Pillared Derivatives of γ-Zirconium Phosphate Containing Nonrigid Alkyl Chain Pillars

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Abstract: Pillared derivatives of γ-zirconium phosphate, having the general formula $ZrPO_4[O_2P(OH)_2]_{1-x}[O_2POH-(CH_2)_n-HOPO_2]_{x/2}\cdot mH_2O$ ($n = 4$, 6, 8, 10, 12, and 16), were prepared by soft topotactic reactions between colloidal dispersions of exfoliated lamellae of $\gamma-ZrPO_4[O_2P(OH)_2]\cdot 2H_2O$ and 1,*n*-alkanediphosphonic acid solutions. In these compounds the interlayer distance can be easily modulated almost continuously by increasing the number of the carbon atoms in the alkyl chain, while the lateral distance of the pillars can be varied over a large interval according to the degree of pillaring. The interlayer distance of compounds with a low percentage of pillaring decreased appreciably when the intercalated solvent was eliminated (e.g., by dehydration). The reversible elongation and shortening property of the interlayer suggests that the alkyl chains, being nonrigid pillars, tend to fill up empty spaces created by the loss of interpillar solvent by adopting different conformations in the interlayer region. The large interpillar spaces filled by solvent can be seen as “tailor-made molecular vessels,” in which specific reactions could be carried out in a restricted environment.

Introduction

Study of the chemistry of metal phosphonates began in the mid-1970s with the pioneering works of Yamanaka et al. on γ-zirconium phosphate derivatives[1] and Alberti et al. on γ-zirconium phosphate and phosphate ester derivatives.[2] Because of existing knowledge of the layered structure of γ-metal (IV) phosphates, the initial development of metal phosphonate chemistry was essentially based on γ-metal (IV) phosphonates.[3,4] These phosphonates are ideal starting precursors for the molecular design of structures with specific properties, given the great variety of organic groups that can be attached to the γ-layers. Hosts for the intercalation of a large variety of guests, protonic conductors, photochemically and catalytically active materials, and micro- and mesoporous solids have already been prepared.[3,4] Furthermore, supramolecular assembly between layers and layer-by-layer formation of very thin films[5] have stimulated further interest in the chemistry of these organic derivatives of γ-metal(IV) phosphates.

After elucidation of the structure of γ-metal (IV) phosphates,[6] currently formulated as $M^{IV}PO_4[O_2P(OH)_2]\cdot 2H_2O$ (hereafter referred to as γ-MP), and after the discovery that these layered solids are exfoliated in water−acetone medium at 80 °C,[7] it became evident that these organic derivatives are formed through the gradual replacement of the bidentate anionic ligand $O_2P(OH)_2^-$ with similar $O_2P(OH)R^-$ ligands.[8a,b]

As result of these discoveries, the chemistry of γ-zirconium phosphate derivatives began to increase rapidly in the early 1990s. As was the case with γ-metal phosphonate chemistry,[4] considerable growth can be expected soon. It is now possible to design and prepare γ-organic derivatives with predicted properties,[8] including derivatives containing crown ethers[9] in the interlayer region, by choosing the appropriate organic radical, R.

The possibility of obtaining γ-pillared derivatives by topotactic reactions with diphosphonic acids has also been investigated.[10] Through the use of rigid organic radicals such as biphenyl groups, γ-pillared compounds with high interlayer microporosity (320 m^2/g) have been prepared.[11] The mechanism of the formation of γ-pillared compounds by topotactic reactions has been clarified recently.[12]

We decided to investigate the preparation of γ-derivatives containing nonrigid pillars because of expected changes in their conformation as a function of the degree of pillaring and the amount of solvent included in the interpillar spaces. In the present paper, we describe the synthesis and some preliminary characterization of a series of γ-zirconium phosphate derivatives of the general formula: $ZrPO_4[O_2P(OH)_2]_{1-x}(O_2POH-(CH_2)_n-HOPO_2)_{x/2}\cdot mH_2O$ (**1**), where $n = 4$, 6, 8, 10, 12, and 16.

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Table 1. General Conditions for the Topotactic Reaction between 0.25 g of γ−ZrP and 1,10-Decanediphosphonic Acid

x^a	c^b, mol/L^{-1} × 10^3	t, min^c	x^d	x^e	x^f
0.12	3.10	∞	0.096	0.094	0.095
0.25	6.30	360	0.24	0.22	0.23
0.50	13.0	15−20	0.47	0.42	0.44
1.00	26.0	10	0.80	0.80	0.80

[a] Programmed degree of pillaring. [b] Concentration of 15 mL of 1,10-decanediphosphonic acid solution in 1:1 water:acetone mixture. [c] Flocculation time. [d] Degree of pillaring obtained by ion chromatography. [e] Degree of pillaring obtained by liquid ^{31}P NMR. [f] Average degree of pillaring.

Experimental Section

Chemicals. Zirconyl chloride octahydrate was a Merck pro analysis product. All other chemicals were C. Erba RPE grade.

Preparation of 1,*n*-Alkanediphosphonic Acids. All the 1,*n*-alkanediphosphonic acids used were prepared by an Arbuzov[13] type phosphonation reaction: 0.036 mol of 1,*n*-dibromoalkane was mixed with 12 g (0.072 mol) of triethyl phosphite and the final solution was heated for 6 h at 150 °C.[14] The mixture was then cooled and 120 mL of concentrated HCl was added. The mixture was refluxed for 12 h. After cooling at 0 °C, the precipitate was filtered off, washed with cool water, and dried by rotatory evaporation. In some cases, the first precipitate was purified by treatment with HCl solution, obtaining a purity degree of 85−95%.

Preparation of γ−$ZrPO_4[O_2P(OH)_2]\cdot 2H_2O$. The compound was prepared in its diammonium form by thermal decomposition of zirconium fluorocomplexes and then converted into its hydrogen form by elution in HCl solution. The detailed procedure was described previously.[12]

Topotactic Reaction with 1,*n*-Alkanediphosphonic Acids. γ−ZrP (0.25 g) was dispersed in 35 mL of a 1:1 water:acetone mixture under shaking at 80 °C for ∼15−20 min in a closed vessel to allow formation of a colloidal dispersion. To the dispersion was quickly added, with shaking, 15 mL of 1,*n*-alkanediphosphonic acid solution that had been heated to 80 °C. The concentration of this solution was varied to obtain compounds with increasing degrees of pillaring. As an example, Table 1 reports the experimental concentrations used with 1,10-decanediphosphonic acid. Shown are the x values in **1**, calculated by assuming a quantitative exchange of the diphosphonic acid, as well as the values found experimentally. Similar concentrations were also used for all the other acids. After a certain time, the flocculation time, which depends on the degree of pillaring involved and the length of the alkyl chain used (see later), initial flocculation of the colloidal dispersion was observed. To allow for complete flocculation, the reaction was continued, without shaking, for another 3 days. If no flocculation was observed the first 2 days, acetone was allowed to evaporate slowly through a hole (of ∼2 mm^2), which allowed a slow flocculation to be observed; the reaction was then continued for another 3 days. The solids were finally separated by centrifugation.

Instrumental and Analytical

X-ray powder diffraction (XRD) patterns of samples were recorded with the step-scanning procedure (step size 0.03°, counting time 2 s) and use of a computerized Philips PW1710 diffractometer with a graphite monochromated CuKα radiation (40 kV, 30 mA). Diffraction patterns of samples at high temperatures were recorded with an A. Paar HTK camera. Phosphonate to phosphate molar ratios in the solids were obtained by quantitative ^{31}P liquid NMR analysis with a Bruker AC 200 spectrometer; for this procedure, weighed amounts of sample (30 mg) were dissolved in 1 mL of 4M HF acid in deuterated dimethyl sulfoxide. The spectra showed a singlet at 3.1 ppm for phosphoric acid and an unresolved multiplet at the following positions: 1,4-butanediphosphonic acid, 34.8 ppm; 1,6-hexanediphosphonic acid, 35.6 ppm; 1,8-octanediphosphonic acid, 36.3 ppm; 1,10-decanediphosphonic acid, 37.7 ppm; 1,12-dodecanediphosphonic acid, 39.3 ppm; and 1,16-hexadecanediphosphonic acid, 42.1 ppm. The shifts were relative to 85% D_3PO_4 in D_2O.

^{31}P magic angle spinning (MAS) NMR spectra were recorded on a Varian spectrometer operating at 161.9 MHz, with a magnetic field modulation of 9.4 T, at room temperature, MAS in the range 7−7.4 kHz, and $\pi/2$ of 8 μs.

The phosphate groups exchanged by the diphosphonates were determined in the mother liquor by ion chromatography with a DIONEX series 2000 I/sp, AS4A column, and an eluent $NaHCO_3$ (1.7 mM) − Na_2CO_3 (1.8 mM) solution.

Thermogravimetric analyses were performed with a Stanton Redcroft STA780 thermoanalyzer, using a heating rate of 5 °C/min in a constant oxygen flow (30 cm^3/min). The samples were first conditioned over a saturated solution of NaCl at 75% relative humidity (r.h.).

The x values in **1** were calculated as the average of the results obtained by NMR and by ion-chromatographic analysis. The percentage of the substitution (or the percentage of pillaring) was defined as 100x.

Results and Discussion

Topotactic Reactions of Pillaring with Diphosphonate Groups. Since each diphosphonate must replace two $O_2P(OH)_2^-$ groups belonging to two different γ-lamellae, the topotactic reactions of pillaring are more complicated than the reactions of substitution for $O_2P(OH)_2^-$ by monophosphonate groups.[15]

We have recently found that the pillaring reaction occurs in at least two steps.[12] In the first step, each diphosphonic group behaves like a monovalent anionic ligand, replacing only one $O_2P(OH)_2^-$ group of exfoliated γ-lamellae. This reaction is very fast, the $t_{1/2}$ being a few minutes. The colloidal derivatized lamellae can interact with each other, including replacing a second $O_2P(OH)_2^-$ for each acidic diphosphonate group taken up and forming a pillared bilamellar particle. This bilamellar particle can react with other derivatized lamellae or with another bilamellar particle, giving rise to tri- or tetralamellar particles and so on. Therefore, the number of pillared lamellae increases over time and, when this number exceeds a given value (usually 5−6), flocculation of the pillared γ−ZrP takes place. The substitution reaction of the dihydrogen phosphate diphosphonate can also continue, though very slowly, after flocculation. The number of pillared lamellae continues to increase over time and the compound becomes progressively more crystalline.

We also assumed that the above mechanism held for the reaction between γ−ZrP and 1,*n*-alkanediphosphonic acid and made no further investigation of this mechanism. We confirmed that in the final compounds two dihydrogen phosphate groups were replaced by each entering diphosphonic group. Therefore, regardless of the mechanism, the total topotactic reaction of pillaring can be written as:

$$ZrPO_4[O_2P(OH)_2]\cdot 2H_2O + x/2[(CH_2)_n(PO_3H)_2]^{2-} \overset{(m\text{-}2)H_2O}{\rightleftharpoons} Zr\,PO_4[O_2P(OH)_2]_{1-x}\,[O_2POH-(CH_2)_n-HOPO_2]_{x/2}\cdot mH_2O + xH_2PO_4^-$$

Figure 1 shows the ^{31}P MAS NMR spectrum of a 1,4-butanediphosphonate derivative with 90% pillaring. Three

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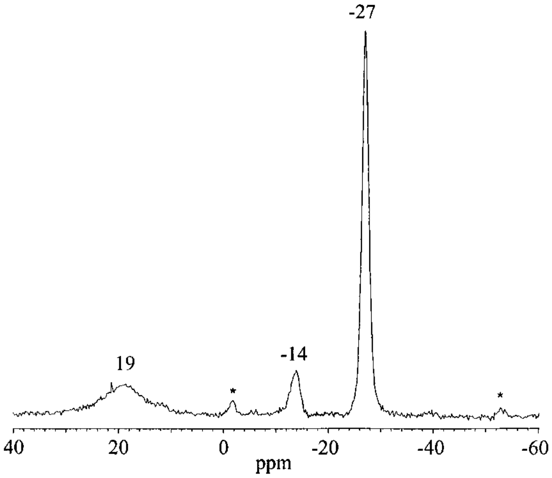

Figure 1. ^{31}P MAS NMR spectrum of 1,4-butanediphosphonate derivative with 90% pillaring percentage. The asterisked peaks refer to spinning side-bands.

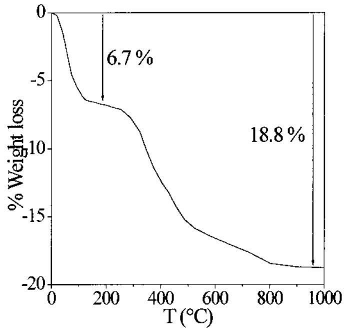

Figure 2. Thermogravimetric curve of $ZrPO_4[O_2P(OH)_2]_{0.14}[HO_3P(CH_2)_6PO_3H]_{0.43}\cdot1.2H_2O$ conditioned at 75% r.h. Heating rate: 5 °C/min, under static atmosphere.

signals are present: one at −27 ppm, from the PO_4 groups, the second at −14 ppm, from the H_2PO_4 groups of the γ-layer; and the third at 19 ppm, which can be ascribed to the diphosphonate groups.[16] In agreement with our model, the signal at 35 ppm characteristic of free 1,4-butanediphosphonic acid is not observed. We can conclude that the diphosphonate groups covalently join adjacent layers.

The value of the hydration of the pillared derivatives, previously conditioned at 75% r.h., was determined by thermogravimetry. A typical thermogravimetric curve of 1,6-hexanediphosphonate derivatives having a high percentage of pillaring (86%) is shown in Figure 2.The first weight loss, at temperatures up to 200 °C, is due to the dehydration process; the second, at ~300 °C, is due to the oxidation of the organic moieties. The weight loss after 400 °C can be attributed to the condensation of −P−OH groups and the final formation of cubic pyrophosphate at 1000 °C.

The variation of hydration (*m*) with the degree of pillaring of derivatives with different chain lengths is shown in Figure 3.

For γ−1,4-butanediphosphonate derivatives the hydration followed the equation: $m = 2-x$. We conclude that there is one water molecule for each P−OH group in the derivative. For derivatives with longer chains, these was more than one water molecule for each P−OH group.

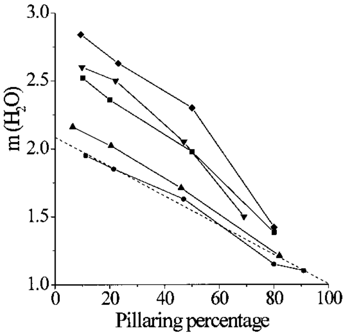

Figure 3. Water content (*m*) of some 1,*n*-alkanediphosphonate derivatives as a function of the pillaring percentage. Circles, $n = 4$; triangles pointing up, $n = 6$; squares, $n = 8$; triangles pointing down, $n = 10$; and diamonds, $n = 12$.

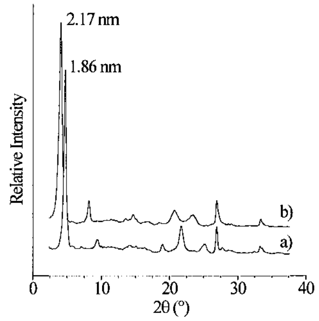

Figure 4. XRD patterns of (a) 1,8-octanediphosphonate derivative and (b) 1,12-dodecanediphosphonate derivative, with 80% pillaring percentage and conditioned at 75% r.h.

In the absence of structural data, the reason for the greater hydration is not clear. It may be related to a decrease in the degree of crystallinity or an increase in hydrolytic phenomena (or both) with the increasing chain length of the pillared derivative.

Since flocculation time and interlayer distances of the dehydrated derivatives were found to depend on the degree of pillaring, we will discuss derivatives with high and low degrees of substitution separately.

Derivatives with a High Percentage of Pillaring (≥60%). The flocculation time of all the derivatives with pillaring >60% was ~10 min. The maximum *x* value, regardless of chain length, was ~1. This confirmed that *n*-alkyl chains could be accommodated in the γ-layers without appreciable steric hindrance up to full conversion.

The degree of crystallinity increased with the reaction time and decreased with increasing chain length. After the flocculation, we continued the reaction for another 3 days to obtain pillared derivatives sufficiently crystalline for determination of their interlayer distances. As an example, the XRD patterns of samples with $x = 0.8$ are shown in Figure 4 for $n = 8$ and 12. The interlayer distance was found to depend essentially on the number of carbon atoms of the alkyl chain; the effects of dehydration and degree of pillaring were negligible.

Figure 5 shows the variation in the interlayer distance with increasing numbers of carbon atoms in the alkyl chain for derivatives with a percentage of pillaring of ~80%. The interlayer distance increases linearly with *n*, which means that alkyl chains exhibit the same conformation and are inclined at the same angle with respect to the layer plane. The experimental data reported in Figure 5 fit the straight line $d = 0.93 + 0.101\ n$, where *d* is the interlayer distance in nm. Assuming an extended conformation for the alkyl chain, this equation can be rewritten[17] as $d = 0.93 + 0.127\ n \sin \alpha$, where α is the

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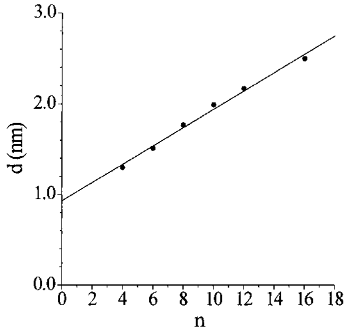

Figure 5. Interlayer distance as a function of the number of carbon atoms in the alkyl chain (n) for derivatives with maximum degree of pillaring, conditioned at 75% r.h.

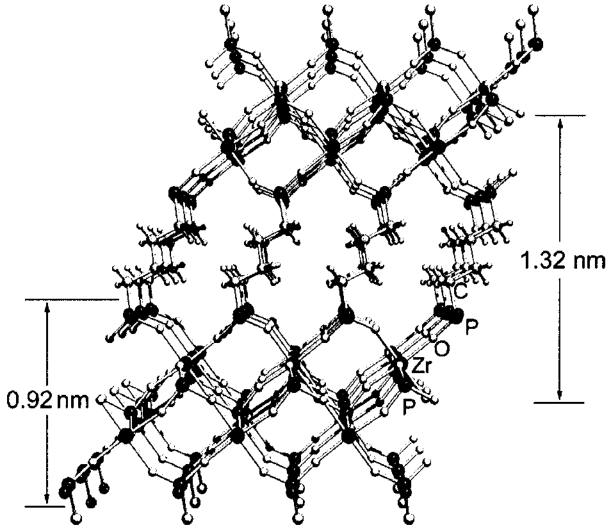

Figure 6. A structural model of an ideal 1,4-butanediphosphonate derivative with 100% pillaring.

angle between the alkylchain axis and the plane of γ-layer; for this case, $\alpha = 52.7°$.

To obtain structural information on pillared derivatives of γ−ZrP, we tried to increase the degree of crystallinity by hydrothermal treatment. Good results were obtained only for the 1,4-butanediphosphonate derivative, which was successfully treated at 250 °C under nitrogen atmosphere for 6 days in 1 mM 1,4-butanediphosphonic acid. The structure of this pillared derivative was determined ab initio by Patterson methods with final Rietveld refinement.[18] The results confirmed that (*a*) the structure of the γ-inorganic backbone was maintained after the topotactic reaction and (*b*) the alkyl chains act as pillars covalently joining adjacent γ-lamellae.

Computer models based on the structure of γ−ZrP, experimental composition, interlayer distance, and inclination angle were made with the help of the Hyperchem program. The interlayer distance is in agreement with alkyl chains in extended conformation, bonded to both sides of the γ-layers. Figure 6 shows the model optimized for the 1,4-butanediphosphonate derivative with 100% pillaring which is very similar to the actual structural model we reported previously.[18] The γ-layer thickness determined (0.91 nm) is in good agreement with the extrapolation of the straight line of Figure 5 to $n = 0$, which gives a thickness of 0.93 nm.

Derivatives with a Low Percentage of Pillaring (≤50%). The flocculation times of samples with 50% pillaring were in the range 20−40 min. The time increased considerably with a decreasing percentage of pillaring. At percentages <25%, no flocculation was obtained, even after 10 days. In these cases, we induced the pillared derivatives to flocculate as described in the *Experimental Section*.

Table 2. Composition and Interlayer Distances under Different Conditions of Some Samples with the General Formula: $ZrPO_4[O_2P(OH)_2]_{1-x}[O_2POH-(CH_2)_{10}-HOPO_2]_{x/2}\cdot mH_2O$

		d, nm			
x	m[a]	wet	conditioned[a]	dried[b]	rehydrated[c]
0.098	2.60	1.92	1.41	1.12	1.93
0.22	2.50	1.94	1.65	1.43	1.97
0.47	2.05	1.97	1.94	1.84	2.00
0.68	1.50	1.99	2.00	1.93	2.00

[a] Samples conditioned at 75% r.h. [b] Samples dehydrated at 100 °C. [c] Samples contacted with water again after dehydration.

XRD patterns clearly showed that the original γ−ZrP phase was always completely converted into monophasic pillared derivatives, even for very low percentages of pillaring. The absence of the original γ−ZrP phase can be attributed to the fact that even a few pillars randomly distributed over the whole surface of the exfoliated lamellae are sufficient to prevent the recomposition of the original γ−ZrP phase during flocculation.

The free interpillar space depends on the pillaring percentage and can be roughly evaluated by simple geometrical calculations based on the positions of the phosphorus atoms in the γ-layer structure. If we assume a uniform distribution for the alkyl chains in their extended conformation, the interpillar distance can range from 0.54 nm in compounds with 100% pillaring to ∼1.6 nm at 12% pillaring. Therefore, van der Waals interactions between adjacent alkyl chains, especially at a low degree of pillaring, should be negligible, and the disposition of the chains in the interlayer region should be determined only by the γ-layer inorganic backbone.

Reversible Conformational Changes of the Pillars during Hydration−Dehydration Processes: Accordion-like Movement. The interlayer distance of the derivatives with a low degree of pillaring showed a strong dependence on the amount of interpillar water. To illustrate this typical behavior, we examine in detail 1,10-decanediphosphonate derivatives of the general formula: $ZrPO_4[O_2P(OH)_2]_{1-x}[O_2POH-(CH_2)_{10}-HOPO_2]_{x/2}\cdot mH_2O$. The results are summarized in Table 2.

Note that the interlayer distance of a fully hydrated derivative does not depend on the percentage of pillaring. This behavior can be explained by assuming that the alkyl chains are in their extended conformation when the solvent fills the interpillar spaces. When the water is partially or totally removed (e.g., by conditioning the samples at low r.h. or by dehydration at 110−150 °C), the alkyl chains cannot remain in their extended conformation any longer. The chains tend to reduce the void interpillar spaces and assume conformations that decrease the interlayer distance (Figure 7). This reduction depends on the interpillar spaces and hence on the degree of pillaring. The conformation of the alkyl chains in the absence of reciprocal interactions is of interest, and solid-state ^{13}C NMR measurements are in progress to obtain some preliminary information.

The reversibility of the conformational change can be followed by XRD with the use of a high-temperature camera. For the derivatives with $n = 10$ and pillaring in the range 90−40%, only a small decrease (∼0.1 nm) was observed during dehydration. Greater variation (∼0.5 nm) was found in the pillaring range 30−20%, and a decrease of 0.8 nm was obtained in the range 15−8%.

As an example, Figure 8 shows the XRD patterns of 1,10-decanediphosphonate derivative with a pillaring percentage of

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(18) Alberti, G.; Murcia-Mascarós, S. Vivani, R. *J. Mol. Struct.* (in press).

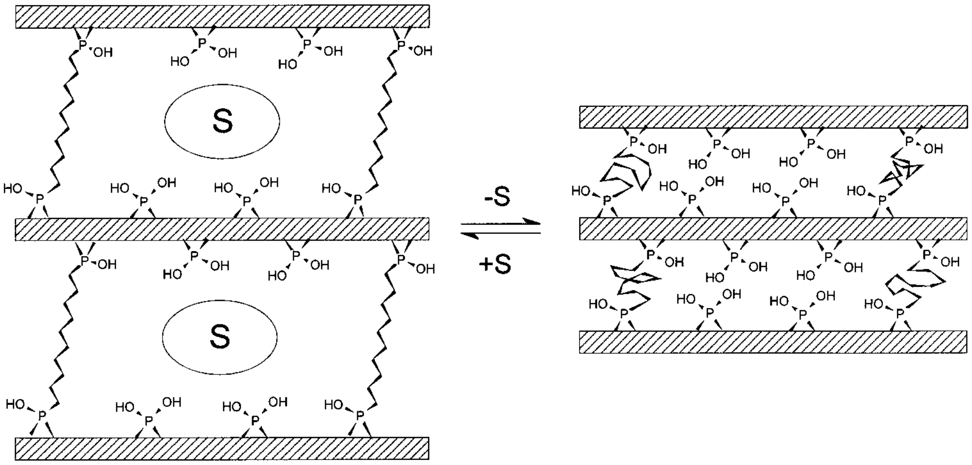

Figure 7. Schematic representation of "accordion effect" for a 1,10-decanediphosphonate derivative with 12% pillaring percentage. The different conformations of the alkyl chains can be observed in the presence and absence of solvent in the cavities.

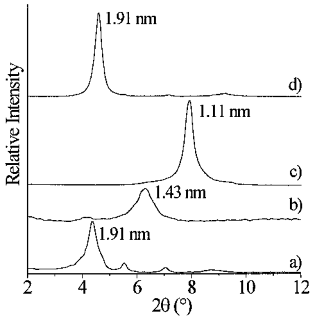

Figure 8. XRD patterns of 1,10-decanediphosphonate derivatives with 12% pillaring percentage: (a) initial wet sample, (b) conditioned at 75% r.h., (c) dried at 100 °C, and (d) contacted again with water:acetone 1:1 at 80 °C for 15 min.

12%. The maximum interlayer distance of the completely hydrated sample, 1.91 nm, decreases to 1.43 nm after conditioning at 75% r.h. and to 1.11 nm when dehydrated at 100 °C. When the dried sample is contacted with water again, the original interlayer distance is restored and the term "accordion-like movement" is given to this reversible elongation and shortening of the interlayer distance.

Compounds at low pillaring percentages can be considered layered solids with chained adjacent layers. As in layered solids, the interlayer distance depends on the size and amount of the intercalated species. However, unlike layered solids, where infinite swelling is possible, the maximum interlayer distance of chained solids is fixed by the length of the alkyl chain joining the layers; thus intercalation of large species may not occur, at least when intercalation processes are not very energetic. Therefore, these particular pillared derivatives exhibit behavior intermediate between that of layered and rigid three-dimensional solids.

Conclusion

γ-Zirconium phosphate pillared with alkyl chains may be very easily prepared by soft topotactic reactions with colloidal dispersions of $\gamma-$ZrP. These derivatives constitute a large class of pillared compounds in which the maximum interlayer distance can be very easily modulated in an almost continuous manner by increasing the length of the alkyl chains joining the layers. In the derivatives described, the gallery height can vary from 0.36 to 1.4 nm; on the other hand, the lateral distance of the pillars can also be changed over a very large range by controlling the degree of pillaring. Furthermore, the interlayer distance of these compounds, unlike those containing rigid pillars, is strongly dependent on the conformation of the nonrigid pillars, which, in turn, depends on the amount of solvent present in the interpillar space.

These pillared compounds are very interesting because their large interpillar spaces may be seen as tailor-made molecular vessels, which can be filled with various solvents. Some selective reactions could be carried out in these interpillar spaces, especially if catalytic sites are present on the surface of the γ-layers or fixed to the alkyl chains (molecular reactors). In the compounds obtained with low pillaring percentage, acid P−OH groups are already present, both on the surface of $\gamma-$ZrP and at the bases of the alkyl chains.

The formation of insoluble solids inside these tailor-made molecular vessels is also conceivable. Thus, clusters of different sizes and shapes, dispersed in the ordered spaces, could be obtained.

Reversible movement related to conformational change may resemble muscle contraction. Perhaps some application of this anisotropic mechanical movement is possible with the use of suitable pillars and electrical or chemical command.

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