



Covalent Bonding of Aza-18-Crown-6 to γ -Zirconium Phosphate. A new Layered Ion-exchanger with Potential Recognition Capabilities

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Abstract: The preparation of γ -zirconium phosphate exchanged with *N*-(2-ethylphosphonic)-aza-18-crown-6 is reported as well as its ^{31}P NMR data, powder XRD pattern, molecular modeling and preliminary ion-exchange experiments.

Layered inorganic materials such as that formed by γ -zirconium phosphate constitute a rigid framework able to incorporate organic molecules, thus forming highly ordered supramolecular assemblies which can be used for a great variety of practical purposes.¹ 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 and amine intercalation.

We describe in this communication the incorporation for the first time of a crown ether to γ -zirconium phosphate. The starting γ -phase was prepared as previously reported² (Figure 1, trace A, shows its powder X-ray diffraction pattern) and exchanged with *N*-(2-ethylphosphonic)-aza-18-crown-6 hydrochloride.³ ^{31}P -NMR of the resulting solid in $\text{HF}/\text{H}_2\text{O}^4$ evidenced the incorporation of the phosphonate as the spectrum showed two signals at 22.1 (organic phosphonic acid) and -0.4 ppm (phosphoric acid) in 1:7 intensity ratio. The mother liquors of the exchange reaction displayed the same signals but in 4.8:1 intensity ratio showing the loss of phosphoric acid from the starting γ -phase that must take place in the exchange reaction. Elemental analysis of the solid gave C, 10.43%, H, 2.89% and N, 0.89% corresponding to a molecular formula of $\text{ZrPO}_4(\text{H}_2\text{PO}_4)_{1-n}(\text{C}_{14}\text{H}_{29}\text{NO}_8\text{P})_n(\text{H}_2\text{O})_x$ with $n = 0.23$ and $x = 1.36$, *i.e.* replacement of *c.a.* 12% phosphate groups (relative to total phosphorous) by phosphonates occurred, a value which is in excellent agreement with the signals intensity ratio (1:7 or 12.5:87.5) observed in its $\text{HF}/\text{H}_2\text{O}$ ^{31}P -NMR spectrum (see above). The presence of chloride in the sample (the starting crown ether phosphonate was in hydrochloride form) is uncertain from these data but it is presumably not present because the positive charge of the crown ammonium can be easily compensated by deprotonation of the OH group of its phosphonate.

^{31}P CPMAS NMR of the exchanged sample showed signals at 9.4 (phosphonate), -13.3 (unexchanged exchangeable phosphate) and -27.2 ppm (non-exchangeable phosphate) similarly to other γ -zirconium phosphate phosphonates previously described.² The powder X-ray diffraction pattern of the solid (Figure 1, trace B) clearly shows incorporation of crown-ether phosphonates in that the interlayer distance of exchanged

γ -zirconium phosphate increased to 18.8 Å. The relatively broad signals indicate that the material has a low degree of crystallinity and is not very well-ordered. However, the diffractions at $2\theta = 7.12^\circ$ (12.4 Å) and 15.16° (5.84 Å) suggests that the material may contain some unchanged γ -phase. Provided both the starting and the exchanged γ -phase give similar diffraction responses, integration of the signals at $2\theta = 4.70^\circ$ (18.8 Å) and 7.12° (12.4 Å) yields a 0.89:0.11 ratio of exchanged to starting γ -phase. Recalculation of the molecular formula on these grounds gives $n = 0.26$ and $x = 1.39$ which corresponds to a slightly higher replacement (*c.a.* 13%) of phosphate by phosphonates in the exchanged γ -layers than that previously considered.

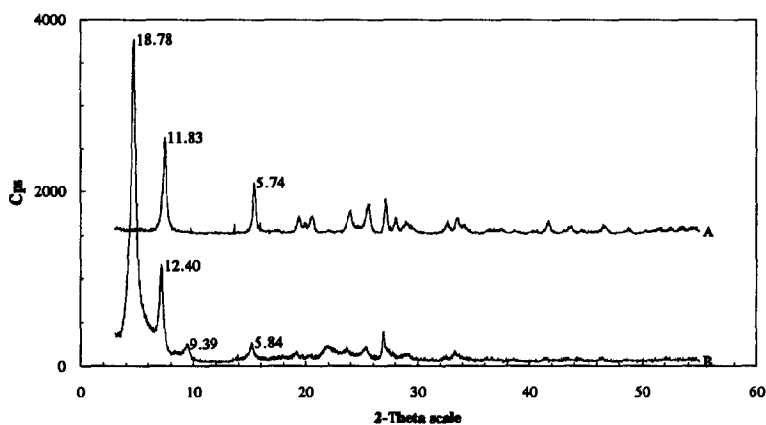


Figure 1

Figure 2 shows HyperChem molecular modeling of the γ -zirconium phosphate containing *N*-(2-ethylphosphonic)-aza-18-crown-6 units.

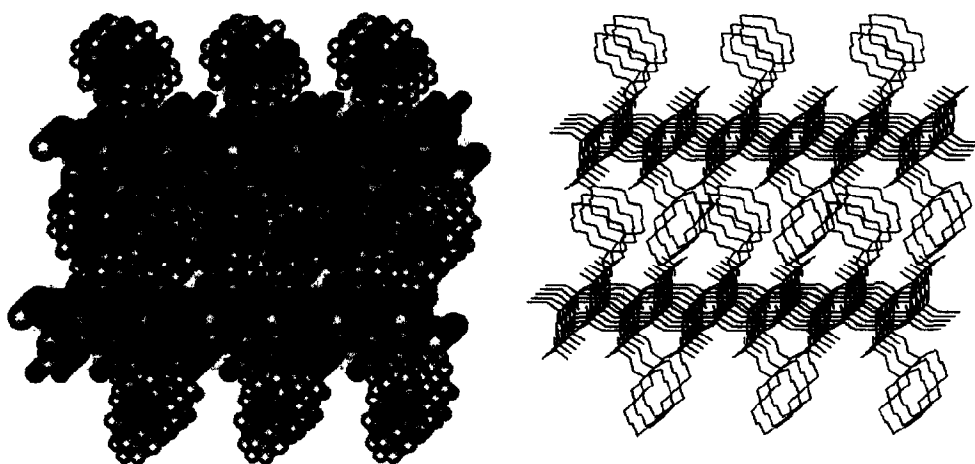
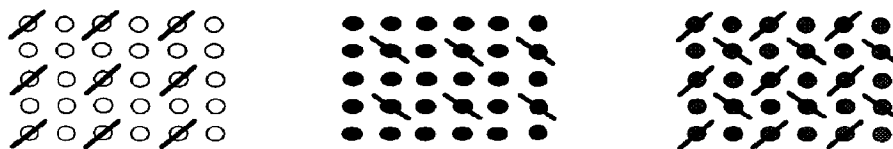


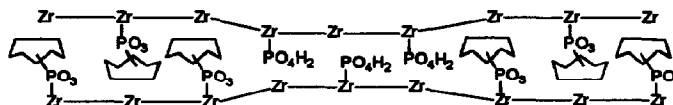
Figure 2

The model was constructed from previously reported geometries of the γ -layer⁵ and on the assumption that its structure remains essentially unaltered with the inclusion of organic phosphonates. *N*-(2-ethylphosphonic)-aza-18-crown-6 was minimized by AM1/AMBER procedures⁶ prior to its incorporation in the γ -phase. From the represented 60 units of exchangeable phosphate in each layer (30 per face), we found that a maximum of 18 can be regularly replaced by phosphonate. Scheme 1 shows one of the possible arrangements.



Scheme 1

The crowns (straight lines) bonded to the phosphonic groups of the down face in the upper layer (white circles) leave void places where the crowns of the up face in the lower layer (black circles) may rest without severe steric interference (top view of upper and lower layers in gray). This is equivalent to a predicted maximum exchange of 18 phosphonates in 120 phosphates, *i.e.* 15% relative to total phosphorous. This number seems reasonable in view that phenylphosphonic acid, which is sterically much smaller than our crown-ether derived phosphonic acid, was reported to exchange only to a maximum extent of 33% relative to total phosphorous.⁷ Therefore, it appears that is not necessary to use a great excess of organic phosphonic acid in the exchange reaction since with only an approximate 2.3 molar excess of it relative to γ -zirconium phosphate,³ a value of exchange (12-13%) very close to the possible maximum predicted by the model was attained in our case. Nevertheless, the permanence of some starting γ -phase in the sample (see above) suggests the existence of 'bubbles' or parts of the layers devoid of crowns (Scheme 2) whose presence might be minimized with a higher excess of organic phosphonic acid and/or by previous delamination by amine intercalation.⁸



Scheme 2

Setting the different torsion angles of the $\text{PCH}_2\text{CH}_2\text{N}$ fragment of each phosphonate to reasonable values to achieve minimum steric interactions amongst crowns and not invading van der Waals distances between layers, the model predicts a minimum interlayer separation of 18.6 Å, in excellent agreement with the XRD pattern.

Finally, Figure 3 shows the titration curves with NaOH of the starting γ -layer (circles) and the exchanged one with the crown-ether phosphonate (crosses). It may be seen that the ion-exchange properties of both materials are quite different in that the capacity of the crown-ether containing material is much higher. At pH 10, where hydrolysis of the zirconium phosphate framework is assumed to take place at a very

low level⁹, the exchanged γ -layer is able to contain *c.a.* 1.5 meq of Na⁺ compared to *c.a.* 0.9 meq for the non-exchanged material. Research is in progress concerning selectivity studies towards cations.

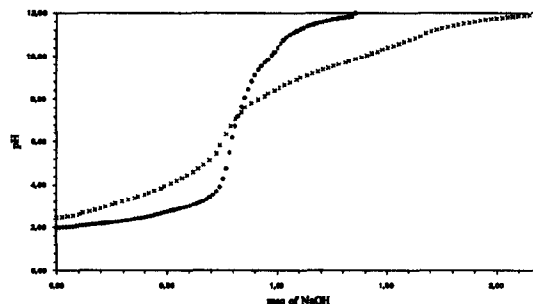


Figure 3

Acknowledgment. We thank *Ministerio de Educación y Ciencia* for financial support under grants PB90-0176 and PB93-0264.

References and Notes

- 1 See for example refs. 1-5 in Kim, R.M.; Pillion, J.E.; Burwell, D.A.; Groves, J.T.; Thompson, M.E. *Inorg. Chem.* **1993**, *32*, 4509.
- 2 Clayden, N.J. *J. Chem. Soc., Dalton Trans.* **1987**, 1877.
- 3 Exchange conditions: a suspension of 200 mg of γ -phase and 600 mg of 2(1-aza-18-crown-6)ethyl phosphonic acid hydrochloride in 20 mL of water/acetone (1:1) was refluxed for 20 h. The solid was filtered, washed with 20 mL of water and stored overnight under P₂O₅.
- 4 Sample referenced to external Ph₃P/CDCl₃ at -5.3 ppm
- 5 See for example Alberti, G.; Casciola, M.; Vivani, R.; Biswas, R.K. *Inorg. Chem.* **1993**, *32*, 4600.
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