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PERSPECTIVE

Organically pillared microporous zirconium phosphonates

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There is great technological interest in the design of multifunctional microporous materials, particularly those with pores in the 10–20 Å range. The many attempts to achieve this goal through cross-linking zirconium phosphate-like layers by use of several types of diphosphonic acids will be described. A variety of functionalized pillared materials are also described with potential as sorbents and catalysts. The advances in synthetic methods now achieved promises to produce a wide variety of porous materials with controlled pore sizes and varying degrees of hydrophilic–hydrophobic character whose chemical behavior will be mediated by the incorporation of diverse functional groups as part of the pillars.

1. Introduction

Organic–inorganic hybrids constitute an important class of compounds in the exploratory research area of advanced materials design. In this connection, metal phosphonates represent a particularly versatile field for investigation because of the great latitude open to the investigator. A variety of di-, tri-, tetra-, penta- and hexa-valent metals readily combine with phosphonic acids. Furthermore, almost any desired organic compound may be converted to a phosphonic acid by known reactions. It is thus possible to introduce organics with different functional groups into the hybrid structure. Much of our work has been exploratory in nature, beginning with zirconium as the principal metal. Choice of this metal arose naturally from our work with zirconium phosphates. Early on, we synthesized a layered zirconium phosphate[1] of composition $Zr(HPO_4)_2 \cdot H_2O$ that is referred to as α-ZrP. Subsequently, we discovered a second layered zirconium phosphate, $Zr(PO_4)(H_2PO_4) \cdot H_2O$, or γ-ZrP.[2] The structures of both compounds are now well known.[3–5] The first zirconium phosphonates prepared by direct precipitation of a phosphonic acid with a soluble Zr(IV) salt[6] were later shown to have the α-ZrP structure.[7] For a more comprehensive overview of this chemistry, refer to ref. 8. It is extremely difficult to synthesize organic derivatives of γ-ZrP by direct precipitation. Instead, a great variety of such derivatives have been prepared by ester interchange reactions where the dihydrogen phosphate group of γ-ZrP is replaced by the organic phosphonate. An excellent review of these types of reactions has been presented by Alberti.[9] In this perspective, we will summarize the work that has been carried out to produce porous pillared metal phosphonates. As a necessary preliminary, the crystal structures of the α- and γ-zirconium phosphates will be described. A schematic representation of the structures is given as Fig. 1a and 1b.

Abraham Clearfield

Abraham Clearfield was born in Philadelphia, Pennsylvania, USA and received a B.A. and M.A. in chemistry from Temple University. He received his Ph.D. in 1954 from Rutgers University in inorganic chemistry and crystallography. Upon graduation, he joined the U.S. Army Quartermaster Corp. Laboratories in Natick, Massachusetts for one year. He then joined the research staff of NL Industries in their Titanium Alloy Manufacturing Division in Niagara Falls, where he rose to the rank of Senior Scientist. In 1963, he joined the faculty of Ohio University in Athens, Ohio and was promoted to full professor in 1968. In 1976, he moved to Texas A&M University. Professor Clearfield's, and his students', field of interest are inorganic ion exchange materials, metal phosphonates and materials chemistry.

Zhike Wang

Zhike Wang was born in Guangzhou, Guangdong Province, P.R. China. She received her B.S. in chemistry from Fudan University, Shanghai, P.R.China, in 1993 and her M.S. in chemistry from Peking University, Beijing, P.R.China, in 1996. She came to Texas A&M University in 1997 and conducted studies on the catalytic properties of zeolites using solid state NMR techniques in Prof. James F. Haw's group. She joined Prof. Abraham Clearfield's research group in 1999 and performed her research on the synthesis and characterization of porous layered solid acids, such as sulfonated zirconium phosphonates and pillared clays. She characterized the surface acidity of those materials and monitored catalysis through solid state NMR spectroscopy. She is graduating soon with her Ph.D. in chemistry.

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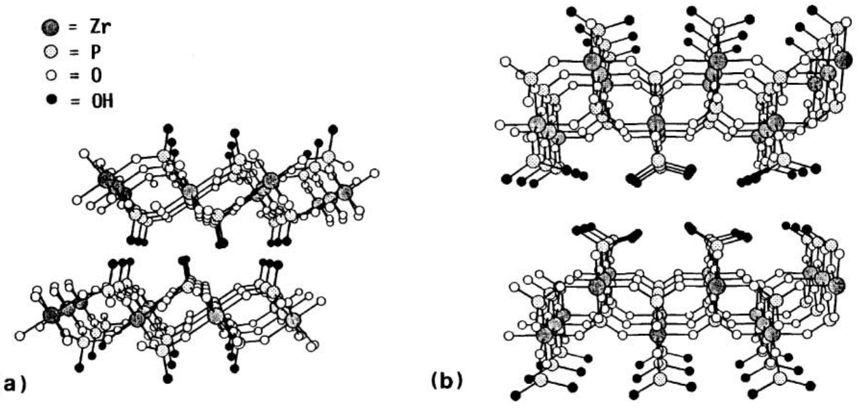


Fig. 1 (a) Crystal structure representation of α-zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$, interlayer spacing 7.6 Å. (b) Crystal structure representation of γ-zirconium phosphate, $Zr(PO_4)(H_2PO_4) \cdot 2H_2O$, interlayer spacing, 12.2 Å.

The α-ZrP compound was first prepared by refluxing zirconium phosphate gels in 10–12 M phosphoric acid.[2] Single crystals were formed hydrothermally in 10 M H_3PO_4 at 170 °C. The crystals are monoclinic, space group $P2_1/n$ with a = 9.060(2), b = 5.297(1), c = 15.414(3) Å, β = 101.71(2)°. The layers consist of metal atoms lying slightly above and below the mean plane and bridged by phosphate groups from above and below. Three oxygen atoms of each phosphate group are bonded to three different zirconium atoms, which form a distorted equilateral triangle. Each zirconium atom is thus octahedrally coordinated by six oxygen atoms from six different phosphate groups. The fourth phosphate oxygen bonds to a proton and points into the interlayer space. The layers are staggered such that a phosphorus atom on one layer lines up with a zirconium atom in the adjacent layer. A water molecule resides in the interlayer space, hydrogen bonded to monohydrogen groups all from the same layer, alternately, at about $+1/4c$ and $-1/4c$. There are no hydrogen bonds between layers, so that only van der Waals forces hold the layers together. Similar metal phosphates are formed by Ti, Hf, Si, Ge, Sn and Pb[9b] and they all behave as ion exchangers.

Although γ-ZrP was discovered many years ago,[2] its structure was not uncovered until recently because of the difficulty in obtaining single crystals. It was known from ^{31}P NMR solid state spectra that the two phosphate groups in γ-ZrP are different and are assigned as an orthophosphate and a dihydrogen phosphate.[10] The structure of the layers was determined for α-titanium phosphate[11] and later a complete structure, including the water molecules, was obtained for γ-ZrP[5] using powder data. The crystals are monoclinic, a = 5.3825(2), b = 6.6337(1), c = 12.4102(4) Å, β = 98.678(2)°, space group $P2_1$, and Z = 2. The structure indeed contains alternating orthophosphate groups and dihydrogen phosphate groups as predicted from the NMR spectra. The zirconium atom is octahedrally coordinated by four oxygen atoms from four different PO_4^{3-} and two oxygens from two different $H_2PO_4^-$ groups. Two of the oxygens of the orthophosphate group bridge zirconium atoms in the a-axis direction and the other two do so in the b-axis direction. These groups are alternately located 0.65 Å above and below the mean plane of the layers. The dihydrogen phosphate groups reside on the outer periphery of the layer utilizing two of its oxygen atoms to bridge across zirconium atoms in the a direction. The two hydroxyl groups extend into the interlamellar space. The location of the water molecules and the hydrogen-bonding scheme is shown in Fig. 1b. Both protons are replaceable through ion exchange reactions.[12,13]

2. Pillared zirconium aryldiphosphonates

Pillaring is achieved by use of diphosphonic acids as the ligand. This concept was first introduced by Martin Dines, *et al.*[14] in an effort to cross-link the inorganic $-PO_3Zr$ layers with rigid aryl groups. The ligand of choice was 4,4′-biphenyldiphosphonic acid. In the fully pillared state, the biphenyl rings would be spaced 5.3 Å apart so that no porosity would result. However, by introducing spacer molecules such as phosphorous acid, $-O_3PH$ groups would occupy a number of spaces on the layers and thus introduce porosity by separating the pillars (Fig. 2).

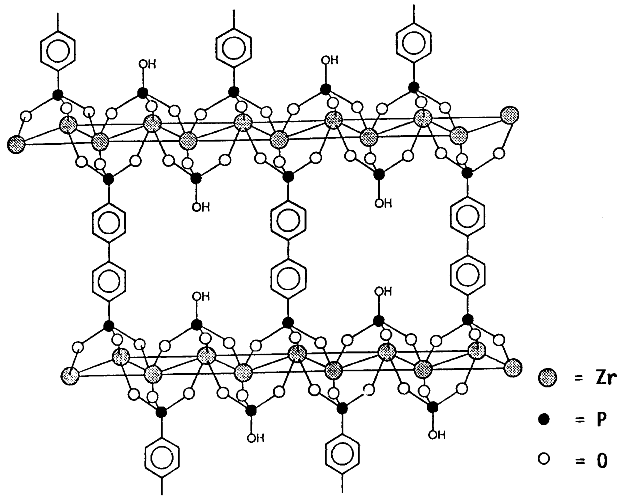


Fig. 2 Idealized representation of α-zirconium phosphate type layers pillared by diphenyl groups. The pillars are spaced 10.6 Å apart by mononhydrogen phosphate groups to create microporosity.

This indeed was the case. However, it turns out that the porosity arose from a broad distribution of mesopores and not the expected microporosity. In fact, after many attempts[15] we have concluded that microporous materials cannot be obtained by similar reactions in aqueous media. However, by carrying out the reactions in DMSO or DMSO–C_2H_5OH mixtures, products with high surface areas and a significant portion of micropores could be obtained.[16] More recently, we have achieved the desired for combination of high surface area with a narrow pore size distribution.[17] A non-aqueous solvent such as DMSO or alcohol or their combination is required. The difference is that an excess of Zr(IV) is required in the reactant mix. The pores lie between 1–2 nm with the maximum in the dV/dr curve from ≈13 Å to as high as 19–20 Å, depending on conditions of synthesis. Typical isotherm and pore size distribution curves are shown in Figs. 3a and 3b, respectively.

The phenyl groups are readily sulfonated either by dispersion of the porous zirconium phosphonate in fuming sulfuric acid[18] or by exposing the solid to gaseous SO_3 in a closed vessel.[17] The latter technique was chosen to obtain samples for determination of the acid strength of the sulfonic acid groups. For this purpose, we emulated the methodology of Haw *et al.*[19,20]

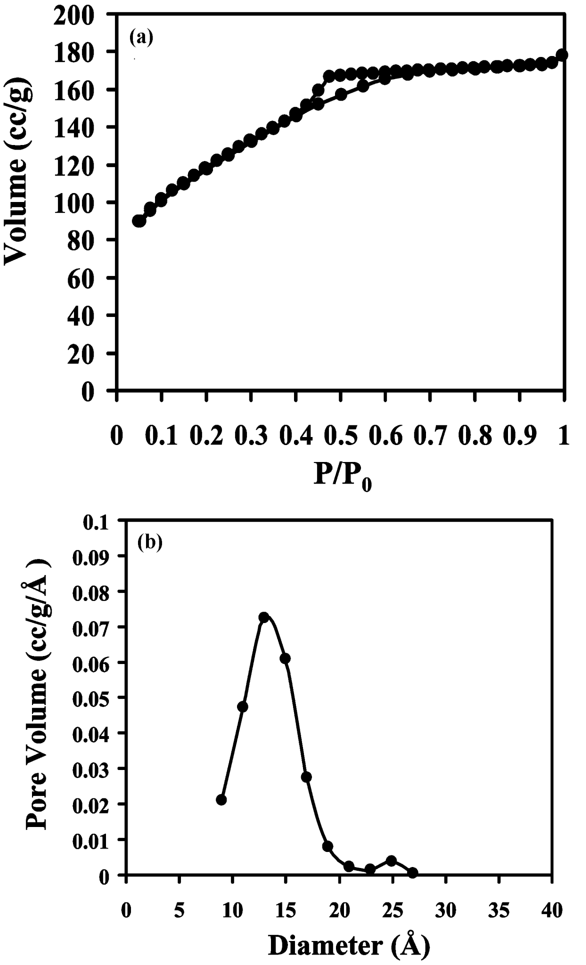


Fig. 3 (a) N_2 sorption–desorption BET isotherm of microporous zirconium biphenylene diphosphonate prepared in a mixed ethanol–DMSO solvent. (b) Pore size distribution as determined by de Boer t-plot. The maximum is at 13 Å.

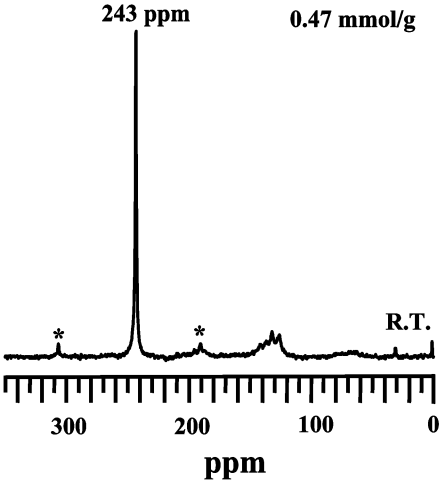
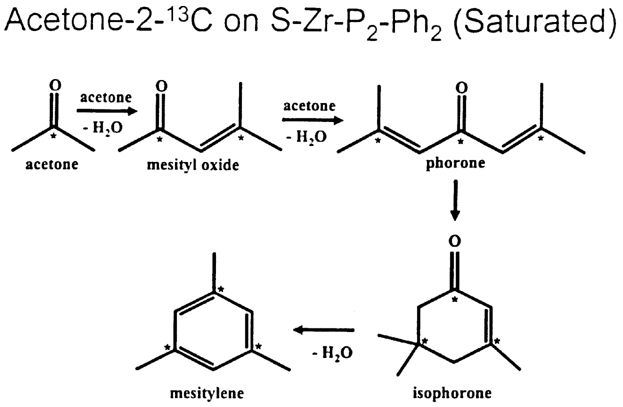


Fig. 4 Solid state MAS NMR spectrum of acetone-2-^{13}C sorbed on pillared sulfonated zirconium biphenylenebis(sulfophosphonate) at room temperature at a level of 0.47 mmol per gram. The resonance at 243 ppm represents the protonated acetone species and the minor peaks are the same for polymerized acetone derivatives. Starred peaks are spinning side bands.



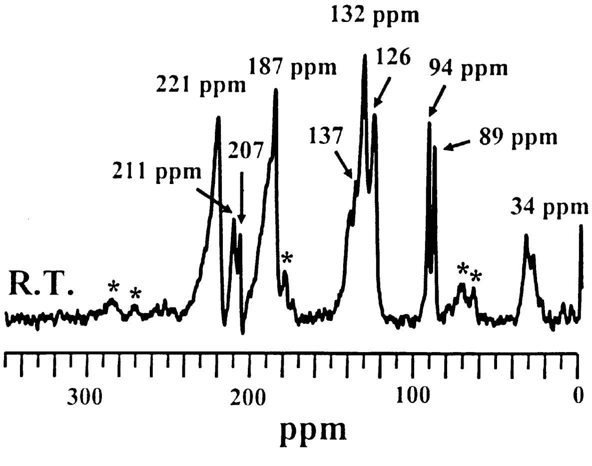
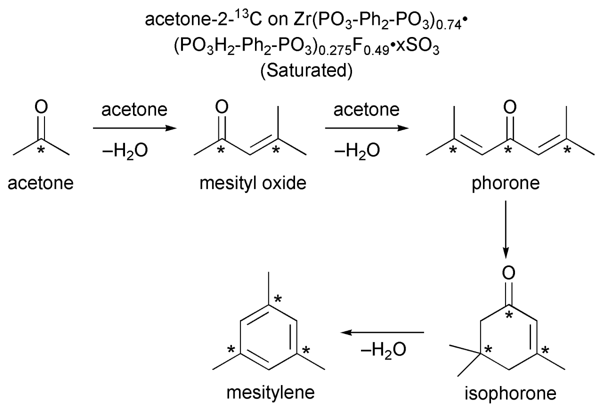


Fig. 5 Solid state MAS NMR of acetone-2-^{13}C sorbed on zirconium biphenylenebis(sulfophosphonate) in which the surface is saturated by the acetone (see text for explanation).

Acetone-2-^{13}C is exposed to the catalyst and the ^{13}C chemical shift observed. This shift arises from the protonation of the carbonyl group imparting carbenium ion character to it. As a result, the ^{13}C resonance shifts downfield. The magnitude of this shift at a given temperature is compared to that of a catalyst of known acidity. For example, zeolite HY exhibits a shift to 220 ppm and HZSM-5 to 223 ppm at 298 K. 100% H_2SO_4 gives a shift of 244 ppm and our porous sulfonate gave a ^{13}C shift of 243 ppm, hardly distinguishable from that of pure sulfuric acid, as shown in Fig. 4. The minor peaks in the figure arise from condensation of the protonated acetone. This effect is seen more clearly in Fig. 5, where the surface of the catalyst has been saturated with acetone. Under these conditions, the acetone molecules are near enough to each other to undergo condensation–polymerization reactions. Mesityl oxide is identified by two peaks at 211 (carbonyl) and 187 ppm, the peaks at 207 and 187 ppm are the chemical shifts of the carbonyl and β-carbon, respectively, of isophorone with the shift of the third ^{13}C in isophorone at 34 ppm (Scheme 1). The peak at 137 ppm arises from mesitylene (1,3,5-trimethylbenzene) and the region 126 to 140 ppm is associated with the presence of olefins and other aromatic products. The large peak at 221 ppm is that of protonated acetone. It now has a much lower shift because of the lower catalyst acid strength arising from the presence of water, which creates an equivalent amount of hydronium ion.

It is also possible to sulfonate zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$, to create a strong Brønsted acid catalyst. We had prepared this compound much earlier.[18] It is an excellent proton conductor at high relative humidity.[21] This compound exfoliates completely in water to particles of about 5 × 5 nm and 1.5 nm thick as shown by recent light scattering measurements. To moderate the deliquescence of this sulfonate, Curini *et al.*[22,23] prepared $Zr(O_3PCH_3)_{1.2}(O_3PC_6H_4SO_3H)_{0.8}$. This compound was found to be a very effective catalyst for a number of organic reactions including conversion of oximes, semicarbazones and tosylhydrazones to their respective carbonyl compounds. It has also been utilized for the tetrahydropyranylation of alcohols and phenols.[24] The starting compound is merely added to the catalyst in an inert solvent and kept at 80 °C with shaking.

This method of utilizing the strong acid character of the sulfonated zirconium aryl derivatives as a catalyst would be



Scheme 1

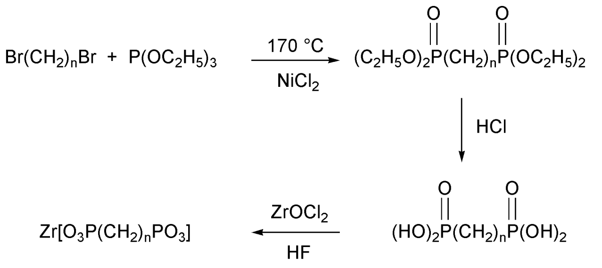
ideal for a number of reasons. The reactions are run under mild, reflux conditions. The acidity can be adjusted by increasing the ratio of phenyl to methyl groups and the catalyst is easily recovered and re-used. The porous materials prepared by us have the added benefits of much greater surface area and the possibility that they will display size and shape selectivity. The pores are in the 10–20 Å range, the region inaccessible to zeolites. Furthermore, the Brønsted acidity is greater than that of ZeY and ZSM-5. Temperatures as high as 130 °C may be utilized without loss of SO_3. This should allow for the use of these catalysts for many acid catalyzed reactions with large molecules. Since the phosphonate chemistry of Ti is similar to that of Zr, this less expensive metal may be utilized to lower the cost of the catalysts. We are pursuing these options.

Mutin and co-workers[25] utilized a sol–gel procedure to obtain porous pillared materials that require comment since they utilized propanol as solvent, where our results were obtained with varying levels of ethanol relative to DMSO. They used phosphoric acid as a spacer group. By employing a non-hydrolytic condensation between the $Zr(OC_3H_7)_4$ and P–OH groups, they were able to obtain a range of compositions from low to high phosphate content. In the general formula, $Zr(O_3PC_{12}H_8PO_3)_x(HPO_4)_{2-2x}$, those compositions for which x varied from 0.2 to 0.6 yielded high surface areas (262 to 307 $m^2\ g^{-1}$) with about 45% micropores with a range of 5 to 15 Å and a maximum at ≈6 Å. These results are similar to the results obtained by Alberti *et al.*[26] who used 3,3′,5,5′-tetramethylbiphenyldiphosphonic acid as the pillaring agent and (HPO_3) as spacer group. However, this compound had almost no mesoporosity, whereas the sol–gel products contained extensive interparticle mesoporosity. This result may stem from the fact that the particles produced without HF are claimed to be 10–20 nm in size.[25]

Odobel *et al.*[27] prepared pillared zirconium phosphite (2,2′-bipyridine-5,5′-diphosphonates) by varying the ratio of phosphorous acid to the bipyridine phosphonic acid in the presence of HF. A single phase of composition $Zr(O_3PH)_{0.8}$-$(O_3P\text{-bipy-}PO_3)_{0.6}$·$5.3H_2O$ was obtained when the ratio of phosphorous acid to the bipyridinephosphonic acid was $5 \le r \le 15$. This compound, termed MAT1, had a surface area of 420 $m^2\ g^{-1}$ of which 330 $m^2\ g^{-1}$ was due to mesopores of ≈40 Å average diameter. The micropores (90 $m^2\ g^{-1}$) were small, radius ≈5 Å. A fully pillared product was also obtained by omitting the phosphorous acid. This compound had a surface area of 130 $m^2\ g^{-1}$, average diameter, 40 Å, with no micropores.

3. Zirconium alkyldiphosphonates

Just as the aryldiphosphonic acids were used to prepare hybrid pillared layered derivatives, so alkyl analogues may be prepared in a similar way. This was done by converting α,ω-alkyldibromides to diphosphonic acids by means of an Arbusov–Michaelis reaction. The phosphonic acids were then reacted with zirconyl chloride solutions at reflux temperatures with HF added to obtain better, crystallized products.



Compounds with n = 6, 8, 10 and 20 were synthesized and the diphosphonic acid with n = 2 was purchased. Fig. 6 is a plot of the observed interlayer spacings *versus n*, the number of carbon atoms in the alkyl chain. The slope is 1.071 Å per carbon atom. That value indicates the chains are tilted about 32° from the perpendicular to the planes or 58° to the mean plane. All these preparations were carried out in aqueous media. The question arises at to whether highly porous pillared materials can be prepared in non-aqueous media as is the case for the aryl-pillared materials. An attractive feature would be control of the interlayer distance by choice of alkyl chain length.

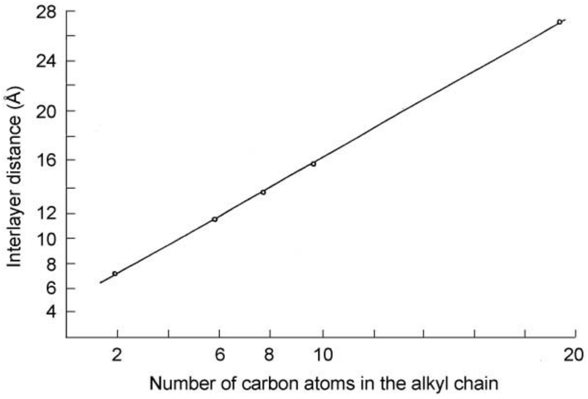


Fig. 6 Plot of basal spacing of zirconium n-alkylbis(phosphonates) as a function of the number of carbon atoms in the alkyl chain (after C.-Y. Yang, Ph.D. dissertation, Texas A&M University, Dec. 1986).

Derouane and Jullien-Sardot[28] prepared a series of alkyl-pillared zirconium phosphonates from mixtures of n-alkyl diphosphonic acids (n = 6–12) and phosphoric acid in which the ratio PA/DPA varied from 0 to 10 (PA = H_3PO_4 and DPA is the diphosphonic acid). The reactions were carried out in methanol as solvent and HF/Zr ≤ 6. The C_8 preparations were studied extensively as representative of the group. As the ratio PA/DPA increased, the X-ray patterns showed increased line width indicative of increased disorder. Decreasing particle size was ruled out as the size remained relatively constant. Surface areas decreased from 236 $m^2\ g^{-1}$ for PA/DPA = 0.75 to 132 $m^2\ g^{-1}$ for a ratio of 0.29. The porosity was mainly of the mesopore type (68% for PA/DPA = 0.29 and 90% for a ratio of 0.75). The overall mean pore diameter was 38–39 Å. The *d*-spacing for the dry C_8 compound (no phosphoric acid) was 13.9 Å in good agreement with the value in Fig. 6, but on sorption of amine, the interlayer spacing increased to as high as 15.5 Å. Assuming a perpendicular orientation of the chains the expected interlayer spacing is calculated to be 15.7 Å. Thus, the chains must be tilted when dry and perpendicular to accommodate the sorbent filling the pores.

Derouane and Jullien-Lardot proposed three possible models to account for the structure of these mixed derivatives (Fig. 7). Model A is one in which the two groups segregate into separate layers. Although a reflection appears in the X-ray patterns at

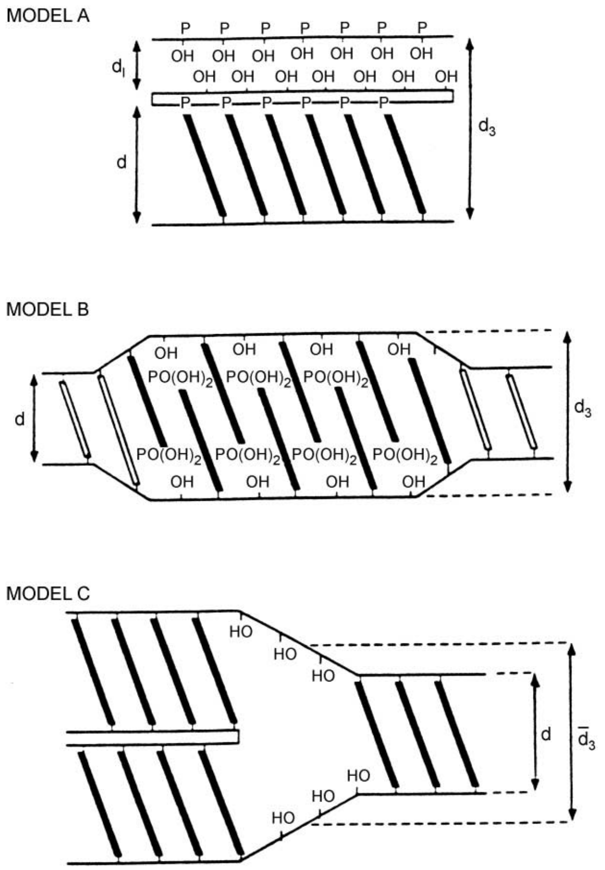


Fig. 7 Possible structural models explaining the generation of mesoporosity and larger interlayer spacings in zirconium n-alkyldiphosphonates (with permission from ref. 28).

21 Å at high PA/DPA ratios, the authors reject this model as not being as capable of explaining the X-ray data as the other models. Model B contains microdomains in which the diphosphonic acid binds to Zr through only one of its acid groups because a phosphate group occupies the position on the opposite layer. This model is rejected as not showing a ^{31}P resonance for free $-PO_3H_2$ groups. By elimination, Model C is accepted. This model explains the two interlayer spacings and the internal porosity, but not the fact that P/Zr is normally greater than two. An alternate model is presented in the Discussion section.

4. Pillared structures of divalent elements

Both the aryl and alkyl pillared zirconium phosphonates are insufficiently crystallized to allow structure determination by X-ray diffraction methods. Even in the presence of HF as solubilizing agent, crystal growth does not develop sufficiently to yield many Bragg type reflections. This is not the case for divalent elements where the structures of many compounds have been reported.[8] The ready crystallization of many divalent phosphonates stems from their solubility in acid solution. By proper adjustment of the pH, it is sometimes possible to even obtain single crystals. Otherwise, the structures may be solved from powder diffraction data. We report here our results with the alkyl copper compounds of general formula $Cu_2[(O_3P(CH_2)_nPO_3)(H_2O)_2]$. In the first two members of the series, $n = 2$, 3, the copper atom is five-coordinate.[29] Four of the coordinating oxygens are phosphonate oxygens and the fifth is a water molecule. The coordination polygon is that of a distorted square pyramid with the Cu^{2+} slightly out of the equatorial plane in the direction of the capping atom. The Cu atom lies in a plane and is bridged by phosphonate groups above and below the plane. The third phosphonate oxygen is directed away from the direction of these Cu–O–P–O chains and bonds to two Cu atoms in an adjacent row, forming layers. The layers are then bonded together into a three-dimensional whole by the carbon chains. A schematic drawing of the C_3 representative is shown in Fig. 8. The connectivity, in this compound, is such as to form tunnels that are filled with water molecules.

Table 1 Unit cell dimensions (Å) and space groups of copper alkylene phosphates, $Cu_2[O_3P(CH_2)_nPO_3(H_2O)_2]\cdot xH_2O$

n/*x*	2/0	3/1	4/2	5/2.8
a/Å	8.0756(1)	17.3181(8)	20.0305(6)	22.3773(2)
b/Å	7.5872(1)	6.7624(3)	6.6713(2)	6.7633
c/Å	7.4100(1)	4.3276(2)	4.39661(1)	4.3529(1)
β/°	116.319(1)	90.00	91.379(1)	90.00
Space group	$P2_1/c$	$Pnc2$	$C2/m$	$Pmmn$

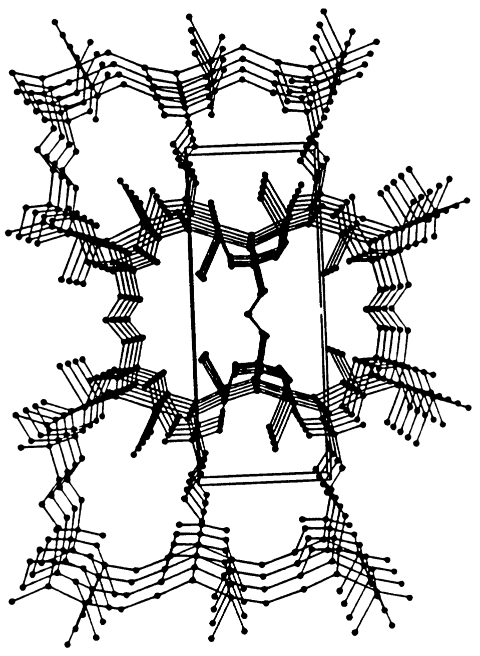


Fig. 8 Representation of the structure of $Cu_2[(O_3PC_3H_6PO_3)(H_2O)_2]$ as viewed down the *a*-axis illustrating the tunnel-like pores. The Cu–O_3P columns form wavy chains running in the horizontal direction and are cross-linked by the alkyl C_3 groups.

In the C_4 and C_5 members of this family, the Cu atoms are located on centers of symmetry, octahedrally coordinated by four phosphonate oxygens and a water molecule at half occupancy.[30] These octahedra are then bonded into layers in the same way as described for the C_3 compound. The layers are linked together by the alkyl chains as shown in Fig. 9. The alkyl pillars form channels that run parallel to the *c*-axis direction as shown in the figure. The distance between pillars in the *b*-axis direction is 6.6 Å and in the *c*-axis direction, 4.4 Å.

The unit cell dimensions and space groups of the four copper compounds are listed in Table 1. We note that the odd number compounds (*n*) are monoclinic and those with an even number of carbons in the pillars are orthorhombic. The interlayer distances are half the *a*-axis dimension for the orthorhombic compounds and 1/2*a* sin β for the monoclinic cells. The values are 7.238, 8.659, 10.012 and 11.189 Å for the 2, 3, 4 and 5 carbon compounds, respectively. The average increase per carbon atom is 1.316 Å compared to a *trans–trans* expected value of 1.27 Å.

The water content of the tunnels increases as the length of the carbon chain increases from zero to 2.8 for the four compounds listed in Table 1. This is undoubtedly the result of the increased tunnel volume accompanying the increase in alkyl chain length. Removal of the water by heating destroys the crystallinity without collapse of the layers. The process appears to be irreversible as 24 hour immersion in water did not restore

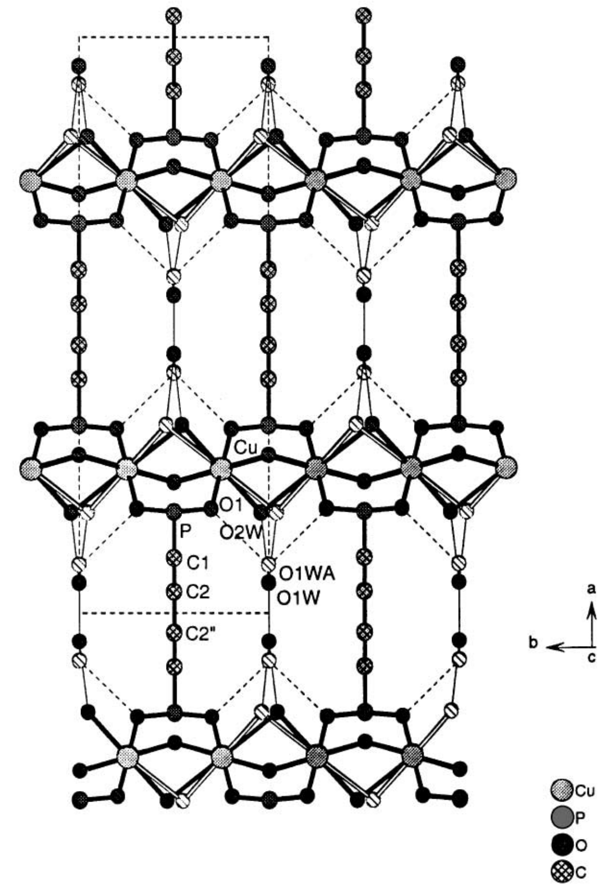
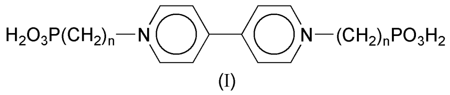


Fig. 9 A view of $Cu_2(O_3PC_4H_8PO_3)\cdot 2H_2O$ down the *c*-axis direction showing the tunnels and associated water molecules.

the crystallinity. It would be advantageous to do so as the anhydrous compounds have two open coordination sites on the copper atoms that might be used in catalytic reactions. In this connection, it is relevant to observe the results with similar lanthanide compounds of general composition[31] $LnH(O_3P\text{-}[O_3P(CH_2)_nPO_3]$, $n = 2, 3$. These compounds have similar structures as to the disposition of the alkyl chains in the copper compounds, but are anhydrous. The bonding in the cross-linked compounds is similar to that in the non-cross-linked $LnH(O_3PC_6H_5)_2$.[32] The alkyl pillars in these lanthanides are ≈5.3–5.4 Å apart in one direction and 4.2 Å apart in the perpendicular direction as compared to 6.7 and 4.3–4.5 Å in the copper compounds. This narrowing of the tunnels in the lanthanides is the result of the chelation–donation type bonding. A number of ethylene and propylene pillared compounds of V, Co, Sb(II), Cr, Zn and Fe(II) have been synthesized and structurally characterized as listed in ref. 30.

5. Pillaring by combined aryl–alkyl pillars

Vermeulen and Thompson[33] prepared diphosphonic acids of the type:



(I)

with $n = 2, 4$. Two types of compounds were synthesized with (I) in aqueous HF containing Zr(IV) and phosphonic acid for which $n = 2$. Refluxing this mixture yielded a solid with a composition $Zr(HPO_4)(I)_{0.5}X$ and an 18 Å interlayer spacing.[34] A schematic representation is shown in Fig. 10a. The layer has the α-ZrP structure with alternating ethylviologen and monohydrogen phosphate groups bonded to the layers. The viologen nitrogens are positively charged so that the net charge of the ethylviologenphosphonate is +2. Therefore, a halogen is required for charge balance and was found to be a mixture of F^- and Cl^-.

The second phase was prepared hydrothermally at 190–200 °C and was crystalline.[34] It's crystal structure was solved from powder diffraction data and was found to contain well-defined pores as illustrated in Fig. 11. Its composition is $Zr_2(PO_4)(I)F_3\cdot 3H_2O$. The layers are unique in that orthophosphate groups bridge to four Zr atoms within the layer as in γ-ZrP and the phosphonate groups bond as in α-ZrP. Two-thirds of the fluoride ions are bonded to zirconium. The Zr atoms are octahedrally coordinated by two phosphate oxygens, three oxygen atoms from the phosphonate groups in a facial geometry and a fluoride ion that points into the tunnels. The viologen phosphonate molecules bridge the inorganic layers and form a criss-cross stack as shown in Fig. 10b. This type of stacking reduces the electrostatic repulsions of adjacent viologen groups. The closest face-to-face contact between viologen groups in the *c*-axis direction is 4.6 Å. The closest viologen–viologen contact across the pore (*b*-axis direction) is about 8 Å and the basal spacing is 13.6 Å, leading to a fairly large pore. The positioning of the F^- and three water molecules in the cavity is shown in Fig. 11. This fluoride ion is exchangeable.

Thompson and co-workers[34–36] prepared catalysts from the porous zirconium viologen compound by incorporation of active metal species such as platinum and palladium. This was accomplished by exchange of anionic metal halides, $[MX_4]^{2-}$, for the fluoride ions in the cavity. Treatment of the exchanged solid with hydrogen gas reduces the salts to colloidal metal particles. In the process, the violgoen groups are 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[37] or silver[38] 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.

It is readily obvious that any combination of alkyl and aryl groups can be assembled, with some effort, by the investigator to use as pillars. Alkyl groups may be placed in *para*-positions of aromatics or even in between rings such as $H_2O_3PC_6H_4\text{–}(CH_2)_n\text{–}C_6H_4PO_3H_2$ or $H_2O_3P(CH_2)_nC_6H_4\text{–}(CH_2)_m\text{–}C_6H_4\text{–}(CH_2)_nPO_3H_2$. Whether the use of such ligands in our new synthetic procedure can be utilized to fine tune the porosity remains to be tested.

6. Pillared structures with γ-ZrP layers

Organically pillared structures of the γ-ZrP type are very difficult, if not impossible, to prepare by direct synthesis. Instead, they are produced by topotactic replacement of $O_2P(OH)_2$ by the phosphonic acid ligand.[39] Our interest is in the diphosphonic acid ligands that allow for cross-linking of the layers. Alberti found that two pathways were possible. At low concentrations of ligand, cross-linking of the layers occurs, while at concentrations greater than 1 M, a bilayer forms in which half the phosphonic acid groups, one from each ligand, are non-bonded. A schematic drawing of a biphenyl cross-linked γ-ZrP is shown in Fig. 12. It was found[9,40] that a solid solution of composition $Zr(PO_4)(H_2PO_4)_{1-x}[C_{12}H_8(PO_3H)_2]_{x/2}\cdot nH_2O$ with $x = 0.1\text{–}0.58$ could be synthesized. However, if the value of x was less than 0.25, the compound was unstable to dehydration. At higher levels of x, the products could be dehydrated and

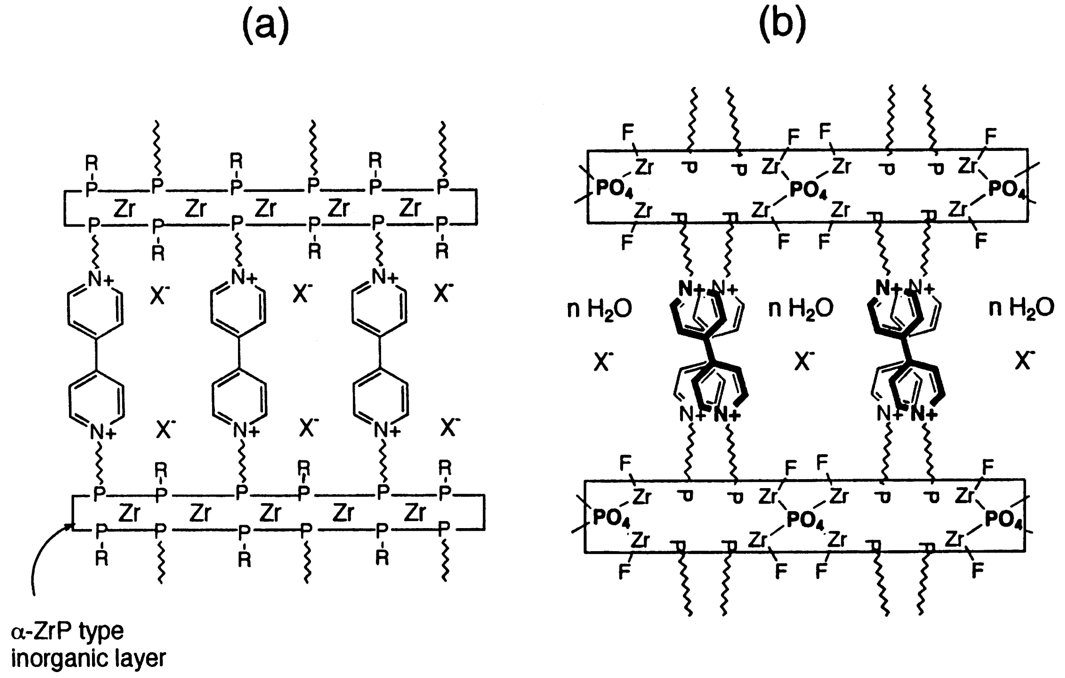


Fig. 10 (a) Schematic representation of zirconium *N*,*N*′-ethyl-4,4′-bipyridyl diphosphonate obtained by a reflux procedure spaced by O_3PR groups, R = OH or alkyl group. (b) Representation of zirconium *N*,*N*′-ethyl-4,4′-bipyridyl diphosphonate phosphonate fluoride, $Zr_2(PO_4)(PV)F_3$, where PV = *N*,*N*′-ethyl-4-4′-bipyridyl diphosphonate group.

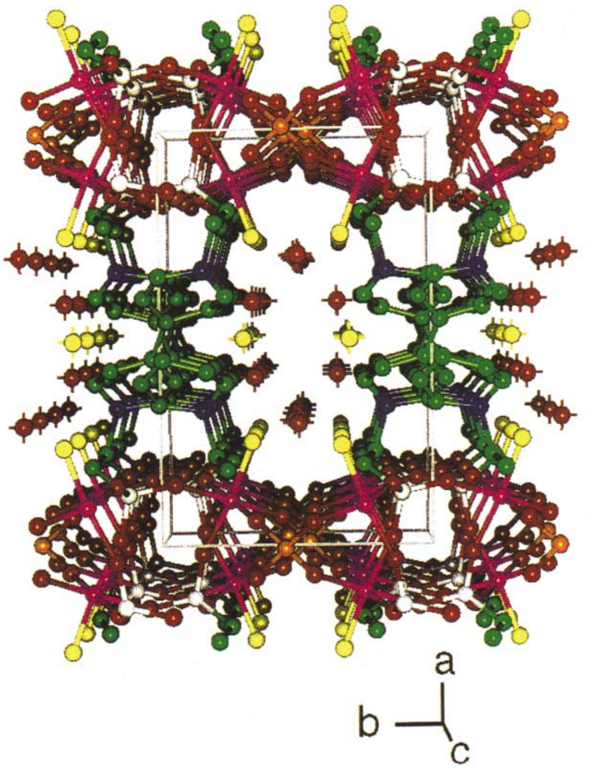


Fig. 11 Ball and stick representation of $Zr_2(PO_4)(PV)F_3$ as viewed down the *c*-axis showing the cavities with water and F^-, yellow; oxygens, brown; Zr, violet; P as PO_4 tetrahedra are orange, and ethylviologen has C, green; N, purple.

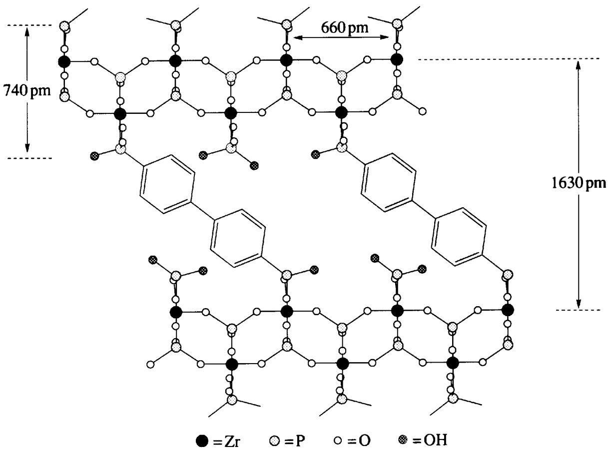


Fig. 12 Computer generated model of two layers of γ-zirconium phosphate pillared by 4,4′-biphenyldiphosphonate of composition $Zr(PO_4)(H_2PO_4)_{0.75}(HO_3PC_{12}H_8PO_3H_2)_{0.125}$ (reproduced with permission from ref. 40, Copyright 1994, VCH).

exhibited porosity as shown in Fig. 13. The surface area was found to increase up to 25% pillaring, maximum surface area 320 m^2 g^{-1}, and then decrease as more space was occupied by increased levels of pillaring. Because the in-plane dimensions were found to be unchanged by the degree of pillaring and the interlayer spacing expanded to 16.3 Å, it was concluded that the γ-type layers were intact. The larger interlayer spacing of the γ-pillared compound, compared to the α-type (16.4 *versus* 13.8 Å) results from the greater thickness of the γ-type layer. However, the pillars are close to perpendicular in the α-type compounds, but highly tilted in the γ-type.

An efficient way of carrying out the pillaring reactions was discovered by Alberti *et al.*[41] in that γ-ZrP exfoliates in water–acetone media at 80 °C. These workers found that the reaction occurs in two steps.[42] A very rapid reaction occurs initially, in which one phosphonate group of the diphosphonic acid displaces one dihydrogen phosphate group on an exfoliated layer. The layers then come together slowly by displacement of additional dihydrogen phosphate groups to build stacks of layers one at a time. When the stack contains five or six layers, flocculation occurs. The crystal structure of the C_4 compound has been solved from X-ray powder data.[43] In order to obtain a crystalline product suitable for X-ray studies, the original precipitate was treated hydrothermally in a 0.01 M solution of the butanediphosphonic acid at 250 °C for three days. The layers are essentially of the γ-ZrP type.[5] The butyl groups have

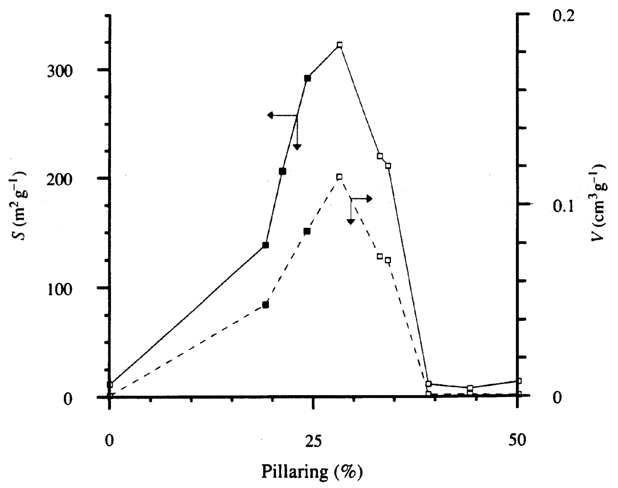


Fig. 13 Specific surface area S and volume V of the micropores for anhydrous samples of $Zr(PO_4)(H_2PO_4)_{1-x}(HO_3PC_{12}H_8PO_3H)_{x/2}$ as a function of the degree of pillaring. [□] and [■] refer to monophase and biphase systems, respectively. Reproduced with permission from ref. 40, Copyright 1994, VCH.

an almost *trans–trans* conformation and are tilted relative to the perpendicular. The interlayer spacing is 13.01 Å. The basal spacings for a series of alkyl pillared compounds of general composition $Zr(PO_4)(H_2PO_4)_{0.1}(HO_3P(CH_2)_nPO_3H)_{0.45}\cdot mH_2O$ at 75% relative humidity are plotted against m in Fig. 14.

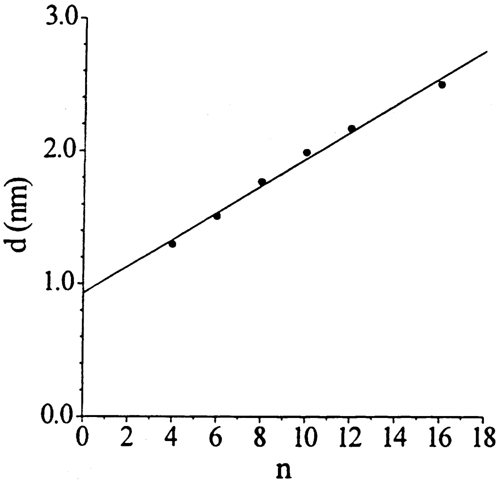


Fig. 14 Interlayer spacings as a function of the number of carbon atoms in the alkyl chain of pillared γ-zirconium alkyldiphosphonates of general formula $Zr(PO_4)[HO_3P(CH_2)_nPO_3H]_{x/2}[(HO)_2PO_2]_{1-x}$. (After ref. 42, copyright ACS, 1998).

The compounds for which the basal spacings are recorded in Fig. 14 are 90% pillared. In such cases, the chains are in the *trans–trans* conformation and the pillars may be considered to be at their greatest extension but at an angle of 52.7° to the layers. However, the interlayer distances of those derivatives with a low degree of pillaring (less than 50%) were shown to exhibit a variable interlayer spacing depending on the water content. For example,[42] when thoroughly wet the ten carbon derivative, $Zr(PO_4)(H_2PO_4)_{0.56}[HO_3P(CH_2)_{10}PO_3H]_{0.22}\cdot nH_2O$, had a water content of $n = 2.5$, and a basal spacing of 19.4 Å. Conditioned at 75% relative humidity, the spacing reduced to 16.5 Å and dried at 100 °C, 14.9 Å. On rehydration, the spacing returned to 19.7 Å. Alberti has termed this phenomenon the "accordion effect" and indicated that the organic pillars crinkle as shown in Fig. 15. Our opinion is that severe twisting or compression of the pillars requires a great deal of energy. A lesser amount of energy would be required if the layers slid laterally relative to one another. That is, the angle that the pillars make to the plane decreases. For example, the interlayer spacing of the pillared derivatives as a function of the number of carbons in the n-alkyl chain can be represented as $d = 9.3\ \text{Å} + 1.27\ \text{Å}\cdot n\cdot \sin a$, where n is the number of carbon atoms in the pillar, a is the angle between the layer and the alkyl chain and 9.3 Å is the layer thickness. In Fig. 14, the basal spacings shown are for nearly full pillared derivatives at 75% relative humidity. For this case, $a = 52.7°$ is the normal angle of inclination. To achieve a value of 16.5 Å for the interlayer spacing, this angle would be 48.5°. To accomplish this change in angle, the layers would need to shift by ≈0.72 Å. The comparable shift to achieve a level spacing of 14.3 Å would require a shift of ≈2 Å to obtain an a value of 40.5°. These shifts would be easily achievable given the large spaces between pillars.

We have already described MAT1, an α-layer pillared ZrP in which the pillars are 2,2′-bipyridyl. Odobel *et al.*[27] also prepared γ-layer versions by exfoliating γ-ZrP in the presence of 4,4′-bis(dihydroxyphosphoryl)-2,2′-bipyridine. Two derivatives were prepared of composition $Zr(PO_4)(H_2PO_4)_{0.8}[HO_3P\text{-bipy-}PO_3H]_{0.1}\cdot 2H_2O$ (MAT 2) and $Zr(PO_4)(H_2PO_4)_{0.5}[HO_3P\text{–bipy–}PO_3H]_{0.25}\cdot 2H_2O$ (MAT 3). MAT 2 had a surface area of 60 m^2 g^{-1}, apparently largely mesoporous in nature, and MAT 3 had a surface area of 380 m^2 g^{-1}. In this latter compound, the pillars alternate with $H_2PO_4^-$ groups creating micropores of ≈5 Å diameter. These pores account for 90% of the surface area. The pores are about the same size as those obtained by Alberti in zirconium 3,3′,5,5′-tetramethylbiphenyldiphosphonate phosphite.[44] It is curious that MAT 2, with very few pillars, yielded such a low surface area and a lack of micropores.

The reason for preparing porous pillared materials using 2,2′-bipyridyl pillars is their ability to complex many metals. The porosity of these materials allows access of the metal to the active sites. Odobel and co-workers[27] found that for MATs 1 and 3, a very rapid uptake of Fe(II) or Cu(I) occurred, accompanied by a change in color, pink for the iron compound and brown for the copper compound. In addition, a very broad MLCT charge transfer band was found in the UV spectra of these complexes. The bipyridine-pillared compounds may be considered as functionalized pillared materials. Another example is the sulfonic acid compounds treated in an earlier section. We now turn to two other functionalized pillared derivatives, those with polyether and polyimine pillars.

7. Functionalized pillared hybrids: polyethers and polyimines

Early in the history of zirconium phosphate-organic derivatives, Yamanaka reported that ethylene oxide reacts with γ-ZrP to produce derivatives of the type $Zr(PO_4)(H_2PO_4)_{1-x}(O_3POCH_2CH_2OH)_x\cdot H_2O$.[45] Propylene oxide also reacted similarly[46] and these organic derivatives were able to undergo ester interchange on refluxing in the presence of other organic phosphates.[47,48] Subsequently, we were able to prepare α-type hybrids of polyether glycols by direct precipitation.[49] The polyether phosphates were prepared by treatment of a polyether glycol with $POCl_3$ in carbon tetrachloride followed by a hydrolysis reaction.

$$\begin{aligned}&H(OCH_2CH_2)_nOH + POCl_3 \rightarrow\\ &\quad H(OCH_2CH_2)_nOPOCl_2 \xrightarrow[\Delta]{H_2O}\\ &\qquad H(OCH_2CH_2)_nOPO_3H_2 \xrightarrow{Zr(\text{IV})}\\ &\qquad\quad Zr[O_3PO(CH_2CH_2O)_nH]_2\cdot H_2O\end{aligned}$$

To obtain the organodiphosphates, an excess of phosphorus oxychloride was used. The non-bridged compounds were difficult to recover because of their hydrophilic nature. They swell in water and exfoliate spontaneously for $n \geq 9$. In contrast, the

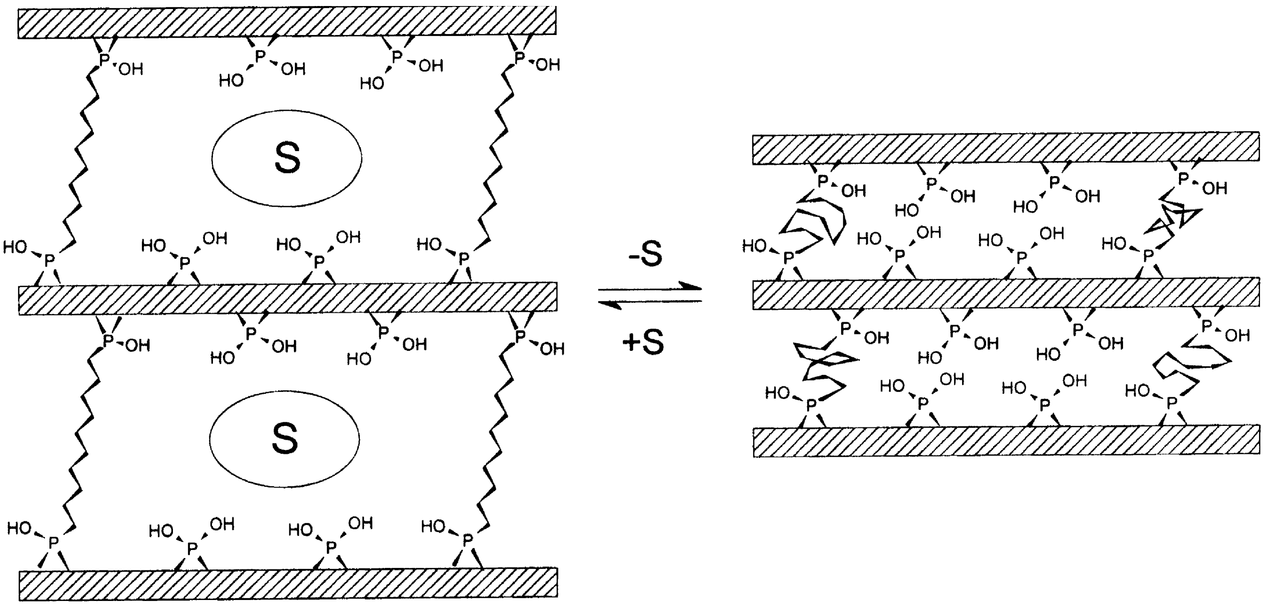


Fig. 15 Schematic of the accordion-effect for a zirconium 1,10′-decanediphosphonate derivative with 12% pillaring. The change in interlayer spacing results from presence or absence of solvent (after ref. 42, copyright ACS).

Table 2 Interlayer spacing data for $Zr[O_3PO(CH_2CH_2O)_nPO_3]_x$-$[HPO_4]_{2-2x}$

	x from		Interlayer spacing/Å	
n	Elemental analysis	TGA	Anhydrous	Wet
2	0.96	0.96	12.3	15.5
3	0.83	0.87	14.0	16.1
4	0.97	1.0	16.1	17.2
9	0.73	0.71	20.1	21.3
13	1.02	1.0	33.3	>44

cross-linked products readily precipitate and are easily recovered and when dried, are free flowing powders. Table 2 presents data on the interlayer spacings for a number of the cross-linked products.[50] These data yield a straight line with slope 1.92 indicating that the chains are inclined from the perpendicular to the planes by 39.5° for the anhydrous compounds. On immersing in water, the interlayer spacings increase. The thickness of the α-layer is 6.3 Å, so for the compound with n = 3, the gallery height (the free space between the bottom of one layer to the top of the layer below it) is 7.7 Å in the dry state. If the polyether chain were perpendicular to the layer, the interlayer spacing would be 9.97 + 6.3 = 16.3 Å, a value close to the interlayer spacing for the wet, swollen form. The minor amount of monohydrogen phosphate in the formula must arise from hydrolysis of the diphosphate during the synthetic process since no H_3PO_4 was added. Similar phosphonates have also been prepared.[49,50] A schematic representation of the structure is shown in Fig. 16.

The structure of these polyether complexes has not been established. The chains are 5.3 Å apart in the α-type layers with three such adjacent pillars lying in a triangular arrangement.[3] Thus, there are six oxygens per polyether group of three pillars *i.e.* $O(CH_2CH_2O)$ units that could act cooperatively to sorb salts akin to crown ether behavior. In fact, the compound with n = 4 did sorb $CuCl_2$ from methanolic solutions at a level of 0.2 moles per mole of Zr. However, the compound with n = 9 sorbed one tenth of this amount. In contrast, the non-pillared polyether compounds increased the amount of $CuCl_2$ sorbed as n increased, as expected. The polyether chains with one end untethered may be free to coil and uncoil to sorb salts, but the pillared polyether chains may be constrained to not behave similarly because of their dual attachment to the layers.

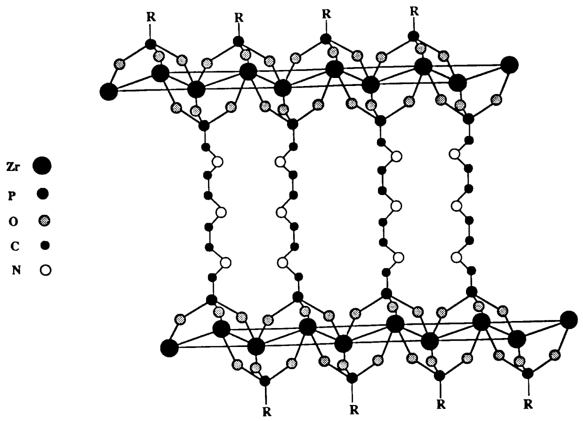


Fig. 16 Schematic representation of zirconium polyether or polyimine diphosphonates.

Polyimine phosphonic acids were prepared by reacting polyimines with chloromethylphosphonic acid:

$$NH_2(CH_2CH_2NH)_nH + ClCH_2PO_3H_2 \xrightarrow[pH=7.5]{} H_2O_3PCH_2NH(CH_2CH_2NH)_nH$$

To obtain disphosphonic acids, a two to one ratio of $ClCH_2PO_3H_2$ to diamine is required. Pillared compounds with n = 1–3 were prepared[50,51] and exhibited interlayer spacings of 14.3, 17.7 and 19.2 Å for n = 1, 2 and 3, respectively. In acid solution, protonation of the amino groups takes place with addition of a charge neutralizing anion in the interpillar spaces. These protonated phases behave as anion exchangers. Titration of the protons in the presence of an ion such as Cu^{2+} results in uptake of Cu^{2+} together with its accompanying anion. The unpillared zirconium polyimine derivatives exfoliate in acid solution and complex a variety of polyanions and heteropoly acid anions with accompanying precipitation.

8. Discussion

In this short perspective, we have tried to convey the types of reactions that can be carried out to obtain a variety of organically pillared metal phosphonates with a range of properties and chemical behavior. The general procedure is to prepare a diphosphonic acid of the pillar and combine it with a layer forming cation. We have found that four valent metals readily form such layers and those formed from zirconium are quite stable. The choice of pillar depends on the use to which the end product is to be put. One of our objectives was to produce pores in the 10–20 Å diameter range with a narrow pore size distribution. Such a group of materials could be used as sorbents and molecular sieves with pores larger than those supplied by zeolites and smaller than those provided by the new MCM type materials.

Upon sulfonation, very strong Brønsted acid materials are obtained. These compounds undoubtedly can be used as acid catalysts for a variety of reactions. The uniqueness of these materials lie in the fact that they have intermediate size pores and therefore may be useful for catalyzing desired transformations of large molecules that do not fit into zeolite pores. The frameworks are stable in air to 350 °C and to 400 °C in an inert atmosphere. However, SO_3 is lost at about 150 °C. We envision the use of these compounds at temperatures below 100 °C because of their high acidity and perhaps dispersed in inert solutions of the organic compound that is to be transformed. We have carried out additional catalytic reactions with a variety of molecules that will be reported upon shortly.

Several questions arise at this juncture. Will the alkyl-pillared compounds form similar porous type materials when synthesized as designated for the aryl-pillared complexes? What role does the fluoride ion play in formation of the pores and the overall acidity and catalytic behavior? In our synthesis, there are no spacer groups included as reactants. How then, can we account for the formation of the micropores? Earlier, we had proposed a structure[16] similar to that of Derouane. However, we did not observe a larger interlayer spacing than that of 13.8 Å, a value expected for the biphenyl pillar. Therefore, this interlayer spacing had to be preserved as shown in Fig. 17. The aryl pillars are designated as double lines in that figure. It is proposed that the pores develop by a coming together of layers of unequal size during particle growth. Many of the pillars are seen to be bonded by only one of the phosphonic acid groups. Because an excess of Zr was used in the preparation, the outer surfaces terminate with a layer of Zr. However, some of the single-bonded internal pillars may terminate in phosphonic acid groups. This would have the effect of increasing the ratio of phosphorus to Zr as is actually observed. Our hypothesis needs to be given a more quantitative character and such studies are underway.

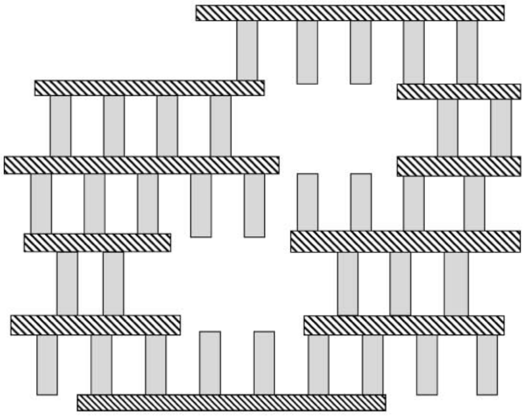


Fig. 17 Conceptual model of pore formation in zirconium biphenyldiphosphonate. The double vertical lines represent biphenyl groups, and the horizontal striped bars represent the inorganic PO_3ZrO_3P layers. The biphenyl groups protruding into the pore have free PO_3H_2 groups signified by connecting the two parallel vertical lines.

As a final word, we have shown in a preliminary way, that prefunctionalized pillars may be utilized for pillaring. If these compounds can also be made microporous, then new classes of such materials with interesting properties would result.

Acknowledgements

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References

1 A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1964, **26**, 117.
2 A. Clearfield, R. H. Blessing and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1968, **30**, 2249.
3 A. Clearfield and G. D. Smith, *Inorg. Chem.*, 1969, **8**, 431.
4 J. M. Troup and A. Clearfield, *Inorg. Chem.*, 1977, **16**, 3311.
5 D. M. Poojary, B. G. Shpeizer and A. Clearfield, *J. Chem. Soc., Dalton Trans.*, 1995, 111.
6 G. Alberti, U. Costantino, S. Allulli and N. Tomassini, *J. Inorg. Nucl. Chem.*, 1978, **40**, 113.
7 M. D. Poojary, H.-L. Hu, F. L. Campbell, III and A. Clearfield, *Acta Crystallogr., Sect. B*, 1993, **49**, 996.
8 A. Clearfield, in *Progress in Inorganic Chemistry*, K. D. Karlin, ed., John Wiley, New York, 1998, pp. 371–510.
9 (*a*) G. Alberti, in *Comprehensive Supramolecular Chemistry*, G. Alberti and T. Bein, eds., Pergamon, New York, 1996, vol. 7, p. 151; (*b*) A. Clearfield and U. Costantino, *ibid*, p. 107.
10 N. J. Clayden, *J. Chem. Soc., Dalton Trans.*, 1987, 1877.
11 A. N. Christensen, E. K. Andersen, I. G. Andersen, G. Alberti, M. Nielsen and M. S. Lehmann, *Acta Chem. Scand.*, 1990, **44**, 865.
12 A. Clearfield and J. M. Garces, *J. Inorg. Nucl. Chem.*, 1979, **41**, 903.
13 G. Alberti, in *Inorganic Ion Exchange Materials*, A. Clearfield, ed., CRC Press, Boca Raton, FL, 1982.
14 M. B. Dines, P. M. DiGiacomo, K. P. Callahan, P. C. Griffith, R. H. Lane and R. E. Cooksey, in *Chemically Modified Surfaces in Catalysis and Electrocatalysis*, J. S. Miller, ed., ACS Symposium Series 192, American Chemical Society, Washington, DC, 1982, p. 223.
15 A. Clearfield, in *Design of New Materials*, A. Clearfield and D. A. Cocke, eds., Plenum Press, New York, 1986, pp. 121–134.
16 A. Clearfield, *Chem. Mater.*, 1998, **10**, 2801.
17 A. Clearfield, Z. Wang and P. Bellinghausen, *J. Solid State Chem.*, in press.
18 C.-Y. Yang and A. Clearfield, *React. Polym.*, 1987, **5**, 13–21. Ack: Army.
19 J. F. Haw, J. B. Nicholas, T. Xu, L. W. Beck and D. B. Ferguson, *Acc. Chem. Res.*, 1996, **29**, 259.
20 T. Xu, E. J. Munson and J. F. Haw, *J. Am. Chem. Soc.*, 1994, **116**, 1962.
21 E. W. Stein, Sr., A. Clearfield and M. A. Subramanian, *Solid State Ionics*, 1996, **83**, 113.
22 M. Curini, O. Rosati, E. Pisani and U. Costantino, *Synlett*, 1996, 333.
23 M. Curini, M. C. Marcotullio, E. Pisani, O. Rosati and U. Costantino, *Synlett*, 1997, 769.
24 M. Curini, F. Epifano, M. C. Marcotullio, O. Rosati and U. Costantino, *Tetrahedron Lett.*, 1998, **39**, 8159.
25 D. Medoukali, P. H. Mutin and A. Vioux, *J. Mater. Chem.*, 1999, **9**, 2553.
26 G. Alberti, U. Costantino, F. Marmottini, R. Vivani and P. Zappelli, *Microporous Mater.*, 1998, **21**, 297.
27 F. Odobel, B. Bujoli and D. Massiot, *Chem. Mater.*, 2001, **13**, 163.
28 E. G. Derouane and V. Jullien-Lardot, *Stud. Surf. Sci. Catal.*, 1994, **83**, 11.
29 D. M. Poojary, B. Zhang and A. Clearfield, *J. Am. Chem. Soc.*, 1997, **119**, 12550.
30 D. I. Arnold, X. Ouyang and A. Clearfield, *Chem. Mater.*, 2002, **14**, 2020.
31 F. Serpaggi and G. Ferey, *J. Mater. Chem.*, 1998, **8**, 2749.
32 R.-C. Wang, Y.-P Zhang, H. Hu, R. R. Frausto and A. Clearfield, *Chem. Mater.*, 1992, **4**, 864–871.
33 L. A. Vermeulen and M. E. Thompson, *Nature*, 1992, **358**, 656.
34 D. M. Poojary, L. A. Vermeulen, E. Vicenzi, A. Clearfield and M. E. Thompson, *Chem. Mater.*, 1994, **6**, 1845.
35 K. P. Reis, V. K. Joshi and M. E. Thompson, *J. Catal.*, 1996, **161**, 62.
36 A. Dokoutchaev, V. V. Krishnan, M. E. Thompson and M. Balasubramanian, *J. Mol. Struct.*, 1998, **470**, 191.
37 A. Clearfield and S. P. Pack, *J. Catal.*, 1978, **51**, 431.

38 S. Cheng and A. Clearfield, *J. Catal.*, 1985, **94**, 455.

39 G. Alberti, R. Vivani and F. Marmottini, *J. Porous Mater.*, 1998, **5**, 205.

40 G. Alberti, F. Marmottini, S. Murcia-Mascaros and R. Vivani, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1594.

41 G. Alberti, C. Dionigi, E. Giontella, S. Murcia-Mascaros and R. Vivani, *J. Colloid Interface Sci.*, 1997, **188**, 27.

42 G. Alberti, S. Murcia-Mascaros and R. Vivani, *J. Am. Chem. Soc.*, 1998, **470**, 81.

43 G. Alberti, R. Vivani and S. Murcia-Mascaros, *J. Mol. Struct.*, 1998, **470**, 81.

44 G. Alberti, U. Costantino, F. Marmottini, F. Vivani and P. Zappelli, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1357.

45 S. Yamanaka, *Inorg. Chem.*, 1976, **15**, 2811.

46 S. Yamanaka and M. Tsujimoto, *J. Inorg. Nucl. Chem.*, 1979, **41**, 605.

47 S. Yamanaka, H. Maeda and M. Tanaka, *J. Inorg. Nucl. Chem.*, 1979, **41**, 1187.

48 S. Yamanaka and M. Hattori, *Chem. Lett.*, 1979, 1073.

49 C. Y. Ortiz-Avila and A. Clearfield, *Inorg. Chem.*, 1985, **24**, 1773.

50 A. Clearfield and C. Y. Ortiz-Avila, in *Supramolecular Architecture*, T. Bein, ed., ACS Symposium Series 499, American Chemical Society, Washington, DC, 1992, p. 178.

51 C. Y. Ortiz-Avila, C. Bhardwaj and A. Clearfield, *Inorg. Chem.*, 1994, 2499–2500.