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Preparation and first characterization of a layered γ-zirconium phosphate derivative containing benzo 15-crown-5 groups covalently attached to inorganic layers

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A layered derivative of γ-zirconium phosphate containing benzo-15-crown-5 groups covalently attached to inorganic layers has been prepared by replacement of the interlayer dihydrogen phosphate groups of the above layered compound, partially in F^- form, by a topotactic reaction in water-acetone solution at 80°C with 4-dihydroxyphosphorylbenzo-15-crown-5. According to the degree of the topotactic replacement, two different phases with interlayer distances 15.7 − 16.7 Å and 26.3 − 27.1 Å, and approximate percentages of replacement 5% − 22% and 45% − 69%, respectively, were obtained. A computer structural model of the phase with the ideal topotactic replacement of 50% was derived. Although it is too early to predict any practical uses of this derivative, the demonstration that crown ethers can be covalently attached to the inorganic layers of γ-zirconium phosphate opens new prospects in the heterogenization of crown ethers in the surface and interlayer regions of layered solids.

INTRODUCTION

Uncharged organic molecules exhibit a tendency to aggregate to one another, usually giving rise to organic crystals of a molecular type in which the structures are essentially determined by weak interactions amongst these molecules (hydrogen bonds, van der Waals forces). However, if organic groups are covalently bonded to a rigid structure of an inorganic type, the above natural tendency is partially or completely lost because the covalent bonds are considerably stronger than hydrogen bonds or van der Waals forces.

A case of particular interest is that in which the inorganic structure is an inorganic lamella of a layered crystal. When organic groups are covalently attached to this layer, the weak interactions of the organic groups belonging to adjacent lamellae of the inorgano-organic compound so formed are determined by the fixed positions of these groups in the two faces of the lamellae. In other words, the inorganic lamellae can be considered as planar "clothes-hooks" to which R organic groups, or mixtures of organic groups of different natures, can be covalently attached to fixed positions that are determined by the structure of the inorganic layer.[1] This fact may allow the realisation of quite singular organic structures and conformations in the interlayer region. It could also be of interest to use these particular interlayer regions of an organic type as hosts for the intercalation of other molecules since particular selectivity could be expected, and even well-ordered supramolecular structures in these interlayer regions could be obtained.

Layered inorganic structures particularly suitable to be used as "clothes-hooks" for organic groups are both α- and γ- zirconium phosphate.[2] This explains the increasing interest given to these compounds, first obtained by Alberti et al. in 1978.[3] A large number of organic radicals, as well as their mixtures, have already been attached to the inorganic lamellae of α- and γ-zirconium phosphate. In particular, it is now known that the

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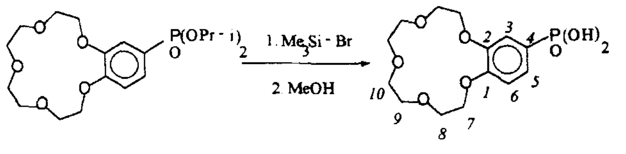
$O_2P(OH)_2^-$ groups of γ-zirconium phosphate, recently[1,4] formulated as zirconium phosphate dihydrogenphosphate dihydrate γ-$ZrPO_4$ $O_2P(OH)_2{\cdot}2H_2O$, can easily be replaced by $O_2PR'R$ groups even by simple topotactic reactions of these layered compounds with phosphonic acids[1,2,5] according to the process: γ-$ZrPO_4$ $O_2P(OH)_2{\cdot}2H_2O$ + $HO_2PR'R \rightleftharpoons$ γ-$ZrPO_4$ $O_2PR'R$ + H_3PO_4 (R, which can be different or equal to R', is H, OH, or some different kind of organic radical).

It was of interest to examine the possibility of preparing γ-zirconium phosphate derivatives containing crown ethers in the interlayer region. This fact could allow the heterogenisation of the crown ethers in the well-ordered interlayer structures which might even find practical applications.

EXPERIMENTAL

Reagents and Materials.

Except for zirconyl chloride octahydrate (E. Merck), all other reagents were C. Erba R.P.E. Diisopropoxyphosphoryl benzo-15-crown-5 was prepared as previously described.[6] Trimethyl bromosilane was synthesised from hexamethylsilixane and $AlBr_3$[7] and distilled before using. Acetonitrile was distilled under phosphorus pentoxide before using.



Synthesis of 4-Dihydroxyphosphoryl benzo-15-crown-5, 1: Phosphonic acid **1** was obtained from diisopropoxyphosphoryl benzo-15-crown-5 by reaction with trimethyl bromo silane and methanol according to the method reported in ref. 7

Trimethyl bromo silane (19 g, 0.124 mol) was slowly added (about 30 min in a nitrogen atmosphere) to a stirred solution of diisopropoxyphosphoryl benzo-15-crown-5 (21.46 g, 0.0496 mol) in CH_3CN (250 mL). The reaction mixture was then stirred for 5 h at 75°C. After cooling to room temperature, methanol (20 mL) was added, the solution was evaporated and the residuum crystallised from C_2H_5OH (60 mL). After filtration, the solid was first treated with boiling CH_3CN (300 mL) and then filtered off again in order to give 11.0 g of white crystals. Melting point 172 ÷ 175 °C; ^1H NMR (DMSO-d_6, δ): 3.55 c (8H, $H^{9,10}$), 3.71 m (4H, H^8), 4.00 m (4H, H^7), 6.95 dd (1H, H^6, $^3J_{HH}$ 7.0 Hz, $^4J_{PH}$ 4.0 Hz), 7.05 d (1H, H^3, $^3J_{PH}$ 15.3 Hz), 7.20 dd (1H, H^5, $^3J_{HH}$ 7.0 Hz, $^4J_{HH}$ 13.0 Hz), 8.51 broad s (2H, OH). ^{31}P NMR (DMSO-d_6, δ) 18.9 ppm, t $^2J_{PH}$ ^{13}Hz. Elemental analysis: calculated for $C_{14}H_{21}O_8P$: C, 48.28; H, 6.08; P, 8.89. Found: C, 48.18; H, 5.90; P, 8.68. The crystals are soluble in water (pK_1 2.22; pK_2 7.52), water-acetone-mixtures and in polar organic solvents such as dimethylsulfoxide and methanol.

Preparation of layered γ-zirconium phosphate in hydrogen form: the compound was prepared by direct precipitation in the presence of ammonium fluoride according to the method described in a previous paper.[8] The microcrystalline compound was obtained in the monoammonium form and therefore converted into the hydrogen form by eluting the ammonium ions with hydrochloric acid as described in ref. 8. From the elemental analysis of zirconium, total phosphate groups and fluorides, as well as by solid state ^{31}P M.A.S. NMR (Fig.1), X-ray powder diffraction patterns, thermogravimetric analysis, and ion-exchange of acid protons with Na^+ ions, 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 307.2 was assigned. The high content of fluoride anions in the compound obtained 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 the eventual procedures to be used to reduce or to eliminate the F^- from γ-zirconium phosphate will be reported and discussed elsewhere.[9] It must be pointed out that, for the purposes of the present investigation, it was decided to use the batch of γ-zirconium phosphate as directly obtained in the synthesis; in fact, possible steric effects between the large anion groups of the acid **1** and monovalent anions present in adjacent sites of a same lamella could be decreased if some $O_2P(OH)_2^-$ groups were previously replaced by the smaller fluoride anions.

Analytical and Instrumental Data:

X-ray powder patterns were recorded with a computerised Philips PW 1710 Diffractometer using CuK_α 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 (2°C/min). An oxygen flux (30 mL/min.) was used to facilitate the oxidation of the benzo crown groups.

^{31}P liquid-state NMR spectra were taken with a Bruker AC200 instrument. The relative percentages of the phosphonate and total phosphate (sum of PO_4 and $O_2P(OH)_2$) groups in the γ-zirconium phosphate derivatives were thus obtained: 50 mg of the sample were first dissolved in about 0.1 mL of concentrated hydrofluoric acid and dimethylsulfoxide as solvent. The shifts of the signal of compound 1 and phosphoric acid are 18.9 and 3.2 ppm,

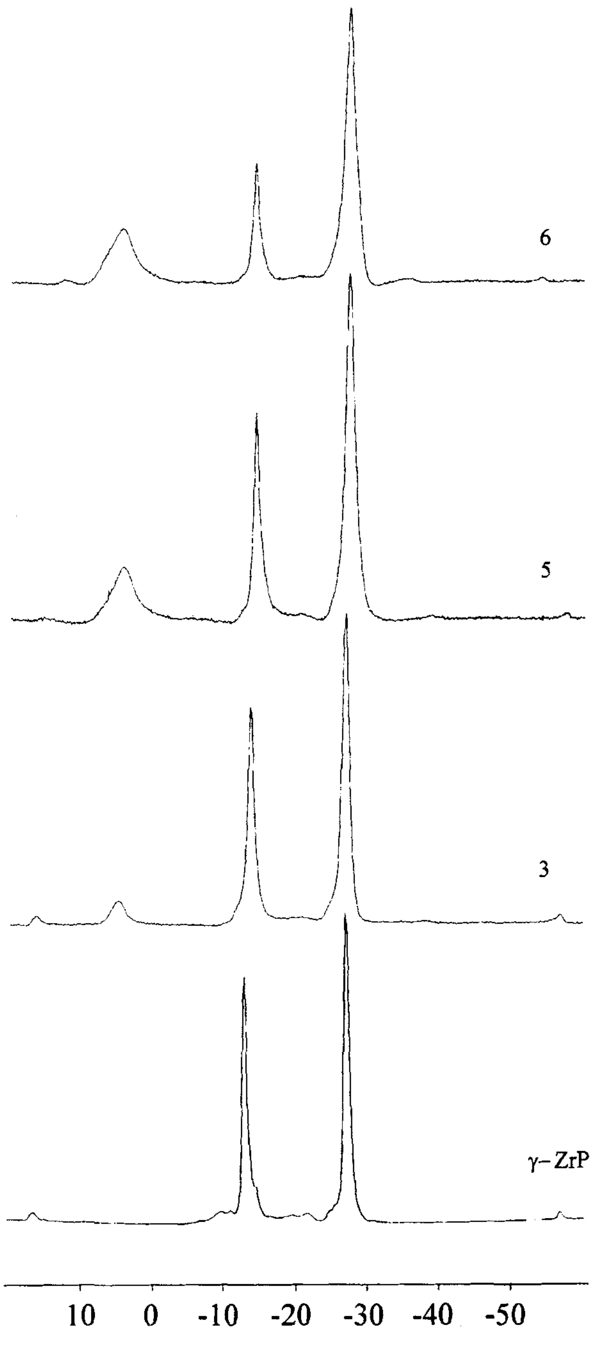


Figure 1. ^{31}P M.A.S. NMR spectra of some γ-zirconium phosphate BC derivatives. The samples are numbered as in Table 1.

respectively. The shifts are relative to 85% D_3PO_4 in D_2O, with a positive sign indicating a shift to lower field.

The ^{31}P MAS. NMR spectra were recorded on a 400 MHz Varian Spectrometer; chemical shifts are reported in ppm with respect to diluted H_3PO_4. Zirconium was determined as described in ref. 10. For the determination of the fluoride anions, 100 mg of sample were refluxed for 3 hr with 10 mL of 1 M NaOH: after filtration, 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.

The cation exchange capacity (CEC) of the γ-zirconium phosphate was determined by titrating (Mettler DK Autotitrator) its acid POH groups with NaOH in the presence of 0.1M NaCl (500 mg of γ-zirconium phosphate in 100 mL). Since 50% of the acid protons are titrated at pH values higher than 6.1, where hydrolytic processes also take place, the total amount of acid protons was calculated by multiplying by 2 the CEC found at the above pH value (inflection point of the titration curve). For the batch used in this investigation, the total experimental CEC was 5.13 m mol/g.

RESULTS AND DISCUSSION

On the basis of the successes obtained in the preparation of organic derivatives of γ-zirconium phosphate by simple topotactic reactions of these layered compounds with phosphonic and phosphinic acids,[1,2,11-14] the preparation of the derivative containing crown ethers in the interlayer region was attempted in a similar manner using phosphonic acid **1**. Hereafter, the monovalent anion of acid **1** will be simply indicated as the $O_2P(OH)BC^-$ group, where BC is $C_{14}H_{19}O_5$. The reaction was performed in water-acetone (1:1 in volume) solution at 75°C for at least a week.

In order to obtain samples with various content of $O_2P(OH)BC^-$ groups, different concentrations of acid **1** and different volumes of solutions were used for the topotactic reaction. To avoid the eventual formation of α-zirconium phosphonate phases,[14] solutions of phosphonic acid **1** more concentrated than 0.1 M were not used. To reach the highest degree of replacement, it was preferred to repeat the topotactic reaction several times with new solutions of acid **1**.

The experimental conditions used for 6 different samples with an increasing crown ether content are summarised in Table 1. After washing with water-acetone (1:1 in volume) the samples were conditioned over a saturated NaCl solution (75% relative humidity). The ^{31}P MAS. NMR spectra of samples 4, 6 and 7, as well as that of γ-zirconium phosphate before the topotactic reaction, were determined in advance (Fig. 1). The comparison of these spectra clearly shows that the original $O_2P(OH)_2^-$ groups, as expected, can be gradually replaced by $O_2P(OH)BC^-$ groups.

On the basis of this encouraging result, the compositions of all the derivatives obtained at different degrees of topotactic replacement were formulated as $ZrPO_4[O_2P(OH)_2]_{1-x-y}(O_2P(OH)BC)_x(A \cdot H_2O)_y \cdot nH_2O$, where A

TABLE 1. Experimental conditions used for the preparation of the γ-ZrP benzocrowns of composition $ZrPO_4[O_2P(OH)_2]_{(1-x-y)}(O_2P(OH)BC)_x(A{\cdot}H_2O)_y{\cdot}nH_2O$. The x 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
1	$4{\cdot}10^{-3}$	78.3	0.31	0.32	0.24	0.10
2	$4{\cdot}10^{-3}$	130.0	0.52	0.52	0.24	0.16
3	$2{\cdot}10^{-2}$	112.0	2.24	0.78	0.24	0.24
4	$1{\cdot}10^{-2}$	376.0	3.76	1.10	0.24	0.34
5	$5{\cdot}10^{-2}$	54.6 × 2**	2.73 × 2**	1.53	0.25	0.47
6	1.10^{-1}	26.0 × 4**	2.60 × 4**	2.01	0.26	0.62

*data referred to 1 g of γ-ZrP
**number of contacts

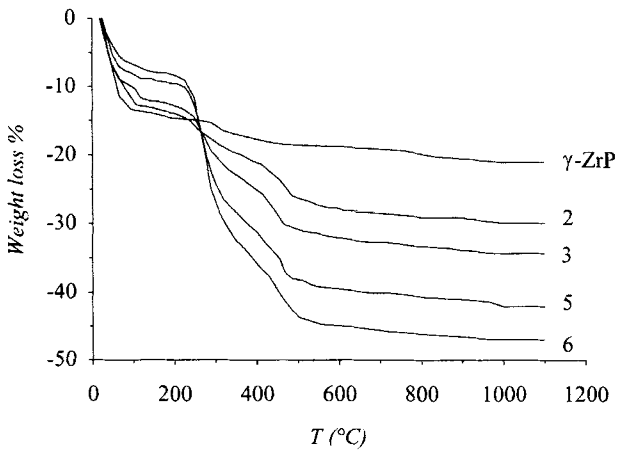


Figure 2. Thermogravimetric curves in oxygen flux (30 mL/min.) of the γ-zirconium phosphate BC derivatives (rate 2°C/min.). The samples are numbered as in Table 1.

represents the sum of the monovalent F^- anions still present and of the OH^- introduced by hydrolysis during the topotactic exchange. The y coefficient was found to vary in the range 0.23 − 0.27 (see later). A first estimation of the coefficient x was derived by ^{31}P liquid-state NMR analysis in the solution obtained by dissolving the sample in HF (see experimental part). From the relative fraction of the peak at 18.9 ppm (see experimental part) the molar fraction of the phosphorus atoms of the phosphonate groups (X_{Ph}), as compared with the total phosphorus atoms in the solid, was obtained and hence the x value calculated by the relation $X_{Ph} = x/[1+(1-x-y)+x] = x/(2-y)$. The x values obtained in this way are summarised in table 1, where the y values used for the various samples are also reported. Note that the $O_2P(OH)BC$ groups are taken up by γ-zirconium phosphate with high selectivity and that, in spite of their large size, the highest percentage of replacement (about 60%) is comparable to that previously obtained with $O_2P(OH)C_6H_5$ groups.[14]

The thermogravimetric curves of some samples in oxygen flux are shown in Fig. 2. The hydration water of the derivatives obtained was found to be completely lost at temperatures higher than 110°C. Since the decomposition of the derivatives starts at a temperature higher than 200°C, the coefficient n was evaluated by the weight losses at 150°C. Taking into account the x and y values reported in Table 1, as well as the n values obtained by thermogravimetric analysis, the estimated compositions of some characteristic samples are summarised in Table 2. In the same table, the experimental weight losses at 1100°C are compared with the values calculated from the reported compositions, assuming the following total decomposition $ZrPO_4\ [O_2P(OH)_2]_{1-x-y}\ (O_2P(OH)BC)_x(A{\cdot}H_2O)_y\ {\cdot}nH_2O \rightarrow (2-y)/2\ ZrP_2O_7 + y/2\ ZrO_2 +$ gaseous products ↑.

Note that a good agreement is found, thus lending further support to the compositions estimated.

Additional information on the gradual topotactic replacement was also obtained by determining the X-ray powder diffraction patterns of the samples at room temperature and 110°C. From the pattern at room temperature it was found that the degree of crystallinity of γ-zirconium phosphate is strongly decreased by the topotactic reaction; furthermore the interlayer distance of 12.2 Å of the original γ-ZrP disappears completely just because of very low insertion of the $O_2P(OH)BC^-$ groups and a new phase with interlayer distance of 15.7 Å is formed. The interlayer distance of this latter phase (hereafter called phase *a*) was found to progressively increase to 16.6 Å with increasing $O_2P(OH)BC^-$ group content. At degrees of exchange higher than a value corresponding to about x = 0.22, the 16.6 Å phase is then discontinuously converted into a new phase (hereafter called phase *b*) with an interlayer distance 26.3 − 27.1Å. This fact seems indicate than no more room for the solubilization of the $O_2P(OH)BC^-$ groups in the interlayer region of the phase *a* is available and, hence, these latter groups must assume a new disposition in order to permit further replacement of the original

TABLE 2. Experimental and calculated weight losses at 1100°C of some γ-ZrP benzocrowns previously conditioned at 75% r.h. The compositions are obtained by using the x and y values reported in Table 1 and the n values calculated by the weight loss at 150°C.

Sample	Composition	MW	% W.L calculated	% W.L found
γ-ZrP	$ZrPO_4[O_2P(OH)_2]_{0.78}(F{\cdot}H_2O)_{0.22}{\cdot}2.1H_2O$	307.8	−19.0	−20.5
2	$ZrPO_4[O_2P(OH)_2]_{0.60}(O_2P(OH)BC)_{0.16}(A{\cdot}H_2O)_{0.24}{\cdot}2.6H_2O$	355.7	−30.3	−29.9
3	$ZrPO_4[O_2P(OH)_2]_{0.52}(O_2P(OH)BC)_{0.24}(A{\cdot}H_2O)_{0.24}{\cdot}2.7H_2O$	377.5	−34.3	−34.3
5	$ZrPO_4[O_2P(OH)_2]_{0.28}(O_2P(OH)BC)_{0.47}(A{\cdot}H_2O)_{0.25}{\cdot}2.2H_2O$	425.5	−41.9	−42.0
6	$ZrPO_4[O_2P(OH)_2]_{0.12}(O_2P(OH)BC)_{0.62}(A{\cdot}H_2O)_{0.26}{\cdot}2.1H_2O$	460.6	−46.5	−46.9

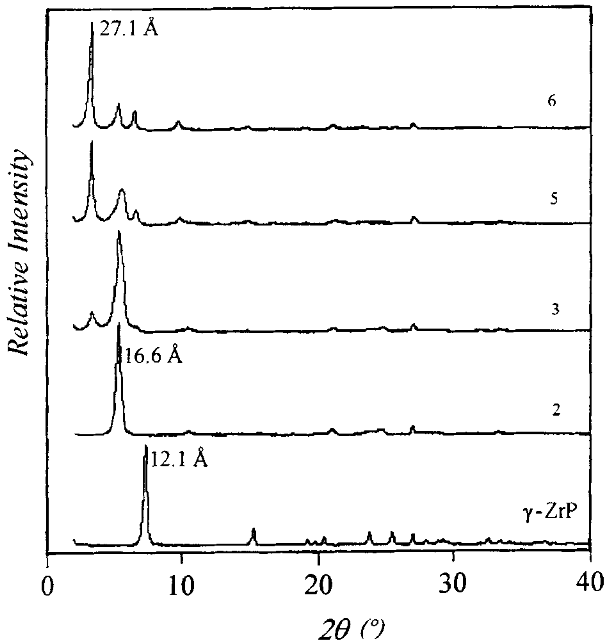


Figure 3. X-ray powder diffraction patterns of some γ-zirconium phosphate BC derivatives. The samples are numbered as in Table 1. The pattern of the original γ-ZrP is also shown for comparison.

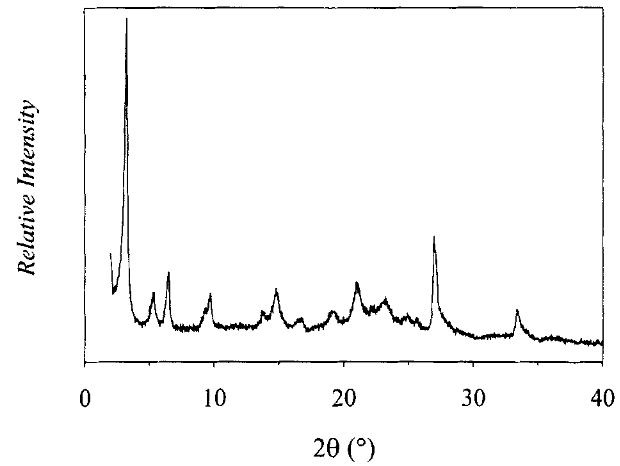


Figure 4. X-ray powder diffraction pattern of the γ-zirconium phosphate BC derivative obtained by repeating the topotactic reaction for eight times with new solutions (sample n. 7).

$O_2P(OH)_2^-$ groups. Typical X-ray powder patterns of some samples are shown in Fig. 3.

On the basis of these preliminary results, an attempt was made to prepare phase *b* in purer form by repeating the topotactic reaction eight times, each time with 32 mL of 0.1 M acid **1**. The X-ray powder diffraction pattern (fig. 4) showed that only a negligible percentage of phase *a* was still present after such a drastic procedure. However the crystallinity of the sample turned out to be very poor and an interlayer distance of 24.5Å, i.e. even slightly lower than in the previous samples (27.1Å), was found. In our opinion, a high hydrolytic replacement of $O_2P(OH)_2^-$ with smaller OH^- groups could be responsible for the decrease of the degree of crystallinity and of the interlayer distance.

An approximate evaluation of this hydrolytic replacement was therefore made by determining the phosphate groups released when γ-ZrP is contacted eight times under the same conditions used for the preparation of phase *b*, except that phosphonic acid **1** was replaced by an equivalent amount of hydrochloric acid, whose monovalent anion possesses a very slight tendency to be taken up by γ-ZrP. The total of the phosphate groups released in these contacts, corresponding to 8% of replacement, was found while no appreciable amount of fluoride anions was present in the solutions; furthermore, no appreciable amount of chloride ions was found in the solid. It was therefore concluded that only $O_2P(OH)_2^-$ groups are essentially involved in the hydrolytic reactions. The fluoride content in sample no. 7 was determined and an amount corresponding to 20% of the exchangeable sites was found.

On the basis of these analytical results, the following composition was assigned: $ZrPO_4\ [O_2P(OH)_2]_{0.03}\ (O_2P(OH)BC)_{0.69}(F{\cdot}H_2O)_{0.2}\ (OH{\cdot}H_2O)_{0.08}{\cdot}1.8\ H_2O$. This composition was also supported by thermogravimetric analysis (expected W. loss 47.9%; experimental W. loss 48%,). Note that all the $O_2P(OH)_2^-$ groups of the original γ-ZrP have in practice been replaced with $O_2P(OH)BC^-$, F^- and OH^- groups.

In order to have an additional insight into the phase *a* too, a larger amount of sample no. 2 (hereafter indicated as sample 2') was again prepared and also characterised for its F^- content and the approximate hydrolytic replacement of the $O_2P(OH)_2^-$ groups. A fluoride content as in the original γ-ZrP and a very moderate hydrolytic replacement of about 2% were found. On the basis of these analytical results obtained, this compound was more precisely formulated as $ZrPO_4\ [O_2P(OH)_2]_{0.60}\ (O_2P(OH)BC)_{0.16}(F{\cdot}H_2O)_{0.22}\ (OH{\cdot}H_2O)_{0.02}{\cdot}2.6H_2O$. X-ray powder diffraction patterns of sample 2 (corresponding to phase *a*) and of sample 7 (corresponding to a nearly pure phase *b*), previously conditioned at 75% r.h., are reported in Table 3, where the patterns at 110°C are also reported. Note that the lost of the hydration water in phase *a* causes a decrease in the interlayer distance from 16.64 to 13.10 Å, while, for phase *b*, there is a decrease from 27.09 to 24.57 Å.

Structural Aspects.

In previous papers,[12,13,15] it was demonstrated that the **a** and **b** parameters of the $\gamma\text{-}ZrPO_4\ O_2P(OH)_2{\cdot}2H_2O$ cell (5.386 and 6.636Å, respectively) remain essentially unaltered after the replacement of the interlayer $O_2P(OH)_2^-$ groups with $O_2P(OH)R^-$ groups of differing

TABLE 3. X-ray powder diffraction patterns, at room temperature and at 110°C, of the γ-ZrP benzocrown phases *a* and *b* (see text), previously conditioned at 75% r.h. Phase *a* (sample 2')

Room temperature d (Å)	Intensity	110°C d (Å)	Intensity
16.64	vs	13.10	vs
8.42	w	5.91	ms
4.86	vw	4.58	w
4.22	w	3.75	ms
3.61	w	3.28	ms
3.30	w	2.67	w
2.69	vw		

Phase *b* (sample 7)

Room temperature d (Å)	Intensity	110°C d (Å)	Intensity
27.09	vs	24.57	vs
13.63	s	12.74	ms
9.48	mw	8.58	w
9.08	mw	7.40	vw
6.45	w	3.27	vw
5.98	mw		
5.34	w		
4.65	w		
4.22	mw		
3.82	w		
3.57	vw		
3.47	vw		
3.30	s		
2.68	s		

nature. Only a variation in the interlayer distance, which depends on the length, size and conformation of the organic groups present can be expected. Thus, if the composition of the phases under investigation and the molecular structure of the R group present in the derivative are known, computer models can be derived using the **a** and **b** cell parameters of the original γ-ZrP. While more precise structural information is still not available from single crystal X-ray diffraction, these models can be used to check on whether the calculated interlayer distances correspond or not to the experimental interlayer distance of the obtained derivatives. Furthermore they can be useful for explaining possible steric hindrance between adjacent phosphonate groups and to gain initial information on the conformation assumed by the R group in the interlayer regions of the investigated phases.

A computer structural model of phase *b*, with an ideal composition $ZrPO_4\ [O_2P(OH)_2]_{0.50}[O_2P(OH)BC]_{0.5}$, was therefore derived (Fig. 5). Note that a good agreement between the expected and the experimental interlayer distance of phase *b* (27.9 and 27.09 Å, respectively) can be only obtained if a double layer of benzocrown groups in their extended conformation is assumed. On the other hand, phase *a* seems to be formed with only a monolayer of interpenetrated benzocrown groups (see Fig. 6).

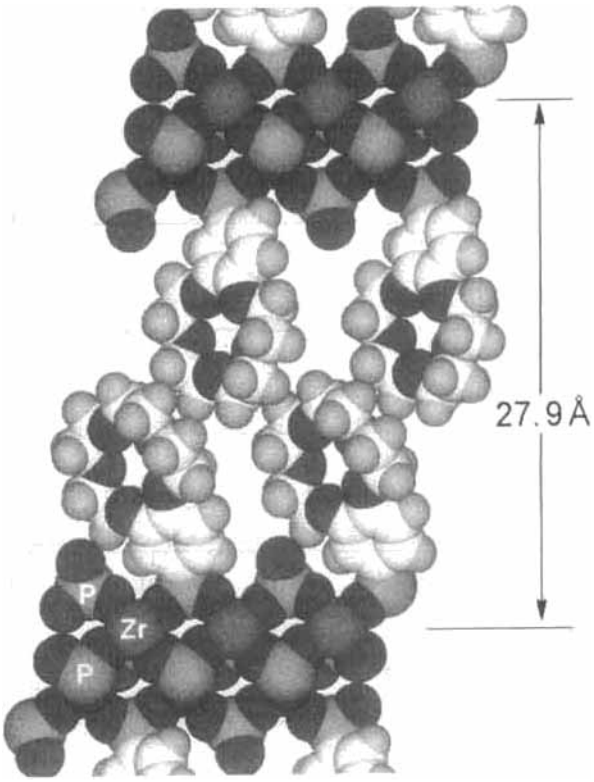


Figure 5. A computer structural model of phase *b* with an ideal composition $ZrPO_4\ [O_2P(OH)_2]_{0.5}\ [O_2P(OH)BC]_{0.5}$. Benzocrown groups are assumed to be in their extended conformation.

The interlayer decrease with dehydration deserves some additional consideration. In fact, since the hydration water is not expected to be interposed between the two layers of benzocrown groups, but rather placed between benzocrowns of the same layer, the above decrease could be explained either by a decrease in the angle formed by the benzocrown groups with respect to the inorganic plane, or by a variation of the conformation

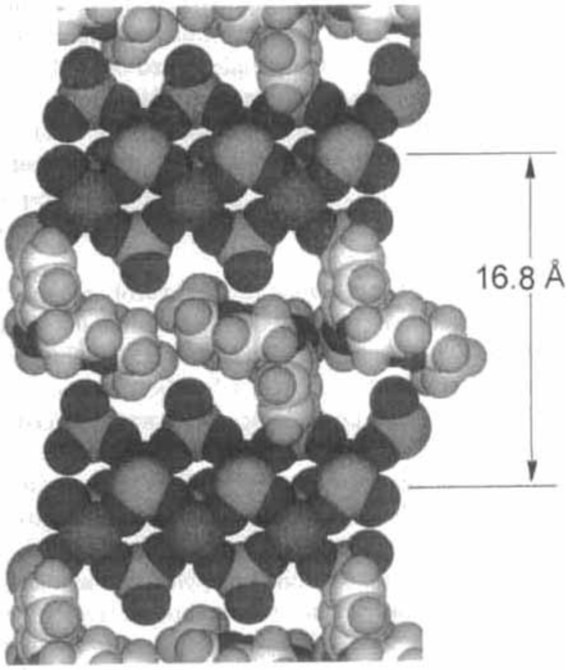


Figure 6. A computer structural model of phase *a* with an ideal composition $ZrPO_4\ [O_2P(OH)_2]_{0.78}\ [O_2P(OH)BC]_{0.22}$.

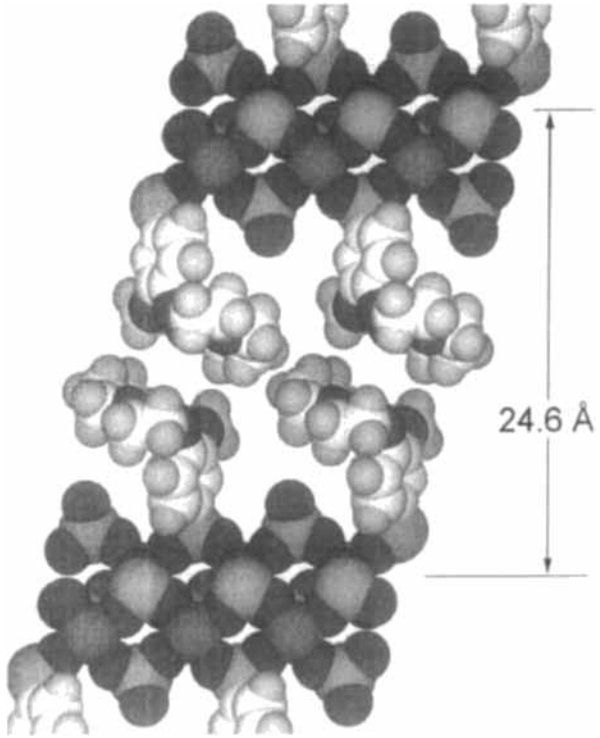


Figure 7. A computer structural model of phase *b* showing the conformational change of benzocrown group due to dehydration.

of these groups as shown in Fig. 7. Support for this eventuality is afforded by the good agreement of the experimental interlayer distance with that calculated. The eventual conformational change with dehydration deserves further attention because, if confirmed, it could be related to the presence —or not— of H_3O^+ counter ions within the crown. It can be pointed out that this might be the first example in which the charge of the cations inserted in the crowns are balanced by the negative fixed charges of a polymeric inorganic layer. Even practical implications could be expected since, in this case, the ion exchange selectivity could be considerably increased by the presence of the crown. In other words, a coupling between an ion-exchange process, occurring in a heterogeneous phase, and the selective solvation of cations in the crowns, presently used in solution, could be possible. Note that both phases *a* and *b*, because of the presence of acid -POH groups, can be considered cation exchangers with an appreciable ion-exchange capacities, the calculated values being 3.8 and 1.6 m-equiv/g, respectively. Although it is too early to predict some practical uses of the compounds obtained in the present work, the demonstration that these groups can be covalently attached to the inorganic layers of γ-zirconium phosphate opens new prospects in the heterogenization of crown ethers in the surface and in the interlayer regions of layered solids.

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