

Preparation and Characterization of Zirconium Phosphate Phosphonates, $ZrPO_4(H_2PO_4)_{1-x}(RPO_2OH)_x \cdot nH_2O$, with γ -Layer Structure (R = CH₃, C₃H₇, C₆H₁₁)

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The γ -zirconium phosphate phosphonates, $ZrPO_4(H_2PO_4)_{1-x}(RPO_2OH)_x \cdot nH_2O$ (R = CH₃, C₃H₇, C₆H₁₁), have been prepared by total or partial replacement of the interlayer dihydrogen phosphate groups of γ -ZrPO₄H₂PO₄·2H₂O with RPO₂(OH)⁻ groups of the corresponding phosphonic acids. The following compounds: γ -ZrPO₄CH₃PO₂-OH·2H₂O (interlayer distance = 12.8 Å); γ -ZrPO₄C₃H₇PO₂OH·1.2H₂O (interlayer distance = 15.1 Å) and γ -ZrPO₄(H₂PO₄)_{0.33}(C₆H₁₁PO₂OH)_{0.67}·H₂O (interlayer distance = 16.9 Å) were obtained. The partial replacement of H₂PO₄⁻ groups when cyclohexyl phosphonic acid was used seems to be due to steric hindrances in the interlayer region. Some considerations on the structure of these compounds as well as some preliminary ion exchange and intercalation properties are also reported.

Introduction

Two zirconium acid phosphates with a layered structure (usually distinguished by α - and γ -prefixes) are presently known.^{1,2} Organic derivatives of α -zirconium phosphate have been obtained by direct synthesis since 1978;³ their chemistry is now well developed,⁴ and even exciting applications in the field of tailor-made molecular sieves,^{5,6} "shape selective catalysis",⁷ and protonic conduction⁸ seem now to be possible.

As concerns the organic derivatives of γ -zirconium phosphate, information on their preparation by direct synthesis is not available. However the preparation of a mixed γ -zirconium phosphate phenylphosphonate by a topotactic reaction between already preformed γ -zirconium phosphate (γ -ZrP) and a solution of phenylphosphonic acid was reported by Yamanaka et al.⁹ as long as 1981 and then, in the following years, some other organic derivatives of γ -ZrP were also prepared by the same research group.^{10,12}

At that time, the γ -ZrP dihydrate was however erroneously formulated as γ -Zr(HPO₄)₂·2H₂O and its structure was therefore believed to be similar to that of α -Zr(HPO₄)₂·H₂O, but with a different packing of the layers.¹³ For this reason it was not possible

for these authors to give a correct interpretation of their experimental data.

After the recent advances in the formulation^{14,15} and structural characteristics of γ -metal(IV) phosphates,¹⁶ the chemistry of these layered compounds can today be better understood.

Now we know that γ -ZrP must be formulated as ZrPO₄H₂-PO₄·2H₂O and that the structure of a γ -layer consists of PO₄ groups sandwiched between two planes of zirconium atoms (see for example Figure 2) while PO₂(OH)₂ groups are bonded to the zirconium atoms in the external part of the sandwich. It is therefore clear that, unlike α -metal(IV) phosphonates, pure γ -M^{IV}(RPO₃)₂ cannot exist; however, the existence of γ -mixed organic derivatives of composition γ -M^{IV}PO₄RPO₂OH is possible. The previous literature was therefore again revisited, and it became clear that many of the considerations there reported, being based on a wrong formula and structure, were incorrect.

It was thus thought of interest to investigate once again the preparation of mixed organic derivatives of γ -ZrP in the light of this new knowledge. All our attempts to prepare these compounds by direct synthesis were however unsuccessful.¹⁷ It was therefore decided to prepare these compounds by topotactic reactions on already preformed γ -ZrP by a procedure similar to that described by Yamanaka et al.⁹

It was found that the interlayer dihydrogen phosphate groups of γ -ZrP can easily be exchanged by the smaller phosphite groups giving a compound of composition ZrPO₄[HPO₂(OH)]₂·2H₂O.¹⁷ However, when the same exchange was attempted with C₆H₅-PO₂OH groups, the maximum obtained replacement was not higher than 67% and the compound γ -ZrPO₄(H₂PO₄)_{0.33}(C₆H₅-PO₂OH)_{0.67}·2H₂O was obtained.¹⁸

It was believed that complete replacement of interlayer PO₂(OH)₂ groups was not obtained in this case only because of steric hindrance created by the large benzene ring.¹⁸ Since organic

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derivatives of γ -ZrP are of interest for their ion exchange and intercalation properties⁴ and since they could also find many practical applications, as in the case of organic derivatives of α -ZrP, it was thought of interest to collect more information on the effect of the nature and size of the organic radical on the formation of $ZrPO_4 \cdot RPO_2OH$ compounds by topotactic reactions.

In particular, a short R group, such as $-CH_3$, an aliphatic chain ($-C_3H_7$), and a large cyclic radical ($-C_6H_{11}$) were chosen and the results compared with those already obtained using the aromatic ring $-C_6H_5$.

Experimental Section

Reagents and Materials. Except for zirconyl chloride octahydrate (E. Merck) and methylphosphonic, propylphosphonic, and cyclohexylphosphonic acids (Alfa-Ventron Division, Hoechst and Fluka AG, 98% respectively), all other chemicals were C. Erba R.P.E. grade. γ -ZrP was prepared according to the procedure reported earlier.¹⁵

Preparation of the Organic Derivatives of γ -ZrP. 1. γ -Zirconium Phosphate Methylphosphonate. About 1 g of γ -ZrP was mixed with 200 mL of 0.5 M $CH_3PO_3H_2$ and heated on a water bath at 80 °C for 72 h. The solid was then separated, washed several times with distilled water to pH \approx 4, left in air overnight, and conditioned over saturated $BaCl_2$ solution (r.h. 90%).

2. γ -Zirconium Phosphate Propylphosphonate. A 1-g sample of γ -ZrP was refluxed with 100 mL of 1 M $C_3H_7PO_3H_2$ in a water-acetone (50:50) solution for at least 10 days. In this case, since the interlayer distances of the original γ -ZrP and that of γ -zirconium phosphate propylphosphonate are different, the progression of the topotactic reaction can be followed simply by X-ray powder diffraction (XRD). The exchanged solids were then conditioned as above.

3. γ -Zirconium Phosphate Cyclohexylphosphonate. A 1-g sample of γ -ZrP was refluxed in 100 mL of 1 M aqueous cyclohexylphosphonic acid for 3 days. The product was conditioned as above.

To obtain more crystalline samples, the solids, after the topotactic reaction, were maintained at 80 °C for an additional 48 h in 10^{-2} M HCl solution.

Instrumental Data. XRD patterns of the samples were recorded according to the step scanning procedure (step size 0.03°) with the help of a computerized Philips PW1710 Diffractometer using $Cu K\alpha$ radiation. Diffraction patterns at 200 °C were taken with a high temperature camera used in static conditions.

The weight loss curves were taken at a heating rate of 5 °C/min using a Stanton Redcroft Thermal Analyser STA780.

The sodium exchange and intercalation experiments were done either by the automatic titration method (Mettler DK Autotitrator), as previously described,¹⁷ or by the batch procedure.¹⁹

The relative proportions of phosphate to phosphonate in the exchanged products were obtained by ³¹P liquid-state NMR analysis with a Bruker AC200 instrument, after dissolving 0.1 g of the sample in about 1 mL of concentrated hydrofluoric acid and dimethyl sulfoxide as solvent. The shifts of the signals of methylphosphonic, propylphosphonic, cyclohexylphosphonic, and phosphoric acids were 32.3, 33.4, 33.8, and 1.6 ppm respectively. The shifts are relative to 85% D_3PO_4 in D_2O , with a positive sign indicating a shift to lower field.

Results and Discussion

Preparation of γ -Zirconium Phosphonates. Preliminary attempts to replace the interlayer $PO_2(OH)_2$ groups of γ -ZrP with CH_3PO_2OH groups by refluxing γ -ZrP directly either with dimethyl methylphosphonate alone or mixed with hydrochloric acid of different concentrations were carried out without success; the methylphosphonic acid was therefore used in its pure form.

It was found that with high concentrations of the methylphosphonic acid (>1 M), at 80–100 °C, γ -ZrP is completely transformed into γ -zirconium phosphate methylphosphonate (γ -ZrPMeP) in less than 24 hrs; however the reaction goes on with formation of the α -phase as indicated by the appearance of a peak at 8.9 Å characteristic of the α -zirconium methylphosphonate.² It was supposed that, as an analogy to our experience with the preparation of γ -zirconium phosphate phosphite,¹⁷ the

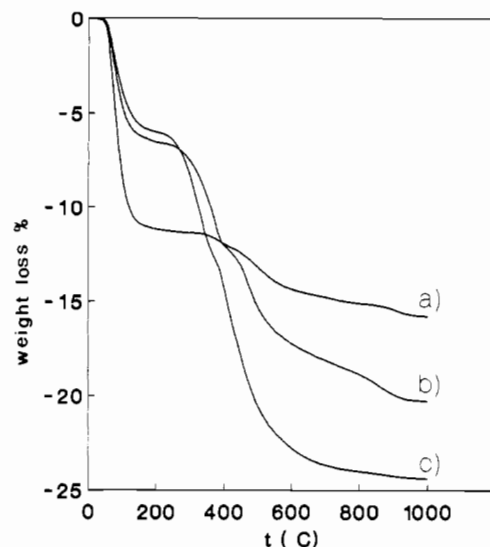
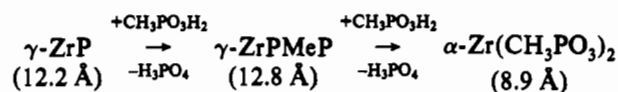


Figure 1. Thermogravimetric curves for γ -ZrPMeP (curve a), γ -ZrPPrP (curve b) and γ -ZrPCHP (curve c).

Table I. Comparison between Experimental and Calculated Weight Losses for the Pyrolysis of γ -Derivatives to ZrP_2O_7 , Where the Compositions of the Anhydrous Compounds Were Derived by NMR Analysis

composition of the anhydrous γ -derivative	expt wt loss, %	calcd wt loss, %
$ZrPO_4CH_3PO_2OH$	5.2	5.6
$ZrPO_4C_3H_7PO_2OH$	14.7	14.2
$ZrPO_4(H_2PO_4)_{0.33}(C_6H_{11}PO_2OH)_{0.67}$	19.4	18.9

transformation proceeds as follows:



where the numbers in parentheses are the interlayer distances (corresponding to the first reflection in the X-ray powder diffraction pattern).

To avoid the formation of the α -phase, the topotactic reaction was therefore carried out at a moderate temperature and concentration. Since the interlayer distances of γ -ZrP and γ -ZrPMeP are very close to each other, it was difficult to follow the progression of the topotactic reaction by X-ray analysis of the samples at various times. Therefore X-ray powder diffraction was only used to control the initial formation of the α -phase (appearance of a peak at 8.9 Å), while the progression of the reaction was followed by NMR analyses of the samples. It has been found that using 0.5 M $CH_3PO_3H_2$ at 80 °C, complete transformation into γ -ZrPMeP takes place within about 60–70 h without a detectable formation of the α -phase.

Similar trends were observed also for γ -zirconium phosphate propylphosphonate (γ -ZrPPrP) and γ -zirconium phosphate cyclohexylphosphonate (γ -ZrPCHP).

Typical procedures of preparation of these three organic derivatives are reported in the Experimental Section.

Characterization. NMR analyses showed that full replacement of the dihydrogenphosphate groups was obtained with methyl- and propylphosphonic acids, while only two-thirds were replaced in the case of cyclohexylphosphonic acid.

On the basis of these results, the anhydrous products were formulated as γ -ZrPMeP ($fw = 281$), γ -ZrPPrP ($fw = 309$) and γ -ZrPCHP ($fw = 327$).

The products were conditioned at 90% relative humidity and their waters of hydration, as well as their thermal decomposition, were determined thermogravimetrically in air (curves a–c of Figure 1).

Table II. X-ray Powder Diffraction Patterns of γ -Zirconium Phosphate Methylphosphonate, γ -Zirconium Phosphate Propylphosphonate and γ -Zirconium Phosphate Cyclohexylphosphonate at Different Degrees of Hydration

$d(\gamma\text{-ZrMeP}\cdot n\text{H}_2\text{O}), \text{\AA}$			$d(\gamma\text{-ZrPrP}\cdot n\text{H}_2\text{O}), \text{\AA}$		$d(\gamma\text{-ZrChP}\cdot n\text{H}_2\text{O}), \text{\AA}$	
90% r.h. $n = 2$	53% r.h. $n = 1.35$	200 °C $n = 0$	90% r.h. $n = 1.2$	200 °C $n = 0$	90% r.h. $n = 1$	200 °C $n = 0$
12.75 (s)	12.50 (s)	10.01 (s)	15.14 (s)	14.8 (s)	16.87 (s)	16.4 (s)
5.938 (m)	5.931 (m)	5.464 (w)	6.073 (m)	6.80 (w,b)	8.454 (m)	8.30 (m)
5.842 (m)	5.832 (m)	4.710 (m)	4.991 (m)	6.41 (vw)	6.186 (ms)	6.41 (w)
4.672 (m)	4.658 (w)	3.641 (m)	4.777 (m)	5.40 (w)	5.216 (w)	5.64 (w)
4.564 (m)	4.586 (m)	3.323 (w)	4.698 (m)	4.35 (vw)	4.887 (w)	4.95 (vw)
4.112 (w)	4.545 (m)	3.219 (m)	4.057 (m)	4.19 (w)	4.829 (w)	4.79 (w)
3.721 (m)	4.118 (w)	2.804 (w)	3.980 (m)	3.70 (w,b)	4.242 (m)	4.68 (w)
3.659 (m)	3.727 (m)	2.686 (m)	3.874 (w)	3.30 (w)	4.170 (m)	4.17 (m)
3.310 (m)	3.680 (m)	2.591 (m)	3.830 (w)	2.93 (vw)	3.916 (w)	3.56 (m)
3.217 (w)	3.620 (m)	2.509 (m)	3.404 (m)		3.617 (m)	3.34 (w)
3.193 (w)	3.310 (m)	2.271 (w)	3.336 (w)		3.557 (m)	3.28 (w)
3.032 (w)	3.223 (w)	2.093 (w)	3.309 (m)		3.316 (m)	3.21 (w)
2.771 (w)	3.186 (w)	2.071 (vw)	3.235 (m)		3.257 (m)	3.05 (vw)
2.732 (vw)	3.031 (w)	1.879 (vw)	3.029 (m)		3.171 (w)	2.95 (vw)
2.696 (m)	2.782 (w)	1.832 (w)	2.981 (w)		2.803 (w)	2.78 (vw)
2.659 (vw)	2.752 (vw)		2.680 (w)		2.690 (w)	
2.556 (w)	2.695 (w)		2.641 (w)		2.661 (w)	
2.497 (vw)	2.657 (vw)		2.600 (vw)		2.603 (vw)	
2.448 (vw)	2.547 (vw)		2.373 (w)		2.485 (vw)	
2.364 (vw)	2.499 (vw)		2.350 (w)		2.441 (w)	
2.259 (vw)	2.445 (vw)		2.317 (vw)		2.193 (vw)	
2.166 (vw)			2.183 (w)		2.138 (vw)	
2.138 (vw)			2.120 (w)		2.040 (vw)	
			2.060 (w)		1.959 (vw)	
			2.031 (w)		1.920 (vw)	
			1.988 (w)		1.875 (vw)	
			1.822 (w)		1.793 (vw)	

Note that the weight losses due to hydration water (<180 °C) are well separated from the losses due to the hydroxyl condensation and to the concomitant oxidative decomposition of the organic radicals (>300 °C).

Taking into account the losses under 200 °C and the formula weights of the anhydrous products determined by NMR, the compositions of the hydrated compounds are as follows: $\gamma\text{-ZrPO}_4\text{-CH}_3\text{PO}_2\text{OH}\cdot 2\text{H}_2\text{O}$ (12.8 Å), $\gamma\text{-ZrPO}_4\text{-C}_3\text{H}_7\text{PO}_2\text{OH}\cdot 1.2\text{H}_2\text{O}$ (15.1 Å) and $\gamma\text{-ZrPO}_4\text{(H}_2\text{PO}_4\text{)}_{0.33}\text{(C}_6\text{H}_{11}\text{PO}_2\text{OH)}_{0.67}\cdot \text{H}_2\text{O}$ (16.9 Å), where the numbers in brackets are their interlayer distances determined by XRD. As confirmed by X-ray analysis, the final product of the decomposition at 1000 °C was cubic zirconium pyrophosphate in all the investigated compounds. It was therefore possible to make a comparison between the percentages of the losses found in the range 200–1000 °C and those calculated for the decomposition of the anhydrous products to ZrP_2O_7 (fw = 265.2). As can be seen from the data reported in Table I, good agreement is obtained in all the cases, this being a further confirmation of the above compositions.

In the case of $\gamma\text{-ZrPMeP}$ the hydration and the X-ray powder diffraction pattern were also determined for a sample conditioned over a saturated $\text{Mg}(\text{NO}_3)_2$ solution (53% r.h.). It was found that the hydration water was dependent on the relative humidity; however, the x-ray pattern was only slightly modified when the relative humidity was decreased from 90% to 53% (see Table II). On the other hand, when the last molecule of water was lost, a decrease of the interlayer distance from 12.5 to 10.0 Å was observed. The dehydration behavior of $\gamma\text{-ZrPMeP}\cdot \text{H}_2\text{O}$ is thus very similar to that of the original $\gamma\text{-ZrPO}_4\text{H}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$ where the interlayer distance decreases from 11.3 to 9.4 Å when the last water molecule of hydration is removed. This behavior is typical of layer compounds in which the water molecules are interposed between groups of adjacent layers so that their removal causes the layers to come close together. On the other hand, as shown in columns 4–7 of Table II, the interlayer distances of $\gamma\text{-ZrPPrP}\cdot 1.2\text{H}_2\text{O}$ and $\gamma\text{-ZrPChP}\cdot \text{H}_2\text{O}$ do not change appreciably when their hydration water is removed. This behavior seems to indicate that the packing of γ -layers containing large R groups in their surface may create a permanent free porosity in the interlayer region, where a limited number of water molecules

Table III. Comparison of the Unit Cell Dimensions for Five Different γ -Layered Compounds

compound	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	β , deg
$\text{ZrPO}_4\text{H}_2\text{PO}_4\cdot 2\text{H}_2\text{O}$	5.386	6.636	24.806	98.70
$\text{ZrPO}_4\text{HPO}_2\text{OH}\cdot 2\text{H}_2\text{O}$	5.448	6.621	27.688	113.92
$\text{ZrPO}_4\text{(H}_2\text{PO}_4\text{)}_{0.33}\text{(C}_6\text{H}_5\text{PO}_2\text{OH)}_{0.67}\cdot 2\text{H}_2\text{O}$	5.387	6.626	32.394	109.51
$\text{ZrPO}_4\text{C}_3\text{H}_7\text{PO}_2\text{OH}\cdot 1.2\text{H}_2\text{O}$	5.364	6.621	30.710	98.86
$\text{ZrPO}_4\text{(H}_2\text{PO}_4\text{)}_{0.33}\text{(C}_6\text{H}_{11}\text{PO}_2\text{OH)}_{0.67}\cdot \text{H}_2\text{O}$	5.379	6.637	34.082	98.17

can be accommodated without appreciable increase of the interlayer distance. The XRD patterns of anhydrous and conditioned (90% r.h.) samples of $\gamma\text{-ZrPPrP}$ and $\gamma\text{-ZrPChP}$ are reported in Table II.

Structural Aspects. The unit cell of $\gamma\text{-ZrP}$ and a structural model of γ -titanium phosphate have been reported in previous papers.^{15,16} On the basis of these data and on the hypothesis that the *a* and *b* parameters of the $\gamma\text{-ZrP}$ cell (5.386 and 6.636 Å respectively) remain essentially unaltered after the replacement of the interlayer H_2PO_4 groups with HPO_2OH or $\text{C}_6\text{H}_5\text{PO}_2\text{OH}$ groups, structural models for $\gamma\text{-ZrPO}_4\text{HPO}_2\text{OH}$ and for $\gamma\text{-ZrPO}_4\text{C}_6\text{H}_5\text{PO}_2\text{OH}$ were derived.^{17,18}

Because these models were useful for explaining the steric hindrance between adjacent phosphonate groups, the hypothesis that the *a* and *b* parameters do not change appreciably for the topotactic exchange of the H_2PO_4 groups present in the interlayer region has been subjected to experimental testing. Samples of $\gamma\text{-ZrPO}_4\text{HPO}_2\text{OH}\cdot 2\text{H}_2\text{O}$, $\gamma\text{-ZrPO}_4\text{(H}_2\text{PO}_4\text{)}_{0.33}\text{(C}_6\text{H}_5\text{PO}_2\text{OH)}_{0.67}\cdot 2\text{H}_2\text{O}$, $\gamma\text{-ZrPPrP}$, and $\gamma\text{-ZrPChP}$ with a good degree of crystallinity were prepared and their unit cell dimensions determined from their X-ray powder patterns using the TREOR program.²⁰

A comparison of the unit cell dimensions of these derivatives with those of $\gamma\text{-ZrP}$ (Table III) indeed shows that the structure of the γ -layer remains essentially unchanged and that the interlayer groups, as expected, have an influence only on the

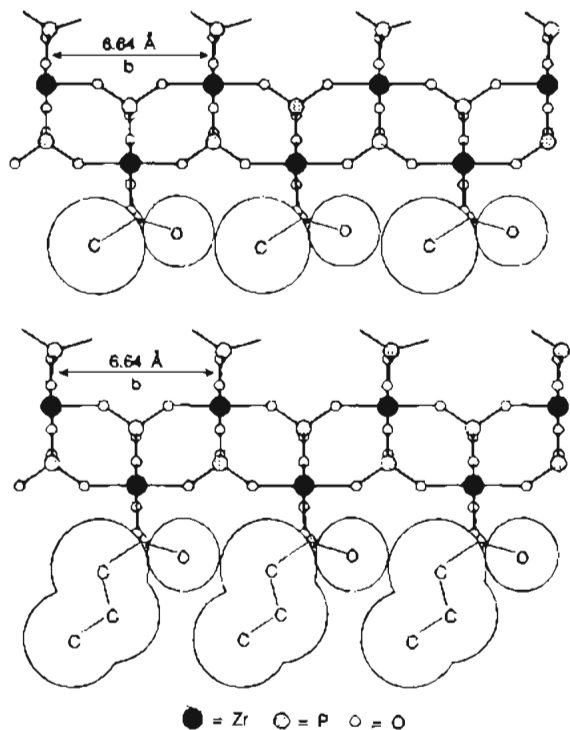


Figure 2. Structural models of γ -ZrPMeP (upper) and γ -ZrPPrP (lower) viewed perpendicular to the b axis. The radii of oxygen and methyl group were assumed to be 1.5 and 2 Å, respectively.

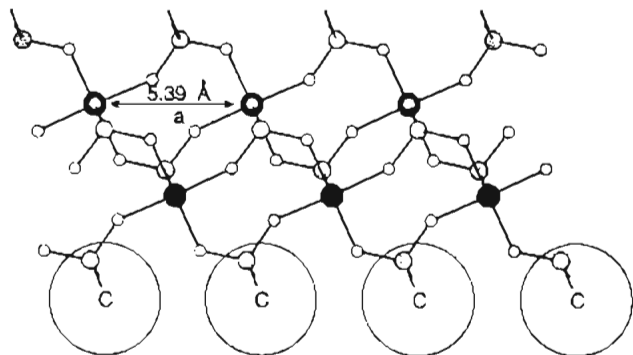


Figure 3. Structural model of γ -ZrPMeP viewed perpendicular to the a axis.

interlayer distance. It was concluded that useful models can be made with the aid of a computer by simply introducing into it the structural data of the γ -layer (taken from refs 15 and 16) and replacing H_2PO_4 with RPO_2OH groups.

The models obtained for γ -Zr $\text{PO}_4\text{CH}_3\text{PO}_2\text{OH}$ and γ -Zr $\text{PO}_4\text{-C}_3\text{H}_7\text{PO}_2\text{OH}$ are reported in Figures 2 and 3. These models indicate that the a and b dimensions are instead sufficiently large to accommodate adjacent alkyl chains, so replacements of 100% of the interlayer H_2PO_4^- groups can be expected. The experimental data confirm this expectation.

More data are instead required for organic derivatives containing groups larger than alkyl chains. Similar to the observation with phenylphosphonic groups,¹⁸ a partial replacement (66%) of the H_2PO_4 groups was attained with cyclohexylphosphonic groups, thus confirming the steric hindrance of large groups. Since less steric hindrance for a given large R group is expected if phosphinate, RPO_2H , groups are used, we are now examining such a possibility, and the first results with $\text{C}_6\text{H}_5\text{PO}_2\text{H}$ groups seem to confirm this expectation.

In conclusion, the simple structural models derived as described above are useful for predicting the formation of γ -organic derivatives according to the nature of the R organic group. For

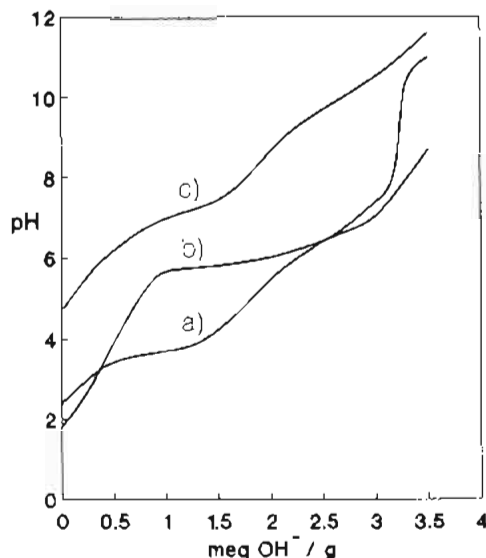


Figure 4. Titration curve of γ -ZrPMeP (curve a), γ -ZrPPrP (curve b), and γ -ZrPCHP (curve c) with 0.1 M NaOH in the presence of 0.1 M added NaCl. Experimental conditions: solid/liquid ratio = 1 g/250 mL.

Table IV. Compositions and Interlayer Distances of Na-Exchanged and Amine Intercalated Forms of γ -Derivatives, Where the Hydrated Compounds Were Obtained at 90% Relative Humidity

compound	d , Å
Zr $\text{PO}_4\text{CH}_3\text{PO}_2\text{OH}_{0.5}\text{Na}_{0.5}\cdot 1.3\text{H}_2\text{O}$	11.7
Zr $\text{PO}_4\text{CH}_3\text{PO}_2\text{OH}_{0.5}\text{Na}_{0.5}$	10.1
Zr $\text{PO}_4\text{CH}_3\text{PO}_2\text{ONa}\cdot 2.2\text{H}_2\text{O}$	13.8
Zr $\text{PO}_4\text{CH}_3\text{PO}_2\text{ONa}$	10.7
Zr $\text{PO}_4\text{C}_3\text{H}_7\text{PO}_2\text{ONa}\cdot 2\text{H}_2\text{O}$	15.9
Zr $\text{PO}_4\text{C}_3\text{H}_7\text{PO}_2\text{ONa}$	15.4
Zr $\text{PO}_4(\text{HPO}_4)_{0.33}(\text{C}_6\text{H}_{11}\text{PO}_2\text{O})_{0.67}\text{H}_{0.5}\text{Na}_{0.5}\cdot 1.4\text{H}_2\text{O}$	17.2
Zr $\text{PO}_4(\text{HPO}_4)_{0.33}(\text{C}_6\text{H}_{11}\text{PO}_2\text{O})_{0.67}\text{Na}\cdot 2\text{H}_2\text{O}$	18.3
Zr $\text{PO}_4\text{CH}_3\text{PO}_2\text{OH}(\text{C}_6\text{H}_{13}\text{NH}_2)_{0.6}\cdot 2\text{H}_2\text{O}$	22.6
Zr $\text{PO}_4\text{C}_3\text{H}_7\text{PO}_2\text{OH}(\text{C}_6\text{H}_{13}\text{NH}_2)_{0.6}\cdot 1.3\text{H}_2\text{O}$	21.8
Zr $\text{PO}_4(\text{H}_2\text{PO}_4)_{0.33}(\text{C}_6\text{H}_{11}\text{PO}_2\text{OH})_{0.67}(\text{C}_7\text{H}_{15}\text{NH}_2)_{0.8}\cdot 0.6\text{H}_2\text{O}$	25.6
Zr $\text{PO}_4(\text{H}_2\text{PO}_4)_{0.33}(\text{C}_6\text{H}_{11}\text{PO}_2\text{OH})_{0.67}(\text{C}_{10}\text{H}_{21}\text{NH}_2)_{0.9}\cdot 0.7\text{H}_2\text{O}$	32.0

example, the length of the alkyl chain, a part from its direct relation to the interlayer distance of the γ -compound and some effect on the rate of the topotactic reaction, is not expected to have an appreciable influence on the extent of the replacement of H_2PO_4 so that many other organic derivatives of γ -ZrP containing alkyl chains of different lengths are expected to exist.

Preliminary Characterization of Ion Exchange and Intercalation Behavior. Due to the presence of acid P(OH) group in these compounds, some preliminary investigations of their ion-exchange and intercalation properties were carried out. The theoretical capacities are 3.15 mequiv/g for γ -ZrPMeP (dihydrate), 3.06 mequiv/g for γ -ZrPPrP (monohydrate), and 3.85 mequiv/g for γ -ZrPCHP (monohydrate).

Curves a-c of Figure 4 show the potentiometric titration curves of the compounds with NaOH solution. Note that the experimental uptakes at $\text{pH} \approx 8$ for γ -ZrPMeP, $\text{pH} \approx 10.6$ for γ -ZrPPrP and $\text{pH} \approx 11$ for γ -ZrPCHP correspond to the theoretical amounts. However, sodium exchange in γ -ZrPPrP is probably very slow, since the batch titrations (6 days of equilibration) with 1.5 and 3.0 mequiv/g of NaOH showed that the equilibrium pH values, 5.6 and 7.7, respectively, were much less than those represented by the titration curves.

The curves do not show well-defined plateaus, as have already been found for γ -Zr $\text{PO}_4\text{HPO}_2\text{OH}\cdot 2\text{H}_2\text{O}$. As previously discussed,¹⁷ this indicates that the γ -phases, due to the rigidity of their γ -layers, have less tendency than the α -phases to give

discontinuous phase transitions. XRD patterns of γ -ZrPMeP samples titrated at different loadings confirmed this behavior. It was found that, in the range 0–50% Na conversion, there is only a continuous and slight decrease of the interlayer distance from 12.8 to 12.6 Å, and then from 50 to 90% of conversion, there is a slight increase to 12.8 Å; finally, from 90 to 100%, there is an abrupt change from 12.8 to 13.4 Å. However, since the pH reached high values, entrance of water in the interlayer region, as a consequence of a hydrolytic attack of the γ -phase, cannot be excluded in this latter case. The same sample was therefore titrated to pH = 11 and again examined by XRD; a further large increase of the interlayer distance to 17.7 Å was found. The large increase of the interlayer distance in an alkaline medium seems to support the possibility of a hydrolytic attack. More detailed investigations, with careful control of hydrolytic phenomena, are therefore necessary. Similar trends were found for γ -ZrPPrP and γ -ZrPCHP.

The interlayer distances and water content of 50 and 100% Na-exchanged forms are reported in Table IV.

The preliminary intercalation behavior of the γ -derivatives obtained was only investigated with hexylamine (heptylamine for the cyclohexyl derivative). The intercalation processes seem to be very slow as seen in the case of the Na⁺ exchange process. Investigations of the mechanism of intercalations are in course.

The composition of some of the intercalate compounds obtained and their interlayer distances are reported in Table IV.

Conclusions

The results obtained in this work seem to confirm that topotactic reactions between γ -ZrPO₄H₂PO₄ and phosphonic acids can be employed to prepare an enormous variety of organic derivatives with γ -layered structure having a general formula ZrPO₄(H₂PO₄)_{1-x}(RPO₂OH)_x \cdot *n*H₂O, where R can be chosen from among a large variety of organic radicals.

It is likely to expect that similar compounds can also be obtained using γ -TiP. The value of *x* seems to be dependent on the size and nature of the R group. Alkyl chains, for their flexibility, may adapt their orientation in the interlayer region to give the minimum steric hindrance with adjacent groups; therefore, full replacement of H₂PO₄ groups is obtained. With large or long rigid groups, steric hindrance seems instead to prevent complete exchange; therefore, a certain percentage of the smaller H₂PO₄ groups originally present remains in the interlayer region.

Finally, we believe that even pillared derivatives can be prepared by topotactic reactions between γ -ZrP and diphosphonic acids. Owing to the practical importance of molecularly engineered layered solids (MELS) in the field of molecular sieves and shape-selective catalysis, we are presently investigating such a possibility.

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