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Preparation and First Characterisation of a Pillared γ-Zirconium Phosphate Derivative Containing Dibenzo 18-Crown-6 Groups Covalently Bound to Inorganic Layers

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A pillared crown ether derivative of γ-zirconium phosphate containing 4,4′-bis(dihydroxyphosphoryl)dibenzo-18-crown-6 groups covalently bound to inorganic layers has been prepared by a topotactic reaction in 1:1 water-acetone mixture at 80°C. It was found that the original γ-zirconium phosphate was already completely converted into a pillared phase (interlayer distance 1.9 nm) when ~15% of the interlayer dihydrogen phosphate groups were replaced with 4,4′-bis(dihydroxyphosphoryl)dibenzo-18-crown-6. The interlayer distance of this phase was found to increase progressively up to 2.1 nm with the gradual increase of the replacement to 50%. For higher replacement, a discontinuous transition of this latter phase to a new one (interlayer distance 2.6 nm) was finally observed. Some preliminary computer structural models of the crown ether conformations in the interlayer regions of these pillared phases were derived.

Keywords: γ-zirconium phosphate, γ-zirconium phosphate phosphonates, 4,4′-bis(dihydroxyphosphoryl)dibenzo-18-crown-6

INTRODUCTION

Over the last two decades, a new large class of α and γ layered inorgano-organic materials with a general formula α-$Zr(O_3PR)_x(O_3PR')_{2-x}$ and γ-$ZrPO_4(O_2PRR')$, (where R, R′ can be monovalent inorganic or organic radicals, e.g., H, —OH, —CH_3, —C_6H_5 etc.), has been developed [1–3].

This class of compounds can be considered one of the rare examples where an inorganic layered matrix covalently binds organic groups that, depending on their functionality, can improve or modify inorganic framework properties.

While α-zirconium phosphonate compounds have only been prepared by direct synthesis [1, 4], γ-zirconium phosphate phosphonates have usually been obtained simply by a topotactic

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replacement [5, 6] of the monovalent dihydrogen phosphates with monovalent phosphonate groups in the parent inorganic solid γ-Zr PO_4O_2-$P(OH)_2{\cdot}2H_2O$, according to the process:

$$\begin{aligned}&\gamma\text{-}ZrPO_4\,O_2P(OH)_2 + HO_2PRR'\\&\rightleftharpoons \gamma\text{-}ZrPO_4[O_2PRR'] + H_3PO_4\end{aligned} \quad (1)$$

The fully converted γ-zirconium phosphate-phosphonate compound can be obtained or not, depending on the amount of phosphonic acid available in solution and on the steric hindrance of the phosphonate groups [6b].

The topotactic reaction (1) already allowed the preparation of several γ-derivatives, often exhibiting interesting architectures of the organic groups in the interlayer region [1, 7, 8].

A transformation of γ-$ZrPO_4O_2P(OH)_2 \cdot 2H_2O$ from bidimensional inorganic into tridimensional inorgano-organic solids was also recently performed using a divalent diphosphonic acid for joining adjacent γ-layers [8–10]. These compounds, also called pillared compounds, can exhibit microporosity in the interlayer region depending on the length and the rigidity of the organic group and on the degree of the conversion which, in turn, determines the lateral relative distance of diphosphonate groups acting as pillars [11].

Recently, even a γ-derivative containing benzo 15-crown-5 groups covalently bound as monophosphonate to the inorganic lamellae of γ-zirconium phosphate was obtained in our laboratory [1, 7, 8]. After this success, which is an example of etherogenization of a crown ether in a well ordered inorganic framework, it was thought of interest to examine the possibility of preparing pillared compounds in which a crown ether, namely 4,4′-bis(dihydroxyphosphoryl)dibenzo-18-crown-6, could act as a pillar to join adjacent γ-layers. Some preliminary data on these compounds have been already reported [1, 8].

In this paper, the syntheses and characterisation of the phases obtained at various degrees of topotactic replacement are reported and some preliminary models of the conformations of the crown in the interlayer region are given.

EXPERIMENTAL

Reagents and Materials

Except for zirconyl chloride octahydrate (E. Merck), all other reagents were C. Erba RPE. 4,4′(5′)-bis(diisopropoxyphosphoryl)dibenzo-18-crown-6 was prepared as previously described [12]. Trimethyl-bromosilane was synthesised from hexamethylsilixane and $AlBr_3$ and distilled before use. Acetonitrile was distilled under phosphorus pentoxide before use.

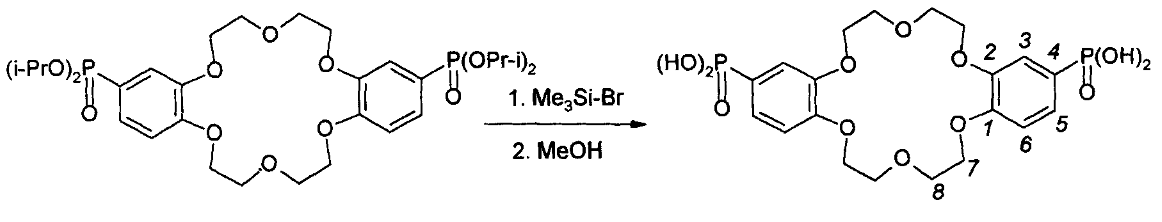
Layered γ-Zirconium Phosphate (γ-ZrP)

Microcrystals (particle size 0.5–2 μm) were prepared by thermal decomposition of zirconium fluorocomplexes according to the procedure described in a previous paper [13].

The compound was formulated as $ZrPO_4[O_2P(OH)_2]_{0.78}(F{\cdot}H_2O)_{0.22} \cdot 2.1H_2O$ and the formula weight of 307.6 was assigned [7]. The high content of fluoride anions in this compound is due to the high concentration of ammonium fluoride in the solution used for the synthesis. The topotactic exchange $O_2P(OH)_2^-/F^-$, as well as possible procedures that may be used to eliminate the F^- from γ-zirconium phosphate, will be reported and discussed elsewhere. Since the topotactic reaction does not seem to be appreciably influenced by the presence of F^- (see later), the batch of γ-ZrP obtained was directly used in this research without additional treatments for the elimination of F^-.

Fluoride-Free γ-Zirconium Phosphate

This compound was prepared by hydrothermal synthesis, as described in ref. [14].



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SCHEME 1

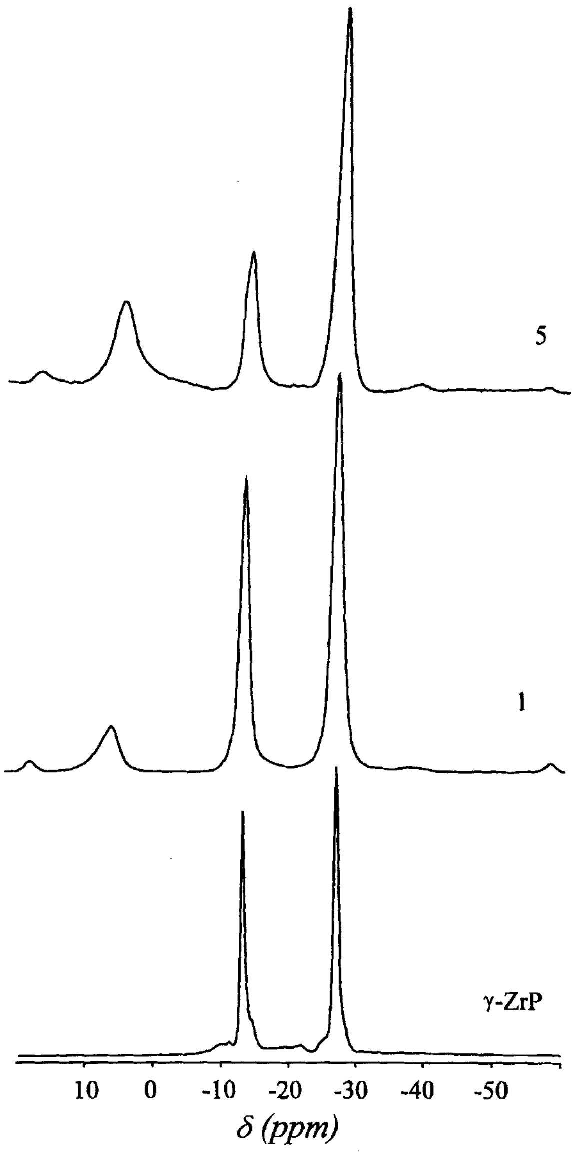

FIGURE 1 ^{31}P MAS NMR spectra of some γ-zirconium phosphate DBC derivatives. The samples are numbered as in Table I.

Synthesis of 4,4′-bis(dihydroxyphosphoryl) dibenzo-18-crown-6,1

Diphosphonic acid **1** was obtained from 4,4′(5′)-bis(diisopropoxyphosphoryl)dibenzo-18-crown-6 by reaction with trimethyl bromo silane and methanol according to the method reported in ref. [15].

Trimethyl bromo silane (334.5 g, 0.224 mol) was slowly added (about 30 min. in a nitrogen atmosphere) to a stirred solution of 4,4′(5′)-bis(diisopropoxyphosphoryl)dibenzo-18-crown-6 (30.85 g, 0.0448 mol) in CH_3CN (200 mL). The reaction mixture was then refluxed for 5 h. After cooling to room temperature, methanol (20 mL) was added, and the mixture kept overnight at room temperature, then refluxed for 5 h and finally evaporated to a volume of 50 mL. A solid was filtered off and washed with CH_3CN (300 mL); about 22.7 g of white crystals were finally collected. Melting point 230÷240°C; ^1H NMR (DMSO-d_6, δ): 3.78 c (8H, H^7), 4.02 m (4H, H^8), 6.95 dd (2H, H^6, $^3J_{HH}$ 7.8 Hz, $^4J_{PH}$ 3.6 Hz), 7.08 d (2H, H^3, $^3J_{PH}$ 13.8 Hz), 7.20 dd (2H, H^5, $^3J_{HH}$ 7.8 Hz, $^3J_{PH}$ 12.0 Hz), 7.25 broad s (6H, $OH+H_2O$). ^{31}P NMR (DMSO-d_6, δ) 18.9 ppm.

Elemental analysis: calculated for $C_{20}H_{28}O_{13}P_2$: C, 44.62; H, 5.24; P, 11.51. Found: C, 44.70; H, 5.31; P, 11.55.

The crystals are weakly soluble in water-acetone mixtures but soluble in polar organic solvents such as dimethylsulfoxide and CH_3CN.

Preparation of Pillared Crown-Ethers Derivatives

The preparation was carried out topotactically by putting, at 80°C under shaking, a weighed amount of γ-ZrP in contact with a known amount of the diphosphonic acid **1** dissolved in a mixture water acetone (1:1 in volume).

Samples with an increasing crown ether content were obtained, as summarised in Table I, by increasing the concentration of acid **1** in a fixed volume of solution (144 mL/g of γ-ZrP). Due to the low solubility of acid **1** in the 1:1 water acetone mixture, samples with crown ether content higher than 0.16 mol per mol of γ-ZrP, were obtained by increasing the volume of the saturated acid solution. The reaction times depend on the final conversion. As reported in Table I, the values can range from one day, for $x/2 \leq 0.1$, to two weeks, for $x/2 \geq 0.5$. After separation and washing with water-acetone (1:1 in volume), the samples were conditioned over a saturated NaCl solution (75% relative humidity).

Analytical and Instrumental Data

X-ray powder diffraction (XRD) patterns were recorded with a computerised Philips PW 1710 diffractometer using CuKα radiation. Diffraction patterns at 110°C were taken with a high temperature camera used in static conditions.

The weight loss curves were taken with a Stanton Redcroft Thermal Analyser STA 780

TABLE I Experimental conditions used for the preparation of the γ-ZrP dibenzocrowns of composition $ZrPO_4[O_2P(OH)_2]_{(1-x-y)}(DBC)_{x/2}(A\cdot H_2O)_y\cdot nH_2O$. The $x/2$ values were determined by ^{31}P NMR analysis using the y values reported in the column 6 (see the text)

Sample	Conc. of acid 1 (M)	Volume* (mL)	Initial m mol of 1 in solution*	m mol of 1 in the solid*	y	$x/2$	Reaction time (day)
1	$2.01\cdot10^{-3}$	144	0.29	0.23	0.24	0.075	1
2	$2.99\cdot10^{-3}$	144	0.43	0.43	0.24	0.13	5
3	$3.75\cdot10^{-3}$	144	0.54	0.53	0.24	0.16	7
4	$3.75\cdot10^{-3}$	238	0.89	0.67	0.24	0.21	7
5	$3.75\cdot10^{-3}$	272	1.02	0.79	0.24	0.24	7
5bis	$3.75\cdot10^{-3}$	272	1.02	0.72	0.04	0.23	7
6	$3.75\cdot10^{-3}$	504	1.89	0.98	0.24	0.30	15

*data referred to 1 g of γ-ZrP.

(2°C/min). An oxygen flux (30 mL/min.) was used to facilitate the oxidation of the dibenzo crown groups.

The relative percentages of the phosphonate and total phosphate (sum of $O_2P(OH)_2$ and PO_4) groups in the γ-ZrP derivatives were obtained by ^{31}P liquid-state NMR spectra taken with a Bruker AC200 instrument; 50 mg of the sample were first dissolved in about 0.1 mL of concentrated hydrofluoric acid in dimethylsulfoxide as solvent. The shifts of the signal of compound **1** and phosphoric acid are 18.9 and 3.2 ppm, respectively. The shifts are relative to 85% D_3PO_4 in D_2O, with a positive sign indicating a shift to lower field. An appropriate delaytime between two acquisitions was set in order to ensure quantitative measurements.

The ^{31}P MAS NMR spectra were recorded on a 400 MHz Varian Spectrometer; chemical shifts are reported in ppm using diluted H_3PO_4 as reference.

Zirconium was determined as described in ref. [16].

For the determination of the fluoride anions, 100 mg of sample were first refluxed for 3 hr with 10 mL of 1 M NaOH. After separation of the solid, the F^- content in the solution was obtained by ion chromatography, with a Dionex series 2000 i/sp instrument using an Ion PAC AS4A column and a buffer solution ($1.8 \cdot 10^{-3}$ M in Na_2CO_3 and $1.7 \cdot 10^{-3}$ M in $NaHCO_3$) as eluent.

RESULTS AND DISCUSSION

It was recently found in our laboratory that γ-ZrP undergoes a process of exfoliation when it is put in contact with water-acetone mixtures with an acetone content higher than 35% in volume and a temperature higher than 55°C [17]. The formation of a colloidal dispersion of γ lamellae greatly facilitates the topotactic replacement of $O_2P(OH)_2$ groups with phosphonate or diphosphonate groups. Consequently, the topotactic reaction with the diphosphonic anion of acid **1** (hereafter DBC) was carried out in this solvent according to the procedure described in the experimental section.

The process can be schematically written as:

$$\begin{aligned}&\gamma\text{-}ZrPO_4O_2P(OH)_2+(1/2)H_2DBC\\&\rightleftharpoons\gamma\text{-}ZrPO_4[O_2P(OH)_2]_{1-x}(DBC)_{x/2}+H_3PO_4\end{aligned}\qquad(2)$$

The details of the mechanism of the topotactic reaction between diphosphonic acids and colloidal dispersion of γ-ZrP are still under investigation in our laboratory. For this reason this mechanism is not discussed here, but it will be reported elsewhere. The experimental conditions used and the analytical results obtained for 6 samples containing an increasing amount of DBC pillars are summarised in Table I. Note that for $x/2 \leq 0.16$ (corresponding to a topotactic replacement of $O_2P(OH)_2$ groups $\leq 32\%$) almost all of the DBC groups present in the initial solution are taken up by γ-ZrP. This result, in agreement with previous findings for biphenyldiphosphonic acid [11], is a further indication that γ-ZrP exhibits a very high selectivity for diphosphonate groups.

The ^{31}P MAS NMR spectra of samples 1, 5 and that of γ-zirconium phosphate before the topotactic reaction, are shown in Figure 1. These spectra show three signals at 4.3 ppm, −13.5 ppm and −26.4 ppm, that can be assigned to DBC, $O_2P(OH)_2$ and PO_4 groups, respectively. Comparison with the parent γ-ZrP spectra shows that, while the relative intensity of the signal related to the PO_4 groups remains practically the same in all the reported spectra, the relative intensity of the $O_2P(OH)_2$ signal decreases with the increasing intensity of the DBC peak that, in turn, increases with the degree of replacement. This confirms that the original $O_2P(OH)_2$ groups are indeed replaced by DBC groups.

All the derivatives obtained at different degrees of topotactic replacement were formulated as $ZrPO_4[O_2P(OH)_2]_{1-x-y}(DBC)_{x/2}(A \cdot H_2O)_y \cdot nH_2O$, where A represents the sum of the monovalent anions F^- still present and

OH^- (introduced by hydrolysis during the topotactic reaction). On the basis of chemical analyses, the values of the coefficients y and $x/2$ were calculated and summarised in Table I. Note that y is practically constant (y=0.24) for all the examined samples. Furthermore, F^- analysis showed that about 80% of the latter value is due to this anion. This means that the fluorides present in the original γ-ZrP are scarcely involved in the topotactic reaction and that the hydrolysis of γ-ZrP, under the experimental conditions used in this research, is relatively modest ($\leq$5%).

The thermogravimetric curves of some samples in oxygen flux are shown in Figure 2. Their hydration water was found to be completely lost at temperature $\leq$110°C. Since the decomposition of the derivatives starts at a temperature higher than 200°C, the water content in the samples was evaluated by the weight losses at 150°C. Taking into account the x and y values reported in Table I, as well as the water molecules obtained by thermogravimetric analysis, the estimated compositions of some characteristic samples were derived and summarised in Table II. In the same table, the experimental weight losses at 1100°C

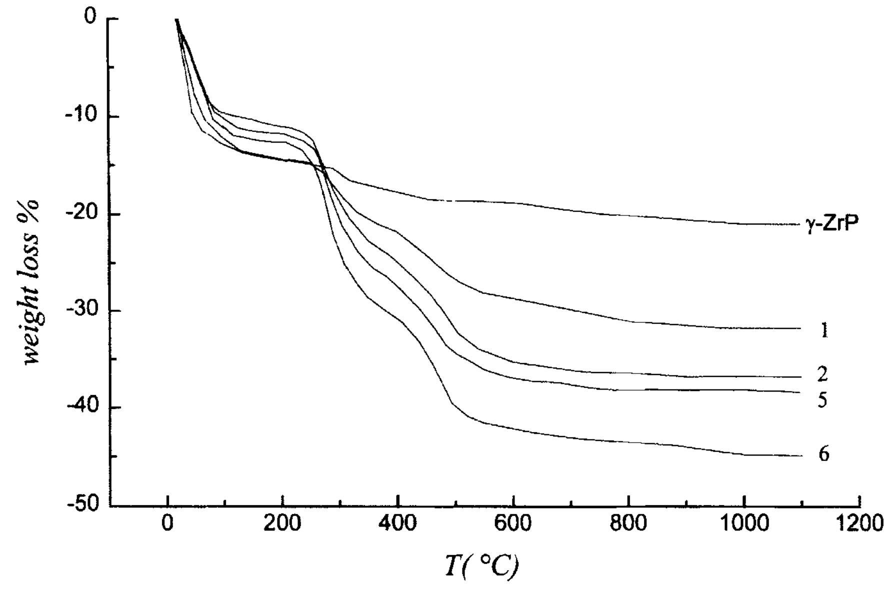

FIGURE 2 Thermogravimetric curves in oxygen flux (30 mL/min.) of the γ-zirconium phosphate DBC derivatives (rate 2°C/min.). The samples are numbered as in Table I.

TABLE II Experimental and calculated weight losses (W.L.) at 1100°C of some γ-ZrP dibenzocrowns previously conditioned at 75% of relative humidity. The compositions are obtained by using the x and y values reported in Table I and the n values calculated by the weight loss at 150°C

Sample	Composition	MW found	MW Calcul.	% W.L. Calcul.	% W.L. found
γ-ZrP	$ZrPO_4[O_2P(OH)_2]_{0.78}(F \cdot H_2)_{0.22} \cdot 2.1H_2O$		307.6	−19.0	−20.5
1	$ZrPO_4[O_2P(OH)_2]_{0.61}(DBC)_{0.075}(A \cdot H_2O)_{0.24} \cdot 3H_2O$	363.4	348.3	−28.5	−31.8
2	$ZrPO_4[O_2P(OH)_2]_{0.50}(DBC)_{0.13}(A \cdot H_2O)_{0.24} \cdot 2.7H_2O$	392.8	359.6	−31.0	−36.9
5	$ZrPO_4[O_2P(OH)_2]_{0.28}(DBC)_{0.24}(A \cdot H_2O)_{0.24} \cdot 2.2H_2O$	400.6	393.6	−37.0	−38.1
6	$ZrPO_4[O_2P(OH)_2]_{0.16}(DBC)_{0.30}(A \cdot H_2O)_{0.24} \cdot 2.9H_2O$	431.6	427.1	−41.9	−42.6

are compared with the values calculated from the reported compositions, assuming the following total decomposition:

$$\mathrm{ZrPO_4[O_2P(OH)_2]_{1-x-y}(DBC)_{x/2}(A{\cdot}H_2O)_y{\cdot}nH_2O} \rightarrow (2-y)/2\mathrm{ZrP_2O_7}+y/2\mathrm{ZrO_2}+\text{gaseous products}\uparrow.$$

Note that a good agreement is found, thus giving further supports to the compositions estimated.

To find out whether the presence of F^- in γ-ZrP influences the topotactic reaction, the sample 5 was prepared again (sample 5bis) using fluoride free γ-ZrP [15]. In this γ-ZrP the y parameter was estimated to be lower than 0.04 and only due to the presence of OH^- groups introduced by the hydrolytic replacement of $O_2P(OH)_2^-$. Since $x/2$ value of sample 5bis was found to be practically coincident with that of sample 5 (see Tab. I), the topotactic reaction seems not to be appreciably influenced, at least up to 50% of $O_2P(OH)_2$ replacement, by the presence of fluorides in γ-ZrP.

Additional information on the topotactic replacement was also obtained by determining the XRD patterns of the samples at room temperature (conditioned at 75% of relative humidity) and at 110°C. From the pattern at room temperature it was found that the crystalline degree of γ-ZrP is greatly decreased by the topotactic reaction; furthermore the interlayer distance of 1.22 nm of the original γ-ZrP was found to disappear completely after the insertion of a small amount of DBC groups and a new phase with interlayer distance of 1.9 nm was formed, with only 15% of $O_2P(OH)_2$ replacement (sample 1). The interlayer distance of this phase was found to progressively increase up to 2.1 nm by increasing replacement to 50%. For replacement higher than 50%, a discontinuous transition of this latter phase to a new one with interlayer distance of 2.6 nm was finally observed. The discontinuous change of the interlayer distance will be discussed in the next section.

The XRD patterns at 110°C of the samples with low DBC loading showed a drastic decrease of their interlayer distance. For example, the interlayer distance of sample 2 collapsed from 1.9 nm to 1.5 nm. However, only a negligible reduction was observed for samples with high DBC loading (e.g., sample 5). The variation of the interlayer distance at low DBC loading may be related to conformational changes and will be discussed in the next section.

Typical XRD patterns of some samples at room temperature are shown in Figure 3.

Structural Aspects

In previous papers, [6d, 11, 18] it was demonstrated that the **a** and **b** parameters of the γ-$\mathrm{ZrPO_4O_2P(OH)_2{\cdot}2H_2O}$ cell (0.5386 and 0.6636 nm respectively) remain essentially unaltered after the replacement of the interlayer $O_2P(OH)_2$ groups with $O_2P(OH)R$ groups of differing nature. As expected, only a variation in the interlayer distance, which depends on the length, size and conformation of the organic groups present in the interlayer region, was found.

If the composition of the phases and the molecular structure of the R group are known, computer models can be derived using the **a** and **b** cell parameters of the original γ-ZrP and the experimental interlayer distance of the obtained derivatives. These models can even be used to gain initial structural information on the conformations assumed by the R group in the interlayer regions. They are especially useful when, as in the present case, this information cannot be extracted from XRD patterns, due to the low crystallinity degree of compounds.

A computer structural model of the phase with an ideal composition $\mathrm{ZrPO_4[O_2P(OH)_2]_{0.50}[DBC]_{0.25}}$ was therefore derived using the *Hyperchem* program (Fig. 4). The model was built in two steps: the geometry of DBC moiety was optimised using MM + force field [19]. The DBC group was then used to replace H_2PO_4 groups in γ-ZrP layers. When the experimental interlayer distance was imposed, the DBC group

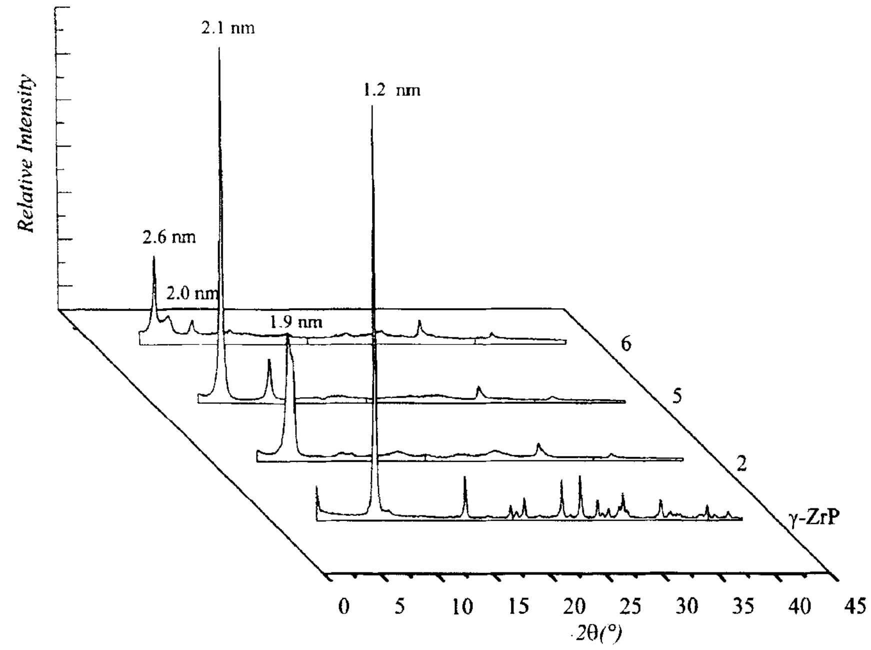

FIGURE 3 X-ray powder diffraction patterns of some γ-zirconium phosphate DBC derivatives and of the original γ-ZrP. The samples are numbered as in Table 1.

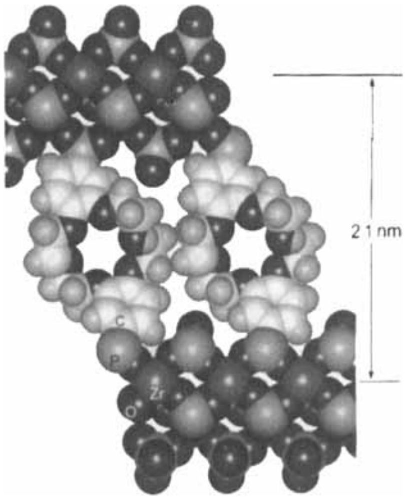

FIGURE 4 A computer structural model of the phase of ideal composition $ZrPO_4[O_2P(OH)_2]_{0.50}[DBC]_{0.25}$, to which the experimental interlayer distance of sample 5 has been attributed.

exhibited the right size to be bound to adjacent layers with a dihedral angle between the layer plane and DBC axis close to that found in γ-ZrP [20].

The decrease of the interlayer distance with dehydration, observed for sample 1, 2, 3, deserves some additional consideration. Indeed, since the intercalated water molecules are expected to be placed between DBC pillars, the above decrease could be explained either by a decrease in the angle formed by the DBC groups relative to the inorganic plane, or by a variation of the conformation of these groups as shown in Figure 5. A possible fold conformation can be found by computer models in agreement with the experimental interlayer distance. This means that crown ethers in anhydrous conditions can change their conformations filling the free interpillar spaces which are created by the loss of the intercalated water. In this context, we recall that a marked and reversible change of the interlayer distance was recently observed in derivatives containing a low percentage of non-rigid pillars, such as alkyl chains, during their dehydration and rehydration [1,8]. Thus, non-rigid pillars may assume different conformations depending on the free interpillar space available in the interlayer region. In the particular

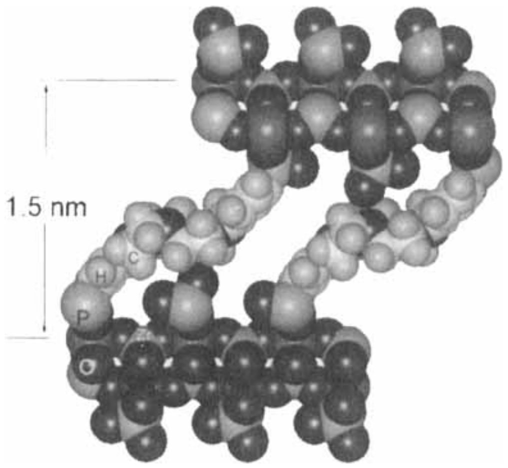

FIGURE 5 A computer structural model of the phase of ideal composition $ZrPO_4[O_2P(OH)_2]_{0.75}[DBC]_{0.125}$, to which the experimental interlayer distance of the dehydrated sample 2 has been attributed.

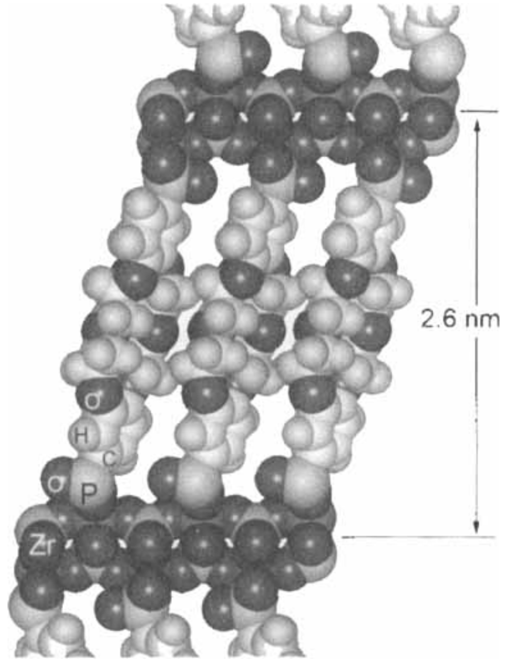

FIGURE 6 A computer structural model of the phase of ideal composition $ZrPO_4[DBC]_{0.5}$ to which an interlayer distance of 2.6 nm has been attributed.

case of partially converted DBC derivatives, H_3O^+ counter ions of the layers could be inserted in the crown ether. Accordingly, the dehydration of the H_3O^+ is also expected to facilitate the conformational changes of the crown. This possibility deserves further attention because it could be the first example in which the charge of the cations inserted in the crowns is balanced by the negative fixed charges of a polymeric inorganic layer.

A structural model for the phase with interlayer distance of 2.6 nm was also derived (Fig. 6). In this case, since the replacement is higher than 50%, structural models of the γ-layer show that some DBC pillars can no longer be separated from each other by the smaller $O_2P(OH)_2$ groups. Thus, replacement greater than 50% are only possible if the cross section of the pillar is smaller than the free area surrounding each $O_2P(OH)_2$ group on the surface of the layers (i.e., 0.357 nm^2) or if the pillars can assume a new more elongated conformation which reduces their steric lateral hindrance. The discontinuous phase transition may be explained by taking into account that the insertion of additional pillars in the previous phase at 50% of replacement is expected to start in the external part of the interlayer region of this latter phase and to go on towards its central part with the formation of an advancing phase boundary, similar to that found in ion exchange processes [21]. Therefore, the phase with interlayer distance of 2.6 nm should be finally obtained as a pure phase. However, due to the very low diffusion of the divalent pillars in the interlayer region, the process could require a very long time and the preparation of the pure phase was therefore not attempted.

In conclusion, we can say that the conformations of crown ethers heterogenized in γ-ZrP can be changed not only by varying the water content of the sample, but also by varying the degree of pillaring. Since the tendency of the crown ethers to give complexes with charged or neutral species of various nature also depends on their conformation, an appreciable modification in their selectivity has to be expected with these conformational changes. Encouraging preliminary results on the selectivity of crown ethers in γ-ZrP have been obtained in our laboratory and will be reported elsewhere. Also for this reason, we think that practical applications of the heterogenisation of the crown ethers in well-ordered interlayer structures can really be found.

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