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Layered and pillared zirconium phosphate-phosphonates and their inclusion chemistry

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After a brief account on previous results obtained in this Laboratory in the field of layered and pillared α- and γ-zirconium phosphonates, the perspectives for a development of a "molecular recognition" in porous and in layered solids are examined. In particular, the preparation and the preliminary characterisation of some new zirconium phosphonates more specifically designed for a "molecular recognition", such as: a) layered and pillared derivatives of γ-zirconium phosphate containing crown ethers in the interlayer region, b) α-layered zirconium phosphate containing chiral centres anchored to its surface and c) pillared derivatives of γ-zirconium phosphate containing non rigid pillars, are reported and discussed.

INTRODUCTION

The chemistry of layered M(IV)-phosphates can be considered to have begun in 1964, when the first crystalline member of this class, α-$Zr(HPO_4)_2{\cdot}H_2O$, was obtained by Clearfield and Stynes and its layered structure was clearly established[1].

An important step in the development of this class of compounds was made in 1978 when the first M(IV)-phosphonates and M(IV)-organic phosphates with layered structures closely related to that of zirconium bis monohydrogen phosphate (α-ZrP) were prepared in the author's laboratory[2].

A further development on layered M(IV)-phosphates and phosphonates was made in the years 1987–1990 when it was realised that γ-ZrP, different from zirconium bis monohydrogen phosphate, must be formulated as zirconium phosphate dihydrogen phosphate, $ZrPO_4H_2PO_4{\cdot}2H_2O$, and that its interlayer dihydrogen phosphate groups can be easily replaced by monovalent phosphonate or phosphinate anions by simple topotactic reactions[3]. Many organic derivatives with α- and γ-layered structures have already been prepared[4] and even pillared compounds with regular interlayer porosity have been obtained by a partial replacing dihydrogen phosphates with bivalent diphosphonate groups[5].

After a short discussion of the general aspects of layered and pillared metal phosphonates, a brief account on the more important results recently obtained in this Laboratory, especially on pillared porous materials, will be discussed. Finally, some as yet unpublished results on new zirconium phosphonates more specifically designed for a development of a "molecular recognition" in layered and pillared porous solids, will be reported.

GENERAL ASPECTS OF LAYERED AND PILLARED METAL PHOSPHONATES

Metal (IV) Phosphonates With α-Type Layers

Although α-layered M(IV) phosphonates with M(IV) different than Zr have been obtained, for sake of brevity, we will be concerned only with zirconium compounds.

Layered zirconium monophosphonates

The synthesis of the α-M(IV) phosphonates and organophosphates is closely related to the methods used to prepare α-$Zr(HPO_4)_2{\cdot}H_2O$, (α-ZrP), i.e. the refluxing of amorphous or semicrystalline precipitates[1] and the direct precipitation method in the presence of a complexing agent[6] of Zr(IV). The only change required is the replacement of the H_3PO_4 with the proper phosphonic or organo phosphoric acid.

Just after synthesising the first zirconium phosphonates and zirconium organophosphates of general formula $Zr(O_3P\text{-}R)_2{\cdot}nS$ and $Zr(O_3P\text{-}OR)_2{\cdot}nS$, respectively, where R is an organic group (e.g. $-CH_3$, $-C_6H_5$, $-CH_2COOH$ etc.), S being a polar solvent intercalated

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in the interlayer region, it was realised, by considerations based on their density and interlayer distance[2] that these compounds can be considered to be organic derivatives of α-Zr(O$_3$P-OH)$_2$·H$_2$O in which the inorganic -OH groups have been replaced by R groups, leaving the inorganic structure of the α-layer essentially unchanged. From the known structures of the α-layer and the R radical and from the experimental value of the interlayer distance, it is therefore possible to predict the most probable structural models. Waiting for the definitive structures from X-ray diffraction of single crystals (which are very difficult to obtain, owing to the extremely low solubility of this class of compounds) these model structures are temporarily very useful to understand and/or foresee the properties of the phosphonates obtained. As an example, in Fig. 1 the model structure of α-zirconium phenylphosphonate proposed by Alberti et al.[2] in 1978 (Fig. 1b), is compared with the structure of α-ZrP (Fig. 1a) and with the recent structure reported by Clearfield[7] *et al.* in 1993 (Fig. 1c). Indeed, apart from the orientation of the benzene rings, the recent study essentially confirms the model structure proposed 15 years ago.

If a mixture of two different H$_2$O$_3$P-R acids is used in the synthesis, zirconium phosphonates with two different R groups in the interlayer region are obtained. These compounds can be described by the general formula $M(IV)(O_3P\text{-}R)_x(O_3P\text{-}R')_{2-x}\cdot nS$. As a general rule, the x value can change almost continuously only if the two R and R′ groups are very similar in size and chemical nature, or if the degree of crystallinity of the compound is very low. In the greater part of the compounds studied, discontinuous x-values are therefore observed. Furthermore, very probably for energetic reasons due to the interactions between adjacent layers, asymmetrical layers may be formed in which one side of the layer is richer in R, the other in R′ groups[8]. The packing of the layers is schematically shown in Fig. 2; note the alternation of interlayer regions richer in R and R' pendant groups.

Covalently pillared α-zirconium diphosphonates

Only a few years after that the first organic derivative of α-ZrP was prepared, it was reported that M(IV) diphosphonates, of general formula M(IV)(O$_3$P-R-PO$_3$) could also be obtained with a similar procedure[9].

In these compounds, adjacent inorganic layers of the α-type are covalently joined by the divalent organic group. Given the possibility that "tailor made" materials with interlayer porosity could be prepared by simply changing the length of the organic pillar, the acronym MELS (Molecularly Engineered Layered Structures) was given to M(IV) diphosphonates to emphasise their application potential[10]. A large number of zirconium diphosphonates with divalent R groups of different length was prepared; it was however recognised that, due to the small distance (5.3Å) between adjacent sites in the α-layer, the pillars are too crowded and insufficient free space remains in the interlayer region, independent of the length of the pillar itself.

In order to create the interlayer microporosity, a new strategy, based on the use of pillars with cross sections larger than 24 Å^2, was followed in our laboratory. In such a situation, two adjacent α-positions cannot be occupied by the large pillars and, six phosphite groups were expected to be placed around each pillar (Fig. 3). If the cross section of the large pillar is homogeneous, no interlayer porosity is to be expected. However, if the cross section is not uniform and in particular, if the central cross-section is smaller than the terminal parts (pillars with base), interlayer porosity may be created

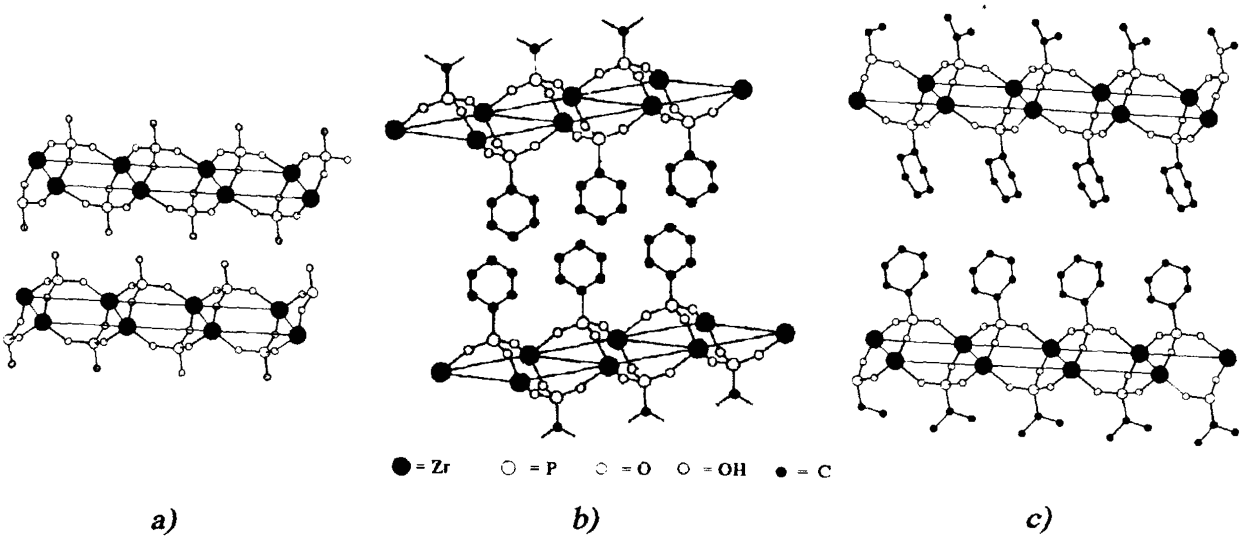


Figure 1 Structural models of: a) α-Zr(HPO$_4$)$_2$·H$_2$O; b) α-Zr(O$_3$PC$_6$H$_5$)$_2$ as proposed in 1978 by Alberti and c) the same compound drawn on the basis of its structural parameters (Clearfield, 1993).

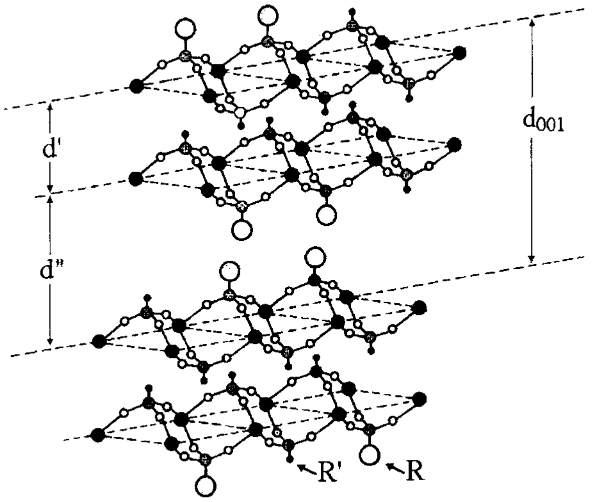


Figure 2 Schematic representation of the structure of a mixed α-zirconium phosphonate with asymmetrical layers. Note that d(001) is the sum of two interlayer distances.

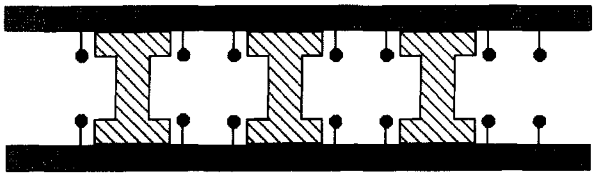


Figure 4 Schematic representation of a porous compound in which the pillars possess a large base. The black dots represent small groups around the large bases (e.g., phosphite groups of Fig. 3).

(Fig. 4). A compound having pillars with bases, recently prepared in our laboratory, indeed confirmed the above expectations. A high phosphite percentage, a good degree of crystallinity, and an interlayer microporosity of 375 m^2 g^{-1} were indeed found[11]. The micropore distribution shows a maximum in the 5–6 Å range. A computer generated structural model of this pillared compound based on its unit cell parameters (a=15.286; b=9.365; c=28.478 Å; β=94.99°) is shown in Fig. 5. Note that its particular molecular architecture is indeed recalling that of a Greek temple.

Zirconium Phosphate-Phosphonates with γ-Type Layers

Preparation and structure of layered γ-zirconium phosphate monophosphonates

Some organic derivatives of γ-zirconium phosphate (γ-ZrP) were first obtained by Yamanaka et. al. already starting from 1975[12]. However, at that time γ-ZrP was believed to be an isomorphous modification of α-ZrP with only a different stacking of the layers and hydration water content, so that it was impossible to give a correct interpretation of the composition and structure of the organic derivatives obtained. The recent advances in the knowledge of the structure of the γ-type layers[3] were fundamental for the development of the chemistry of γ-compounds, that nowadays seems even richer than that of α-derivatives.

We know today that the structure of the γ-layer consists in a rigid framework of $M(IV)O_6$ octahedra placed in two different planes and joined to each other with PO_4 tetrahedra inside and H_2PO_4 outside these planes (see Fig. 6). γ-ZrP must therefore be formulated as $ZrPO_4H_2PO_4{\cdot}2H_2O$. Due to the fact that only three oxygens are available in the phosphonate groups, it is evident that pure γ-zirconium phosphonates cannot exist. On the other hand, mixed organic derivatives of γ- ZrP, such as γ-zirconium phosphate-phosphonate, phosphate-phosphite and phosphate- -phosphinate compounds, are possible. Thus, γ-compounds can be represented with the general formula $ZrPO_4O_2PRR'{\cdot}nS$, where R and R' can be H, OH or organic group and S is the intercalated solvent.

Even if possible in principle, all our attempts to prepare mixed derivatives of γ-ZrP by direct synthesis

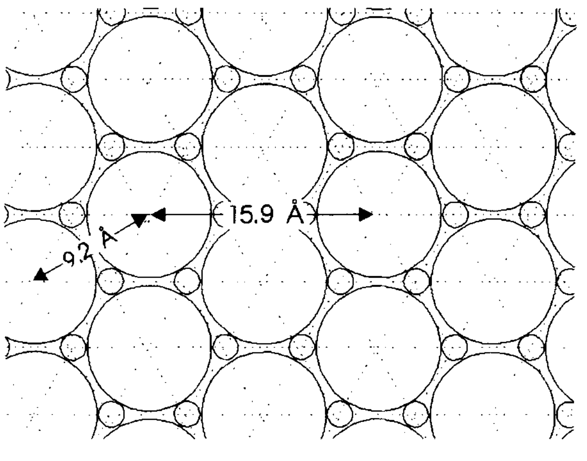


Figure 3 Idealised arrangement of a distribution of 33.3% large R groups (>24$Å^2$) and 66.6% small R' groups on one side of the α-layer.

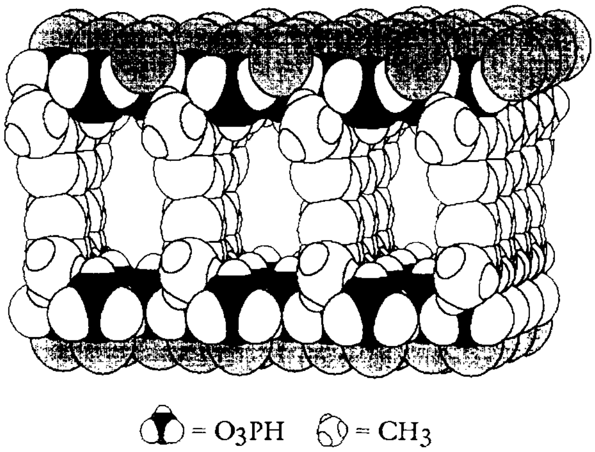


Figure 5 A computer generated view of a microporous α-zirconium phosphite diphosphonate in which are present pillars "with bases".

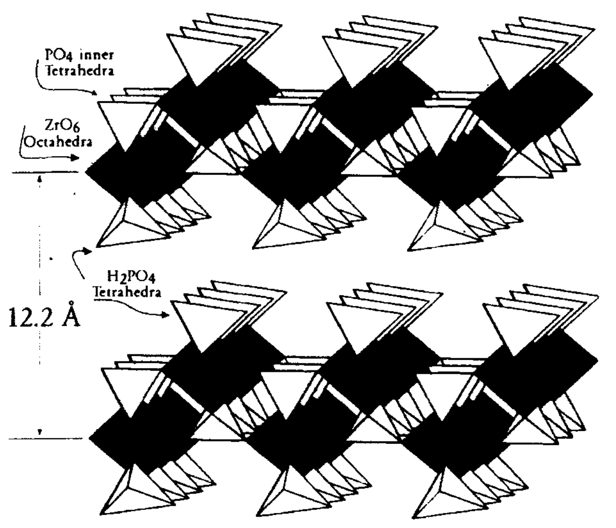


Figure 6 Schematic representation of the structure of γ-ZrP. The hydration water molecules are not shown.

were unsatisfactory, since it was not possible to obtain them as pure phases.

In agreement with Yamanaka's previous work[12], it was found that the interlayer $H_2PO_4^-$ groups of γ-ZrP can be easily exchanged with other $O_2PR'R^-$ groups by means of a topotactic reaction by simply contacting micro crystals of this compound with a solution of a suitable phosphonic acid[13].

It was found that the topotactic replacement of H_2PO_4 groups with other O_2PRR' leaves the γ-layer framework essentially unaltered[13c]. Information about the most probable accommodation of the organic moieties in the interlayer region can therefore be deduced by means of simple computer structural models derived on the basis of the structure of the original γ-ZrP, replacing H_2PO_4 with O_2PRR' groups. These models indicate, for example, that *a* and *b* dimensions of the γ-layer are sufficiently large to accommodate one linear alkyl chain for each O_2PRR' group (see Fig. 7a).

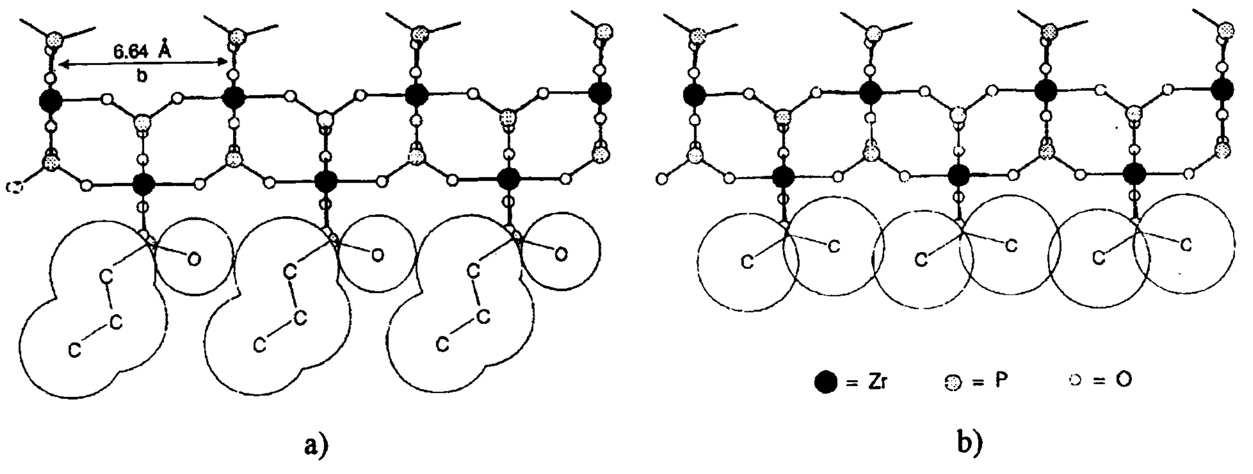
A full conversion in the organic derivative can therefore be expected for n-alkylphosphonic acids. Even though other phosphonic acids with a longer chain must be tested, our data concerning methylphosphonic and propylphosphonic acid confirm these expectations. If both R and R' are alkyl groups, the space around each γ-site is not sufficient to have a fully converted phase, as can be seen in Fig. 7b. A partial replacement was actually observed when dimethylphosphinic acid was used. The same effect is observed when phosphonates are used with one large R group, for instance cyclohexyl phosphonic acid. A similar situation is found for phenylphosphonic acid. In this well studied case, even if the phenyl group is not as large as a long alkyl chain, the rigidity of the aromatic ring causes a steric hindrance with the adjacent OH groups (see Fig. 8); consequently, the full conversion cannot be obtained[13d].

Pillaring of γ-ZrP with diphosphonate groups

If γ-ZrP is contacted with diphosphonic acids, the original $H_2PO_4^-$ groups are replaced by diphosphonate groups and pillared compounds, in which the diphosphonate group is joining adjacent layers, as schematically shown in Fig. 9, are formed. Let us now examine first the pillaring of γ-ZrP with rigid organic pillars, while the case of not rigid pillars will be examined later.

γ-Pillared compounds with rigid pillars: a new way to prepare microporous materials

No appreciable porosity was found in the first prepared pillared γ-compounds[14]; however, it was immediately recognised from the models that the lack of interlayer microporosity was probably due to either the short length of the diphosphonate groups employed, or to their excessive crowding in the interlayer region. Therefore,



a) b)

Figure 7 Structural model of a) γ-zirconium phosphate propylphosphonate and b) γ-zirconium phosphate dimethylphosphinate. The radii of OH and the methyl group were assumed as 1.5 and 2 Å respectively.

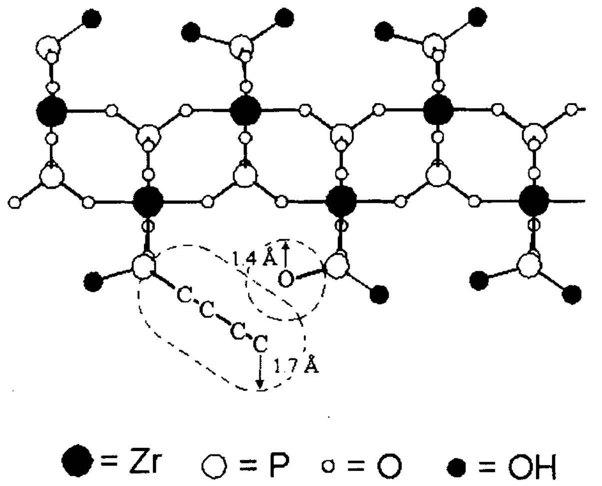


Figure 8 Schematic representation of the possible steric hindrance between adjacent phenyl and OH groups in γ-zirconium phosphate phenyl phosphonate.

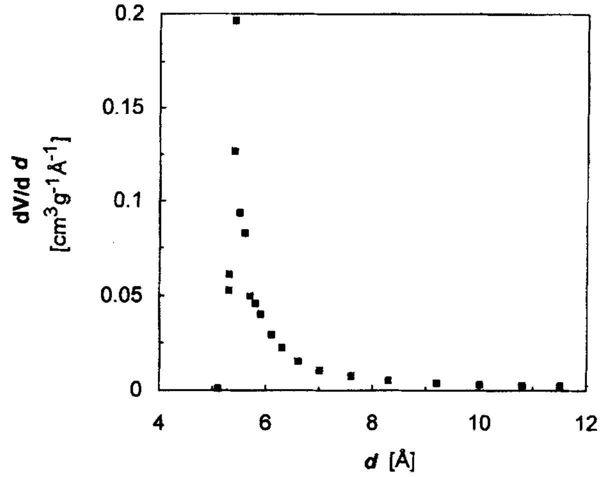


Figure 10 Differential pore volume (D.P.V.) v.s. pore diameter of sample at 28% pillaring percentage.

longer rigid diphosphonate groups were used as pillars and a systematic study of the gradual replacement of the original H_2PO_4 was performed[5]. The hope was that, owing to the high rigidity of the γ-layers, stable solid solutions would be formed in a large composition range, thus making possible the existence of stable materials at very low pillaring percentages. As expected for layered solids with rigid layers, solid solutions were found.

Detailed investigations were performed on the γ-ZrP pillared with biphenyldiphosphonate groups. In the 28–44% pillaring range, the interlayer distance was found not to change appreciably with dehydration. Now, taking into account that the microporosity should increase with the dilution of the pillars, the maximum interlayer microporosity must be expected at the minimum concentration of pillars which can assure the stability of the anhydrous phase, i.e. 25–28% of pillaring. The determination of the volume of the micropores and the specific surface area of anhydrous samples at different pillaring percentages showed that their maximum ($\approx$0.12 cm^3g^{-1} and $\approx$320 m^2g^{-1} respectively) is obtained at the value expected; furthermore, the compound possesses a narrow micropore distribution (Fig. 10) with an average diameter of 5.8 Å. Note that this value too, derived from an experimental surface analysis of the pores, is in good agreement with the free distance between adjacent pillars expected from the computer model for a pillaring percentage of 25% (Fig. 11).

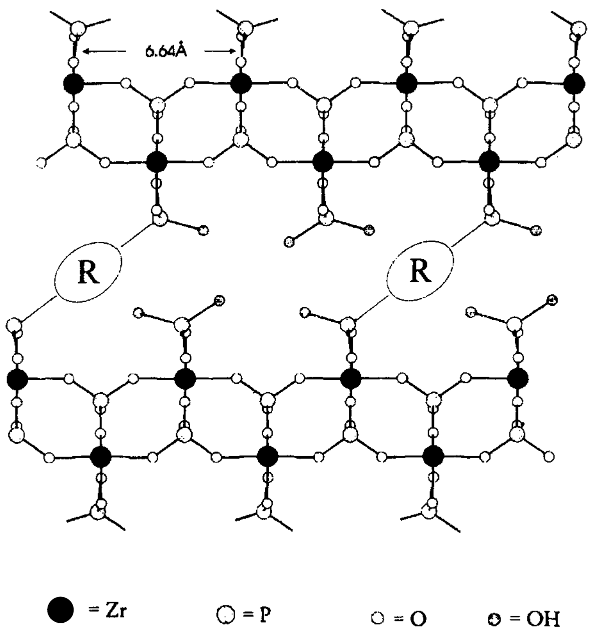


Figure 9 Schematic picture of the structure of γ-zirconium phosphate phenyl diphosphonate.

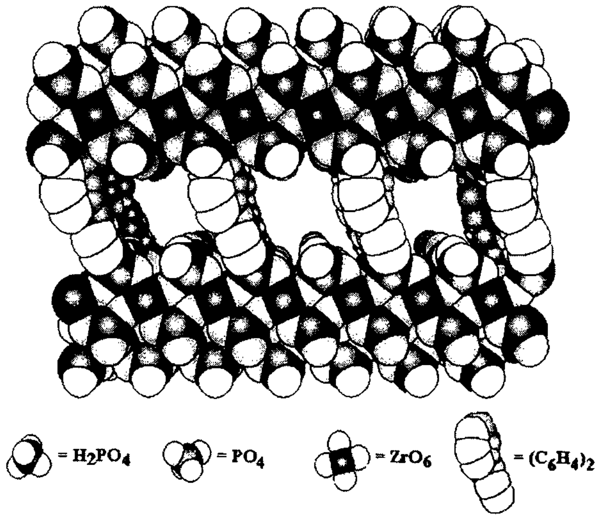


Figure 11 A computer generated view of a microporous γ-compound pillared with rigid pillars and composition: $ZrPO_4(H_2PO_4)_{0.75}(HO_3P\text{-}C_6H_4\text{-}C_6H_4\text{-}PO_3H)_{0.125}$.

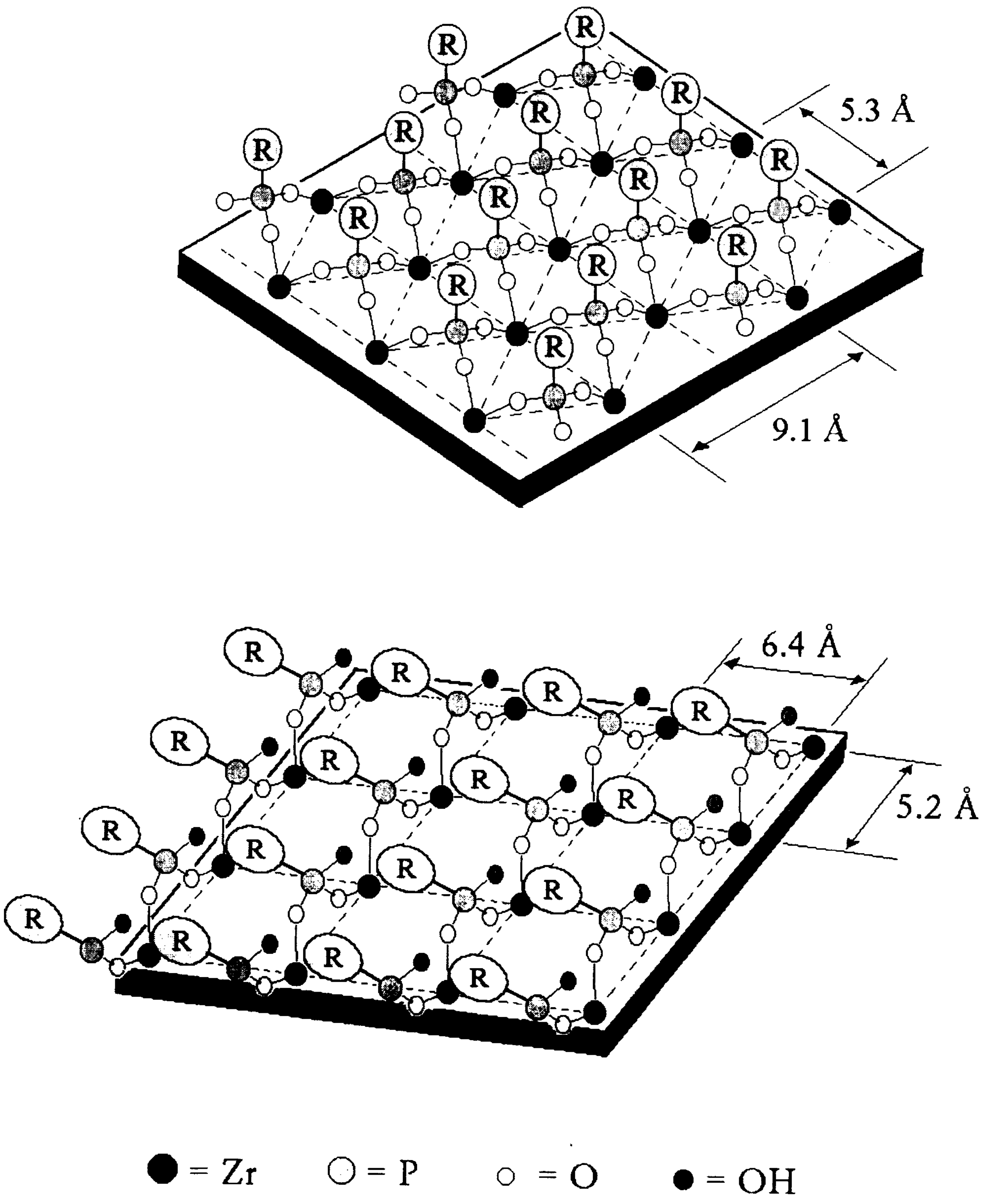


Figure 12 Schematic view of one side of the α-ZrP layer (upper) and of the γ-ZrP layer (down) considered as planar clothes-hooks to which R organic groups, or mixtures of organic groups of different nature, can be covalently attached.

Unfortunately, the degree of crystallinity of this compound was not so good for the unambiguous determination of its cell parameters. It was however found that all the X-ray reflections of a sample at 28% of pillaring can be indexed if a monoclinic cell with a=10.750 Å; b=13.220 Å; c=16.723 Å; β=98.451° is assumed, i.e., with parameters very near to those derived from the ideal model.

Together with the microporous α-pillared compound obtained recently[11], the covalent pillaring of layered structures with organic groups is now opening up an alternative way for the preparation of new molecular sieves and/or shape selective catalysts.

α- and γ-Metal Phosphate Structures Seen as Planar Clothes-Hooks to which a Large Variety of Organic Groups can be Attached

For the large variety of organic groups that can be covalently attached to the α- or γ-layers[4,15], we can consider the inorganic back-bone of α-ZrP and γ-ZrP to resemble planar clothes-hooks with which two different geometrical arrangements of the covalently bound organic molecules, schematically shown in Fig. 12, can be obtained. Some of the organic groups that have already attached to the α- and γ-layered structures are schematically shown in Figs. 13 and 14, respectively. Even two or more pendant organic groups of different size and/or chemical properties can be attached to the surface of the inorganic layers and regular arrangements with well-defined ratios between these groups are usually obtained. The interactions in the interlayer region among organic groups of the adjacent layers are depending both in the structure of the inorganic back-bone and on the arrangements of the different groups attached to the layers.

The success in synthesising M(IV)-phosphonates with α- and γ-layered structure has stimulated the research in the synthesis of other compounds with inorgano-organic layers. Other M(IV)-phosphonates with novel layered structures have been discovered[16], and the research has even been extended to layered M(II)- and M(III)-phosphonates[17], and to vanadyl phosphonates and organo phosphates[18] thus increasing further the number of layered compounds containing inorgano-organic layers.

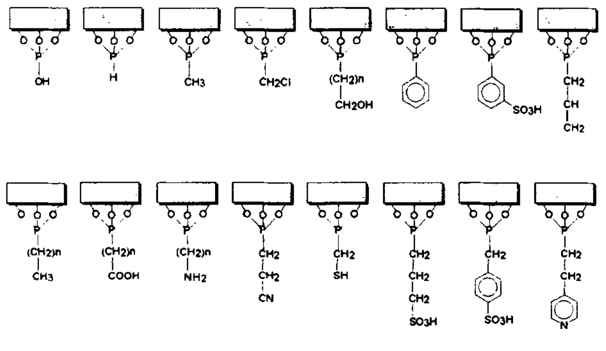


Figure 13 A view of the some organic groups that have already been covalently attached: to α-ZrP layers.

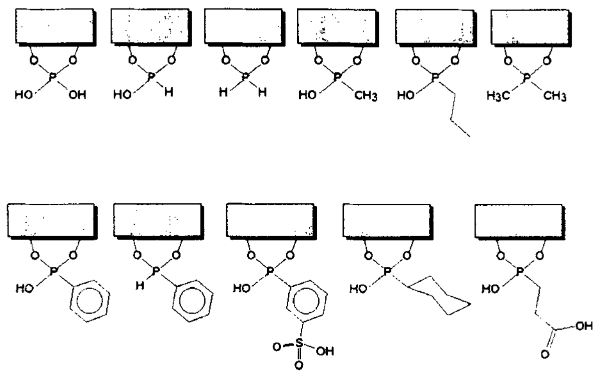


Figure 14 A view of the some organic groups that have already been covalently attached: to γ-ZrP layers.

A large variety of clothes-hooks is already available today and new ones will be prepared in the near future. Owing to the facility with which the surface O_3PR or O_2PRR' groups can be topotactically replaced by other phosphonates, the method may be used to obtain functionalised surfaces and in many cases, this method allows us to choose from among various geometrical arrangements which could be convenient with respect to that of silanization.

SOME CONSIDERATIONS ON “MOLECULAR RECOGNITION” IN POROUS AND IN LAYERED SOLIDS

The molecular recognition in solution is, in large part, based on the use of some host molecules (cyclodextrins, crown ethers, calixarenes, etc.) which possess particular structures (e.g., tubular-, crown- and chalice-shaped) in which some functional group may be present. The molecules that for their shape and/or for their interactions with the inner surface and/or with the functional groups of the host fit these void spaces better than other (i.e., are forming the most stable host-guest complexes), are taken up selectively.

Intra-framework voids (also called cages or pores), where guest molecules can selectively be accommodated, may also be present in some particular solids. If the cage-like voids are not interconnected or are connected by channel openings that are too small for the diffusion of the guest species, these latter remain trapped in the solid (e.g., clathrate or clathrate-like inclusion compounds) and cannot be removed without the decomposition of the host. Vice versa, if the cavities of the host solid are interconnected by openings wide enough for the diffusion of the guest molecules, the latter can be removed without the decomposition of the solid (e.g., zeolites, pillared clays, pillared α- and γ- zirconium diphosphonates, etc.). Note that in such compounds, the number of the void cavities in which guest molecules can be accommodated is of the order 10^{21}–10^{22} per g of porous solid and that to fill up these cavities, the guest molecules must overcome the activation energy for their diffusion in the narrow channels of the solid. It is therefore easy to understand that the more the guest molecule has a suitable size for being accommodated in the cavities and/or the stronger the host-guest interactions, the slower the diffusion process must be. Thus, although from a thermodynamic point of view high selectivities are in principle possible, kinetic factors could prevent a good molecular recognition in porous solids. In order to avoid, as much as possible, steric hindrance to the diffusion of the guest molecules, it could be desirable to have solids with large specific surface area or cavities connected by large openings. If the cavities are too large to give good shape selectivity, their selectivity may be increased by modulating their chemical properties (e.g., hydrophobicity, hydrophilicity, insertion of special functional groups, etc.). In this respect, the pillared α- and γ- zirconium diphosphonates, due to their high variability of both shape and chemical properties of the cavities, seem to have good prospects. As will be discussed later, even very large selective species such as crown ethers can be covalently bonded in the interlayer region of these compounds.

Let us now spend a few words on molecular recognition in layered solids. In this case, the guest molecules are intercalated in the interlayer region and the solid usually adapts its interlayer distance to the dimension of the intercalated species.

The non-rigidity of the interlayer region space permits the intercalation of even very large species at an acceptable intercalation rate but, at the same time, it appreciably lowers the shape selectivity of the host. The adaptation of the interlayer distance to the size of the guest species resembles the pass-key of hotel rooms which opens many locks but, because of this, losses the property to open just a single room selectively.

Taking into account these considerations, it could be of interest to investigate the selectivity of solids which have properties intermediate between those of pillared and layered solids. Solids exhibiting such characteristics have recently been obtained in our laboratory and will be examined later. Finally, molecular recognition can be obtained in solid surfaces if selective sites (e.g., chiral centres) can be anchored on them.

Some layered and pillared zirconium phosphonates, specifically designed for the molecular recognition according to the above considerations, were recently obtained in our laboratory. A brief account of the recent results is here reported.

RECENT RESULTS ON THE PREPARATION OF SOME ZIRCONIUM PHOSPHONATES SPECIFICALLY DESIGNED FOR THE "MOLECULAR RECOGNITION"

Layered and Pillared γ-Zirconium Phosphate Derivatives Containing Crown Ethers in the Interlayer Region

The success obtained in the preparation of a large number of layered and pillared organic derivatives with γ-structure by simple topotactic replacement of the original dihydrogen phosphate groups of γ-ZrP with mono- or diphosphonate groups, has stimulated our interest in the preparation of γ-derivatives containing crown ethers in their interlayer region. A monophosphonic and a diphosphonic acid containing crown ethers in their organic radical, were synthesised in the laboratory of Prof. Kalchenko (Ukraine) and the synthesis of the layered and of the supposed pillared compound were performed in our laboratory.

Preparation of γ-layered zirconium phosphate-phosphonates containing crown ethers

1 g of γ-$ZrPO_4H_2PO_4 \cdot 2H_2O$ was contacted, under shaking at 75°C for 6 days, with 375 mL 5.0×10^{-2} M of 4-dihydroxyphosphoryl benzo-15-crown-5, in 1:1 water-acetone solution. The procedure was repeated three times. Due to steric reasons[13d], a maximum replacement of 50% of the H_2PO_4 originally present in γ-$ZrPO_4H_2PO_4 \cdot 2H_2O$ was expected to take place. The composition of the solid after the topotactic exchange was indeed found to be in good agreement with the above expectation.

The layer compound obtained was enough crystalline and the interlayer distance of the anhydrous compound was 25 Å, which corresponds to a double layer of crown ethers in the interlayer region (Fig. 15).

Definitive results and a more complete characterisation and discussion will be reported elsewhere[19].

Preparation of γ-pillared zirconium phosphate-diphosphonates containing crown ethers

The preparation procedure is analogous to that reported above for the layered compound containing the crown ether, but replacing the solution of the monophosphonic acid with a solution of the diphosphonic acid. In particular, by using 272 mL of an aqueous solution 3.75×10^{-3} M of 4,4′(5′)-bis(dihydroxyphosphoryl)dibenzo-18-crown-6 mono hydrate, (mixture of cis and trans isomers), the topotactic replacement of the original H_2PO_4 groups was found to proceed, as expected, till 50%. The final composition of the anhydrous solid was $ZrPO_4(H_2PO_4)_{0.5}(HO_3P\text{-}R_c\text{-}PO_3H)_{0.25}$, were R_c is dibenzo-18-crown-6. An interlayer distance of 22.2 Å for the hydrated compound (2.5 H_2O moles per mol of

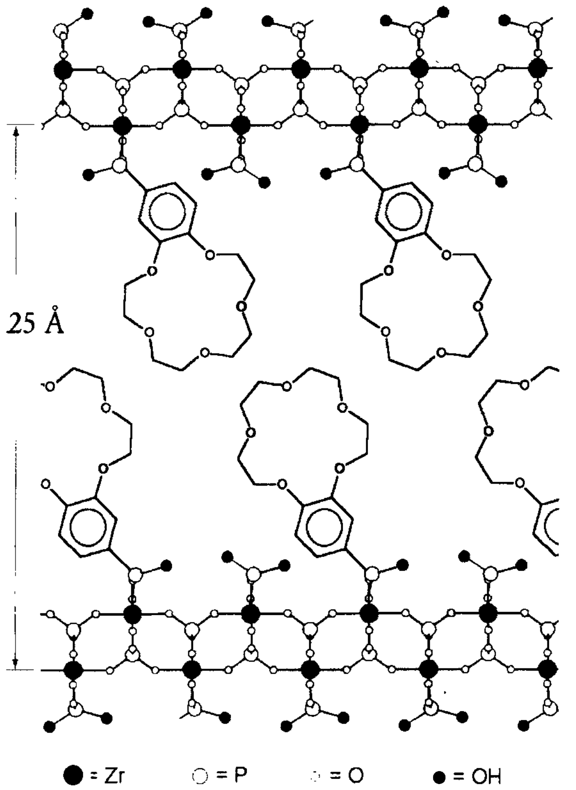


Figure 15 Schematic representation of an anhydrous derivative of γ-ZrP containing a bilayer of crown ethers in its interlayer region.

Zr(IV) when conditioned at 75% relative humidity) and of 20.1 Å for the anhydrous compound were deduced from X-ray powder diffraction of the samples. A model structure of this compound, supposed to be pillared, on the basis of previous results found for the topotactic exchange with other diphosphonic acids, is shown in Fig. 16.

Although the way to the practical applications of these compounds in molecular recognition could still be very long, the demonstration of the existence of layered and pillared solids containing crown ethers in their interlayer regions is, in our opinion, of great interest. We are therefore trying to prepare compounds with lower percentages of topotactic exchange in order to create inter-pillar void spaces, as already obtained for the pillaring of γ-zirconium phosphate with biphenyl diphosphonic acid[5]. Some encouraging results have already been obtained and the results will be published elsewhere[20]. Attempts to prepare α-layered structures too containing crown ethers are currently in progress in our laboratory.

α-Layered Zirconium Phosphate Containing Chiral Centres Anchored to its Surface

In our laboratory it was found that α-zirconium phosphate can be completely delaminated by intercalation of propylamine at about 50% of its maximum capacity[21]. A colloidal dispersion of the constituent lamellae, that can then be used to cover the solid surface of many materials with a very thin layer of α-zirconium phosphate, is obtained in aqueous solution.

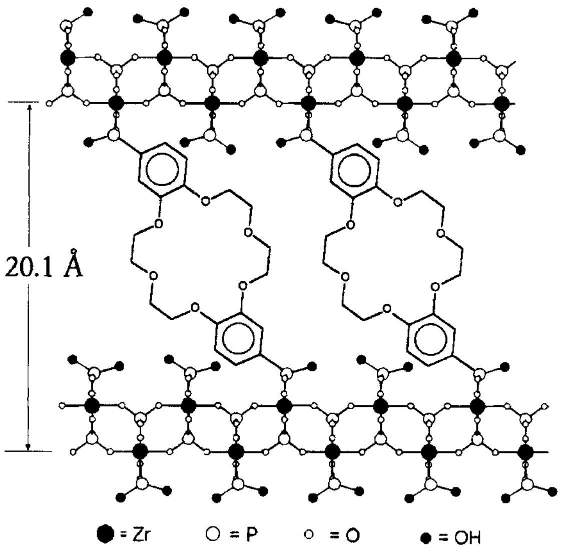


Figure 16 Schematic representation of γ-ZrP pillared with a diphosphonic group containing a crown ether in its organic radical R.

In turn, it is easy to attach a large variety of amines to the surface of the α-zirconium phosphate by a topotactic replacement of other amines eventually anchored to the surface or by the acid-base reaction between amines and the surface -POH groups. It is evident that if some chiral centres are present in the employed amines, the final result is the anchoring of these chiral centres on the zirconium phosphate surface.

We report schematically a typical procedure used in our laboratory[22]: 4 g of silica gel H 5–40 μm (Fluka) were added under stirring to 100 mL of the colloidal dispersion containing 1 g of delaminated α-$Zr(HPO_4)_2 \cdot H_2O$, then another 50 mL of deionised water were added followed by the addition of 49.5 mL of an aqueous solution of d-(+)-α-0.1 M benzylmethylamine. After this latter addition, a colloidal flocculation is observed. The obtained solid is first washed with water / methanol solution, (1:1 in volume), then is degassed under vacuum for about 1h and finally the slurry is stratified, with a thickness of 500 μm, over a glass sheet.

Some enantiomeric separations seem to be encouraging, although reproducible results have not yet been obtained. One of the best separations was obtained for the enantiomeric forms of 2,4 dinitrophenyl hydrazone of the carvone, when eluted in a mixture of toluene/light petroleum 3:1 in volume (Fig. 17).

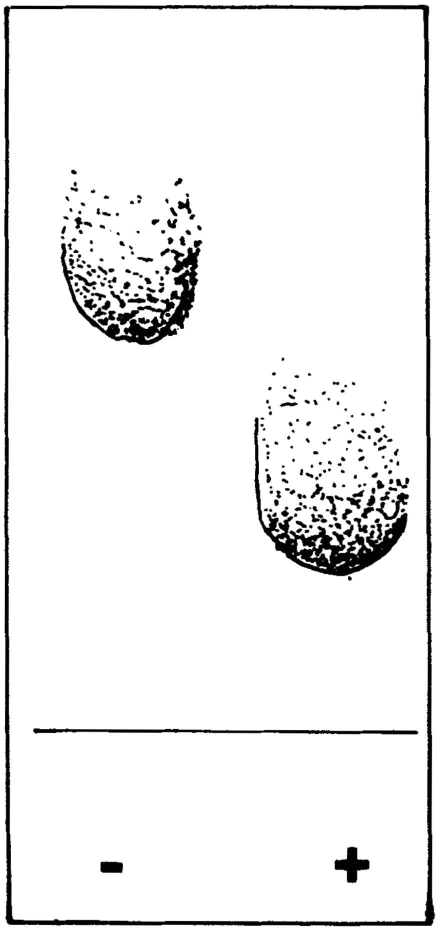


Figure 17 Thin layer chromatographic separation of the enantiomeric forms of 2, 4 dinitrophenyl hydrazon of the carvone on α-ZrP containing benzylmethyl amine anchored to its surface.

Pillared Derivatives of γ-Zirconium Phosphate Containing Non-Rigid Pillars: A Large Class of New Materials in which Different Conformations of the Pillars can be Obtained

As discussed before, γ-ZrP can be pillared by a simple topotactic replacement of the original H_2PO_4 groups with diphosphonate groups. Furthermore, due to the rigidity of the γ-layers, γ-ZrP has a great tendency to the formation of solid solutions. This behaviour, more pronounced in γ- than in α-layered systems, is crucial for significant advances in the design of new architectures, making it is possible to prepare pillared compounds with a very low percentage of pillaring (e.g., 25%), and hence with a very large interpillar lateral distance. Encouraged by our success in introducing rigid pillars in the γ-interlayer region, we have turned our attention to the preparation of compounds with non-rigid pillars, such as alkyl chains, at low pillaring percentages.

The pillaring of γ-ZrP with diphosphonate groups having non-rigid R organic radicals, such as aliphatic chains, was of interest since a variation of the conformation of the pillars as a function of the solvent or of other molecules included in the interpillar spaces, as well as of the pillaring percentages was to be expected.

Very encouraging preliminary results have already been obtained. Pillared compounds of composition $ZrPO_4(H_2PO_4)_{1-x}(HO_3P\text{-}(CH_2)_m\text{-}PO_3H)_{x/2}\cdot nH_2O$, where m = 4, 6, 8, 10, and 12; n ranges from 0.5–3 and x values from 0.1-0.9, have been prepared and the results will be reported elsewhere[23]. A computer generated model of the pillar compound with ideal composition $ZrPO_4[HO_3P\text{-}(CH_2)_{10}\text{-}PO_3H]_{0.5}$, is schematically shown in Fig. 18.

The interlayer distance of hydrated samples conditioned at 90% relative humidity depends linearly on the m value. For the anhydrous samples the dependence on m was only found for samples at very high pillaring percentages (≥ 50%), while an interlayer distance almost independent from m values was found at low pillaring percentages. This fact has been ascribed to the collapsing of the alkyl chains when water is removed in the dehydration process. For example, the interlayer distance of the compound $ZrPO_4(H_2PO_4)_{0.8}(HO_3P\text{-}(CH_2)_{10}\text{-}PO_3H)_{0.1}\cdot 3H_2O$ is decreased from 17.2 Å to 14.0 Å, when the compound is dehydrated. This effect is reversible (Fig. 19). Therefore we jokingly called the alternation of elongation and shortening of the interlayer distance the "accordion effect". The compounds at low pillaring percentages, can be seen as layer solids with chained adjacent layers. If the lateral distance is large enough to permit the collapsing of the chains, the interlayer distance, like in layered solids, depends on the species intercalated. However, in contrast to the layered

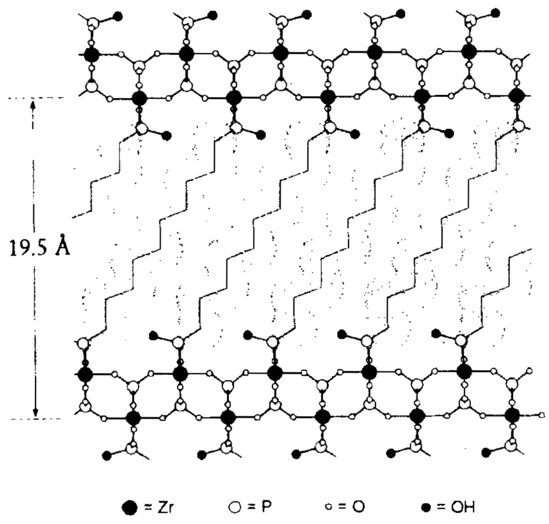


Figure 18 A computer representation of $ZrPO_4[HO_3P\text{-}(CH_2)_{10}\text{-}PO_3H]_{0.5}$, a γ-pillared compound with non-rigid pillars.

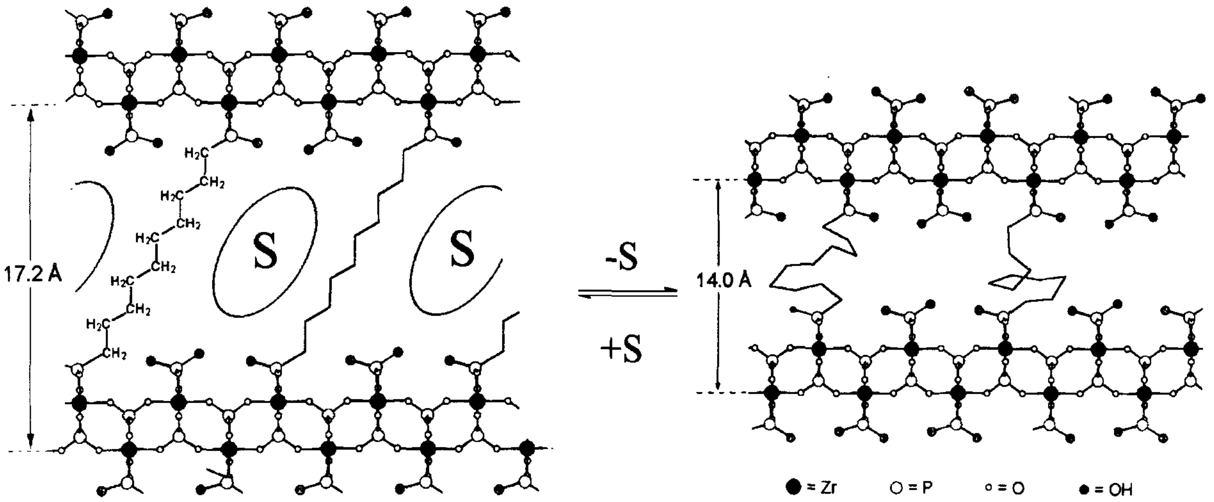


Figure 19 Schematic representation of the reversible shortening and enlargement of the interlayer region of pillared compounds with non-rigid pillars at low (25%) pillaring percentage. Note that an appreciable collapsing of the alkyl chains can only occur if enough large lateral interpillar space is present.

solids, where infinite swelling is even possible, the maximum interlayer distance of chained layer solids, at least for low energy intercalation processes, is fixed by the length of the alkyl chain joining the layers, so that the intercalation of large species may not occur. In this respect, these particular pillared solids are intermediate between layer solids and pillared compounds with rigid pillars. Therefore, according to the previous discussion, a better "molecular recognition" could, in some cases, be obtained. Furthermore, due to the fact that solid solutions are formed even at very low pillaring percentages (<20%) and that very long alkyl chains can be used as non-rigid pillars, interlayer spaces filled by intercalated solvent as large as $30\times20\times10$ Å^3 are, in principle, possible. This fact is fascinating since these interlayer spaces could be seen as "molecular vessels" in which even selective reactions could be carried out (molecular reactors).

APPLICATIONS AND FUTURE PERSPECTIVES

In conclusion, layered and pillared M(IV) phosphonates and organo-phosphates can be considered to be a very large and versatile class of layered inorgano-organic materials. It is evident that, due to the large possibility of choices, both of the structure of the inorganic backbone and of the nature of the organic group attached to these backbones, an enormous variety of conformations of the organic groups in the interlayer region can be realised, in principle. The interlayer region of the M(IV) phosphonates can be seen as a well-ordered region in which many reactions of intercalated molecules between them and/or with the R groups of the layers can be carried out. As discussed by Mallouk et al.[24] the reactivity in layered phosphonates suggests that "it should be possible to engineer solids in which guest molecules bind according to their shape and chemical properties"; e.g. some particular intralayer polymerisation may be facilitated by the nature and disposition of the R groups in the interlayer region. The interactions in the interlayer regions between R groups belonging to adjacent layers are also of great interest. Furthermore, a large variety of molecules can be intercalated in these interlayer regions; thus layered metal phosphonates offer new possibilities for development of an interlayer supramolecular chemistry of the interlayer regions. In this respect, a further development of the supramolecular chemistry in the interlayer region, could come, as discussed before, from the study of the properties of specifically designed layered and pillared compounds, although it is too early to predict the real prospects of these compounds for practical selective separations.

The large surface areas obtained in special preparations of α-ZrP (e.g. α-ZrP/SiO_2 composites prepared from colloidal dispersions of the two components and having surface areas larger than 450 m^2/g) can be topotactically functionalised with R-SO_3H groups. Due to the large surface area and the presence of strong acid sites on their surface, these compounds are of interest as catalysts[25].

The existence of microporous zirconium diphosphonates (zeolite-like compounds) with tailor made cavities of uniform size in their interlayer region, possibly containing catalytic sites, opens the way for their application in molecular sieving and in "shape selective catalysis".

Furthermore, the possibility of preparing zirconium phosphonates containing -SO_3H groups has opened new perspectives in the field of the protonic conductors. Some materials with very good protonic conductivity even in the 100-180°C range, have already been obtained[26].

The recent experiments of Thompson et al. in photochromism via the photoreduction of zirconium phosphate-viologen compounds seem to show exciting promises in the utilisation and storage of solar energy[27].

For other applications and new perspectives of metal phosphonates, such as their structural analogy with Y-type Langmuir-Blodgett films, layer-by-layer growth, topochemical reactivity and non-linear optical effects, the reader is referred to[24].

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