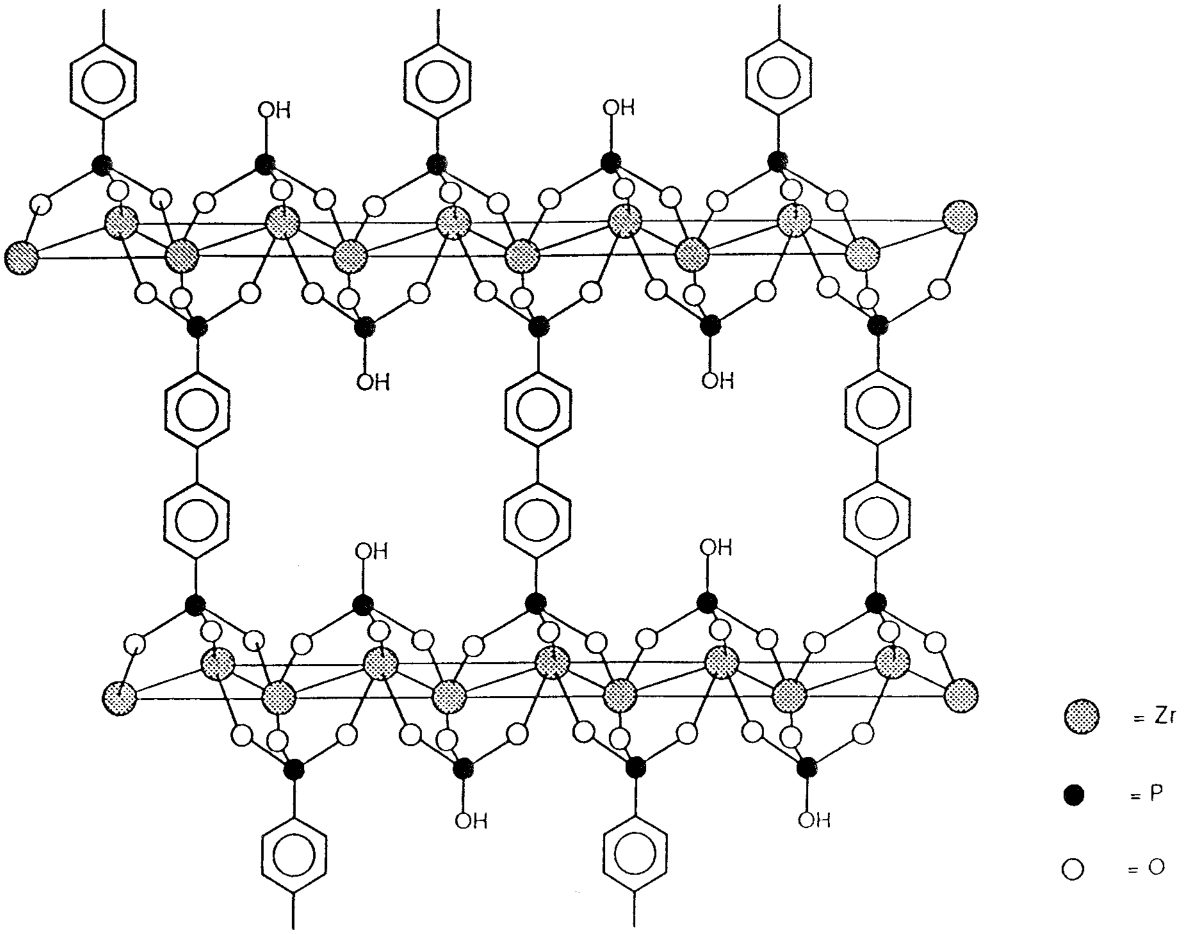


Figure 3. Idealized conception of the structure of $Zr(O_3PC_6H_4C_6H_4PO_3)_{0.5}(HPO_4)$ showing how the pillars may be spaced to produce microporosity.

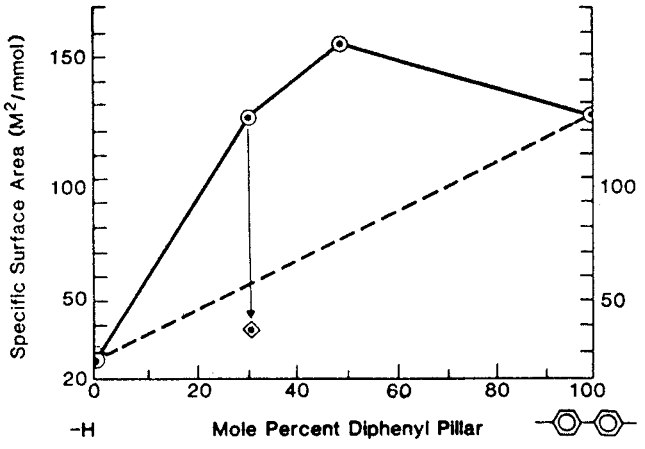


Figure 4. Variation of the specific surface area of the mixed component zirconium phosphite phosphonates, $Zr(O_3PH)_{2-2x}$-$(O_3PC_{12}H_8PO_3)_x$, as a function of the composition. The point denoted with a diamond was measured after sorption of nonane Reproduced with permission from ref 41. Copyright 1982 American Chemical Society.

effects, it may be possible to control the pore size to fit reactions of different sized molecules. In this connection, we have sulfonated these porous materials in fuming sulfuric acid. The resultant products contain about 3% sulfur, which amounts to sulfonation of about 25% of the rings. Thus, we interpret this result to mean that only those groups lining the pores are sulfonated. The pores become highly hydrophilic, and extreme measures are required to obtain dry products. These sulfonates may exhibit interesting catalytic behavior that has yet to be investigated.

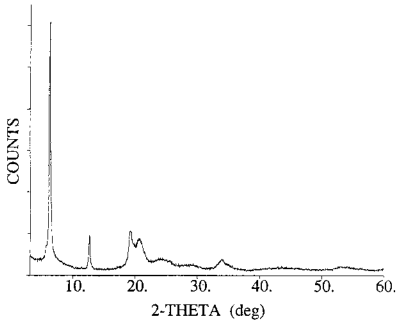


Figure 5. X-ray diffraction pattern of zirconium biphenylenebis(diphosphonate) prepared by refluxing in HF.

There are several major differences between the HF prepared compounds and the refluxed products. With the more crystalline HF treated products, the range of compositions obtained from mixed derivatives containing phosphate or phosphite was limited.[43−46] The bis(phosphonic acid) was always present in greater amount for these reactions. With more amorphous materials (no HF present), the full range of compositions, that is, a complete solid solution, could be prepared. These compounds generally had higher surface areas than the HF treated products, but there was no regular pore structure. Pores ranging in radius from 5 to 100 Å were obtained. In contrast, the HF treated products had a bimodal pure distribution, one range of pore sizes being

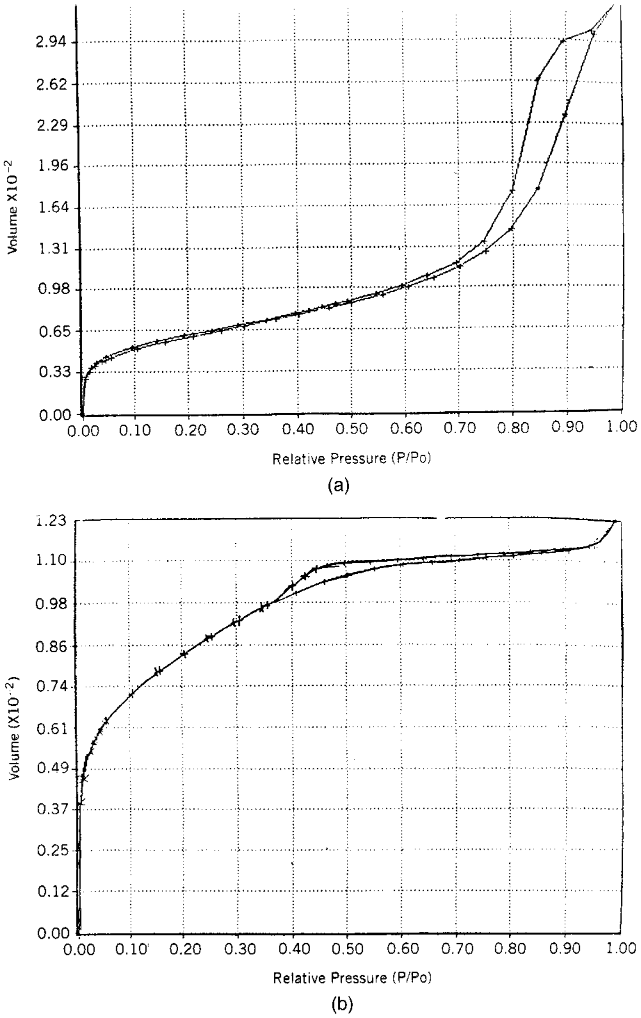


Figure 6. BET sorption–desorption curves of $Zr(O_3PC_{12}H_8PO_3)$: (a) surface area 213 m^2/g, 10 m^2/g in micropores; (b) surface area 308 m^2/g, micropores accounting for 135 m^2/g of the surface area.

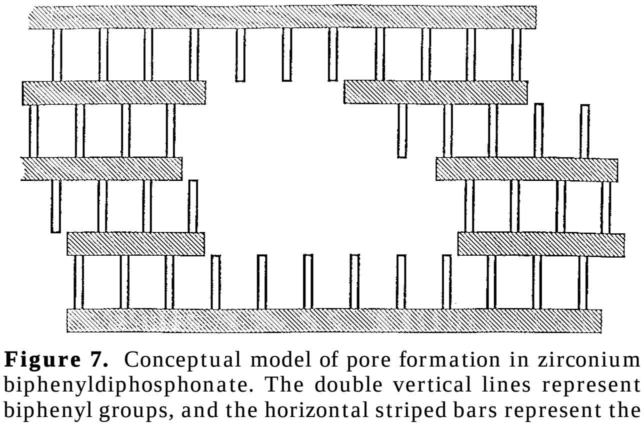


Figure 7. Conceptual model of pore formation in zirconium biphenyldiphosphonate. The double vertical lines represent biphenyl groups, and the horizontal striped bars represent the inorganic PO_3ZrO_3P layers. The biphenyl groups protruding into the pore have free PO_3H_2 groups signified by connecting the two parallel vertical lines.

in the micropore region and the other centered in the mesopore region.[47]

The compounds described above contain a mixture of micropores and mesopores, the ratio depending on the synthetic method. However, Alberti et al.[48] used a clever tactic to obtain a pillared microporous α-type zirconium phosphonate with a very narrow pore size distribution. By placing methyl groups on the ring positions α to the phosphonate groups, they created pillars too large to fit adjacent to each other at a distance of 5.3 Å required by the α-type layer structure. For this purpose 3,3′,5,5′-tetramethylbiphenylenebis(phosphonic acid) (**1**) was synthesized

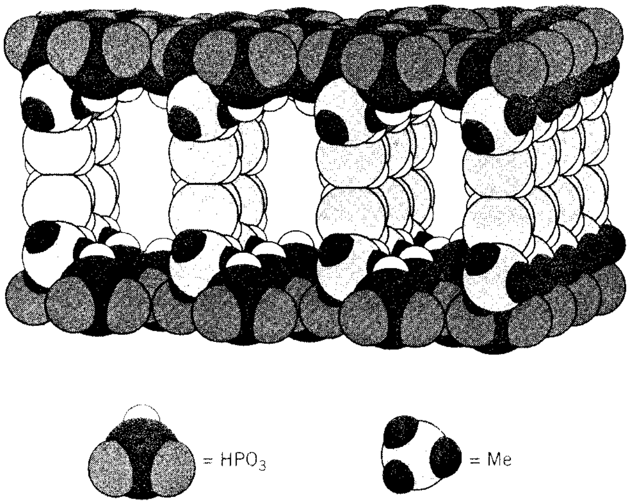
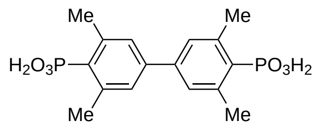


Figure 8. Computer generated model of the pillared microporous compound with ideal composition $Zr(HPO_4)_{1.34}(O_3PRPO_3)_{0.33}$, where R = $-C_{12}H_8-$. Reproduced with permission from ref 48. Copyright 1993 VCH.



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A mixture of **1** and H_3PO_3 in DMSO was reacted with $ZrOCl_2$ in HF as before. The phosphite served to separate the pillars so that they were never adjacent to each other. Otherwise, the methyl groups would sterically hinder each other. It requires a 4:1 ratio of phosphite/phosphonate to avoid steric interactions. Thus, the composition of the product was $Zr(HPO_3)_{1.34}(O_3PRPO_3)_{0.33}$, and a computer drawn model of the structure is shown in Figure 8. The interlayer spacing is 14.5 Å, and a narrow pore size distribution centered at about 6 Å was observed.[48] The specific surface area as determined from BET analysis was 375 $m^2\ g^{-1}$.

Derouane and Jullien-Lardot[49] prepared a series of *n*-alkyldiphosphonate pillared zirconium compounds in methanol containing HF as did Yang.[43] The reactants were treated hydrothermally for 3–175 h, but no temperature of treatment was given. The products had surface areas in the range of 132–314 $m^2\ g^{-1}$ for the octyldiphosphonate and a constant mean pore diameter of 38 Å. One other point needs to be emphasized. Elemental analysis almost always showed a P/Zr greater than 2,[50] and this value was attributed to the fact that over the high observed surface area only one of the acid groups of the bis(phosphonic acid) was bonded to the layer and the other was free. Thus, the formula had to be modified to take this fact into account. For example, if P/Zr = 2.2, then the formula is $Zr(O_3PRPO_3)_{0.9}(O_3PRPO_3H_2)_{0.2}\cdot nH_2O$. This excess of phosphated organic could also be observed by the increased weight loss measured by thermogravimeric analysis (TGA).[44,46] Al-

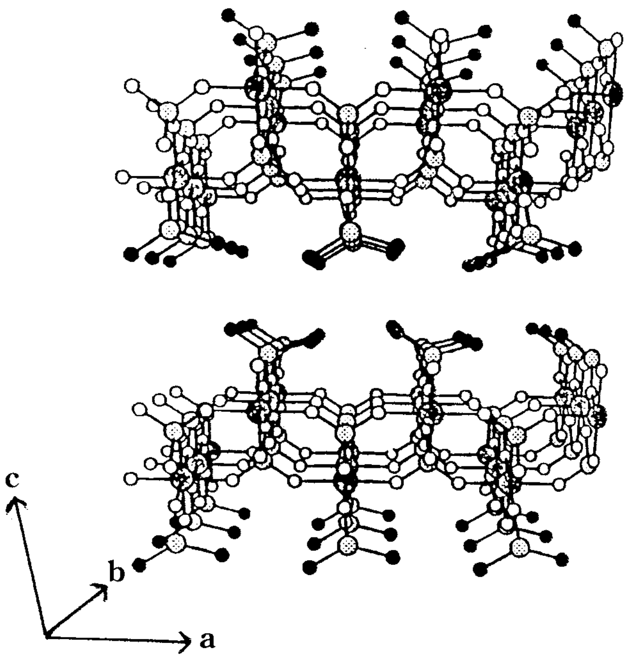

Figure 9. Schematic representation of γ-zirconium phosphate, $Zr(PO_4(H_2PO_4)\langle 2H_2O$. The water molecules are omitted for clarity.

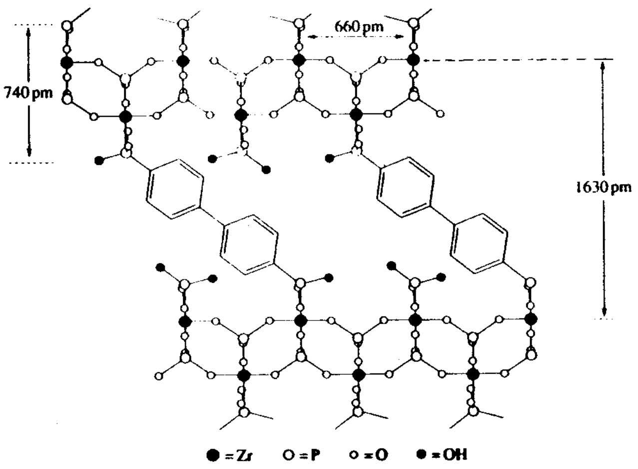

Figure 10. Computer generated model of two layers of γ-zirconium phosphate pillared by 4,4′-biphenyldiphosphonate groups. The approximate formula is $Zr(PO_4)(H_2PO_4)_{0.75}(HO_3PC_{12}H_8PO_3H)_{0.125}$. Reproduced with permission from ref 57. Copyright 1994 VCH.

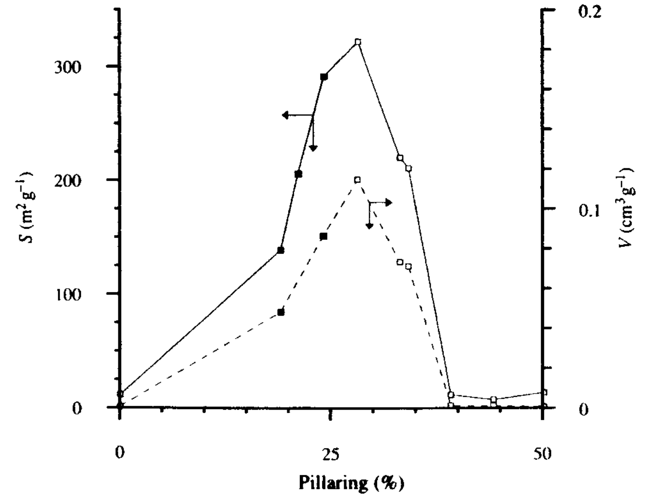

Figure 11. Specific surface area S and volume V of the micropores for anhydrous samples of $Zr(PO_4)(H_2PO_4)_x(HO_3PC_{12}H_8PO_3H)_{1-x/2}$ as a function of the degree of pillaring. [□] and [■] refer to monophase and biphase systems, respectively. Reproduced with permission from ref 57. Copyright 1994 VCH.

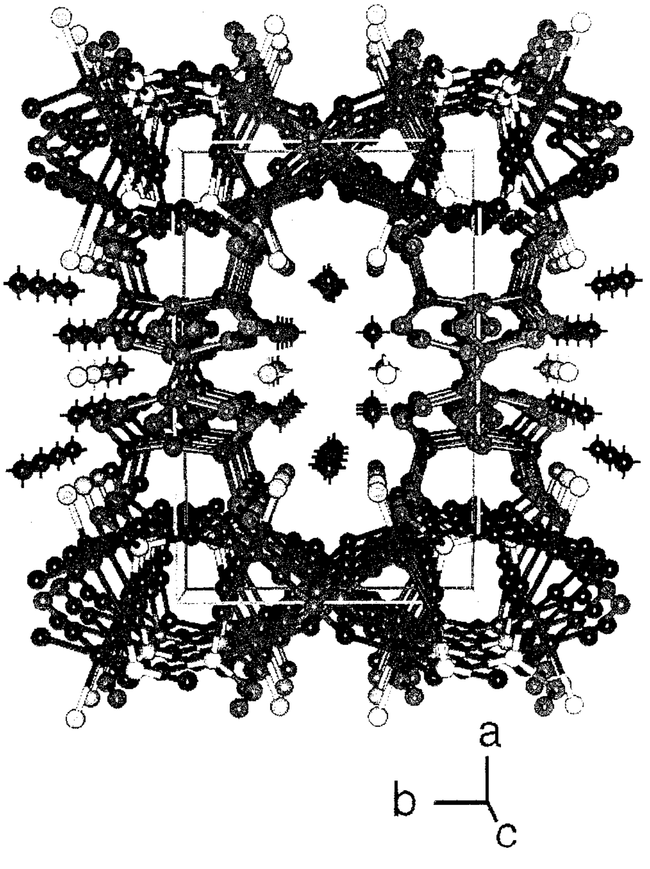

Figure 12. Structure of $Zr_2(PO_4)PVF_3$ viewed down the c-axis showing the cavities filled by water molecules (dark) and fluoride ions.

berti et al.[50] arrived at the same formulation, carried out titrations of the free protons, and found correspondence between the number of free groups determined by titration and elemental analysis. To account for the pore dimensions, surface area, and free groups, we proposed a structure as illustrated in Figure 7 as a working hypothesis. The pores are thought to arise from gaps in the layers that grow at different rates, depending on the availability of reactants. Alberti et al.[48] suggest the hypothesis that DMSO acts as a template around which the layers grow. This hypothesis seems reasonable from our results. Dilution of the DMSO changes the nature of the micelles, accounting for the change in pore size. Also, the very large amount of solvent trapped in the pores, up to 75 wt %, also accords with this idea. Derouane and Jullien-Lardot[49] proposed a somewhat similar but more restricted structural model to account for the pores formed in alkyldiphosphonates and the increased layer spacing.

It was found that addition of excess phosphorous acid in the synthesis of mixed zirconium phosphite/phosphonates in organic solvents induced the formation of a high percentage of mesopores in the products.[50] Compounds with high surface areas in the range of 300−500 m^2/g with a distribution of micropores and mesopores were

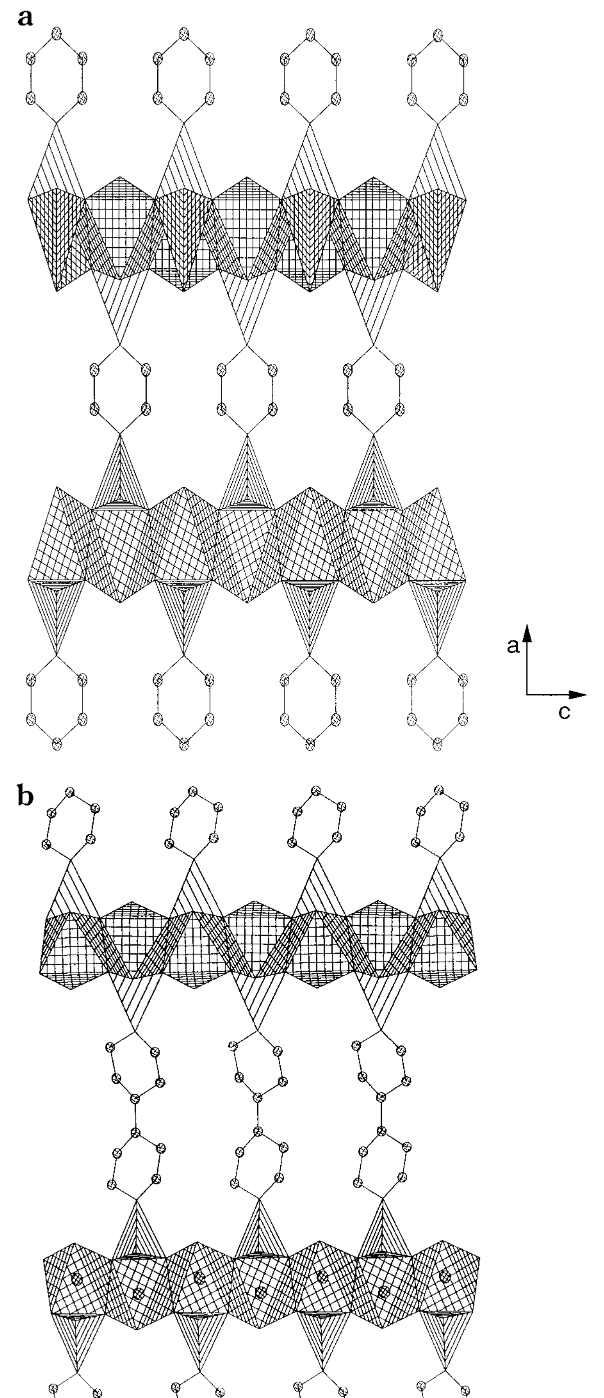

Figure 13. Polyhedral representation of zinc phenylenebis(phosphonate) $Zn_2(O_3PC_6H_4PO_3)\cdot 2H_2O$ (a, top) and $Zn_2(O_3PC_{12}H_8PO_3)\cdot 2H_2O$ (b, bottom).

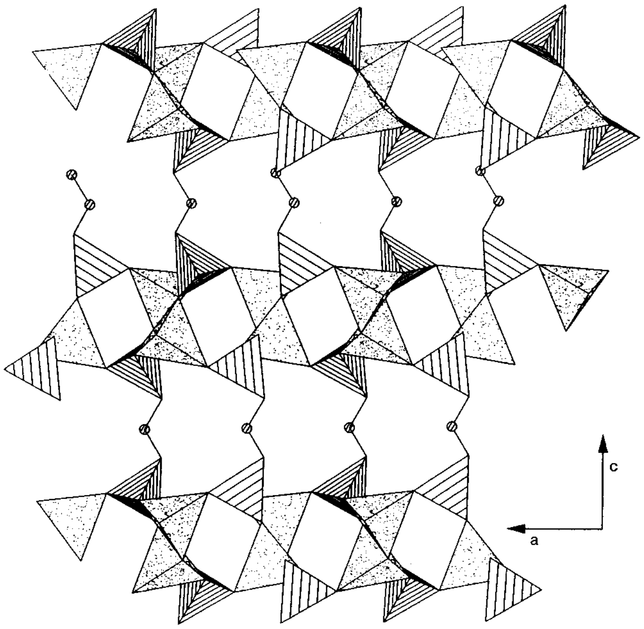

Figure 14. Polyhedral representation of the structure of $Zn_2[(O_3PC_3H_6PO_3]$ viewed down the *b*-axis. The adjacent alkyl groups as seen in this projection are shifted $^1/_2$ along the *b*-axis. The zinc tetrahedra are stippled, and the phosphonate groups are striped.

obtained. The dimensions of the pores could be changed by changing the ratio and concentration of the reagents. These results resemble those already described for the mixed phosphate−phosphonates. Treatment of the aryl pillared products in fuming sulfuric acid introduces sulfonic acid groups into the aromatic rings.[47,51] Even if the interiors of the particles contain no pores, the external surface may be sulfonated. Both the porous and external surface modified particles exhibit ion exchange and catalytic behavior. The non-cross-linked zirconium sulfophenylphosphonate is also an excellent proton conductor.[51b] These qualities of the pillared compounds and the fact that the pore size and structure may be manipulated by the synthetic procedure make this area of research an important and intriguing one.

γ-Zirconium Phosphonates. γ-Zirconium phosphate, $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$, was discovered[52] shortly after the α-compound was crystallized from amorphous zirconium phosphate gels.[53] Its structure has recently been solved[54] as well as that of the titanium analogue.[55] As the formula implies, there are both orthophosphate and dihydrogen phosphate groups within the layers. The orthophosphate group bonds to four different metal atoms, alternating in an up−down fashion, as shown in Figure 9. Two of the phosphate oxygens run parallel to the *a*-axis, and the other two are directed at right angles parallel to the *b*-axis of the monoclinic unit cell. The dihydrogen phosphate groups reside on the outer periphery of the layer utilizing two oxygens to bridge across metal atoms in the *a*-direction. The two hydroxyl groups extend into the interlamellar space and hydrogen bond to the two water molecules holding the layers together in a network of hydrogen bonds.

γ-type phosphonates cannot be formed directly as only α-type derivatives result. This is a consequence of the phosphonate group having only three oxygens available for bonding, whereas four are required in the form of orthophosphate in order to obtain a γ-type layer.[56] However, such derivatives may be formed by topotactic replacement of the dihydrogen phosphate groups, and a large variety of such compounds have been prepared.[56] Of interest in this discourse are the pillaring reactions utilizing diphosphonic acids. Small molecules such as 1,4-phenylene diphosphonic acid and the corresponding biphenyldiphosphonic acid reacted at appreciable rates at 80° C in dilute solution (0.1 M). On this basis it was found that the corresponding biphenyldiphosphonic acid topotactically replaced the H_2PO_4 groups.[57] The amount

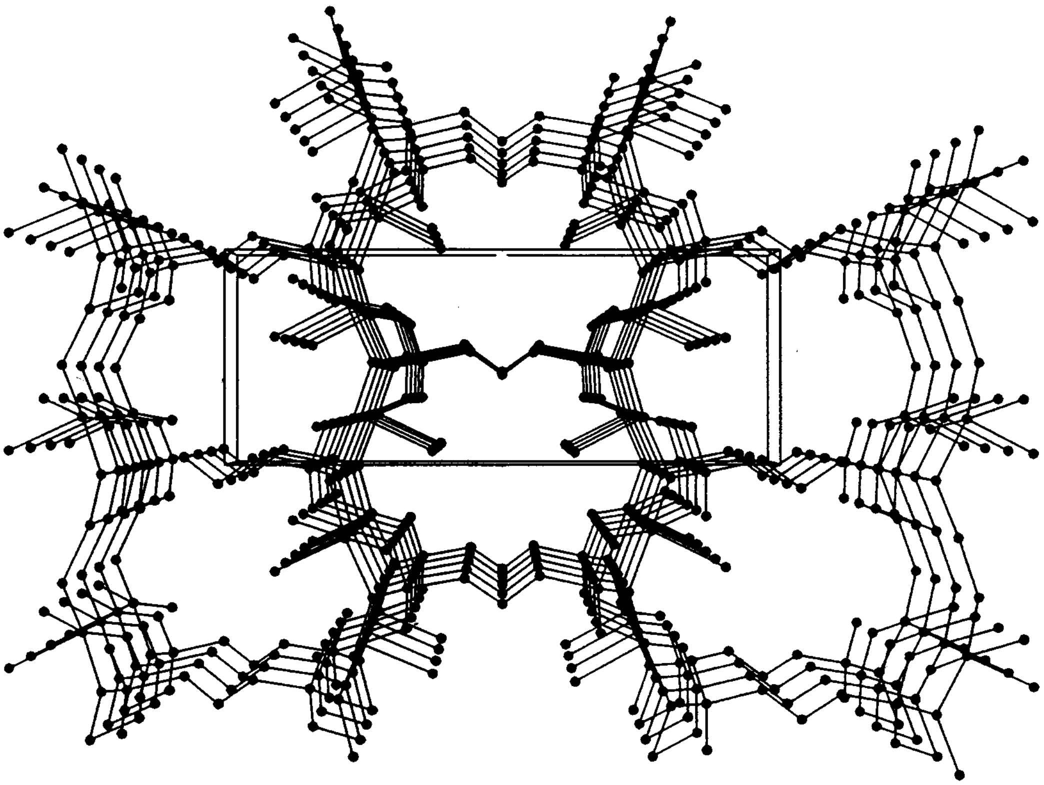

Figure 15. Structure of $Cu_2[(O_3PC_3H_6PO_3)(H_2O)_2]\langle H_2O$ as viewed down the *a*-axis showing the one-dimensional pores. A water molecule (not shown here) occupies the center of these pores and hydrogen bonds to the water molecules coordinated to Cu which are also projected into the pores.

of replacement is conditioned by the concentration of the reactants and steric factors. The distance between phosphorus atoms in the *a*-direction is 5.4 Å and in the *b*-direction 6.64 Å. Thus, if the hydroxyl groups of the dihydrogen phosphates are replaced by alkyl chains, $O_2P(R)_2$, the chains will overlap adjacent positions and only a very limited topotactic reaction can occur. However, if a single chain compound is utilized, the amount of replacement depends on the bulk and rigidity of the organic group.

Alberti et al.[57] was able to prepare a solid solution series of the type $Zr(PO_4)(H_2PO_4)_{1-x}(HO_3P-C_{12}H_8-PO_3H)_{x/2}$ with $x \cong 0.1-0.58$. A schematic representation of the structure is shown in Figure 10. The surface area of these compounds as well as their stability depended upon the degree of pillaring. Figure 11 shows the variation of the specific surface area as a function of the amount of biphenyl cross-linking of the layers. When the degree of pillaring was below 25%, the layers collapsed to γ-zirconium phosphate as dehydration at 200 °C occurred. In the range of 25−44% pillaring the structure was stable to dehydration. The average pore diameter is 5.8 Å. The Alberti group is attempting to introduce functionalized groups (carboxyl, sulfonic) into these microporous materials.

Alkyl Viologen Compounds. We have seen that when the pillaring group is too large to fit into the 24 Å^2 of surface required for a phosphate group in the α-type layer, it could force the pillars to take alternate sites. This was the case for 4,4′-tetramethylphenylenediphosphonic acid.[48] Of course a second spacer group such as phosphate or phosphite is required to occupy sites adjacent to the pillars. Thompson and co-workers[58] inadvertently made use of this principle in efforts to impart photochemical character to the compounds. They reacted *N*,*N*′-dibutyl viologen bis(phosphonic acid) with aqueous H_3PO_4 and HF in a Teflon lined pressure vessel at 190−200 °C. The compound obtained, $Zr_2(PO_4)(PV)F_3{\cdot}3H_2O$, where PV = the viologen phosphonate group, had the structure schematically depicted in Figure 12. The structure was solved from X-ray powder data and refined by Rietveld methods.[58] The viologen phosphonate molecules bridge the inorganic layers and form a criss-cross stack. This stacking reduced the electrostatic repulsions of adjacent viologen groups. The closest face-to-face contact between viologen groups in the *c*-axis direction (perpendicular to the page in Figure 10) is 4.6 Å. The layers contain orthophosphate groups that bond to four Zr atoms in much the same way as in γ-zirconium phosphate. The phosphonate groups then bridge to three different Zr roughly parallel to the *a*, *b*, and *c*-unit cell directions and the sixth coordination site on Zr is occupied by F^-. The distance from viologen group to viologen group across the pore is about 8 Å, and this space is occupied by the three water molecules and the remaining fluoride ions.

Thompson et al.[59] prepared catalysts from this porous zirconium viologen compound by incorporation of active metal species such as Pt and Pd. This incorporation was accomplished by exchange of anionic metal halides $[MX_4]^{2-}$ for the F^- in the pore. Treatment of the exchanged solid with hydrogen gas reduces the salts to colloidal metal particles. In the process, the viologen groups were also reduced, taking on a blue or purple color. Exposure of the reduced material to air results in bleaching of the solid with production of hydrogen peroxide. If streams of H_2 and O_2 are passed through an aqueous suspension of the porous metal containing material, H_2O_2 is produced. Mixed platinum–palladium catalysts worked best. This catalytic reaction is reminiscent of the reduction of O_2 by colloidal copper[60a] or silver[60b] metal dispersed on the surface of zirconium phosphate. As a stream of air was passed over these materials, the metal particles were oxidized and diffused back into the zirconium phosphate while the protons present at the exchange sites diffused to the surface forming either H_2O_2 or H_2O.

Pillared Divalent Metal Phosphonates. One of the difficulties in obtaining highly crystalline group 4 pillared or cross-linked phosphonates is their lack of solubility. As a result Ostwald-type ripening is extremely slow. We have indicated that an often used technique is to add HF to the mix as a solubilizing agent in sufficient amount to form the hexafluoro complex MF_6^{2-}. On heating, the metal ion is slowly released, producing a homogeous precipitation effect and a slow resolution–precipitation mechanism. While this technique produces better crystallinity, in many cases the improvement is still insufficient for structure determination. As an illustration, zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$, required 30 days of hydrothermal treatment before a powder pattern with about 35 reflections was obtained.[61] Fortunately, this preparation was sufficient to solve the structure.[62] However, in other cases the hydrothermal treatment results in fluoride bonding to the metal, as with the viologen compounds and others.[62]

In contrast to the group 4 metal phosphonates, divalent metal derivatives are generally soluble in acid solutions and single crystals are often obtained. This fact is illustrated by the detailed structural knowledge that is now available concerning these compounds.[62] Therefore, it was of interest to prepare and crystallize pillared derivatives of these metals. This course of action indeed proved to be fruitful as it was possible to obtain the structures of copper[63] and zinc phenylenebis(phosphonate),[64] $Zn_2(O_3PC_6H_4PO_3)\cdot 2H_2O$, and copper[63] and zinc biphenylenebis(phosphonate),[65] $Zn_2(O_3PC_{12}H_8PO_3)\cdot 2H_2O$ illustrated in Figure 13a,b. The structures were solved from their X-ray powder patterns. In the zinc compounds the layers have the same structure as the parent compound, $Zn(O_3PC_6H_5)\cdot H_2O$[66] with the phenyl ring cross-linking the layers through the aryl rings. The distortion or apparent bending of the biphenyl rings in the diagram results from the fact that the rings are rotated through an angle of 62° relative to each other. This is an unexpected but reasonable result required to facilitate the bonding requirements of the phosphonate groups within the layers.

As expected the zinc pillared compounds are not porous. A start has been made in preparing mixed phosphate/phosphonate derivatives. Initial experiments show that significant mesoporosity results from partial substitution of phosphate for the phosphonate groups.[65] However, the problem is the same as that experienced with mixed zirconium derivatives, with the structure disorder leading to mesoporosity.

A number of zinc and copper alkylene pillared derivatives have now been prepared and their structures determined.[67] In the zinc compounds cross-linked by alkyl chains with even numbers of carbon atoms ($n = 2, 4$) narrow slitlike cavities are formed. The Zn atoms have a distorted octahedral coordination as in the phenylphosphonate compound.[66] However, in the propylenediphosphonate the zinc atoms are four-coordinate and they have a more regular shape, as shown in Figure 14. The distance between propylene chains is too narrow to obtain measurable porosity. However, the corresponding copper compound, $Cu_2[(O_3PC_3H_6PO_3)(H_2O)_2]\cdot H_2O$, does have larger one-dimensional tunnels, as illustrated in Figure 15. The copper atoms are five-coordinate with a distorted pyramidal arrangement similar to that in other copper phosphonates.[68] The copper atoms are separated by the cross-linking propylene chain by 6.76 Å. Each copper atom is coordinated by a water molecule which protrudes into the tunnel. These water molecules on either side of the tunnel hydrogen bond to another water molecule in the center of the tunnel. The compound may be completely dehydrated at 200 °C without loss of its framework structure, leaving an open coordination site on the Cu^{2+} ion and a cavity large enough for small molecules to enter. Using larger alkyl chains and attempting to space the pillars with phosphate, phosphite, or methylphosphonate groups should produce larger pores. However, more needs to be known as to how the smaller units alternate with the cross-linking chains. Since the X-ray powder patterns are maintained at low levels of phosphate substitution, it may be possible, using powder diffractometry and other forms of spectroscopy, to obtain much needed structural information by a combination of X-ray, spectroscopic, and pore size measurements.

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