

Crown Ether Pillared and Functionalized Layered Zirconium Phosphonates: A New Strategy to Synthesize Novel Ion Selective Materials

Baolong Zhang and Abraham Clearfield*

Department of Chemistry, Texas A&M University
College Station, Texas 77843-3255

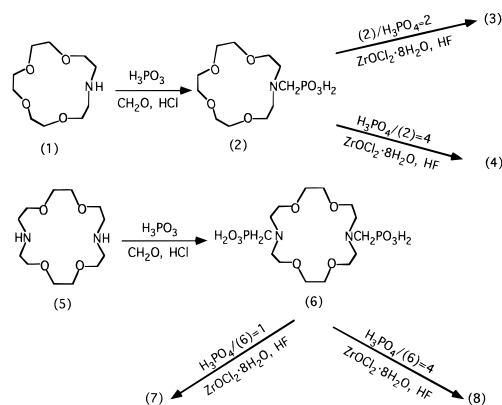
Received October 3, 1996

Crown ethers have been intensively studied during the last 25 years.^{1–3} The interest stems not only from the fact that these studies provide unlimited exploration of structural assembly^{4,5} but also from the chemical and biological potential of these compounds as ion exchangers⁶ and possible agents for transporting ionic species in living tissues.⁷ These macrocyclic ligands are noted for their remarkable selectivity toward metal ions making them excellent choices for the separation of metal ions.^{8,9} However, one of the major problems encountered in using macrocyclic ligands in separation processes is the loss of very expensive macrocycles in the solution due to their solubility.¹⁰ One way to overcome this problem is to attach the macrocyclic ligands covalently to a solid support. Early efforts to accomplish this chemical bonding involved connecting the carbon framework of the macrocycles to the siloxy component of silica gel.^{11,12} However, this method proved to be fraught with preparative difficulties that involves several reaction steps.

Metal phosphonates represent a relatively new class of compounds.^{13,14} Many of them are layered compounds in which inorganic groups build up the layer backbone while the organic portion protrudes into the interlamellar space. One of the noted characteristics of these compounds is their predictable structure skeletons.^{15,16} Other important features are the simple reaction steps required to make them and the ability to affix the various organic groups on a solid support.¹⁷

In this paper, we report our efforts to incorporate crown ethers onto zirconium phosphonate layers. The crown ether precursors used here are 1-aza-15-crown-5 and 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane. They were converted to phosphonic acids by a Mannich type reaction,¹⁸ from which a series of bridged and unbridged zirconium phosphonates were synthesized. Kijima¹⁹ recently reported incorporating the macrocyclic species into the α - and γ -zirconium phosphate by intercalation.

Scheme 1



Brunet *et al.*²⁰ and Alberti^{14,21} also were able to bind the crown ether covalently to γ -zirconium phosphate by an ester exchange reaction. Our synthesis, however, is a new general approach to react macrocycle phosphonic acids with zirconium, and the products obtained are the first examples of bridged and nonbridged crown ether derivatized zirconium phosphonates prepared by direct reaction rather than ester interchange and therefore may be more general.

The preparation is outlined in Scheme 1. Compound **3** was made from phosphonic acid **2** when the ratio of **2** to phosphoric acid was equal to 2. The X-ray diffraction pattern, shown in Figure 1, suggested that it is a layered compound with a d -spacing of 20.0 Å. When the reaction was performed with additional phosphoric acid, a new layered phase, **4**, with d -spacing 13.0 Å, was obtained. The structural difference between these two phases was easily identified from their ³¹P solid state NMR spectra. The ³¹P NMR spectrum of **3** has two main peaks similar to those obtained for zirconium *N*-(phosphonomethyl)iminodiacetic acid layered compounds (ZrPMIDA), in which one peak is at -27.20 ppm due to PO₄³⁻, and another is at -5.98 ppm attributed to the phosphonate phosphorus. In ZrPMIDA it was found²² that the layer backbone in this compound is formed with zirconium bridged by four oxygens from phosphate groups similar to the bonding in γ -Zr(PO₄)(H₂-PO₄)·2H₂O (γ -ZrP).²³ However, the phosphonate binding is similar to that found for α -Zr(HPO₄)₂·H₂O (α -ZrP).²⁴ There is also a minor peak at -19 ppm for HPO₄²⁻ groups. The driving force to form this new layer arrangement is attributed to the bulkiness of the macrocycle phosphonic acid. Like PMIDA, compound **1** is too large to fit into the skeleton of an α -ZrP layer since it exceeds the limit²⁴ of 24 Å² available to the pendant groups. Therefore, the presence of phosphoric acid is necessary to obtain a layered type compound other than α that provides sufficient room for the pendant group by insertion of PO₄ groups. However, the ³¹P NMR of compound **4**, which was made by adding an excess amount of phosphoric acid, has two peaks, one at -21.18 ppm and the other at -9.32 ppm, similar to the spectrum of a layered mixed component zirconium phenylphosphonate/phosphate derivative.²⁵ This suggested that in this case, an α type layered compound is formed with HPO₄²⁻

* Author to whom correspondence should be addressed.

(1) Pedersen, C. T.; Frensdorff, H. K. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 16.

(2) Lehn, J. M. *Acc. Chem. Res.* **1978**, *11*, 49.

(3) Cram, D. J.; Cram, J. M. *Acc. Chem. Res.* **1978**, *11*, 8.

(4) Izatt, R. M.; Christensen, J. J. *Synthesis of Macrocycles: The Design of Selective Complexing Agents*; Wiley-Interscience: New York, 1987; Vol. 3.

(5) Vögtle, F.; Weber, E. *Host Guest Complex Chemistry Macrocycles*; Springer-Verlag: Berlin, 1985.

(6) Lamb, J. D.; Izatt, R. M.; Christensen, J. J. *Progress in Macrocyclic Chemistry*; John Wiley & Sons: New York, 1981; Vol. 2.

(7) Wipf, H. K.; Simon, W. *Helv. Chim. Acta* **1970**, *53*, 1732.

(8) Lehn, J.-M. *Science* **1985**, *227*, 849.

(9) Izatt, R. M.; Brawshaw, J. S.; Neilson, S. A.; Lamb, J. D.; Christensen, J. J.; Sen, D. *Chem. Rev.* **1985**, *85*, 271.

(10) Izatt, R. M.; Bruening, R. L.; Tarbet, B. J.; Griffin, D.; Bruening, M. L.; Krakowiak, K. E.; Bradshaw, J. S. *Pure Appl. Chem.* **1990**, *62*.

(11) Bradshaw, J. S.; Bruening, R. L.; Krakowiak, K. D.; Tarbet, B. J.; Bruening, M. L.; Izatt, R. M.; Christensen, J. J. *J. Chem. Soc., Chem. Commun.* **1988**, 812.

(12) Bradshaw, J. S.; Krakowiak, K. E.; Tarbet, B. J.; Bruening, R. L.; Biernat, J. F.; Bochenska, M. J.; Izatt, R. M.; Christensen, J. J. *Pure Appl. Chem.* **1989**, *61*, 1619.

(13) Clearfield, A. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 268.

(14) Alberti, G. *Comprehensive Supramolecular Chemistry*; Lehn, J. M., Ed.; Pergamon, Elsevier Science, Ltd.: Oxford, U.K., 1996; Vol. 7.

(15) Dines, M. B.; Di Giacomo, P. M. *Inorg. Chem.* **1981**, *20*, 92.

(16) Cao, G.; Hong, H.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420.

(17) Clearfield, A. *Design of New Materials*; Cocke, D. A., Clearfield, A., Eds.; Plenum Press: New York, 1987, p 128.

(18) Tazaki, M.; Nita, K.; Takagi, M.; Ueno, K. *Chem. Lett.* **1982**, 571.

(19) Kijima, T.; Sakoh, K.; Machida, M. *J. Chem. Soc., Dalton Trans.* **1996**, 1245.

(20) Brunet, E.; Huela, M.; Rodríguez-Ubis, C. J. *Tetrahedron Lett.* **1994**, *35*, 8697.

(21) Alberti, G.; Boccali, L.; Dionigi, C.; Kalchenko, V. I.; Vivani, R.; Atamas, L. I. *Supramol. Chem.* **1996**, *7*, 129.

(22) Zhang, B.; Poojary, D. M.; Clearfield, A.; Peng, G.-Z. *Chem. Mater.* **1996**, *8*, 1333.

(23) Poojary, D. M.; Shpeizer, B.; Clearfield, A. *J. Chem. Soc., Dalton Trans.* **1995**, 111.

(24) (a) Clearfield, A.; Smith, G. D. *Inorg. Chem.* **1969**, *8*, 431. (b) Troup, J. M.; Clearfield, A. *Inorg. Chem.* **1977**, *16*, 3311.

(25) Wang, J. D.; Clearfield, A.; Peng, G.-Z. *Mater. Chem. Phys.* **1993**, *35*, 208.

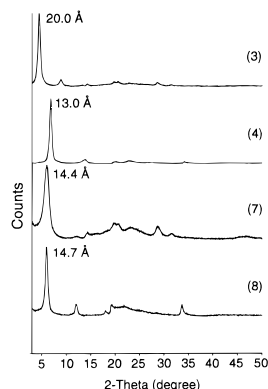


Figure 1. X-ray powder patterns of compounds **3**, **4**, **7**, and **8**.

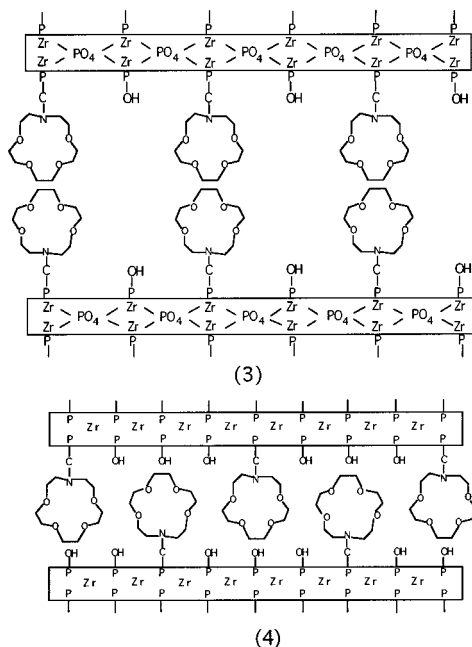


Figure 2. Schematic representation of interlayer arrangement of compounds **3** (top) and **4** (bottom).

(−21.18 ppm) and phosphonate (−9.32 ppm) in the same layer. On the basis of the X-ray diffraction data, elemental analysis, TGA data, solid state ^{31}P and ^{19}F NMR studies, compounds **3** and **4** are formulated as $\text{Zr}_2(\text{C}_{11}\text{H}_{23}\text{NO}_7\text{P})_{1.17}(\text{PO}_4)(\text{HPO}_4)_{0.83}\text{F}_2\text{Cl}_{0.17}\cdot 1.69\text{H}_2\text{O}$ and $\text{Zr}(\text{C}_{11}\text{H}_{23}\text{NO}_7\text{P})_{0.22}(\text{HPO}_4)_{1.78}\text{F}_{0.22}\cdot 1.86\text{H}_2\text{O}$, respectively. The nitrogens in these two compounds are protonated. The fluoride ions are for charge balance. ^{19}F solid state NMR spectra of these two compounds both have a peak at −123 ppm corresponding to free fluoride ion. However, in the ^{19}F NMR spectrum of compound **3** there is a second peak at 45 ppm indicating existence of another kind of fluorine which is bonded to zirconium. This fluorine is labile and can undergo chemical exchange with the nonbonded F^- as shown by NMR line broadening. A small amount of chloride ion is present in this compound because compound **3** was made using zirconyl chloride. A schematic representation of the proposed structural character of compounds **3** and **4** is shown in Figure 2. Evidently, the presence of the small HPO_4 groups on the layers creates enough space to accommodate the bulky phosphonate groups in an α type structure since the bulky phosphonate groups in an α type structure since the bulky phosphonate groups can spread over two phosphorus layer positions.

Similar reactions are observed for the bisphosphonic acid. However, in this case, cross-linked compounds are formed. Unlike the nonbridged compounds **3** and **4**, which easily swell in water due to the hydrophilic character of the macrocycles, the cross-linked compounds **7** and **8** are white insoluble powders. They do not visibly swell due to the fixed distance

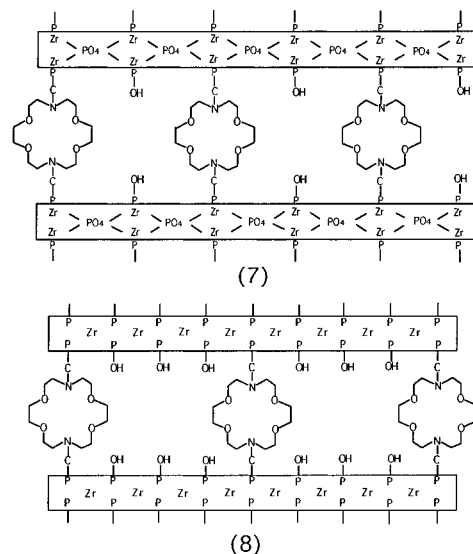


Figure 3. Schematic representation of interlayer arrangement of compounds **7** (top) and **8** (bottom).

prescribed by the cross-linking bisphosphonate groups. When the ratio of H_3PO_4 to compound **6** is equal to 1, a layered compound **7** similar to **3** but with a d -spacing of 14.4 Å, is formed. Compound **8** was obtained from a reaction in which the ratio of H_3PO_4 to **6** was equal to 4. However, unlike compound **4**, the d -spacing of compound **8** remains almost unchanged because the d -spacing, which is dependent on the length of the cross-linking group, has been fixed (it increases slightly to 14.7 Å because the layer thickness of the α -type is 6.3 Å compared to 5.8 Å in the mixed type compound **7**). Similar ^{31}P NMR spectra were observed between compounds **3** and **7** and compounds **4** and **8**, respectively, indicating their structural similarity to each other. On the basis of XRD, elemental analysis, TGA data, solid state ^{31}P and ^{19}F NMR studies, compounds **7** and **8** are formulated as $\text{Zr}_2(\text{C}_{14}\text{H}_{30}\text{N}_2\text{P}_2\text{O}_{10})_{0.75}(\text{HPO}_4)_{0.5}(\text{PO}_4)\cdot\text{F}_{2.5}\cdot 4\text{H}_2\text{O}$ and $\text{Zr}(\text{C}_{14}\text{H}_{30}\text{N}_2\text{P}_2\text{O}_{10})_{0.33}(\text{HPO}_4)_{1.34}\cdot\text{F}_{0.66}\cdot 1.8\text{H}_2\text{O}$, respectively. Their schematic structural representations are shown in Figure 3. Again, the nitrogens in these two compounds are protonated. The fluorine in these two compounds is for charge balance, but both are not bonded to zirconium as suggested by their ^{19}F solid state NMR spectra. A model that was proposed based on the ZrPMIDA structure suggests that the cross-linked compounds **7** and **8** can be regarded as three-dimensional structures with 2.6–2.8 Å uniform pores formed by the macrocycles.

In conclusion, compounds **4** and **8** are the first examples of crown ether pillared α -zirconium phosphonate phosphates. Compound **3** and **7** have new structures other than those reported as γ type macrocycle-derivatized zirconium phosphonates or of those simply pillared by intercalation. This opens up a route to develop novel materials to have special ion exchange and complexing properties. The preliminary results show that they have good selectivity toward transition metals and the interlamellar fluoride ions may be replaced by anion exchange. The details will be reported subsequently.

Acknowledgment. This research was generously supported by the National Science Foundation through grant no. DMR-907715 and by the Robert A. Welch Foundation through grant no. A673. We thank Thomas R. Krawietz for helping with the ^{19}F solid state NMR. We also thank Dr. Renald Guillemette for his assistance with the microprobe analysis and Elizabeth Behrens for AA analysis.

Supporting Information Available: Text describing the synthesis and analytical data of all new compounds (2 pages). See any current masthead page for ordering and Internet access instructions.