Covalent Bonding of Crown Ethers to γ-Zirconium Phosphate—New Layered Ion Exchangers Showing Selective Recognition

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Abstract: The topotactic exchange reactions of γ-zirconium phosphate and γ-zirconium phosphate/methylphosphonate with phosphonic acids derived from azacrown ethers of different sizes was examined. Prior intercalation of hexylamine was necessary in most cases to attain the maximum exchange level predicted by molecular modeling. Materials with imbricated or nonimbricated layers were obtained depending on crown size and exchange level. Exchange of methylphosphonates in γ-zirconium phosphate/methylphosphonate was only observed when hexylamine had previously been intercalated. The exchange with the bisphosphonic acid derived from 1,10-diaza[18]crown-6 gave a material with an interlayer distance compatible with pillaring of the γ-phase. The materials obtained from the exchange reactions of γ-zirconium phosphate with phosphonic acids derived from [12]crown-4 and [18]crown-6 showed thermodynamic selectivities towards Na^+ and K^+, respectively, that were much higher than those observed for the simple crowns in solution. This observation suggests that the inorganic molecular framework enhances molecular recognition by minimization of solvation effects.

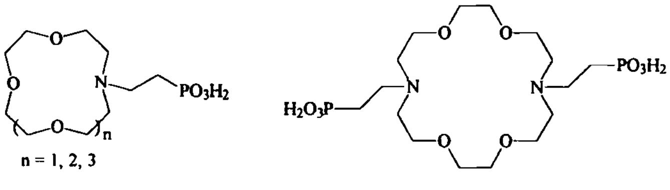
Keywords
crown ethers · layered materials · molecular recognition · zirconium phosphate

Introduction

Macrocyclic polyethers have attracted much attention in the past 30 years because of their large number of potential applications, based on their selective complexation properties with cations. However, the recognition ability of simple crown ethers in aqueous solution is severely diminished by solvation effects. Host–guest chemists have tried to avoid these problems by different approaches, but mainly by increasing the complexity of the host structure (cryptands, lariat ethers, cascade crown ethers, etc.); in most of the cases, their syntheses are difficult and time-consuming.[1]

An alternative approach, which isolates the host–guest recognition phenomena from the solvation environment, is to prepare organic polymers containing crown ethers or to attach the macrocycles to solid matrices.[2] The polymer field has recently been reviewed.[3] In this context, layered inorganic materials might constitute an interesting chemical assembly. γ-Zirconium phosphate has been the focus of a great deal of recent work, because it forms a rigid framework able to incorporate organic molecules by simple phosphate–phosphonate exchange reactions, thus forming highly ordered supramolecular assemblies, which have a great variety of practical applications.[4] Inclusion of macrocycles within the rigid layers of these water-insoluble polymeric compounds may lead to a class of new materials with potentially interesting properties regarding selective ion exchange, amine intercalation, and molecular recognition.

In a preliminary communication[5] we reported the exchange reaction of γ-zirconium phosphate with *N*-(phosphonoethyl)aza[18]crown-6, the first example of covalent inclusion of macrocycles into γ-zirconium phosphate. To our knowledge, only two papers have been published in this field since then,[6] and the recognition properties of the materials have not been reported. The present paper gives a full account of our present research on the exchange reaction of γ-zirconium phosphate and γ-zirconium phosphate/methylphosphonate with phosphonic acids containing crown ethers of different sizes (Scheme 1) and reports the first results concerning their selectivities towards Na^+ and K^+ in aqueous suspensions.



Scheme 1. Crown ether phosphonic acids used in exchange reactions with γ-zirconium phosphate (right: kriptofix).

Results and Discussion

Direct Exchange: Table 1 shows the maximum exchange obtained by refluxing a mixture of γ-zirconium phosphate and the corresponding azacrown *N*-2-ethylphosphonic acid in water/acetone (1:1) under various conditions. Reaction times (up to

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0947-6539/96/0212-1578 $ 15.00+.25/0

Table 1. Level of exchange reached in the direct exchange reaction of γ-zirconium phosphate with phosphonates derived from crown ethers.

Crown	% Exchange [a]	Molecular formula	*d* (Å) [b]
[18]crown-6 [c]	25	$ZrPO_4(H_2PO_4)_{0.75}(C_{14}H_{29}NO_8P)_{0.25}(H_2O)_{2.48}$	18.2
[15]crown-5 [c]	13	$ZrPO_4(H_2PO_4)_{0.87}(C_{12}H_{25}NO_7P)_{0.13}(H_2O)_{0.13}$	20.3
[12]crown-4 [c]	29	$ZrPO_4(H_2PO_4)_{0.71}(C_{10}H_{21}NO_6P)_{0.29}(H_2O)_{0.68}$	16.2
kriptofix [d]	0	–	–

[a] Relative to exchangeable phosphates. [b] Interlayer distances deduced by powder X-ray diffraction. [c] *N*-(phosphonoethyl)azacrown hydrochloride. [d] *N,N*-bis(phosphonoethyl)-1,10-diaza[18]crown-6 dihydrochloride.

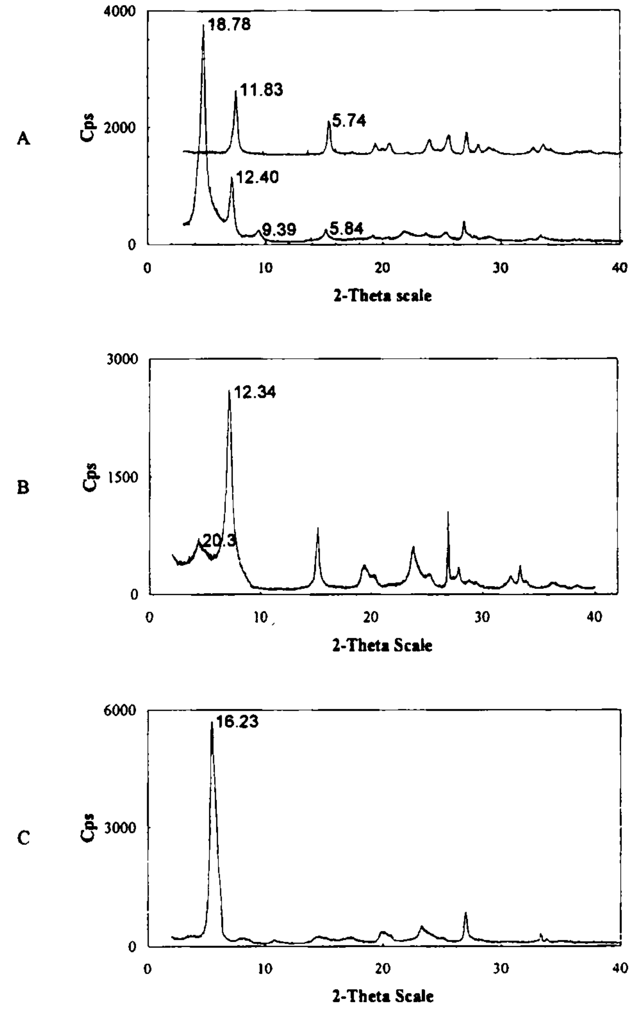
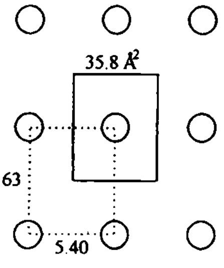


Fig. 1. Powder X-ray diffraction patterns of γ-zirconium phosphate directly exchanged with phosphonates derived from [18]crown-6 (A, lower trace; starting γ-phase in upper trace), [15]crown-5 (B) and [12]crown-4 (C)

three days) and reactants ratio (up to an excess of 8 equiv of phosphonic acid in the case of [15]crown-5; usual excess is 2.5 equiv) were varied. We also tried to force higher exchange levels, especially in the case of the [15]crown-5, by repeating the reaction on already exchanged γ-zirconium phosphates. Molecular formulas were obtained by elemental analyses of the solids. In the case of [18]crown-6 we attained a maximum exchange of 25% relative to the number of exchangeable phosphates or ca. 14% relative to the total number of phosphates. In this case we checked the reliability of the elemental analysis by ^{31}P NMR spectra of the solid dissolved in HF/H_2O (zirconium phosphate matrix is broken by the acid) and of the mother liquor from the exchange reaction. The spectrum of the solid in HF/H_2O showed that phosphonates had been incorporated, since two signals[7] were observed at $\delta \approx 22$ (organic phosphonic acid) and -0.4 (phosphoric acid) in an intensity ratio of 13:87; these figures are in very good agreement with the elemental analysis. The mother liquors displayed the same signals, but in 4.8:1 intensity ratio; this shows that phosphoric acid had been lost from the starting γ-phase in the exchange reaction. CPMAS ^{31}P NMR of the exchanged sample with the phosphonate derived from [18]crown-6 showed signals at $\delta = 9.4$ (phosphonate), -13.3 (unexchanged exchangeable phosphate), and -27.2 (nonexchangeable phosphate), similarly to other γ-zirconium phosphate/phosphonates previously described.[8]

Figures 1 A–C show the powder X-ray diffraction patterns of the material exchanged with [18]crown-6 (together with that of the starting γ-phase, upper trace in Fig. 1 A), [15]crown-5, and [12]crown-4, respectively. The relatively broad signals observed in all cases suggest that the exchanged phases are not ordered or very crystalline. Exchange with the [18]crown-6 and [15]crown-5 phosphonates was not complete, and signals of the hydrated starting γ-phase could be observed in their powder diffraction patterns (compare upper trace of Fig. 1 A with the lower trace and with Fig. 1 B).

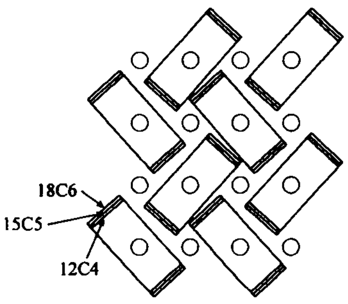
The interlayer distances of the exchanged phases (Table 1) do not follow the trend expected from the crown sizes; the material exchanged with [15]crown-5 has an exceptionally large distance (20.3 Å) compared to that exchanged with [18]crown-6 (18.2 Å).



Scheme 2. Maximum area available per organic residue when all the exchangeable phosphate groups are replaced.

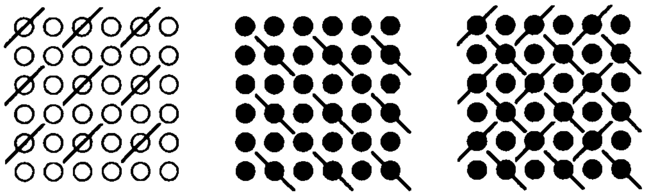
The structure of γ-zirconium phosphate has recently been established.[9] Adjacent exchangeable $H_2PO_4^-$ groups are separated by 5.4 and 6.63 Å along the *a* and *b* axes, respectively, of the unit cell. Therefore, the maximum area available per organic residue when all the exchangeable phosphates are replaced is less than 35.8 Å² (Scheme 2). The crown ethers [18]crown-6, [15]crown-5, and [12]crown-4 can be roughly considered as flat cylinders ca. 4.3 Å high with diameters of ca. 10.7, 9.7, and 8.7 Å, respectively. If the crowns can arrange perfectly perpendicular to the zirconium sheet, their surfaces projected onto the sheet would be 46.0, 41.7, and 37.4 Å², respectively. Hyperchem modeling[10] on the azacrown *N*-2-ethylphosphonic acids shows that, in the most stable conformations, the main plane of the crowns cannot be perpendicular to the zirconium phosphate plane, but at a maximum angle of ca. 68°, which makes their projected areas even larger.

These simple geometric considerations indicate that it should be impossible to replace all exchangeable phosphates of γ-zirconium phosphate by azacrown *N*-2-ethylphosphonic acids. A maximum of 50% of the exchangeable phosphates could be replaced, provided that the crowns arrange themselves perpendicular relative to one another as depicted in Scheme 3.



Scheme 3. Arrangement of crown ethers giving the maximum exchange of phosphates (50% of exchangeable phosphates).

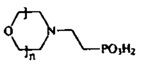
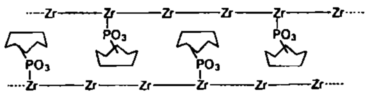
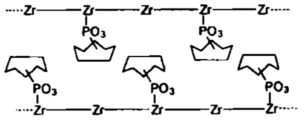
If the exchange is less than 25%, larger voids would be left in the zirconium phosphate surface, which could be occupied by crown ethers pointing downwards from the next layer; this would then give rise to layer imbrication. Scheme 4 shows the crowns (straight lines) bound to the phosphonic groups of the lower face in the upper layer (white circles). The crowns attached to the upper face of the lower layer (black circles) can then occupy the remaining available space without experiencing severe steric interference. Scheme 4, right, shows the top view of the superimposed imbricated upper and lower layers. This arrangement is therefore similar to that in Scheme 3, but the phosphonates are all bound to the same layer in the latter, and the layers are thus not able to penetrate one another.



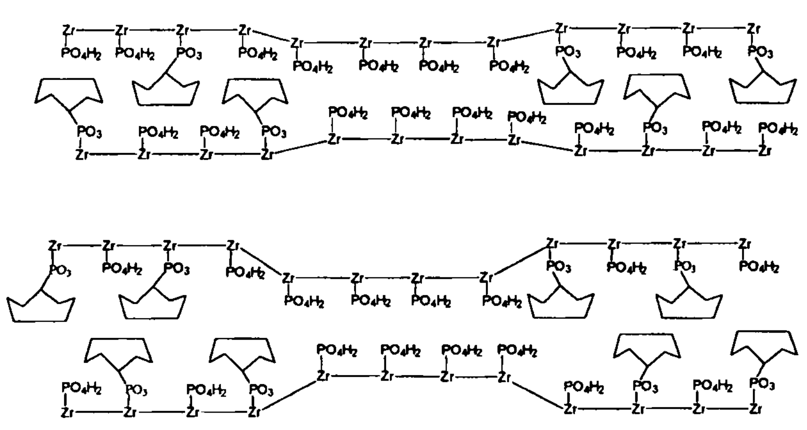
Scheme 4. Left: crowns (straight lines) bound to the phosphonic groups of the lower face in the upper layer (white circles). Center: crowns attached to the upper face of the lower layer (black circles). Right: superimposed imbricated upper and lower layers.

Table 2 shows the approximate interlayer distances predicted by Hyperchem modeling for the zirconium phosphates regularly exchanged with the crown ether phosphonates at low levels ($\leq 25\%$) and at the highest predicted level (50%), that is, for imbricated and nonimbricated layers, respectively. HyperChem modeling suggests that the materials containing [18]crown-6 ($d_{exp} = 18.2$ Å; Table 1) and [12]crown-4 ($d_{exp} = 16.2$ Å) have imbricated layers, whereas that containing [15]crown-5 does not (d_{exp} = 20.3 Å), even though exchange level for the latter was relatively low (13%). It is plausible that the exchange starts at the edge of the zirconium sheets, which eventually have to separate in order to accommodate the phosphonates (Scheme 5).

Table 2. Approximate interlayer distances (*d*) predicted by Hyperchem modeling (see text) for γ-zirconium phosphate exchanged with crown ether phosphonates.

	*n* = 3	*n* = 4	*n* = 5
d imbricated layers (Å) [a]	15	16	18
			
d nonimbricated layers (Å) [b]	18	20	25
			

[a] Exchange ≤25%. [b] 50% exchange.



Scheme 5. Separation at the edge of the zirconium sheets in order to accommodate the exchanged phosphonates. Top: imbricated layers; bottom: nonimbricated layers.

Interestingly, direct exchange with even-numbered crowns gives a pattern that can be compared to that obtained by placing chessmen on alternate squares of a chessboard; this leaves enough room for the upper layer to imbricate (Scheme 5 top). In contrast, in the exchange with the odd-numbered [15]crown-5 all the "chessboard squares" start filling up and this hampers layer imbrication (Scheme 5 bottom). An explanation based solely on crown size cannot account for this odd phenomenon.

Indirect exchange: Hyperchem modeling suggests that the direct exchange reaction of γ-zirconium phosphate with the phosphonates substituted with crown ethers is far from being complete. Assuming that the rate-determining step for the exchange process is increasing the interlayer distance,[11] we planned new exchange experiments in which γ-zirconium phosphate had previously been intercalated with amines. Intercalation with amines from methyl to hexylamine gave similar results to those previously described (Fig. 2).[12]

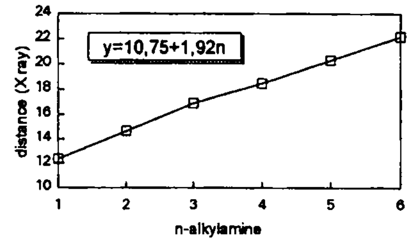


Fig. 2. Plot of interlayer distances against the number of carbons in the intercalated amines and equation for the correlation.

Table 3. Results of the exchange reaction of hexylamine-intercalated γ-zirconium phosphate with crown ether substituted phosphonates.

Crown	% Exchange [a]	Molecular formula	*d*(Å) [b]
[12]crown-4 [c]	47	$ZrPO_4(H_2PO_4)_{0.53}(C_{12}H_{25}NO_7P)_{0.47}(H_2O)_{0.68}$	18.65
[15]crown-5 [c]	45	$ZrPO_4(H_2PO_4)_{0.55}(C_{14}H_{29}NO_8P)_{0.45}(H_2O)_{1.07}$	20.40
[18]crown-6 [c]	28	$ZrPO_4(H_2PO_4)_{0.62}(C_{10}H_{21}NO_6P)_{0.28}(H_2O)_{0.47}$	18.64
kriptofix [d]	22	$ZrPO_4(H_2PO_4)_{0.56}(C_{16}H_{34}N_2O_{10}P_2)_{0.22}(H_2O)_{1.38}$	15.86

[a] Relative to exchangeable phosphate. [b] Interlayer distances deduced by powder X-ray diffraction. [c] *N*-(phosphonoethyl)azacrown hydrochloride. [d] *N*,*N*-bis(phosphonoethyl)-1,10-diaza[18]crown-6 dihydrochloride.

Table 3 shows the degree of exchange observed with γ-zirconium phosphate previously intercalated with hexylamine, and Figure 3 the corresponding powder X-ray diffraction patterns. The resulting materials were dissolved in 40% HF and diluted with water (1:1). Their ^1H NMR spectra displayed only traces of hexylamine, showing that the amine was effectively eliminated in the isolation procedure (see Experimental Procedure). Table 4 summarizes the data of these materials.

Comparison of direct and indirect exchange: Comparing data of direct and intercalation-mediated (indirect) exchange, the phosphonate in-

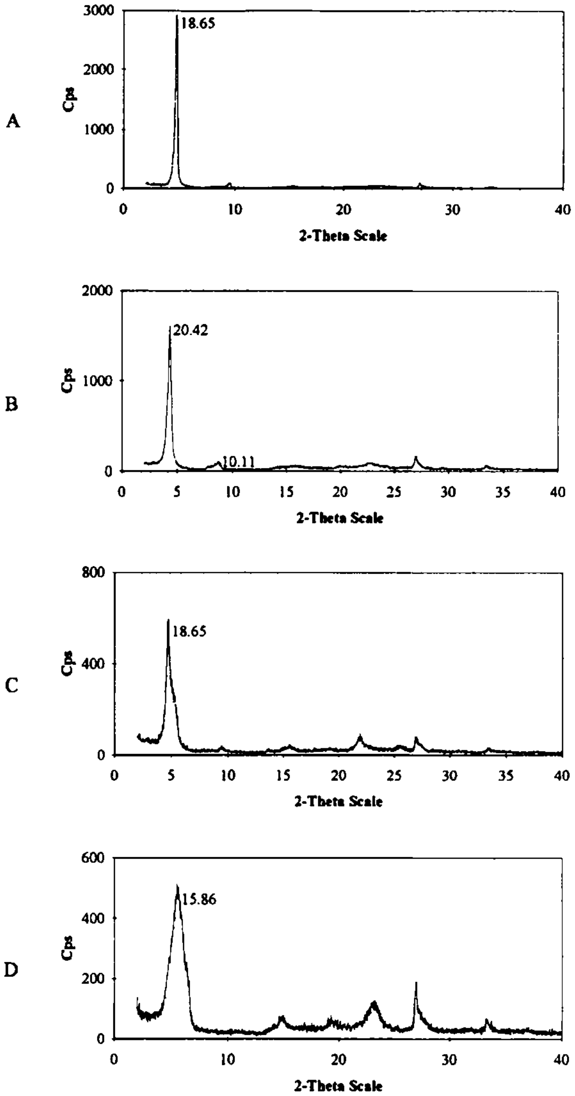


Fig. 3. Powder X-ray diffraction patterns of amine-intercalated γ-zirconium phosphate exchanged with phosphonates derived from [12]crown-4 (A), [15]crown-5 (B), [18]crown-6 (C), and kriptofix (D).

Table 4. CPMAS ^{31}P and ^{13}C NMR chemical shifts of the materials of Table 3.

Crown	$\delta(^{31}P)$	$\delta(^{13}C)$
[12]crown-4 [a]	7.5/−13.3/−27.2	22.2/54.1/64.1/70.1
[15]crown-5 [a]	12.8/−13.3/−27.2	21.8/54.4/65.0/70.8
[18]crown-6 [a]	11.1/−14.8/−28.1	24.9/50.5/64.8/70.3
kriptofix [b]	11.3/−14.2/−27.4	22.4/54.2/65.7/70.1

[a] *N*-(phosphonoethyl)-azacrown hydrochloride. [b] *N*,*N*-bis(phosphonoethyl)-1,10-diaza[18]crown-6 dihydrochloride.

corporation process seems to vary greatly depending on crown size. In the case of the phosphonate derived from [12]crown-4, the exchange appeared to occur in two ways. Direct exchange gave a material (29% exchanged), free from starting γ-phase as shown by its powder diffraction pattern (Fig. 1 C), whose interlayer distance (16.2 Å) suggests layer imbrication (cf. Table 2). Therefore, the phosphonate derived from [12]crown-4 gave direct exchange in such a way that sufficient empty space was left to accommodate the crowns hanging down from the lower face of the next layer. When hexylamine was first intercalated into the γ-zirconium phosphate, which increased the interlayer distance greatly (22.2 Å), a new material was obtained in which 45% of the exchangeable phosphonates were replaced by [12]crown-4-derived phosphonates. This figure is very close to the maximum predicted by our modeling, and the interlayer distance increased to 18.2 Å, a value compatible with nonimbricated layers (cf. Table 2). Intercalation of hexylamine thus made it possible for the [12]crown-4-derived phosphonates to occupy all the available space in the γ-phase, thus avoiding layer imbrication.

In the case of direct exchange with [15]crown-5 phosphonate, incorporation of the phosphonate did not exceed a rather low 13%. The powder diffraction pattern of the resulting material (Fig. 1 B) showed two peaks at low 2θ values, which could be assigned to the starting γ-phase (12.3 Å) and exchanged material (20.3 Å). Interestingly, the interlayer distance of the latter is compatible with nonimbricated layers. This behavior is therefore different to that observed with the phosphonate derived from the smaller [12]crown-4. However, now similarly to its [12]crown-4 counterpart, hexylamine intercalation mediated exchange gave an exchange ratio close to its possible maximum (45%), but the interlayer distance (20.4 Å) did not differ from that obtained by direct exchange. These facts suggest that, even though the degree of exchange was very low, direct exchange with [15]crown-5 phosphonate takes place in such a way that not enough room is left for imbrication.

The phosphonate derived from [18]crown-6 showed a direct exchange level (25%) similar to that of the corresponding [12]crown-4 phosphonate and much higher than that of the [15]crown-5 phosphonate. The interlayer distance (18.2 Å) suggests layer imbrication. Intercalation of hexylamine favored a slight increase of exchange (28%), but the interlayer distance was essentialy unaltered (18.6 Å), and layer imbrication was therefore mantained. Thus, in the case of the [18]crown-6 it seems that the γ-phase was not able to incorporate the number of phosphonate units predicted by our modeling.

Finally, intercalation of hexylamine was critical for the incorporation of kriptofix bisphosphonate into the γ-phase, since direct exchange was unsuccessful. The level of exchange (22%) was similar to that of [18]crown-6. In view of the fact that the two crowns are very much alike in size, this seems reasonable. The interlayer distance is the shortest measured, and Hyperchem modeling shows that separation is compatible with the bisphosphonate crown being bound to opposing faces of consecutive γ-phase layers.

Double exchange: One can replace all exchangeable phosphates of the γ-phase of zirconium phosphate by phosphonates provided the substituents in the latter are small organic groups, such as methyl, ethyl, or propyl.[13] However, the exchange of the resulting material with a second phosphonate has never been tried. The doubly exchanged material might have interesting properties since the overall polarity of the zirconium phosphate should be greatly altered. We therefore tried the exchange reaction of the crown ether phosphonates with a γ-phase entirely exchanged with methylphosphonate. Direct exchange was unsuccessful with all the crown ether phosphonates used in this work. Therefore, we found it necessary to first intercalate alkylamines to separate γ-phase layers. Intercalation of butyl- and hexylamines gave a lower incorporation ratio of amine (0.73 mol per mol of phosphonate) than for the nonexchanged γ-phase (1 mol per mol of exchangeable phosphate) and slightly smaller interlayer separations (18.08 and 21.72 Å, respectively), corresponding to an increase in interlayer distance of 1.82 Å per carbon of amine, a value also slightly lower than that observed with the nonexchanged γ-phase (Fig. 2). Hexylamine gave a reasonable layer separation, and the second exchange was thus performed after its intercalation. Table 5 summarizes the results, and Figure 4 shows the corresponding powder X-ray diffraction patterns.

Table 5. Results of the exchange reaction of hexylamine-intercalated γ-zirconium phosphate with crown ether derived phosphonates.

Crown	% Exchange [a]	Molecular formula	*d* (Å) [b]
[12]crown-4 [c]	16	$ZrPO_4(CH_3PO_3H)_{0.84}(C_{12}H_{25}NO_7P)_{0.16}(H_2O)_{0.95}$	15.83
[15]crown-5 [c]	26	$ZrPO_4(CH_3PO_3H)_{0.74}(C_{14}H_{29}NO_8P)_{0.26}(H_2O)_{1.00}$	20.17
[18]crown-6 [c]	25	$ZrPO_4(CH_3PO_3H)_{0.75}(C_{10}H_{21}NO_6P)_{0.25}(H_2O)_{0.36}$	18.67
kriptofix [d]	16	$ZrPO_4(CH_3PO_3H)_{0.84}(C_{16}H_{34}N_2O_{10}P_2)_{0.08}(H_2O)_{0.36}$	13.01

[a] Relative to exchangeable phosphate. [b] Interlayer distance deduced by powder X-ray diffraction. [c] *N*-(phosphonoethyl)azacrown hydrochloride. [d] *N,N*-bis(phosphonoethyl)-1,10-diaza[18]crown-6 dihydrochloride.

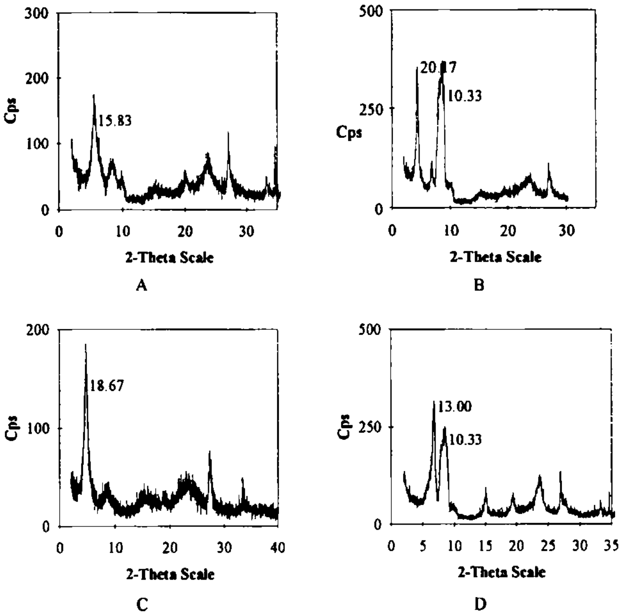


Fig. 4. Powder X-ray diffraction patterns of amine intercalated γ-zirconium phosphate/methylphosphonate exchanged with phosphonates derived from [12]crown-4 (A), [15]crown-5 (B), [18]crown-6 (C) and kriptofix (D).

As for the previous materials obtained by means of amine intercalation, the resulting solids were dissolved in a 1:1 mixture of 40% HF and water, and their solution ^1H NMR spectra were registered. Only traces of amine were detected; this shows that the isolation procedure again washed out the intercalated amine. The spectra showed the signals of both methylphosphonic acid (doublet at $\delta = 0.85$, $J_{H-P} = 18$ Hz) and the crown ether derived phosphonic acid (see Experimental Procedure). The ratios obtained by integrating the peaks at $\delta = 0.85$ and 1.80 (m, CH_2P of the crown ether derived phosphonic acid) were in excellent agreement with the exchange ratios measured from elemental analyses. Therefore, solution ^1H NMR spectra, elemental analyses (Table 4), and powder X-ray diffraction (Fig. 4) showed that the double exchange did take place with prior amine intercalation. The observed exchange ratios are lower that those obtained from the nonexchanged γ-zirconium phosphate, and in all cases the signal of the starting γ-zirconium phosphate/methylphosphonate was observed (peak at ca. $2\theta = 8°$ corresponding to 10.33 Å). This shows that the second exchange is far from being complete. Interlayer distances suggest that the materials containing [18]crown-6 and [12]crown-4 phosphonates have imbricated layers, whereas that of [15]crown-5 does not (compare with model values of Table 2). Again, this odd-numbered crown covers the maximum possible space in the exchange process.

Selectivity studies: To check the thermodynamic selectivity of these materials towards Na^+ and K^+ we devised a relatively simple competition experiment. The γ-phase was suspended in deionized water containing Na^+ and K^+ such that the ratio of crown to each alkali metal was ca. 1:2, and the suspension was stirred for 1 h and then centrifuged. Analysis by atomic emission of the supernatant water gave, by difference with the initial values, the amounts of alkali metals retained by the suspended γ-phase. A number of blank measurements and a strict analysis protocol were carried out in order to avoid errors caused by unexpected sources of alkaline metals. Details are given in the Experimental Procedure, and Tables 6 and 7 summarize the results. For reference purposes, Table 6 also contains the unexchanged γ-phase, and Table 7 the methylphosphonate-exchanged material. In these cases Na^+ and K^+ were added in ca. 2:1 molar ratio relative to exchangeable phosphate or methylphosphonate, respectively.

Table 6. Results of the selectivity experiments of the singly exchanged materials towards Na^+ and K^+ (see Experimental Procedure).

Entry	Crown ether exchanged [a]	Na^+ (mol) [b]	K^+ (mol) [b]
1	unexchanged	0.14 [c]	0.16 [c]
2	[12]crown-4 phosphonate (30%)	0.66	0.10
3	[15]crown-5 phosphonate (12%)	0.94	1.27
4	[18]crown-6 phosphonate (23%)	0.27	0.99
5	kriptofix phosphonate (32%)	0.42	0.86

[a] Percent exchanged relative to exchangeable phosphate in parentheses. [b] Per mol of crown ether unless otherwise indicated. [c] Per mol of exchangeable phosphate.

Table 7. Results of the selectivity experiments of the doubly exchanged materials towards Na^+ and K^+ (see Experimental Procedure).

Entry	Crown ether exchanged [a]	Na^+ (mol) [b]	K^+ (mol) [b]
1	methylphosphonate (100%)	0.06 [c]	0.02 [c]
2	methylphosphonate (84%)/ [12]crown-4 phosphonate (16%)	0.50	0.23
3	methylphosphonate (82%)/ [18]crown-6 phosphonate (18%)	0.84	0.68
4	methylphosphonate (84%)/ kriptofix phosphonate (16%)	0.72	0.22

[a] Percent exchanged relative to exchangeable phosphate in parentheses. [b] Per mol of crown ether unless otherwise indicated. [c] Per mol of methylphosphonate.

It can be seen in Table 6 that the unexchanged γ-phase (entry 1) retained similar amounts of Na^+ (0.14 mol) and K^+ (0.16 mol) and therefore did not show any intrinsic selectivity for these metals. The unexchanged material thus retains 0.3 mol of ions per mol of exchangeable phosphate. The crown ether phosphonate exchanged γ-phases (entries 2–5, Table 6) showed similar capacities (0.20–0.29 mol, values of Table 6 corrected for crown contents of each exchanged material) to that of the unexchanged γ-phase (0.3 mol) and displayed selectivity towards the studied metals: 1) [12]crown-4 phosphonate exchanged material (entry 2) retained almost seven times as much

Na^+ (0.66 mol) as K^+ (0.10 mol); 2) in the case of the [15]crown-5 phosphonate exchanged γ-phase (entry 3) the selectivity was reversed and slightly favored K^+ (1.27 mol) over Na^+ (0.94 mol); 3) the materials containing [18]crown-6 ethers (entries 4 and 5) exhibited clear K^+ selectivities by factors of 3.6 (0.99:0.27; entry 4) and 2.0 (0.42:0.86; entry 5). It is also noteworthy that in the cases of the [18]crown-6-containing materials (entry 4), the amount of retained K^+ almost coincided with the crown ether content per molecular formula of the material; this suggests that each crown in the γ-phase is coordinated to a K^+ ion.

Qualitatively speaking, the selectivities shown by the singly exchanged materials containing [12]crown-4 and [18]crown-6 ethers agree with those shown by the crowns in water solution,[14] a consequence of adequate matching between the size of the metal and that of the crown cavity. However, the thermodynamic selectivities are substantially higher. We believe that this can be attributed to the minimization of solvation effects owing to the protected environment of the crowns provided by the γ-phase. This superstructure could be responsible for the unexpected selectivity towards K^+ shown by the material containing [15]crown-5.

The case of the doubly exchanged materials (Table 7) is more puzzling. Methylphosphonate-exchanged γ-phase showed a much lower capacity for retaining the metals (0.08 mol; entry 1). This is reasonable because this phase should be much less polar that the unexchanged γ-phase. Its apparent selectivity towards Na^+ could be attributed to measurement errors due to the low levels of ions in the samples. The materials containing both methyl- and crown-derived phosphonates (entries 2–4, Table 7) showed higher capacities (0.12–0.27 mol), and all of them displayed moderate Na^+ selectivities, regardless of crown size. This behavior contrasts with that displayed by the materials of Table 6. The electronic density in the surface of the zirconium sheet evidently plays an important role in controlling the selectivity of the encapsulated crowns. Research is in progress in order to understand the effect of methylphosphonates upon selectivity and to determine the dynamic selectivities of these materials.

Conclusion

The present paper demonstrates that crown ethers can be covalently linked to the inorganic framework of γ-zirconium phosphate or γ-zirconium phosphate/methylphosphonate in various ways leading to a new class of materials. The recognition selectivities of the macrocycles are substantially altered/enhanced by the controlled microenvironment of the rigid framework. The results presented open new horizons in the chemistry and properties of γ-zirconium phosphate based materials. Work is in progress to include other interesting molecules (chiral, luminescent, etc.) in these inorganic frameworks and to use the properties and recognition capabilities of the resulting materials in different practical applications.

Experimental Procedure

General: ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively, on a Bruker AC-200 instrument (Organic Chemistry Department, UAM) using a 5 mm dual probe and TMS as internal standard. ^{31}P NMR solution spectra were recorded at 121 MHz in H_2O on a Bruker AMX-300 instrument (Servicio Interdepartamental de Investigación, SIdI, UAM) using a standard BB 10 mm probe and 10 mm tubes containing a 5 mm tube with a solution of Ph_3P in $CDCl_3$ used as internal lock and external reference ($\delta = -5.4$ relative to phsphoric acid). CPMAS ^{31}P and ^{13}C NMR spectra were recorded on a Bruker CPX-400 instrument (Ciencias del Medioambiente, CSIC, and Bruker, Karlsruhe) or on a Varian UNITY INOVA 500 (Varian, Palo Alto), and chemical shifts are given in ppm relative to external phosphoric acid or TMS. Powder X-ray diffraction analyses were performed in a Siemens D 5000 diffractometer (Servicio Interdepartamental de Investigación, SIdI, UAM) with Cu tubes and scintillation detector, sweeping a 2θ range of 5–70°, in 0.02° steps and with a time sweep of 30 min. Elemental analyses were performed in a Perkin-Elmer 2400 instrument (Servicio Interdepartamental de Investigación, SIdI, UAM). Atomic emission analyses were carried out in a Hitachi Z 8200 instrument (Analitical Chemistry Department, UAM).

General method for the preparation of phosphonic acids derived from azacrown ethers: The azacrown ether (4.56 mmol) was added to a solution of diethyl vinylphosphonate (1.12 g, 6.84 mmol) in a 1:1 mixture of ethanol/water (50 mL). The mixture was refluxed for 24 h and the solvent was removed in vacuo. The residue was heated at 70 °C under reduced pressure to eliminate the excess of diethyl vinylphosphonate, and the resulting oil was refluxed overnight in concentrated hydrochloric acid (30 mL). The solvent was then removed in vacuo, and the product was dried overnight under reduced pressure. ^1H and ^{13}C NMR spectra showed that the products could be used without further purification. Quantitative yields were obtained in all cases.

2-(1-Aza-4,7,10-trioxacyclododecane)ethylphosphonic acid. ^1H NMR (D_2O): $\delta =$ 3.65 (m, 2H, NCH_2CH_2P), 3.50 (m, 12H, CH_2O crown), 3.25 (m, 4H, CH_2NCH_2), 1.95 (m, $J_{P-CH} = 16$ Hz, 2H, NCH_2CH_2P); ^{13}C NMR (D_2O): $\delta = 68.9$, 68.7, 63.6 (CH_2O crown), 53.2 (CH_2N crown), 48.2 (CH_2N), 21.5 (d, $J_{C-P} = 135$ Hz, NCH_2CH_2P). Elemental analysis for $C_{10}H_{23}ClNO_6P \cdot H_2O$: C, 35.56; H 7.46; N, 4.15. Found: C, 35.56; H, 7.53; N, 3.70.

2-(1-Aza-4,7,10,13-tetraoxacyclopentadecane)ethylphosphonic acid: ^1H NMR (D_2O): $\delta = 3.60$ (m, 2H, NCH_2CH_2P), 3.45 (m, 16H, CH_2O crown), 3.20 (m, 4H, CH_2NCH_2), 1.90 (m, $J_{P-CH} = 16$ Hz, 2H, NCH_2CH_2P); ^{13}C NMR (D_2O): $\delta = 72.2$, 71.8, 71.3, 66.7 (CH_2O crown), 56.4 (CH_2NCH_2 crown), 52.1 (CH_2N), 24.3 (d, $J_{C-P} = 135$ Hz, NCH_2CH_2P). Elemental analysis for $C_{12}H_{27}ClNO_7P \cdot H_2O$: C, 37.78; H 7.67; N, 3.67. Found: C, 37.66; H, 7.42; N, 3.42.

2-(1-Aza-4,7,10,13,16-pentaoxacyclooctadecane)ethylphosphonic acid. ^1H NMR (D_2O): $\delta = 3.65$ (m, 2H, NCH_2CH_2P), 3.50 (m, 20H, CH_2O crown), 3.15 (m, 4H, CH_2NCH_2), 1.93 (m, $J_{P-CH} = 16$ Hz, 2H, NCH_2CH_2P). ^{13}C NMR (D_2O): $\delta = 72.6$, 72.5, 72.3, 72.2, 66.2 (CH_2O crown), 55.9 (CH_2NCH_2 crown), 47.6 (CH_2N), 23.2 (d, $J_{C-P} = 135$ Hz, NCH_2CH_2P). ^{31}P NMR (H_2O): $\delta = 19.0$. Elemental analysis for $C_{14}H_{31}ClNO_8P. H_2O$: C, 39.49; H 7.81; N, 3.29. Found: C, 38.77; H, 7.74; N, 3.33.

***N,N'*-1,10-Diaza-4,7,13,16-tetraoxacyclooctadecane-bis(2-ethylphosphonic) acid.** ^1H NMR (D_2O): $\delta = 3.60$ (m, 4H, NCH_2CH_2P), 3.50 (m, 16H, CH_2O crown), 3.15 (m, 8H, CH_2NCH_2), 1.85 (m, $J_{P-CH} = 16$ Hz, 4H, NCH_2CH_2P). ^{13}C NMR (D_2O): $\delta = 70.3$, 64.2 (CH_2O crown), 53.2 (CH_2NCH_2 crown), 47.4 (CH_2N), 22 (d, $J_{C-P} = 135$ Hz, NCH_2CH_2P). Elemental analysis for $C_{16}H_{38}ClN_2O_{10}P_2.H_2O$: C, 33.75; H 7.08; N, 4.92. Found: C, 33.85; H, 7.31; N, 4.89.

General procedure for the exchange reaction of γ-zirconium phosphate with crown ether derived phosphonic acids: γ-Zirconium phosphate (200 mg, 0.63 mmol) was added to a solution of the corresponding phosphonic acid (1.57 mmol) in a 1:1 mixture of water/acetone (50 mL). The resulting suspension was refluxed for 20 h, the solid was filtered off onto a filter disk, washed with deionized water (200 mL), and dried for several hours in the air current. The white solid was finally dried until constant weight under vacuum in a desiccator with phosphorous pentoxide. The solvent of the mother liquors was removed to recover the excess phosphonic acid, which could be used in subsequent exchange reactions.

General procedure for amine intercalation in γ-zirconium phosphate and γ-zirconium phosphate/methylphosphonate: γ-Zirconium phosphate or γ-zirconium phosphate/methylphosphonate (1.56 mmol) was added to a solution of *n*-hexylamine (6.25 mmol) in deionized water (50 mL). The resulting suspension was stirred at room temperature for 2 d. The solid was then filtered off and washed with deionized water (200 mL). The white solid was dried under vacuum in a desiccator with phosphorous pentoxide until a constant weight was achieved.

General procedure for the exchange of amine-intercalated γ-zirconium phosphate or γ-zirconium phosphate/methylphosphonate with crown ether derived phosphonic acids: The procedure was identical to that used with pure γ-zirconium phosphate or γ-zirconium phosphate/methylphosphonate. The only difference was that the filtered solid was treated with 10% hydrochloric acid (100 mL) to wash away the intercalated amine.

Analysis protocol for selectivity studies: For each individual data collected in Tables 6 and 7, five different samples were prepared in polypropylene vials and measured by atomic emission:

Sample 1: A suspension of the material under investigation (10 mg) in deionized water (2 mL) was treated with a solution of NaCl/KCl (1 mL) at a concentration such that the molar ratio of crown to each alkali metal was 1:2. The mixture was stirred for 1 h at room temperature and then centrifuged. An aliquot (0.5 mL) of the supernatant solution was diluted to 10 mL with deionized water, and the resulting solution analyzed.

Sample 2: A solution of the material (2.5 mg) in 40% HF (0.06 mL) was diluted to 12.5 mL with deionized water and analyzed. This sample allowed us to determine whether the material intrinsically contained Na^+ and K^+ from the start.

Sample 3: A solution of 40% HF (0.06 mL) was diluted with deionized water (12.5 mL), to determine Na^+ and K^+ content of the 40% HF used in sample 2.

Sample 4: A portion of NaCl/KCl solution (0.5 mL) was diluted to 10 mL with deionized water and analyzed to experimentally measure the Na^+ and K^+ concentration of the prepared solution. Sample 5: Deionized water was measured separately.

Results obtained from these samples were appropriately combined to calculate the data of Tables 6 and 7.

Acknowledgement: We thank Ministerio de Educación y Ciencia for financial support under grants PB93-0264 and PB95-0172. We are indebted to Dr. María Teresa Sevilla (Departamento de Química Analítica, UAM) for the atomic emission measurements and for useful input and discussions. We also thank Bruker Española and Varian España for kindly recording some CPMAS NMR spectra.

Received: May 26, 1996 [F372]

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