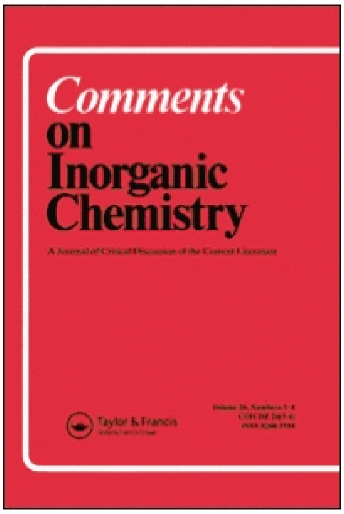

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Layered Phosphates, Phosphites and Phosphonates of Groups 4 and 14 Metals

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To cite this Article Clearfield, Abraham(1990) 'Layered Phosphates, Phosphites and Phosphonates of Groups 4 and 14 Metals', Comments on Inorganic Chemistry, 10: 2, 89 — 128

To link to this Article: DOI: 10.1080/02603599008050860

URL: http://dx.doi.org/10.1080/02603599008050860

Layered Phosphates, Phosphites and Phosphonates of Groups 4 and 14 Metals

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Research dealing with the ion exchange behavior of layered group 4 phosphates dates from World War II. Initially the exchangers were amorphous gels in which the exchange process was poorly understood. Crystallization of the gels and the subsequent determination of their crystal structures had led to an understanding of the ion exchange reactions. The most important group of exchangers have layered structures and can readily intercalate basic molecules in addition to exchanging ions. Their behavior can be used as the basis for understanding the properties of many proton containing layered compounds. The chemistry of these compounds has had a continuous growth in scope, particularly with the synthesis of organic–inorganic layered derivatives. Extension of this organic chemistry to divalent and trivalent metals further broadens the field. Potential applications as sequestrants, ion exchangers, catalysts, sensors and their possible use in the fields of electrochemistry and photochemistry are discussed.

Key Words: *layered tetravalent phosphates, ion exchange, intercalation, layered phosphonates, pillared compounds*

1. INTRODUCTION

Research in chemistry like other forms of human endeavor has its fashions. In the inorganic branch of our field organometallic chemistry has no doubt dominated the arena in the past 25 years with perhaps bioinorganic now running a close second. But at the same

Comments Inorg. Chem.
1990, Vol. 10, Nos. 2&3, pp. 89–128
Reprints available directly from the publisher

Printed in Great Britain

time, research in other less fashionable areas was pursued by those whose training and disposition inclined them in other directions. Such is the case with the research to be described in this paper. Twenty-five years ago solid state chemistry was decidedly not in vogue and the study of layered compounds was pursued mainly by soil and clay chemists. This was precisely the time when Jim Stynes, working for his Master's Degree at Niagara University under my direction, attempted to crystallize gelatinous zirconium phosphate following my suggestion.[1]

Zirconium phosphate had been known since before 1925 when von Hevesy[2] proposed its use for the quantitative determination of zirconium. This idea was abandoned due to the propensity of the precipitate to sequester foreign ions. This propensity was rediscovered in the early 1950's by several groups attempting to obtain ion exchange materials which would not deteriorate on long exposure to radioactive species.[3-5] The first preparations were amorphous gels of variable composition and properties. Many misconceptions about the structure of the gels and their ion exchange behavior abound in the literature, but it was only after the nature of the crystals was understood could the proper deductions concerning the gels be formulated.[6]

At first one might suppose than an understanding of the zirconium phosphate system of compounds constitutes a relatively narrow or restricted field of study. However, 25 years after the crystals of the α-phase were prepared, the field continues to expand and the lessons to be learned apply to broad areas of solid state science, as we shall see. For example, all of the group 4 and 14 elements except carbon form isostructural phosphates[6] as do some of the group 5 and 15 elements.[7] In addition there now exists a huge array of related organic phosphates[8] and phosphonates.[9] The chemistry to be derived from continued study of the organic derivatives could be quite substantial, and lead to numerous applications. Finally we might point out that a large number of proton containing layered compounds are now known.[10] In many respects, such as their ion exchange and intercalation properties, the zirconium phosphates may serve as a model system for understanding their behavior. Further extensions to mixed functionalities and di- and trivalent elements will also be discussed.

2. ZIRCONIUM PHOSPHATES

2.1 α-Zirconium Phosphate, $Zr(HPO_4)_2 \cdot H_2O$

In the usual preparative method for the gel, H_3PO_4 is added to a soluble Zr(IV) salt and the resultant precipitate, washed and dried. Although this procedure seems simple enough, in actuality the properties of the gel depend critically upon the preparative method. The dried particles can vary from hard glassy pieces to a fine white powder and the composition from 1:1 to slightly greater than 2:1 in phosphate–metal ratio. If a metal phosphate is used as precipitant, some of the metal cation will always be present in the precipitate, the amount depending upon the pH. This fact was not taken into account by Burdese and Bolera[11] who misinterpreted their results on heating a precipitate obtained by adding sodium phosphate to zirconyl chloride. On calcination they reported that $Zr_3(PO_4)_4$ was formed whereas their x-ray pattern was that of a sodium zirconium phosphate.[12] In fact we could not make the tetraphosphate, and as far as we know, reports of its existence are incorrect.

Crystallization of the gel is effected by boiling in phosphoric acid.[1] The process is extremely slow, requiring in excess of 14 days for complete crystallization in 12M H_3PO_4.[13] The reaction may be speeded up by either the addition of HF[14] to the solution or by raising the temperature at increased pressure. A teflon lined vessel is best used at the higher temperatures as strong phosphoric acid reacts with glass and other ceramic materials under such conditions. The crystallization reaction is evidently one of dissolution and recrystallization of the gel particles.[15] All of the phosphates of groups 4 and 14 (except carbon) can be prepared in this way. It might be well at this point to remember that a large number of amorphous gelatinous exchangers have been prepared.[16] In the early papers describing gelatinous zirconium phosphate, molybdates, tungstates and antimonates were also described.[4] Since then, the number of ion exchangers of this type that have been synthesized is truly astonishing.[16] However, the authors of these papers almost always fail to properly characterize the gels they have produced, and are contented to describe certain features of their ion exchange behavior.

In order to begin a rational approach to the nature of these gels we need to recall certain features of hydrous oxide structure. These oxides may be classified into two types; particle hydrates and framework hydrates.[17] Particle hydrates are those for which ion exchange occurs only on the surface, the interior or bulk being quite similar to the calcined oxide. Examples are the hydrous oxides of groups 4 and 14. Framework hydrates, in contrast, are those which contain cavities or tunnels such as the hydrous oxides of antimony and manganese.[10] Exchangeable ions reside within the cavities and tunnels or between layers. Since exchange in these compounds takes place throughout the surface and interior of the framework hydrates, their exchange capacities are usually much higher than those of particle hydrates. I suspect that the majority of the many ion exchange gels which have been prepared are particle hydrates. To determine whether this is so, attempts should be made to correlate surface areas with ion exchange capacity. Infrared and NMR spectra are but little affected by surface exchange whereas exchange of say Na^+ for H^+ in the interior of a framework hydrate will result in large spectral changes. The most direct procedure, however, remains the conversion of the gels to the crystalline state, generally by hydrothermal methods, followed by elemental analysis, ion exchange titrations, spectral studies and, if possible, structure determination. X-ray diffraction methods remain the definitive way to establish the true nature of the ion exchanger. For example, we crystallized zirconium molybdate and tungstate,[18] and found that they were no longer ion exchangers. Thus, the ion exchange behavior of the gels must have resulted from surface hydroxyl groups. In contrast α-zirconium phosphate in the gel state exhibited the characteristics of a layered framework compound.[19,20] Its conversion to the crystalline state represented an ordering of the layers with extended particle growth.[13,21,22,25]

The crystals are monoclinic[24,25] with $a = 9.060(2)$, $b = 5.297(1)$, $c = 15.414(3)$ and $\beta = 101.71(2)^\circ$, space group $P2_1/n$. The layers consist of metal atoms lying slightly above and below the mean plane and bridged by phosphate groups from above and below as illustrated in Fig. 1. 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 oxygens. The fourth oxygen bonds a

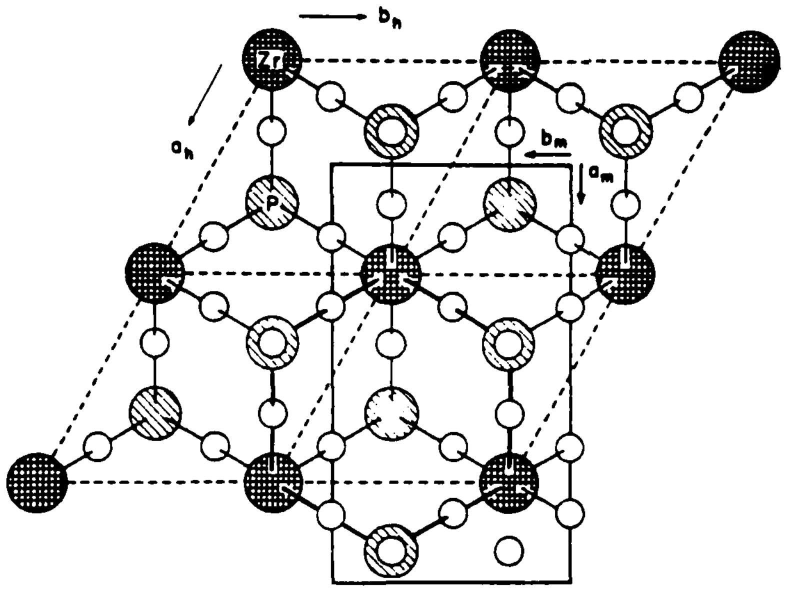


FIGURE 1 Idealized layer in the α-ZrP structure showing relationship of psuedohexagonal cell (a_h, b_h) to the true monoclinic cell (from Ref. 24, with permission).

proton and points into the interlayer space. Reference to Fig. 1 shows that the alternating metal and phosphate arrangement forms twelve-membered rings in a crown arrangement. If the phosphorus atoms are below the mean plane, than the ring is capped by a phosphate group above the plane and vice versa. Figure 1 is an idealized drawing which shows a pseudo-hexagonal cell ($a_h = b_h$) formed by the idealized arrangement. Adjacent layers are shifted relative to each other by $1/3a_h$, $2/3b_h$. This places one twelve-membered ring capped on the top over another capped on the bottom, but rotated 60° so that each phosphate group is above or below a zirconium atom in an adjacent layer. This arrangement creates six sided cavities,[26] illustrated by heavy lines in Fig. 2, of which there is one mole per formula weight. The water molecule sits inside the cavity near its center, forming a hydrogen bonding network with the phosphate groups.[25,27] However, only van der Waals forces hold the layers together as there are no interlayer hydrogen bonds.

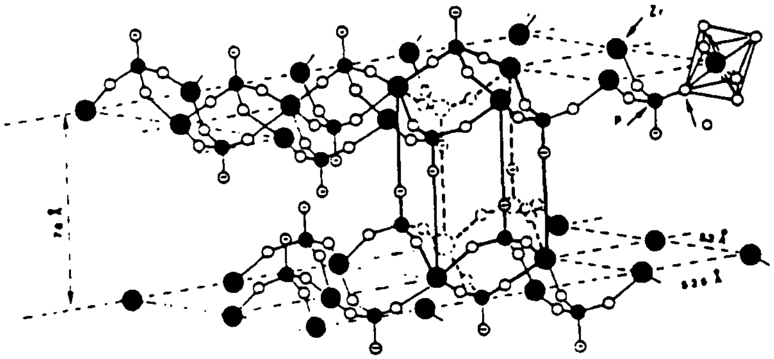


FIGURE 2 Schematic drawing of α-ZrP structure showing relationship between layers which results in formation of six-sided cavities as shown by the heavy solid lines. the P–OH protons and the water molecule have been omitted (from G. Alberti, in *Study Week on Membranes*, ed. R. Passino (Pontifical Academic Scientarum Scripta Varia, Rome, 1976). p. 629, with permission).

Clearfield *et al.*[13,19] have shown that the unit cell changes dimensions as the degree of crystallinity varies, rapidly at first and then more slowly. The first x-ray reflection exhibited by the crystals, (002), is 7.55 Å and represents the interlayer distance. In the gels, where at most only 4 reflections are observed, the (002) reflection may occur at a *d*-spacing as large as 11.2 Å due to water sorption or ~8 Å when dry.[19] As the crystallinity of the preparation increases, the unit cell dimensions progressively decrease[13] as shown in Table I. The effect of this cell volume shrinkage upon the ion exchange behavior of the resultant crystals is shown in Fig. 3. Crystals prepared hydrothermally are considered as having been refluxed for an infinite length of time and yield the titration curve shown as a dashed line. Note that this line has zero slope after a slight initial decrease in pH. The zero slope is dictated by the thermodynamics of the situation. X-ray powder patterns show that along the first zero slope portion of the curve the exchanger of composition $Zr(HPO_4)_2 \cdot H_2O$ is converted into the phase $ZrNaH(PO_4)_2 \cdot 5H_2O$. Both phases are present in the same crystal[6] so that the phase rule requires that the system be invariant. That is, there are three phases present; two crystal phases and the solution phase, and three components are required to describe the system: the H^+ in solution and in the solid and the Na^+ in the

TABLE I

Unit cell dimensions of α-ZrP samples[a]

Dimension	α-ZrP Exchanger				
	12:24[b]	12:48	12:96	12:190	∞
a, Å	9.097 (5)	9.0523 (21)	9.0401 (10)	9.0491 (13)	9.0540 (20)
b, Å	5.307 (1)	5.2853 (16)	5.2775 (7)	5.2845 (9)	5.2843 (15)
c, Å	16.284 (3)	16.2508 (65)	16.2125 (25)	16.1938 (35)	16.1908 (65)
β, deg	111.38 (1)	111.369 (27)	111.414 (11)	111.447 (15)	111.440 (30)
$a \times b$, Å^2	48.278 (27)	47.844 (17)	47.709 (8)	47.820 (10	47.844 (17)
V, Å^3	732.0 (5)	724.1 (4)	720.1 (2)	720.8 (2)	721.0 (4)

[a] Estimated standard deviations in the last significant figures are given in parentheses.
[b] Data taken from Acta Chem. Scand. 23, 1446 (1969).

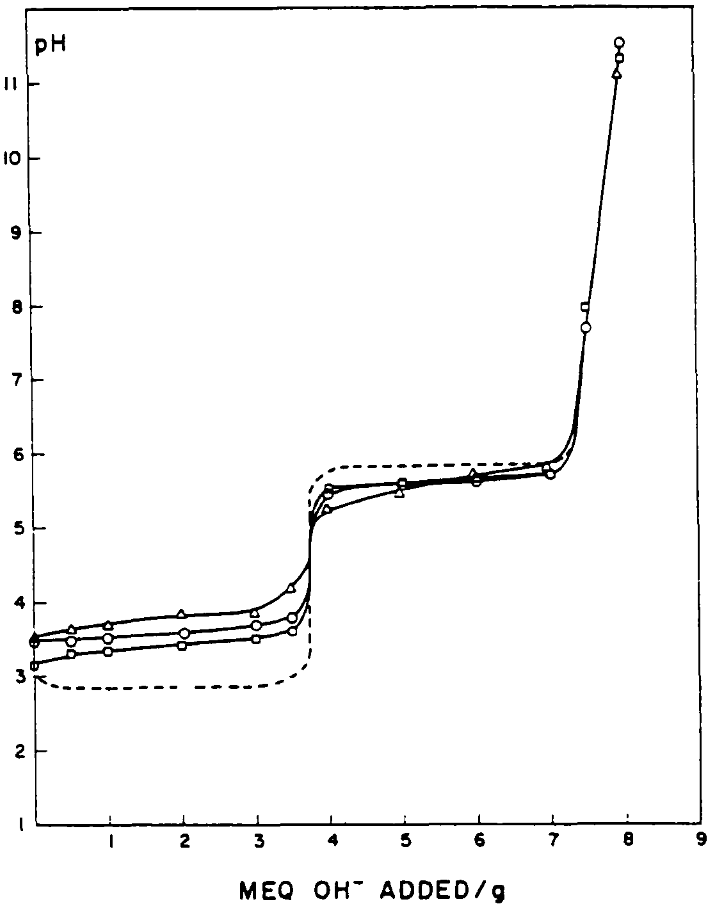


FIGURE 3 Potentiometric titration curves for α-ZrP of different (high) crystallinities. The exchanger samples were prepared by refluxing a gel in 12M H_3PO_4 for 48 h (Δ), 96 h (○), 190 h (□) and more than 300 h (dashed line). Titrant: 0.100M NaOH + 0.1M NaCl (from Ref. 13, with permission).

solid. Since the vapor pressure change is negligible and the temperature is held constant during the titration,

$$f = 3 - 3 + 0 = 0 \tag{1}$$

and the system is invariant.[28] Note that all the other curves in Fig. 3 have a positive slope which means that a degree of freedom is present in the system. This situation arises because, in less crystalline samples of the exchanger, a certain amount of solid solution is present and one more component is necessary to describe the system. The gel forms a complete solid solution, whose composition range decreases as the crystallinity of the exchanger increases. This is reflected in the ion exchange behavior as shown in Fig. 4. For a completely amorphous gel there is observed a large

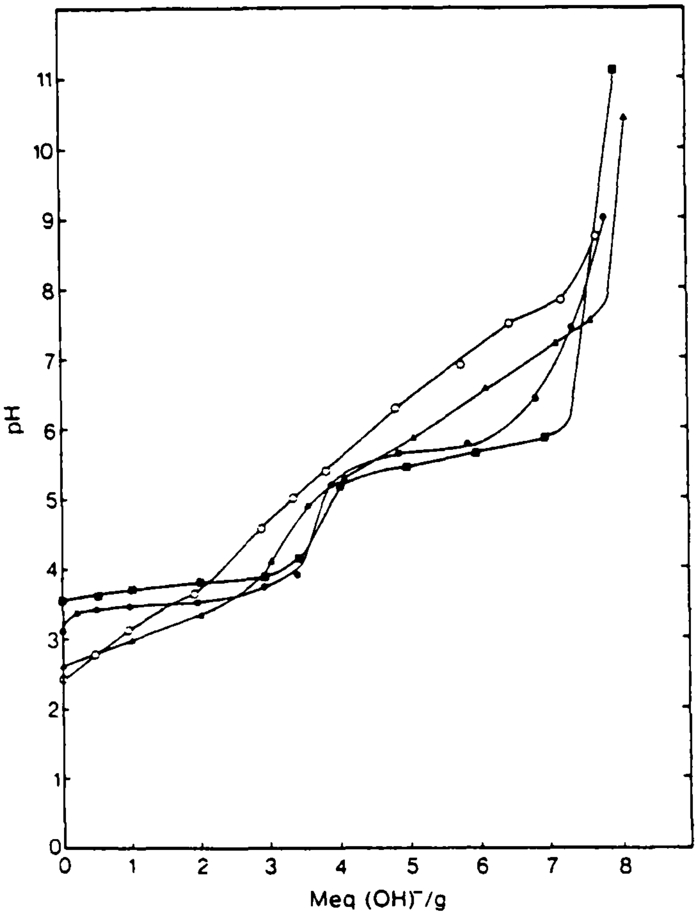


FIGURE 4 Potentiometric titration curves of α-ZrP for exchanger samples of low and intermediate crystallinity. Samples were prepared by refluxing an amorphous gel for 48 h in 0.8M H_3PO_4(O). 2.5M H_3PO_4(▲). 4.5M H_3PO_4(●) and 12M H_3PO_4 (■). Titrant as for Fig. 3 (from Ref. 19. with permission).

increment in pH with each Na^+ uptake by the exchanger. As the crystallinity increases the pH increments decrease and finally approach the constant pH plateaus shown in Fig. 3.

These results provide an explanation for the many contradictory reports in the literature. Subtle changes in gel structure and different degrees of crystallinity show up as differences in the exchange properties which have their roots[28,29] in Eisenman's theory of ion exchange.[30] According to Eisenman the closer the incoming ion approaches the fixed charges of the exchanger, the greater the free energy of exchange. Actually, the free energy depends upon the difference in energies involved in not only bringing the incoming ion from infinity to its equilibrium position inside the exchanger but also taking the co-ion from the exchanger to infinity. In semicrystalline and crystalline samples of α-ZrP[31] the protons are covalently bonded to oxygen.[25,27] Thus, the bond energy should be almost identical and the real difference is the closeness of approach of the incoming ion. Presumably this distance is smaller the smaller the unit cell dimensions, particularly the *c*-axis dimension, of the exchanger. This is reflected in the ion exchange curves of Fig. 3. As the crystallinity increases, the preference of the exchanger for Na^+ (the incoming ion) relative to H^+ increases as shown by the fact that exchange is able to occur at lower and lower pH values. A second factor which determines the free energy of exchange is the difference in hydration energies for the exchanger in the H-form and the Na^+-form. However, for the crystalline and semicrystalline samples this difference is almost constant as the H-form always contains one mole of water and the half-exchanged Na^+ phase 5 moles.[26]

The situation is different in the case of the zirconium phosphate gels. Some swelling of the gels occurs prior to exchange and part of the protons may be present as H_3O^+. Furthermore, the water content may vary depending upon the degree of order in the gel. In Fig. 4, we see that the most amorphous gel initially prefers Na^+ to a greater extent than the crystals. In the swollen state the zirconium phosphate may be considered a weak field exchanger in the Eisenman sense (the electrostatic effect predominates) and the predicted sequence of affinities, $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, is the one actually observed. The dominance of the electrostatic effect may be rationalized on the following grounds. Initially no energy is consumed in breaking an oxygen–hydrogen bond since H_3O^+ is already present. Moreover, the energy in expanding the layers was consumed prior to exchange. Thus, the reaction is strongly exothermic. In addition, only a small amount of water is transferred to the exchanger resulting in negative entropy effects. As exchange proceeds a small amount of swelling occurs followed by a steady decrease in the interlayer spacing.[19] Presumably, the cations initially locate near the most negative sites, but as exchange proceeds less negative sites, where O–H bonds need to be broken, are occupied. At greater than 50% of exchange, cations must necessarily enter already occupied cavities so that cation repulsions come into play. These combined factors reverse the enthalpy to endothermic. In addition water is now transferred from the exchanger to the solution so that the entropy begins to increase. The cavities themselves are probably ill formed due to the disorder in the gel. However, it would be expected that the larger cavities can accommodate two cations but the smaller ones cannot. Thus, phosphate hydrolysis progressively increases with each addition and 100% exchange is not achieved except in fused salts.[32] All of these effects result in selectivity changes which, in the main, follow Eisenman's predictions.

Exchange with crystalline α-ZrP lends itself to exact thermodynamic treatment and the principal thermodynamic quantities for alkali metal exchange have been determined.[6,29] The main feature of the α-ZrP structure is that the layers arrange themselves in such a way as to create cavities between the layers. The largest entranceways into the cavities would allow a cation of 2.61 Å diameter to diffuse unobstructed through the cavities.[25,26] This should allow Li^+, Na^+ and K^+ to diffuse, in an unhydrated state, into the crystal, but Rb^+ and Cs^+ should be excluded. This is indeed the case.[29] However, these larger ions may be exchanged in basic solution. Apparently, in the presence of hydroxide ions, protons of the exchanger near the surface are neutralized with increase in the interlayer spacing, thus allowing the larger ions to enter the crystals.[27]

The mechanism of exchange without base addition can be visualized as taking place in the following way. The hydrated ions exchange with surface P–OH groups introducing protons into the solution. Since the entire surface is available to the incoming ions without obstruction, hydrated ions may exchange and the selectivity sequence for surface exchange is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. However, a small amount of cation will diffuse into the crystal lattice in an unhydrated or partially hydrated condition, provided it is small enough to do so. Rb^+ and Cs^+ are too large and thus exchange only on the surface.[33,34] The ingoing cation forms a solid solution with no phase change. Thus, the equilibrium pH is determined by the amount of solid solution and this is in the order[29] $K^+ > Na^+ > Li^+$. The titration curves for the alkali metal cations indicate that the solubility of these cations in α-ZrP is in this order.[29] The observed lowering of the pH is thus in the same order as the decrease in heat of hydration of the alkali metals. Thus, the extent of exchange without added base depends upon both the size of the cation and its heat of hydration. Polyvalent ions exchange to a very low extent because of their high ΔH_{Hyd} values.

The amounts of ion taken up at equilibrium without added base are quite small but may be as high as 8–10% (of the half-exchanged amount).[35,36] Exchange will not occur beyond this point without adding base to consume the excess protons. However, upon addition of base local concentrations of OH^- near the crystals may occur so that the layers near the crystal surface expand and ions rush in. If the amount of base added is such that the pH remains high for a period of time, the phase that forms may be the fully exchanged one. As the pH falls the high metal-ion-containing phase reverts to the equilibrium (acid stable) phase, e.g., the half-exchanged phase. Indeed such a sequence has been observed for the K^+–H^+ system.[37] Along the plateaus of the titration curves we have seen that two phases with different interlayer spacings coexist. Since exchange occurs from the outer surfaces towards the center and the half-exchanged phases have larger interlayer spacings, the crystal layers may be visualized as in Fig. 5.[38] The region between the two phases is disordered, and even when exchange is complete, some disorder persists. The x-ray diffraction powder pattern reflects this fact in the broadness of the observed peaks. For this reason the crystal structures of the exchanged phases could not be determined from single crystal data. However, we were able to obtain the structures of the anhydrous and monohydrated half-exchanged K^+ and Na^+ phases from powder x-ray data.[39,40]

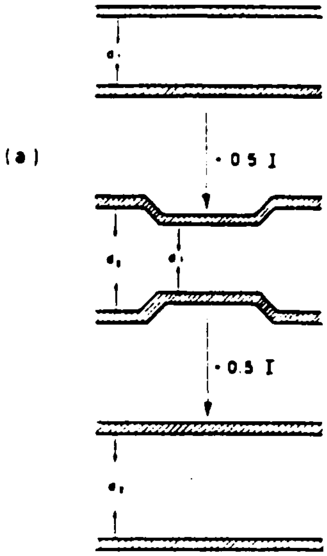


FIGURE 5 Schematic illustration of layer changes in α-ZrP during ion exchange. Exchange occurs from the outer edges inward, increasing the interlayer distance from d_1 to d_2. Both phases exist in the same crystallite. At the completion of the exchange process the crystallites have a single interlayer spacing d_2 (from Ref. 38, with permission).

The structures are shown in Figs. 6 and 7. $ZrNaH(PO_4)_2 \cdot H_2O$ retains essentially the same layer structure as the parent α-ZrP phase. However, the phosphate groups are skewed as shown in Fig. 6. This has the effect of producing alternating wide and narrow cavities. The sodium ions reside in the widened cavities in rows parallel to the *b*-axis.[40] Each Na^+ is loosely held, being surrounded by six atoms; two Na^+ at 2.84 Å in the axial positions, a water oxygen (black circle) at 2.46 Å, two framework oxygens at approximately 3 Å and a $P-O^-$ phosphate oxygen at 2.98(6) Å. One of the framework oxygens coordinating Na^+ forms part of the same phosphate group as the $P-O^-$ group. Thus, these oxygens form a chelating arrangement towards the sodium ions. Nevertheless the strong repulsions of the sodium ions make the structure metastable. Thus, the water molecule is readily given up to form the structure shown in Fig. 7.[39] In the anhydrous phase the Na^+ (and K^+) ions are aligned along the *a*-axis about 1/2*a* or ~5 Å apart.

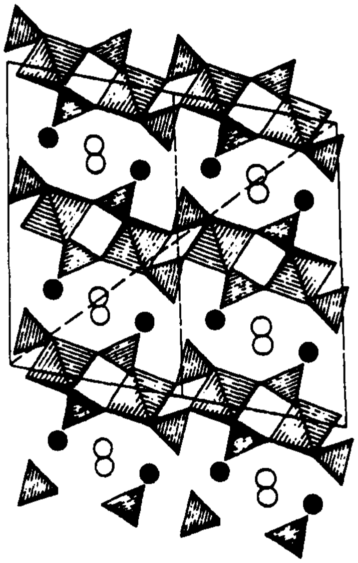


FIGURE 6 Polyhedral representation of $ZrNaH(PO_4)_2 \cdot H_2O$ unit cell contents projected along the *b*-axis, showing the water molecules (dark circles) and sodium ions (open circles) residing between the layers (from Ref. 40, with permission).

This more stable positioning of the ions is brought about by a spontaneous shift of the layers relative to each other by 1/2*b* upon loss of the water.

It should be noted that the alignment of the ions in the monohydrate is in the position closest to the largest opening into the cavities. Thus, we may speculate that the diffusion path followed by the incoming ions is in the zig-zag route through the largest cavity passageways while the protons diffuse outward as hydronium ions along the cavity faces opposite the incoming ions.[40]

Other aspects of the ion exchange behavior of α-ZrP, such as with polyvalent ions, exchange in fused salts and exchange with the expanded layer (θ-ZrP) phase have been summarized in several reviews.[6,38,41]

α-type phosphates (and some arsenates) of all the group 4 and 14 elements have been prepared.[6,7] All of them have been prepared

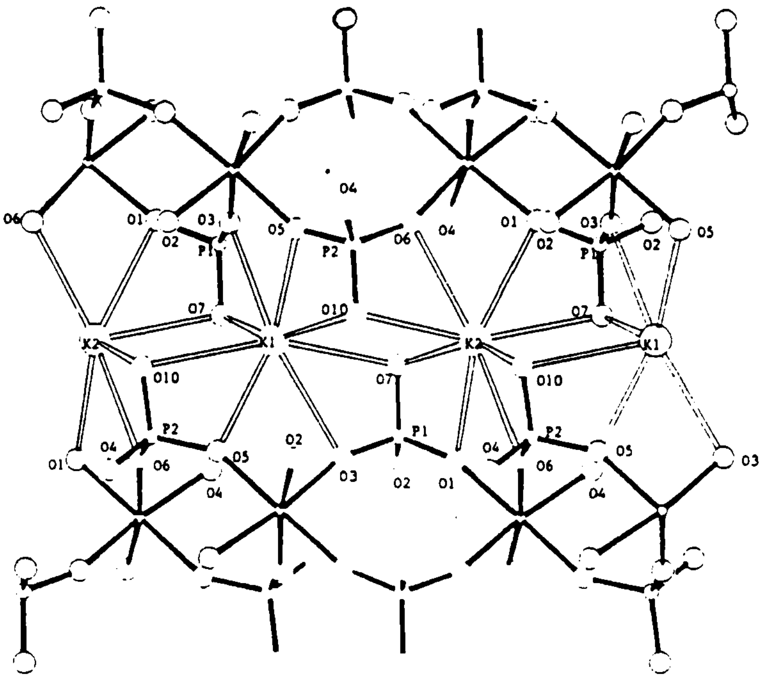


FIGURE 7 Ball and stick representation of the α-ZrKH$(PO_4)_2$ structure showing the K^+ coordination as double lines. The *a*-axis is horizontal and the *b*-axis is perpendicular to the plane of the paper (from Ref. 39a, with permission).

by variants of the methods described for α-ZrP. Pertinent data for these phases are given in Table II. Winkler and Thilo[7] prepared these compounds by dissolving the chlorides [or GeO_2, Pb $(CH_3COO)_4$] in concentrated H_3PO_4 and heating to 150°C (270°C for tin). Small hexagonal platelets were obtained in each case. X-ray diffraction patterns revealed that all these compounds were isomorphous. The silicon compound was found to decompose in water and therefore has been little studied. The ion exchange behavior of these compounds is conditioned by the differences in the distances between the phosphate groups (or the size of the cages) and the ease with which hydrolysis occurs.[42]

TABLE II

Some important acid salts of tetravalent metals with layered structure of the α-type

Compound	Formula	Interlayer Distance (Å)	Ion Exchanger Capacity (meq/g)
Titanium phosphate	$Ti(HPO_4)_2 \cdot H_2O$	7.56	7.76
Zirconium phosphate	$Zr(HPO_4)_2 \cdot H_2O$	7.56	6.64
Hafnium phosphate	$Hf(HPO_4)_2 \cdot H_2O$	7.56	4.17
Germanium(IV) phosphate	$Ge(HPO_4)_2 \cdot H_2O$	7.6	7.08
Tin(IV) phosphate	$Sn(HPO_4)_2 \cdot H_2O$	7.76	6.08
Lead(IV) phosphate	$Pb(HPO_4)_2 \cdot H_2O$	7.8	4.79
Titanium arsenate	$Ti(HAsO_4)_2 \cdot H_2O$	7.77	5.78
Zirconium arsenate	$Zr(HAsO_4)_2 \cdot H_2O$	7.78	5.14
Tin(IV) arsenate	$Sn(HAsO_4)_2 \cdot H_2O$	7.8	4.80

2.2 γ-Zirconium Phosphate and Other Phases

Shortly after the preparation of α-ZrP a second phase of composition $Zr(HPO_4)\cdot 2H_2O$ was prepared.[43] It has an interlayer spacing of 12.2 Å and a fundamentally different layer structure than α-ZrP. This compound has been labeled as γ-ZrP. On dehydration the interlayer distance decreases to 9.4 Å. The γ-phase was prepared by refluxing a solution 0.3M in Zr(IV), in HCl and 6M in NaH_2PO_4. The crystalline solid obtained was the half sodium ion phase, which was converted to the proton phase by washing with 2M HCl. Subsequently very thin rectangular shaped crystals were grown in sealed tubes in this mixed sodium phosphate–HCl solution.

Although the structure of the γ-phase is unknown there is no question that it is layered. This is readily deduced from the fact that it intercalates amines or alkanols readily with expansion of the initial *d*-spacing (002). Yamanaka and Tanaka[44] determined the unit cell of γ-ZrP from electron diffraction patterns to be a = 5.376(2) Å, b = 6.636(4) Å, c = 24.56(1) Å and β = 93.94(5)°. From these values and density considerations, Alberti deduced that the metal atoms were closer together in the γ-type layer than in the α-phase.[42] He pointed out that the γ-phase is favored by high concentrations of $H_2PO_4^-$ and/or HPO_4^{2-} anions and seems to indicate that these ions are involved in the formation of the γ-phase. In fact, a later NMR study[45] on γ-ZrP concluded that half the phosphate groups are dihydrogenphosphate and the other half are orthophosphate, PO_4^{3-}.

Because of its larger interlayer spacing γ-ZrP is able to exchange significant amounts of univalent as well as polyvalent cations without base addition.[46] The selectivity sequences for alkali metal ions are different than exhibited by α-ZrP but still follow Eisenman's predictions.[30] More recently, Lavona *et al.*[47] have carried out very extensive ion exchange studies on α-ZrP and γ-TiP.

A number of other layered zirconium phosphate phases have been synthesized.[48] Some are ion exchangers and others are not. However, in a larger sense there exists a multitude of proton containing layered phases.[10] These include group 5 and 15 phosphates, titanates, antimonates, niobates, tantalates, titanoniobates and mixed valence manganates. The pioneering work carried out in great detail on α- and γ-ZrP serve as model systems for the further study of all these layered solid acids.

3. INTERCALATION BEHAVIOR OF ZIRCONIUM PHOSPHATES

The zirconium phosphates exhibit a rich and varied intercalation chemistry. This behavior arises from the high acidity in the protonic form and the weak forces between the layers. Thus, both α- and γ-ZrP readily intercalate amines but can also be made to interact with less basic compounds such as alcohols, acetonitrile, acetylacetone, etc. The intercalation chemistry of the layered group 4 phosphates has been discussed in a series of reviews[49,50] so that only the salient points will be mentioned here.

n-alkylamines are taken up by α-ZrP from aqueous solutions, the gas phase and from organic solvents. A maximum of 2 moles of amine per formula weight is intercalated forming a bilayer.[51,52] The amines initially lie parallel to the layers at low loadings as the interlayer spacing increases from 7.6 Å to ~10.4 Å irrespective of the amine chain length.[52] As the amount of amine taken up by the host increases, a series of phases is formed in which the amines begin to incline to the layers at increasing angles. At saturation the angle of inclination is ~56°. Under ideal conditions plateaus are observed in the amine titration curves indicating the presence of two solid phases.[53] However, this situation is complicated by the presence of solid solution regions and the slow approach to equilibrium for the intermediate phases. Deintercalation of the amine by addition of acid does not follow the same path as the intercalation. New phases are observed to form as well as more extended solid solution regions.[54] Lesser amounts of secondary and tertiary amines are intercalated because the alkyl chains cover more than one phosphate position. Each phosphate group occupies an area of 24 $Å^2$ and only *n*-alkyl chains can pack tightly enough to not overlap more than one phosphate region.

When propylamine is intercalated into α-ZrP, the lattice becomes progressively disordered and at an uptake of about 2.5 meq/g (~37% of saturation) entirely amorphous.[52] At loadings of 4.5 meq/g, the crystallinity returns with formation of a multiphase system. Alberti *et al.*[55] correctly interpreted this phenomenon as being caused by the exfoliation of the α-ZrP layers. When this colloidal dispersion is treated with acid, very thin platelets of α-ZrP are obtained and these readily adhere to surfaces. Thus, thin coatings and membranes may be formed from the particles, which have been termed "pellicular zirconium phosphate." Aqueous dispersions, as well as coherent films or materials covered with the films of the pellicles, show promise for applications in the fields of ion exchange, catalysis, ion exchange membranes, chromatographic supports, protonic conductors and hydrogen sensors.[56]

Diamines form monolayer intercalates with α-ZrP.[52,57] As with *n*-alkyl amines the diamines initially occupy positions parallel to the layers. The reactions occur in a stepwise fashion as the regions near the edges take up the amine preferentially followed by slow diffusion into the interior. Thus, several intermediate intercalation phases are obtained before the final saturated one. At full intercalation the amines (with even numbers of carbon atoms) are inclined at 58° to the layers with the amino groups protonated by the P–OH groups of the host lattice. At half-saturation it is possible to have the amines evenly distributed throughout the crystals so that spaces remain between the carbon chains. In this condition further uptake of polar molecules such as water and smaller chain alcohols is possible.

α-ZrP itself does not intercalate alcohols because the crystals do not swell, either in water or alcohol. However, the half-sodium ion exchanged phase, $ZrNaH(PO_4)_2 5H_2O$ has an interlayer spacing of 11.8 Å. If this phase is treted with a small chain alcohol protonated with $HClO_4$, the alcohol is intercalated while the Na^+ is displaced by protons.[49,58] Once the alkanol intercalate has been formed, it is easy to replace the intercalated molecule by other alcohols and a variety of polar molecules such as acetonitrile, acetylacetone and dimethylacetone, as well as aromatic amines. The same technique may be used even with amine intercalates to incorporate polyvalent metal ions or large complex ions between the layers.[59,60] Such reactions are facilitated by the increase in the interlayer spacing of the intercalate. In fact, it was possible to pillar α-zirconium and titanium phosphates with the aluminum Keggin Ion, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ by first preparing the butylamine intercalate and then exchanging the Al_{13} cation.[61] This reaction appears to be general, as the hexylamine intercalate of $H_2Ti_4O_9$ was similarly pillared,[62] a reaction suggested by the writer.

Judging from the recent literature, the interest in intercalation reactions with both α- and γ-ZrP continues unabated. Among the intercalates prepared, by both direct and indirect methods, we may mention urea and its derivatives,[63] amides,[63] dimethylsulfoxide[63,64] biopharmaceuticals such as aminoacids,[65] heterocyclic bases (imidazole, histimine, etc.)[66] and cobaltacene.[67] Other molecules have been incorporated between the layers by preparing the ZrP with the molecule of interest in situ[68,69] or with wet freshly prepared ZrP.[70]

4. PILLARING OF LAYERS IN ZIRCONIUM PHOSPHATES

The layered zirconium and titanium phosphates are solid acids of medium acid strength. As such they have been shown to be effective as Bronsted Acid Catalysts.[71-73] Transition metal exchanged phases participate in oxidation reactions[73,74] and in the reduced state in metal catalyzed reactions.[75] However, a limiting factor is the low surface area of the highly crystalline phosphates. Although the more amorphous products have considerably increased surface areas, they are less stable thermally.[76] An effective method which has been applied to smectite clays is to prop the layers open by insertion of an inorganic polymer, thereby creating interlayer pores.[77,78] The smectite clays are eminently suitable to participate in such pillaring reactions because they can be made to swell in water so that barriers to diffusion of the pillaring ions are overcome. Although α-layered compounds resemble clays in structure, they do not swell in water due to their much higher layer charge (exchange capacity of α-ZrP is 6.6 meq/g compared to about 1 meq/g for smectite clays). Therefore it is necessary to pre-swell the layers in order to effect pillaring. We have already mentioned the pillaring of α-ZrP and α-TiP with $[Al_{13}O_4(OH)_{24}(H_2)_{12}]^{7+}$ by pre-swelling with *n*-alkylamines. The zirconium compound was always stuffed, that is, the interlayer space was filled with the aluminum species such that no pores existed other than macropores. In contrast α- and γ-TiP contained pores of diameters between 6 to 8 Å as well as macropores.[61] Much additional study on these systems is required in order to better control the pillaring reactions.

Two other methods of pillaring the phosphates have been described. One method involves the use of diphosphonic acids to crosslink layers and will be discussed in Section 6.2. In the other method a large organic diamine such as 2, 2-bipyridine (bipy)[79a] or 1, 10-phenanthroline (phen)[79b] is used to prop the layers open. These amines cover more than two phosphate groups, leaving open channels between the layers. In order to intercalate such large molecules it was necessary to first prepare the ethyl alcohol intercalate, α-$Zr(C_2H_5OH)_2(HPO_4)_2$, d_{002} = 14.2 Å, and then add an ethanol solution of the amine. The composition of the intercalates was α-$Zr(HPO_4)_2(bipy)_{0.25}\cdot 1.5H_2O$ and α-$Zr(HPO_4)_2(Phen)_{0.5}\cdot 2H_2O$. Addition of transition metal ions (Cu^{2+}, Ni^{2+} and Co^{2+}) then resulted in formation of the bipyridyl and phenanthroline complexes. Further uptake of metal ions was possible by displacement of protons from P–OH groups not covered by the complexes. The conformation of the amines and complexes depended upon compositional factors such as water and metal content. Spectroscopic evidence revealed that the metal complex pillars have very distorted geometries because of the steric constraints imposed by the interlayer region.

More recently the same amines have been intercalated into γ-ZrP.[80] Since the gamma phase has an interlayer spacing of 12.2 Å no pre-swelling was required. Metal complexes were then formed as before but the orientations of the amines in the intercalate differ from those in the α-phase, probably due to the presence of hydrogen bonding by the interlayer water molecules.

While the type of pillaring just described is extremely interesting in delineating guest–host chemistry and in examining "intercalation coordination chemistry" it is not likely to provide porous materials suitable for heterogeneous catalysis. This is so for several reasons. The pores that are created, although not measured, must be fairly small, judging from the slow rate of uptake of transition metal ions. Moreover, the layers are not held apart rigidly and some loss of pillar may occur. However, the thermal stability of the bipy complexes is moderately good to 330°C. A potentially more useful procedure for pillaring the phosphates will be described in Section 6.2.

5. ZIRCONIUM PHOSPHATE PHOSPHITE

Before proceeding to a discussion of organic derivatives of the layered phosphates, we shall describe a hybrid type of layered compound containing both phosphate and phosphite groups. The compounds were prepared by adding $ZrOCl_2 \cdot 8H_2O$ in a 7M HF solution to a mixed H_3PO_4–H_3PO_3 solution followed by heating at 80°C to form crystals.[81] Three types of compounds were obtained depending upon the ratio of phosphate to phosphite added; a phase with essentially the α-ZrP structure but incorporating up 27% of phosphite groups, a phase with essentially the $Zr(O_3P{-}H)_2$ structure but incorporating up to 18% of monohydrogenphosphate groups, and a phase with roughly equal amounts of the two groups.[81,82] Originally it was thought that the phosphate and phosphite groups were randomly dispersed based on chemical evidence.[81] However, Rietveld analysis of the x-ray powder patterns revealed that asymmetric layers are formed.[82] The proposed layer structure of $Zr(HPO_4)_{0.85}(HPO_3)_{1.15}$ is shown in Fig. 8. One layer is of the zirconium phosphite type while the adjacent layer is of the α-ZrP type. This asymmetry is carried over into the phosphite rich phase. One layer type consists of all phosphite groups, while the alternate layers have the phosphite structure but with the phosphate groups randomly distributed within them. In contrast the phase of low phosphite content has the α-ZrP structure with the phosphite groups randomly dispersed throughout.

The ion exchange behavior towards alkali metal ions of $Zr(HPO_4)_{0.7}(HPO_3)_{1.3} \cdot 0.5H_2O$, hereafter referred to as ZrPP, was examined in detail.[83] Only the phosphate containing layer can participate in exchanging ions. However, because of the presence of alternating inert layers more energy is required to form a phase boundary. Consequently, the exchange process occurs at higher pH values in ZrPP than in α-ZrP. Furthermore, ZrPP prefers a continuous expansion of the interlayer distance with large solid solution regions. Thus, in the Na^+–H^+ system a single solid solution exists from 60–100% of exchange. The first step in the Na^+ exchange process occurs in the 0–30% uptake region. A phase with an interlayer spacing of 18.1 Å (5.6 Å for the phosphite layer + 12.5 Å for the Na^+ exchanged layer). From 30–60% of exchange the 18.1 Å phase is converted to a 15.9 Å phase and this

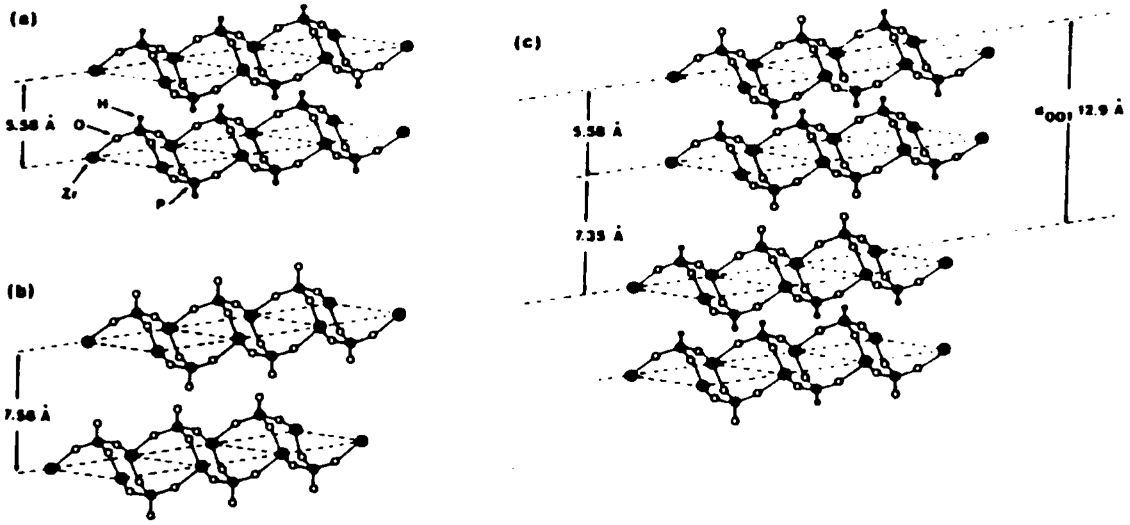


FIGURE 8 Schematic drawing of the structure of (a) zirconium phosphite, (b) α-zirconium phosphate and (c) zirconium phosphate–phosphite (from Ref. 82, with permission).

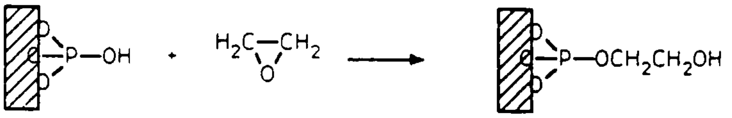
latter one exists from 60% uptake to complete exchange. In the two phase regions, the pH is nearly but not quite constant as the titration curve always exhibits a small positive slope. Thus, even from 0–60% of exchange, solid solution regions are present. Finally, it should be noted that because of the presence of some phosphite groups in the phosphate layer, some of the interlayer cavities are enlarged and provide pathways for the exchange of large cations. This feature allows Cs^+ and Rb^+ to exchange at acid pH values.

The same features carry over into the intercalation of amines.[84] *n*-alkylamines are intercalated more rapidly in ZrPP than in α-ZrP and at higher pH values. Intercalation occurs in two steps. At first, the amines take a position parallel to the layers but at higher loadings form a bilayer. The increase in interlayer spacing is 1.54 Å/C atom. This value is less than observed in α-ZrP and indicates that the alkyl chains assume a certain amount of mixed gauche-trans conformation. This behavior is reasonable considering that more space is available to the chains (average of one alkyl chain per 36 Å^2 in ZrPP as compared to 24 Å in α-ZrP). This additional space imparts a liquid like character to the alkyl chains as shown by the broadened x-ray reflections for planes perpendicular to the layers compared to sharp x-ray reflections for the (00*l*) peaks.

6. ORGANIC DERIVATIVES OF LAYERED GROUP 4 AND 14 PHOSPHATES

6.1 Ester Derivatives

Yamanaka and Koizumi[8,64] demonstrated that γ-ZrP reacts with ethylene oxide to form layered phosphate esters. The reaction may be represented as in Eq. (2).



(2)

Under more severe conditions further reaction to dimerization and trimerization of the ester was achieved to form polyether chains. Subsequently, a similar reaction was carried out with propylene oxide, but only half the hydroxyl groups were esterified.[85] A possible explanation for this difference suggests itself from Clayden's formulation[45] of γ-ZrP as $Zr(PO_4)(O_2P(OH)_2)$. Only one of the hydroxyl groups is esterified since there is insufficient space to satisfy the steric requirements for two such esters on the same phosphate group. Under forcing conditions, polymerization took place with formation of di- and tripropylene oxide chains. Interlayer spacings as high as 30 Å were observed. These ester derivatives were found to undergo facile ester interchange reactions.[85-91] The reactions proceed topotactically by a diffusion process with retention of the original γ-ZrP layer.[90] The original γ-ZrP could be reobtained by refluxing the phosphate esters in H_3PO_4. Conversely refluxing γ-ZrP with an organic orthophosphonic ester ($ROPO_3H_2$) resulted in replacement of $H_2PO_4^-$ by $ROPO_3H$.[88,89] The *n*-alkyl derivatives are able to intercalate *n*-alkanols. Yamanaka *et al.*[91] used the ester interchange reaction to prepare γ-ZrP type derivatives containing ethylene oxide chains by refluxing γ-ZrP with $CH_3(OCH_2CH_2)_n$–OPO_3H_2 (n = 1–3). These derivatives were able to form complexes with alkali metal salts of soft base anions (SCN^-, Br^-, etc.) in a fashion similar to the complexes formed by ethylene oxide polymers.[92]

In the studies by Yamanaka and his co-workers organic analogues of the α-ZrP type were not prepared. This was attributed by Clearfield to the inability of ethylene oxide or phosphate esters to diffuse between the layers of α-ZrP (interlayer spacing 7.6 Å). This in fact was proven correct by first demonstrating that ethylene oxide esterifies the external surface of α-ZrP.[93] However, if the layers are first swollen to larger interlayer spacings, the interior is also esterified by ethylene oxide and ester interchange reactions can also take place inside the expanded lattice.[93,94]

Attempts to incorporate long chain polyethers onto the layers with ethylene oxide were unsuccessful. Presumably the energy required to expand the layers precludes extensive polymerization from occurring. However, if a polyether phosphate is first prepared and allowed to react with Zr(IV) solution, polyether derivatives of α-ZrP are obtained.[94] As the chain length increases the product becomes difficult to isolate from aqueous media due to the strongly hydrophilic character of the polyether chains. In fact when the degree of polymerization of the chains was 9 or greater, complete dispersion of the solid in the aqueous phase occurred. The polyether chains readily incorporate electrolytes, forming conductive films similar to those prepared from polyethylene oxide films.[92]

6.2 Alkyl and Aryl Layered Phosphates and Phosphonates

A very fundamental advance in the development of the chemistry of four-valent metal layered compounds was inaugurated when Alberti *et al.*[95] demonstrated that α-type layered compounds could be prepared with phosphonic acids as well as organic phosphates. A schematic representation of the phenyl compound is shown in Fig. 9. The unit cell dimensions within the layer are similar to those for α-ZrP. However, the interlayer spacing is enlarged to accommodate the phenyl rings. We have prepared similar derivatives with biphenyl and triphenyl rings with interlayer spacings of 23.2 Å and 31.7 Å, respectively.[96] Subsequently a large number of such derivatives were synthesized by Dines and co-workers.[97,98] A partial listing is provided in Table III. Just as it was possible to form a phosphate–phosphite so it is possible to prepare organic derivatives with more than one type of pendant group.[97–100] Three different phases can be prepared: (1) almost pure $Zr(O_3PR)_2$ containing small amounts of $R'PO_3$, (2) almost pure $Zr(O_3PR')_2$ con-

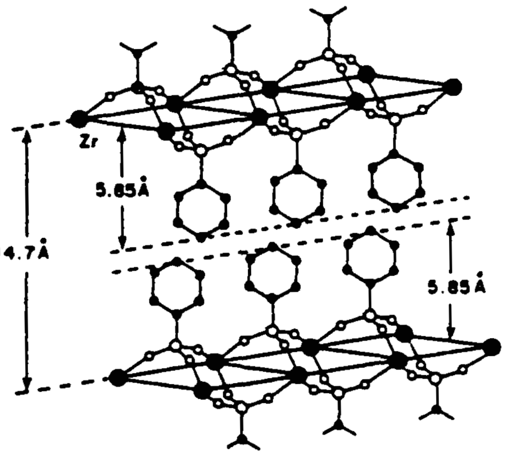


FIGURE 9 Schematic drawing (idealized) of zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$ (from Ref. 95, with permission).

TABLE III

Formulae and interlayer distances (nm) of some organic derivatives of zirconium phosphate having an α-layered structure

Compound	Interlayer Distance (Å)
$Zr(CH_3PO_3)_2$	8.9
$Zr(ClCH_2PO_3)_2$	10.1
$Zr(HOCH_2PO_3)_2 \cdot H_2O$	10.1
$Zr(HOOCCH_2PO_3)_2$	11.1
$Zr(HOOCCH_2CH_2PO_3)_2$	12.8. 13.2
$Zr(C_3H_7PO_3)_2$	14.0
$Zr(CH_2{=}CHPO_3)_2$	10.6
$Zr(C_6H_5PO_3)_2$	14.7, 15.0
$Zr(C_2H_5OPO_3)_2$	11.7
$Zr(C_4H_9OPO)_2$	15.9
$Zr(NO_3NH_3CH_2CH_2PO_3)_{1.68}(OH)_{0.64} \cdot 2H_2O$	14.6
$Zr(HO_3SCH_2CH_2CH_2PO_3)_2$	18.8

taining small amounts of RPO_3, and (3) $Zr(RPO_3)_x(R'PO_3)_{2-x}$ with $x = 0.7-1.3$.

These results resemble those described above for zirconium phosphate phosphite. Furthermore, one layer is generally found to contain mostly R-groups and the adjacent layers a majority of R'-groups. We prepared $Zr(O_3PC_6H_5)(HPO_4)$ in which the layers were staged. The interlayer spacing was 21.4 Å (14.8 Å for the phenyl containing layer and 7.6 Å for the phosphate layer).[101] Butylamine was then intercalated into the phosphate layer producing a new interlayer distance of 33.4 Å (18.6 Å + 14.8 Å for the individual layers).

More severe types of layer staging have been found to occur when one of the two functional groups is phosphate.[100] In order to avoid this staging, we used phosphorus acid to produce layers which contained both functional groups.[101] Upon direct sulfonation of this compound with fuming sulphuric acid, the phosphite groups were converted to phosphate with overall composition $Zr(O_3PC_6H_4SO_3H)(HPO_4) \cdot nH_2O$.[102] A schematic depiction of such a layer arrangement is shown in Fig. 10. This compound behaves as a strong acid ion exchanger insofar as the sulfonic acid groups are concerned (pH range 2–4), while the phosphate protons exchange at higher pH values.[103] Ion exchangers of this type show an in-

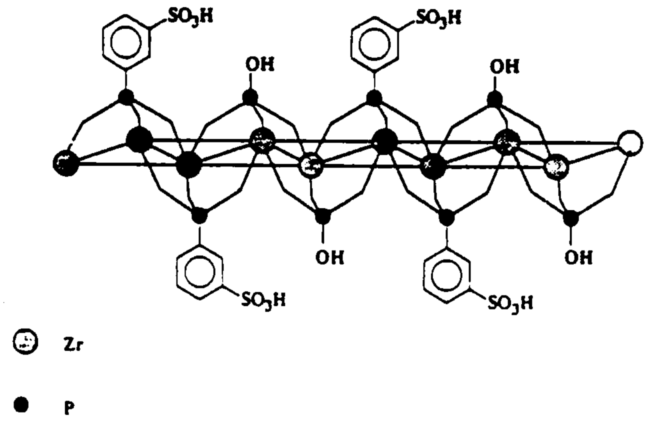


FIGURE 10 Schematic drawings of zirconium phosphate sulfophosphonate. $Zr(HPO_4)(O_3P-C_6H_4SO_3H)$ (from Ref. 103, with permission).

creasing affinity for ions of larger size as shown by the data in Table IV. When added to water, the sulfophenylphosphonate completely disperses as a colloid but reprecipitates upon incorporation of polyvalent ions. $Ru(bpy)_3^{2+}$ (bpy = bipyridine) was readily encapsulated between the layers and used to investigate spectroscopically the chemical microenvironment within zirconium phosphate sulfophenylphosphonate (ZrPS).[104,105] Diffuse reflectance spectroscopy showed that the $\pi \rightarrow \pi^*$ and metal to ligand bonds are red shifted and this shift results from interactions of the pendant phenyl groups with the bipyridyl goups. When methylviologen was also incorporated into the interlamellar space, the rate of electron transfer from the ruthenium complex to the amine depended upon the degree of mobility of the donor and acceptor, particulary the latter.[105] These studies are continuing.

If it is not difficult to imagine that an enormous variety of different organic derivatives of the type described above may be prepared and utilized, not only to examine further aspects of the behavior of layered compounds, but for their potential applications. Membranes have been prepared from these compounds as well as from zirconium phosphate crystals embedded in organic binder.[106] Applications in chromatography,[107] catalysis[108,109] and photochemistry[105] as well as for ion exchange[103] have been sug-

TABLE IV

Distribution coefficients for alkali and alkaline earth metal ions on exchangers MY-IV-95, MY-VI-2, amorphous zirconium phosphate, and AG 50W-X8 at 25°C

Ion	K_d(mL/g)			
	MY-IV-95[a]	MY-VI-2[a]	Amorphous ZrP[a,b]	AG 50W-X8[c]
Li^+	110	–	7	33
Na^+	205	–	11	54
K^+	1500	650	120	99
Cs^+	6500	–	1600	148
Mg^{2+}	21000	9800	–	790
Ca^{2+}	89000	37000	–	1450
Ba^{2+}	400000	190000	–	5000

[a] K_d at pH = 2.00 and a metal loading of 0.1 meq/g.
[b] Calculated from selectivity coefficients given in Ref. 4.
[c] K_d in 0.1 M HNO_3. Data from Ref. 5.

gested. Moreover a new range of intercalation behaviors can be probed.[110,111]

6.3 Pillared Organic Derivatives

Shortly after Alberti's paper on the preparation of layered organic derivatives appeared,[95] Dines *et al.*[97,98] reported the synthesis of alkyl and aryl derivatives which cross-linked the layers. This was achieved by using diphosphonic acids. In these compounds, the layers are held rigidly in place and may be thought of as pillared. Since the distance between phosphate groups is 5.3 Å,[24] there would be no room for inward diffusion of molecules if every position were thusly pillared. By mixing in either phosphoric or phosphorous acid, the Dine's group[98] found it possible to space the pillars so as to create diffusion paths between layers. This is illustrated schematically in Fig. 11. In this depiction each pillar is 10.6 Å apart but in actuality more randomness may be present. The interlayer distances are 9.6 Å for one phenyl ring pillars, 13.6 Å for two and 18.6 Å for three. Thus, ideally the free space would be about 6 Å laterally and 3, 7 and 12 Å vertically for the three pillared types, respectively. The single ring pillared openings are too small to admit N_2 for BET surface area measurements, but

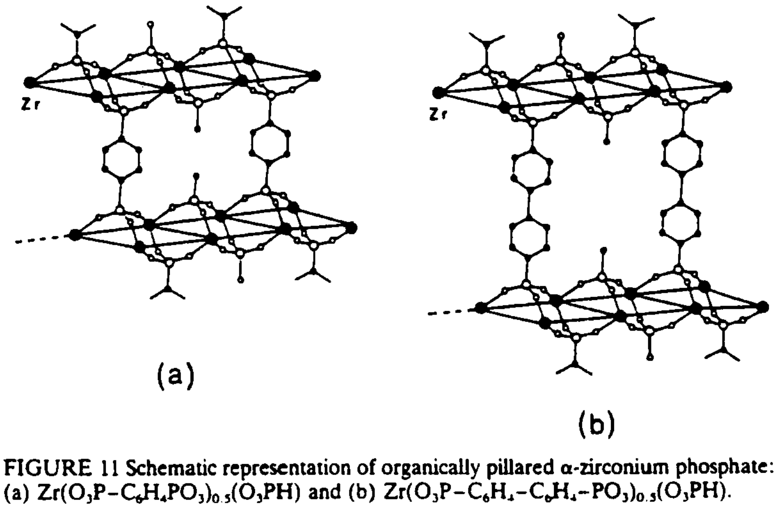


FIGURE 11 Schematic representation of organically pillared α-zirconium phosphate: (a) $Zr(O_3P-C_6H_4PO_3)_{0.5}(O_3PH)$ and (b) $Zr(O_3P-C_6H_4-C_6H_4-PO_3)_{0.5}(O_3PH)$.

surface areas of over 400 Å^2 have been measured for the multi-ring pillared derivatives.[98,101] The idea of spacing the pillars to create cavities is to utilize such compounds as catalysts and sorbants. The aryl pillared compounds are stable to 400°C in reducing atmospheres. Only preliminary catalytic studies have been carried out. The conversion of methanol to hydrocarbons yielded mainly methane and coke with smaller amounts of C_2–C_4 hydrocarbons.[111] However, with ethanol a smooth conversion to ethylene in high yield was obtained.[112]

7. WHAT'S NEXT

We have omitted from this discussion the more solid state aspects of layered tetravalent phosphates since a review article on this subject is in preparation. However, we should mention here that in terms of solid state applications, these compounds show promise for use as separation membranes, H_2 sensors, and proton conductors. The present article will conclude with a description of some new areas that are arising from the earlier work which show promise for future development.

Recently, Tom Mallouk[113] at the University of Texas and my own group[114] prepared a series of layered phosphonates of divalent metals of composition $M(O_3PR){\cdot}H_2O$ and solved the structures of the compounds with $R = C_6H_5$–. An ORTEP diagram of the zinc compound is shown in Fig. 12. Some of the divalent phosphonates had been synthesized earlier[115] but their layered nature was unrecognized. These phosphonates have the same layered structure as those of the $M(O_3PO{\cdot}NH_4){\cdot}H_2O$ inorganic phosphates (M = Fe, Cd, Mn).[116,117] More recently layered trivalent metal phosphonates have been prepared[118,119] and the structure of the lanthanum compound $LaH(O_3PC_6H_5)_2$ determined.[119] A second series of trivalent phosphonates of composition $M_2(O_3PR)_3{\cdot}nH_2O$ has also been discovered.[120] Calcium and cadmium also form two different layered phosphonates whose structures[118] are not the same as those of the zinc[114] and manganese[113] compounds. If we add to these discoveries the growing literature on vanadyl phosphonates,[121] one recognizes that many layered types with interesting properties have now been uncovered. Yet this is not the end of the story. An entirely different type of layer

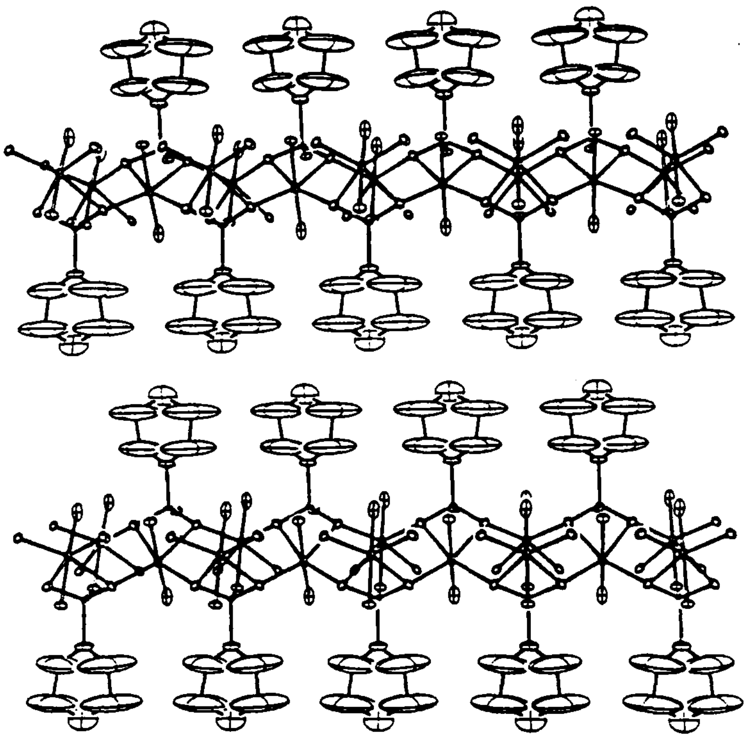


FIGURE 12 ORTEP representation of zinc phenylphosphonate, $Zn(O_3PC_6H_5)\cdot H_2O$, as viewed down the *c*-axis (from Ref. 114, with permission).

was obtained in the compounds $Zn(O_3POC_2H_5)\cdot H_2O$ and $Zn(O_3POC_2H_4NH_3)(O_2CCH_3)$.[122] In thse compounds the zinc is tetrahedrally coordinated by three phosphate oxygens and a water or acetate oxygen. Each phosphate group bridges three zinc atoms to form layers as shown in Figs. 13 and 14. The layers as seen down the *a*-axis (Fig. 14) appear to undulate, alternately rising and falling as one moves along the *c*-axis. This undulation appears as a dual layer structure when viewed down the *c*-axis (Fig. 13).

Since the phosphite ion might be considered the end member of a phosphonate series, we attempted to form layered phosphites of divalent and trivalent metals, and indeed these efforts are prov-

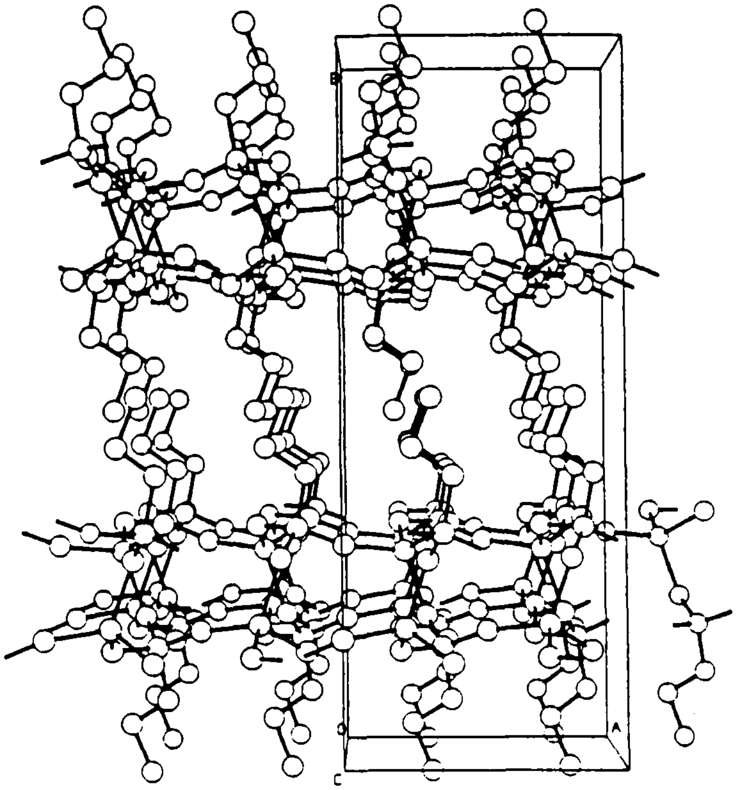


FIGURE 13 Layer arrangement and the unit cell of zinc ethylphosphate as viewed down the *c*-axis (from Ref. 122, with permission).

ing to be successful. A series of papers describing these structures is in the process of being written. Here we wish to mention that in acid solution an entirely unexpected product, $Zn(H_2PO_3)_2 \cdot 3H_2O$, with zeolite-like cavities was obtained.[123] A schematic view of the structure is shown in Fig. 15. When this compound is treated with a variety of cations in exchange for the protons of the P–OH groups, entirely new structures form. These structures depend as much upon the coordination behavior of the added metal as the zinc and phosphite steric requirements.

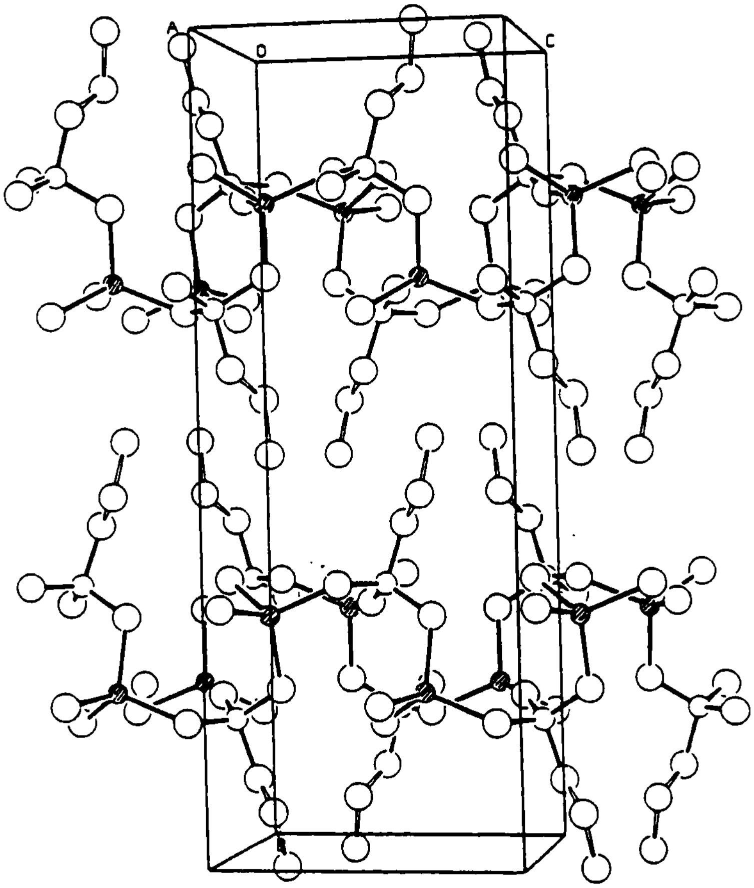


FIGURE 14 Layer arrangement and unit cell of zinc ethylphosphate as viewed down the *a*-axis. The heavy lines outline the Zn and P tetrahedra, while the Zn atoms are designated with stripes (from Ref. 122, with permission).

8. CONCLUSION

After 25 years of research into the nature of the tetravalent metal layered compounds, new discoveries continue to be made. It is evident that an almost endless variety of mixed organic–inorganic structures can be synthesized, and as we learn how to control the reactions, structures by design may be possible.[124] As Professor

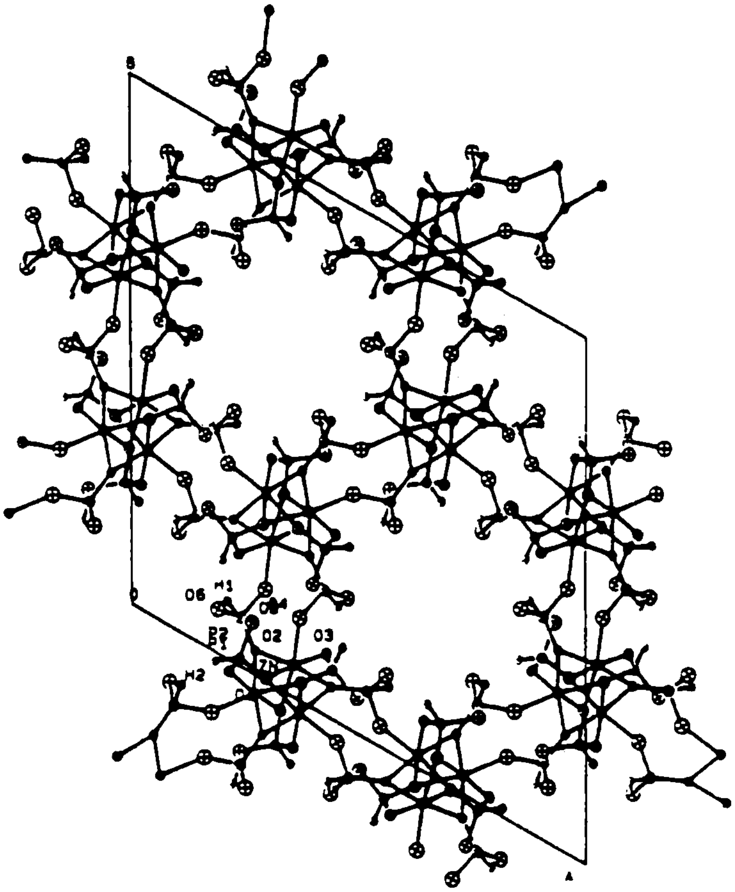


FIGURE 15 Extended view of the $Zn(HO_3PH)_2 \cdot 3H_2O$ structure in the *ab* plane. Note the large (~7 Å) channels running parallel to the *c*-axis in which the water molecules reside (from Ref. 123, with permission).

Alberti has stated,[56] "Till now, the chemistry of tetravalent metal acid salts has been like a mine which becomes richer and richer as one mines deeper and deeper." Now this mine extends to divalent, trivalent and possibly pentavalent metals as well as the tetravalent. An extremely interesting development has been the preparation of inorganic surface-bound mono- or multilayer structures of tetravalent and trivalent phosphonates analogous to Langmuir–Blodgett films.[125] Thus, by attaching such films to electrodes, concomitant absorption electron-transfer reactions may be studied. Add to this potential applications in electrochemistry, ion exchange, membrane technology, catalysis and photochemistry, one recognizes that a very deep mine does in fact exist.

Acknowledgments

I am indebted to the National Science Foundation Chemistry Division for long term support of these studies and more recently the Division of Materials Research (grant no. DMR 8801283) as well as the Office of Army Research for grant no. DAAG-29-85-K-0124.

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