Azacrown Ether Pillared Layered Zirconium Phosphonates and the Crystal Structure of *N*,*N*′-Bis(phosphonomethyl)-1,10-diaza-18-crown-6

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The synthesis of *N*,*N*′-bis(phosphonomethyl)-1,10-diaza-18-crown-6 tetrahydrate (**6**) from the corresponding diazacrown ether is described and the crystal structure of this diphosphonic acid determined. The crystals are triclinic, $P\bar{1}$ with $a = 8.1829(8)$, $b = 8.3092(10)$, $c = 9.1429(10)$ Å, $\alpha = 85.286(9)°$, $\beta = 84.736(9)°$, $\gamma = 73.158(7)°$, and $Z = 1$. The center of the azacrown ether ring coincides with the center of symmetry, requiring that the CH_2PO_3H groups lie trans to each other. One of the acid protons of each phosphonic acid group resides on the aza nitrogens, resulting in a zwitterion arrangement. There are four water molecules per unit cell that participate in an extensive system of hydrogen bonding. An important feature of the H-bonding is that between adjacent phosphonic acid groups to form linear chains along the unit cell diagonal. Reaction of **6** with Zr(IV) in the presence of H_3PO_4 yields zirconium phosphate-type layers cross-linked by the crown ether groups. The types of layers formed were deduced by a combination of ^{31}P NMR and X-ray data. Affixing phosphonic acid groups onto the aza crown ether results in a more rectangular shape to the ring, which is further distorted by the cross-linking of the layers.

Introduction

Crown ethers have been a subject of intense studies for 3 decades[1] because of their selective complexation properties[2] and because their study provides for exploration of structural assembly.[2a,3,4] The recognition ability of crown ethers is somewhat compromised in aqueous solution by the leveling effect of the solvent. Chemists have attempted, and largely succeeded, in increasing the selectivity of the host by synthesizing more complex structures.[4] An alternative approach has involved attachment of the crown to polymers[5] or other solid matrixes.[6] This immobilization of the crown ether tends to limit solvation effects and has the added advantage of relative ease of recovery of the otherwise soluble crown.

Another approach that has been more recently examined is the immobilization of crown ethers or azacrown ethers on ordered layered matrixes. Brunet et al.[7] prepared *N*-(phosphonoethyl)-aza-18-crown-6 (1) and incorporated it into γ-zirconium phosphate, (γ-ZrP), $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$, by an ester-interchange reaction. Alberti et al.[8a,c] carried out similar ester interchange reactions using the phosphonic acid of benzo-15-crown-5 (**2**). The phosphonic acid group is meta to the crown ether ring and was found to replace a maximum of 69% of the dihydrogenphosphate groups in γ-ZrP. The same workers also used the corresponding diphosphonic acid of dibenzo-18-crown-6 (**3**) to prepare $Zr(PO_4)(H_2PO_4)_{0.5}(HO_3P-R_c-PO_3H)_{0.25}$ where R_c is the dibenzo-18-crown-6.[8b,c]

Recently, we prepared both the *N*-(phosphonomethyl) (**4**) and *N*,*N*′-bis(phosphonomethyl)-1,10-diaza-18-crown-6 (**6**) compounds and synthesized layered zirconium derivatives of these acids by direct reaction with Zr(IV) solutions.[9] Phosphoric acid was added to the reaction mix to produce mixed phosphate−phosphonate groups

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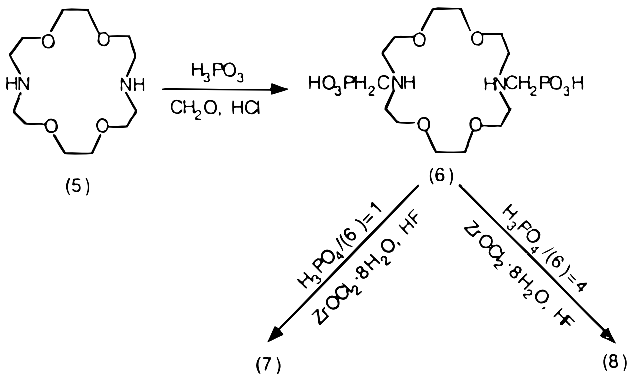
Scheme 1



on the layers. This was done to avoid crowding of the crown ethers on the layers. Because the area of a phosphate group on the layer is only 24 Å^2, and the area per crown is in excess of this value, the presence of the small phosphate groups on the layers allows sufficient room to form layers incorporating the aza crown ethers. Hydrofluoric acid was also added to act as a solubilizer and aid in forming crystals. However, only poorly crystalline compounds were obtained so that indirect methods of structural analysis were utilized to arrive at the type of layers that formed. In this study we report on the crystal structure of the phosphonic acid, compound **6**, and an NMR and modeling study of the same azacrownphosphonic acid immobilized on α-zirconium phosphate-like layers. The structure of α-zirconium phosphate (α-ZrP), $Zr(HPO_4)_2{\cdot}H_2O$, is well documented.[10]

Experimental Section

Materials and Methods. 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**5**) (Scheme 1) was obtained from Aldrich and used without further purification. Deionized water used in all the experiments was purified to a resistivity of 17.6 MΩ cm with a Barnstead Nanopure II System. X-ray powder diffraction (XRPD) patterns were acquired with a Seifert-Scintag PAD V diffractometer using Ni-filtered Cu Kα radiation (λ = 1.5418 Å). Infrared spectra (IR) were recorded with a BIO-RAD FTS-40 spectrometer with the sample in the form of a KBr disk. A DuPont thermal analyst 950 unit was used for thermogravimetric analysis (TGA) at a typical heating rate of 10 °C/min under a flow of oxygen. ^{31}P NMR spectra were recorded on a Bruker MSL-300 and ^{19}F solid MAS NMR was run on a home-built 200-MHz spectrometer, operating with a ^{19}F Larmor frequency of 187.816 MHz using a double-resonance H−F probe from Otsuka Electronics, spinning a 4-mm zirconium rotor. C, H, and N chemical analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN. Zr, P, and F were determined by microprobe analysis. For comparison, F was also analyzed by neutron activation measurements in the Center for Chemical Analysis at Texas A&M University Chemistry Department.

Synthesis of *N,N'*-Bis(phosphonomethyl)-1,10-diaza-18-crown-6 Tetrahydrate (6). First, 4.86 g (18.5 mmol) of **5** and 6.07 g (74 mmol) of phosphorous acid were mixed with 6.4 mL of water and 2.29 mL of concentrated HCl. Second, the mixture was refluxed at 120 °C while 1.67 g (18.5 mmol) of paraformaldehyde was added into the mixture over a 1-h time period. The solution was allowed to reflux for an additional hour. After it cooled to room temperature, the solution was concentrated by rotatory evaporation. A white gel-like solid was obtained. The solid was redissolved in 5 mL of water and purified by an ion-exchange procedure yielding 5 g (9.57 mmol) (51.7%) of a white solid. A column of dimensions 24 × 3 cm^2 was half-filled with Dowex 1-X 8 anion exchanger, 20−50 mesh in the ionic Cl$^-$ form. The resin was treated with 1 L of 1 N NaOH to convert it to the hydroxide form. Then, the redissolved reaction product was passed through the column dropwise followed by rinsing of the column with a 10% acetic acid solution. The effluent was collected and concentrated through rotary evaporation, yielding 5 g (9.57 mmol) of a white solid. Anal. Found: C, 32.04%; N, 5.30%; H, 7.75%. Calcd. for $C_{14}H_{40}N_2O_{14}P_2$: C, 32.19%; N, 5.36%; H, 7.71%. The ^{31}P spectrum of the sample had a single peak at 7.55 ppm.

Synthesis of $Zr_2(C_{14}H_{30}N_2O_{10}P_2)_{0.75}(PO_4)(HPO_4)_{0.5}{\cdot}2.5F{\cdot}4H_2O$ (7) (FW = 781.23). One millimole of compound **6** (0.5 g) was dissolved in 20 mL of deionized distilled water. To this solution was added 1 mmol of phosphoric acid (0.06 mL). In another plastic beaker 3 mmol of $ZrOCl_2{\cdot}8H_2O$ was dissolved in 0.42 mL of HF solution (F/Zr = 4). After the two solutions were slowly mixed together, the resultant solution was kept at 60 °C in an oil bath for 5 days. Then, 0.6 g (0.768 mmol, 57.6%) of a white solid was recovered after filtration, washing, and drying at room temperature. Elemental analysis: C, 15.09%; H, 2.42%; N, 2.51%; P, 12.55%; Zr, 23.3%; F, 6.31% (by microprobe), 7.3% (by neutron activation analysis). Calcd for compound **7**: C, 16.13%; H, 3.97%; N, 2.69%; P, 11.89%; Zr, 23.36%; F, 6.08%.

Synthesis of $Zr(C_{14}H_{30}N_2O_{10}P_2)_{0.33}(HPO_4)_{1.34}{\cdot}0.66F{\cdot}1.8H_2O$ (8). The synthesis procedure for compound **8** is similar to that for compound **7**, but the ratio of phosphoric acid to the bis(phosphonomethyl) crown was 4. Elemental analysis for compound **8**: C, 12.74%; H, 3.15%; N, 2.16%; P, 15.30%; Zr, 23.5%; F, 3.73% (by microprobe); 3.5% (by neutron activation analysis). Calcd for compound **8**: C, 13.43%; H, 3.60%; N, 2.24%; P, 15.03%; Zr, 22.11%; F, 3.04%.

Crystal Structure Analysis of Compound 6. A colorless platelike crystal of compound **6** with dimensions 0.45 × 0.35 × 0.20 mm^3 was mounted on a glass fiber. All crystallographic measurements were carried out on a Rigaku AFC5R diffractometer with graphite monochromated Cu Kα radiation (λ = 1.54178 Å) and a 12-kW rotating anode generator. Unit cell parameters for data collection were obtained from least-squares refinement of 25 reflections chosen from 30° to 38° 2θ. The triclinic refined parameters are a = 8.1829(8), b = 8.3092(10), c = 9.1429(10) Å, α = 85.286(9)°, β = 84.736(9)°, γ = 73.158(7)°, V = 591.47(11) Å^3, Z = 1 (FW = 522.42) in space group $P\bar{1}$. Intensity data were collected at 20 ±2 °C using the $\omega-2\theta$ procedure. Three intensity standards were measured every 150 reflections to monitor crystal decay. Scans of (1.05 + 0.3 tan θ)° were made at a speed of 16°/min in ω. The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 3) for good counting statistics. Of the 3524 reflections that were collected, 1762 were unique (R_{int} = 0.028). The data were corrected for Lorentz, polarization, and absorption effects (ψ−scan).[11] Transmission factors were between 0.90 and 0.99. The structure was solved by direct methods,[12] which revealed the positions of all the non-H atoms. After refinement of these parameters and the anisotropic thermal parameters, all the H atom positions were located by calculation of idealized positions and included in the structure factor calculations as "riding" on the atoms to which they are bonded. After varying the extinction coefficient, the refinements converged at R1 = 0.032 and wR2 = 0.082 and goodness of fit on F^2 of 1.048 for 1762 observed intensities and 146 parameters.[11]

Molecular Modeling. Computer modeling procedures were utilized because the layer immobilized macrocyclic compounds were poorly crystalline. It was therefore necessary to fix the structures more completely so as to create a model to be used to predict and correlate chemical data. Initially, the structure of the diazacrown bis(phosphonic) acid, compound **6**, was optimized in the gas phase using the Universal Forcefield[13]

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Table 1. Selected Intramolecular Distances (Å) and Bond Angles (deg) for Compound 6[a]

P−O12	1.482(2)	O21−C23	1.421(2)
P−O13	1.507(2)	O21−C22	1.427(2)
P−O11	1.572(1)	O22−C25	1.428(2)
P−C11	1.832(2)	O22−C24	1.431(2)
N−C11	1.502(2)	N−C21	1.508(2)
N−H1	0.91(2)	N−C26	1.502(2)
C21−C22	1.503(3)	C25−C26	1.503(3)
C23−C24	1.502(3)		
O11−H111···O13′	2.553(2)	O31−H311···O32	2.753(2)
O31−H312···O22	2.916(2)	O32−H321···O12′	2.679(2)
O32−H322···O13	2.788(2)	N−H1···O31	2.751(2)
O12−P−O13	117.95(9)	O12−P-011	110.96(8)
O13−P−O11	110.12(8)	O12−P−C11	109.60(9)
O13−P−C11	103.65(8)	O11−P−C11	103.32(9)
P−C11−N	118.3(1)	C11−N−C21	110.4(2)
C11−N−C26	115.4(2)	C11−N−H1	106.6(1)
C21−N−C26′	112.1(2)	C26′-N−H1	106.8(14)
C21−N−H1	104.7(14)	N−C21−C22	112.7(2)
C21−C22−O21	108.8(2)	C22−O21−C23	113.5(2)
O21−C23−C24	107.8(2)	C23−C24−O22	107.4(2)
C24−O22−C25	113.0(2)	O22−C25−C26	107.3(2)
C25−C26−N	113.0(2)		

[a] Primed atoms are related to their centrosymmetric similarly numbered atoms.

supplied as part of the Cerius^2 program package.[14] After the minimum geometry was obtained, a conformer search was performed using simulated annealing to explore conformation space. During this procedure, the system was repeatedly heated−cooled and minimized to map different areas of the potential energy surface. The conformer search revealed that the geometry of the crown ether may vary over a wide range, allowing it to bridge across different layers and adjust to the required interlayer separation as determined from X-ray data. On the basis of experimental information presented above for compound **8**, a unit cell was built containing the crown ether molecule bridging between layers with one crown ether per unit cell. Holding the unit cell parameters constant, the geometry of the diazacrown ether was optimized. The layer was considered to have an α-type structure.

Results

Scheme 1 outlines the reactions leading to crown ether cross-linked zirconium phosphonates. The diazacrown ether (**5**) was converted to the diphosphonic acid via a Mannich-type reaction.[9,15] To purify the initial precipitate, it was redissolved in a minimum of water and passed through a bed of Dowex anion-exchange resin.

Crystal Structure of Compound 6. Positional and isotropic thermal parameters are given in Tables 1S (non-hydrogen atoms) and 2S (H-atoms) of the Supporting Information and bond distances and angles are listed in Table 1. Each triclinic unit cell contains one molecule of compound **6** and four water molecules. The center of the diazacrown ring is located on a center of symmetry, which requires that the phosphonic acid groups be trans to each other as shown in Figure 1. The molecule lies along the $[\bar{1}\bar{1}1]$ diagonal. The tetrahedral phosphonate groups contain a short P−O12 bond, 1.482(2) Å, and a long one, P−O11, 1.572(1) Å. O11 is bonded to a proton but the other two oxygens are not. Instead, one of the protons from each phosphonic acid group is donated to the adjacent nitrogen atoms. The bond distances and angles around the ring are normal with the following averages: C−C, 1.503(1) Å; N−C, 1.504(4) Å; C−O, 1.427(3) Å. The comparable values determined for compound **5** are as follows: C−C, 1.501(16) Å; N−C, 1.446(6) Å; C−O, 1.433(16) Å.[16,17] Bond angles range from 103.3(1) Å for O11−P−C11 to 118.3(1) Å for P−C11−N.

Table 2. Comparison of Some Interatomic Ring Distances in Several Forms of 1,10-diaza-18-crown-6 (DA18C6)

compound	interatomic distance (Å)		
	N−N	021−021′	022−022′
DA18C6 (ref 15)	5.841 (6)	5.612 (6)	5.670 (5)
DA18C6 (ref 16)	5.854 (2)	5.612 (2)	5.660 (2)
Da18C6·2HCl (ref 16)	4.174 (1)	6.458 (1)	6.100 (1)
DA18C6(CH$_2$PO$_3$H$_2$)$_2$ (this study)	6.142 (4)	6.081 (3)	5.351 (3)

The two centrosymmetrically related phosphonic acid groups hydrogen bond to adjacent phosphonic acid groups in neighboring unit cells along the $[\bar{1}\bar{1}1]$ diagonal. Oxygen O11 is the donor and O13′ the acceptor oxygen at a distance of 2.553(2) Å. There are two such hydrogen bonds at each end of the cell diagonal (Figure 1). Hydrogen bonds are also formed with the water molecules, O32 and O31. They are located above and below the macrocycle ring as shown in Figure 2. Within the macrocycle ring N−H1 donates to O31 (N−H···O31, 2.751(2) Å) and O31 donates to O22 as an acceptor (O31−H312···O22, 2.916(2) Å). O31 also donates to water oxygen O32 (O31−H311···O32, 2.753(2) Å). O32 is far enough above and below the macrocycle ring to hydrogen bond to the phosphonic acid oxygens O12 and O13, O32−H321···O12′ (2.679(2) Å) and O32−H322···O13′ (2.788(2) Å) where the primes designate bonding to those oxygens in neighboring unit cells.

It is instructive to see how the macrocycle ring is distorted by the attachment of the phosphonomethyl groups. In Table 2 we have collected some interatomic distances between several ring atoms with their centrosymmetric mates of 1,10-diaza-18-crown-6 compounds. The diaza-18-crown-6 is designated in the table as DA18C6 and the HCl derivative as DA18C6·2HCl. The unsubstituted crown ether is conformationally more circular than the derivative structures. The N−N distance and the O−O distances across the center of symmetry are close in value to each other for the two DA18C6 structures. Attachment of the phosphonic acid groups increases the N−N and the O21−O21′ distances but decreases the O22−O22′ distance. These changes have the effect of producing a more rectangular shape for the ring. In the HCl derivative (Table 2) the HCl molecules reside above and below the center of the ring. This results in a drastically shorter N−N distance as the nitrogen protons bond to both Cl atoms of the HCl molecules. A much larger O21−O21′ distance and a smaller O22−O22′ distance result, producing a more elliptical shape to the ring.

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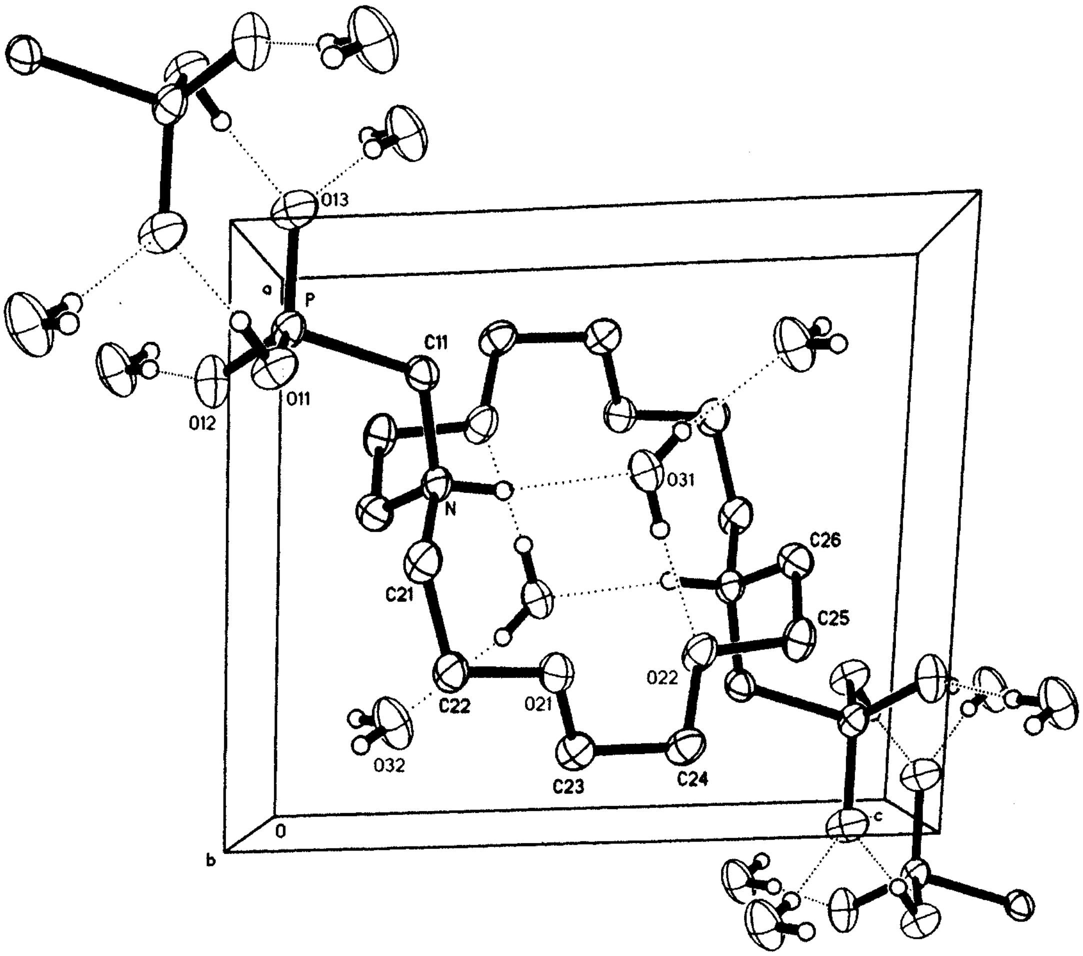

Figure 1. Ball-and-stick representation of the structure of *N*,*N*′-bis(phosphonomethyl)-1,10-diaza-18-crown-6·$4H_2O$ as viewed down the *b* axis. Thermal ellipsoids are at the 30% level. Hydrogen bonding is designated by dotted lines.

Zirconium Crown Ether Compounds

The X-ray powder patterns of the crown ether-immobilized zirconium phosphates contained only a handful of reflections. However, they each exhibited a very intense reflection indicative of the interlayer spacing of a cross-linked layered compound as formulated in Figure 3. The observed interlayer spacings are 14.4 Å for **7** and 14.7 Å for **8**. Apparently, the layers are disordered, resulting in the poorly crystalline powder. To gain further insight into the structure, we examined the solid-state MAS NMR spectra.

NMR Analysis. The ^{31}P spectra of the azacrown bis(phosphonic) acid, compound **6**, and its zirconium-immobilized compound **7** are shown in Figure 4a and b, respectively. The free acid has a peak at +8.4 ppm but there is also a small peak at 11.4 ppm. This peak is probably associated with the presence of some unhydrolyzed ethyl ester of **6**. In contrast, the ^{31}P spectrum of **7** exhibits three main resonances. The peak at −27.0 ppm is assigned to orthophosphate (PO_4^{3-}) groups; the resonance at −19.1 ppm is attributed to monohydrogen phosphate and the peak at −5.9 ppm is due to the phosphonate phosphorus. These assignments are made on the basis of similar resonances in compounds that are structurally well established. In α-zirconium phosphate in which only HPO_4^{2-} groups are present,[10] the ^{31}P resonance occurs at −18.7 ppm.[18] Similarly, the orthophosphate group found in γ-zirconium phosphate[19] exhibits a peak at −27.4 ppm.[18] Zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$, has a structure similar to that of α-zirconium phosphate in which the phenyl group replaces the pendant OH^- group.[20] The phosphorus resonance for this compound occurs at −5.0 ppm whereas the ^{31}P resonance for phenylphosphonic acid occurs at +17.3 ppm. This very large shift for the phosphorus in the free acid and when bonded to Zr is common. So the upfield shift for phosphorus in the azacrown phosphonic acid from +8.4 to −5.9 ppm is within expectations. We cite one more example. The compound zirconium *N*-(phosphonomethyl) iminodiacetic acid (PMIDA) of composition $Zr(PO_4)(O_3PCH_2N[(CH_3COOH)_2)(O_3PCH_2N-(CH_2COOH/CH_2COO^-)]\cdot 2H_2O$ provides a ^{31}P spectrum with resonances at −28 ppm (PO_4^{3-}) and a doublet at −9 and −7 ppm for the two types of phosphonate groups.[21,22] The spectrum also contained a small peak at −20 ppm, which was attributed to the presence of a small amount of monohydrogen phosphate groups. This point was confirmed for a sample prepared with some phosphoric acid added to the reaction mix. The addition

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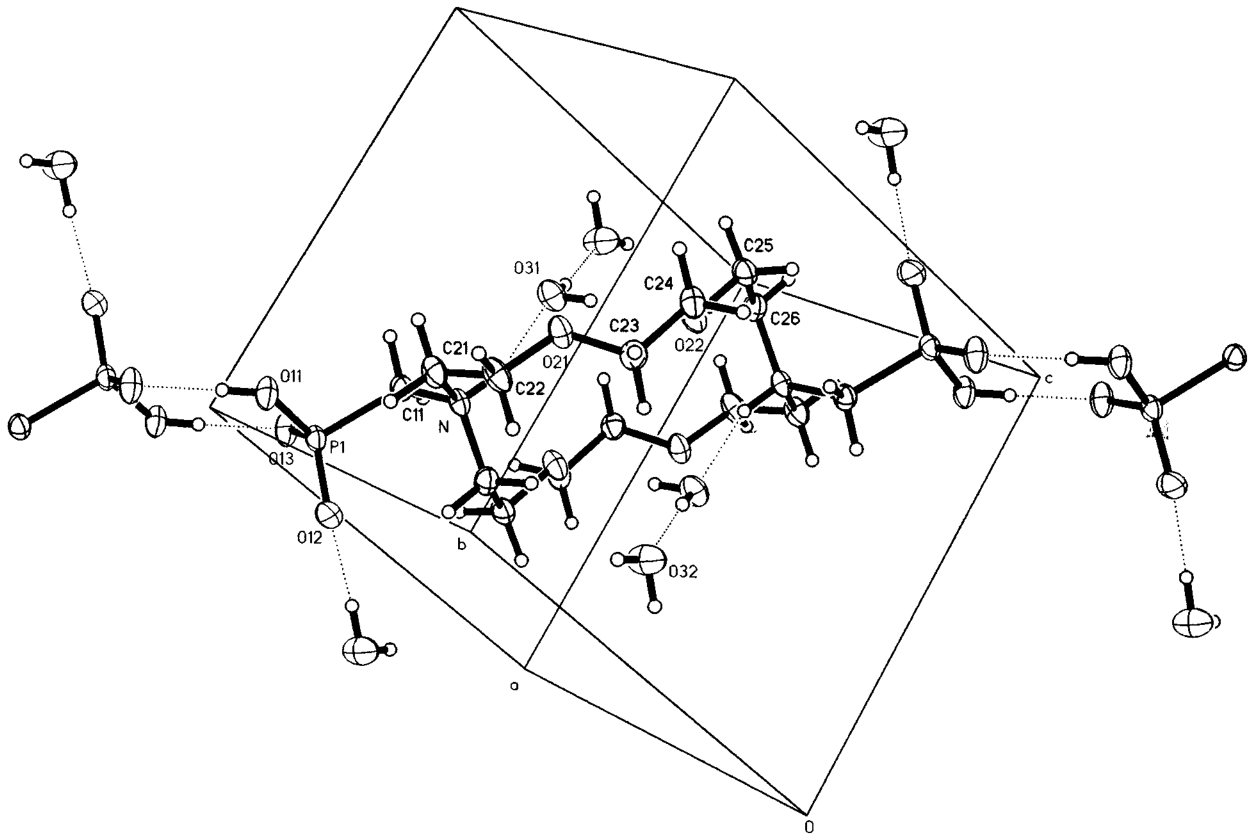

Figure 2. View of the structure of **6** showing its orientation along the cell diagonal and the water molecules above and below the crown ether ring. Hydrogen bonds are designated by dotted lines.

resulted in substitution of HPO_4^{2-} for phosphonate with the resultant spectrum showing a corresponding increase in the intensity of the peak at −20 ppm.

The ^{31}P spectrum for compound **8** is shown in Figure 5. In this case the ratio of added H_3PO_4 to phosphonate was 4 as compared to 1 for compound **7**. The spectrum contains two major resonances at −20.8 and −9.0 ppm. The absence of a peak at −27 ppm and the enhanced intensity at −20.8 ppm indicates that a α-type layered compound was formed. However, the peaks in Figure 5b are not symmetrical but slope toward −8 and −19, respectively, i.e., toward the positions of the peaks for compound **7**. These observations suggest that a small amount of compound **7** is present. A similar change occurred with the zirconium PMIDA derivatives when sufficient monohydrogen phosphate groups replaced PMIDA groups; the ^{31}P NMR spectra indicated a transformation to an α-type layer structure. The picture that emerges from consideration of the X-ray and NMR data is that compound **7** has a PMIDA-type layer structure in which the layers are cross-linked by the bis(phosphonate) crown ether and compound **8** has an α-type layer; both the phosphonate and phosphate groups bridge three Zr atoms. In the PMIDA complex the orthophosphate group bonds to four zirconium atoms whereas the phosphonate groups bond to three different Zr atoms and the last coordination site on Zr is occupied by a water molecule. The difference in interlayer spacing between compounds **7** and **8** is accounted for by the fact that a PMIDA-type layer is 5.8-Å thick whereas the α-layer is 6.3-Å thick.

^{19}F NMR spectra for both compounds have a single peak at −123 ppm, corresponding to that of a free fluoride ion. Since each aza nitrogen is protonated, the F^- ions are required for charge balance.

Consideration of the ^{13}C CP/MAS NMR spectra of both the azacrown phosphonic acid and the cross-linked compound **7** is also instructive (Figure 6). The spectrum contains a doublet resonance at about 47 ppm that is assigned to the C11 methylene carbon. The doublet is due to coupling of the carbon nucleus with its neighboring phosphorus atom. The resonances at 56.3 and 65.2 ppm and the doublet centered at 70.5 ppm are assigned to C21, C22, and C23, respectively. The observation of a doublet at 70.5 ppm indicates that carbons C23 and C24 possess slightly different environments. This NMR observation is consistent with our X-ray crystallographic data. The structure reveals slightly different torsion angles about these two carbon atoms, viz. C22−O21−C23−C24, −176.8°, and C25−O22−C24−C23, +179.7°.

The ^{13}C CP/MAS NMR spectrum of the corresponding crown ether cross-linked compound **7** is shown as Figure 6b. One can still distinguish four resonances but the peaks are considerably broadened and shifted slightly upfield (42.3, 54.6, 65.8, and 70.3 ppm). We believe that the broadening is due to the dispersion of local environments of the crown ether rings between the layers. This effect may result from the disorder in the layers. The ^{15}N spectra show a similar broadening. The largest shift is for C11 attached to ^{31}P and may result from the same effect that results in the very large upfield shift of the phosphonate phosphorus upon bonding with the zirconium.

Molecular Modeling. To fix the structures of the zirconium azacrown ethers more completely, a preliminary molecular modeling study was carried out. The

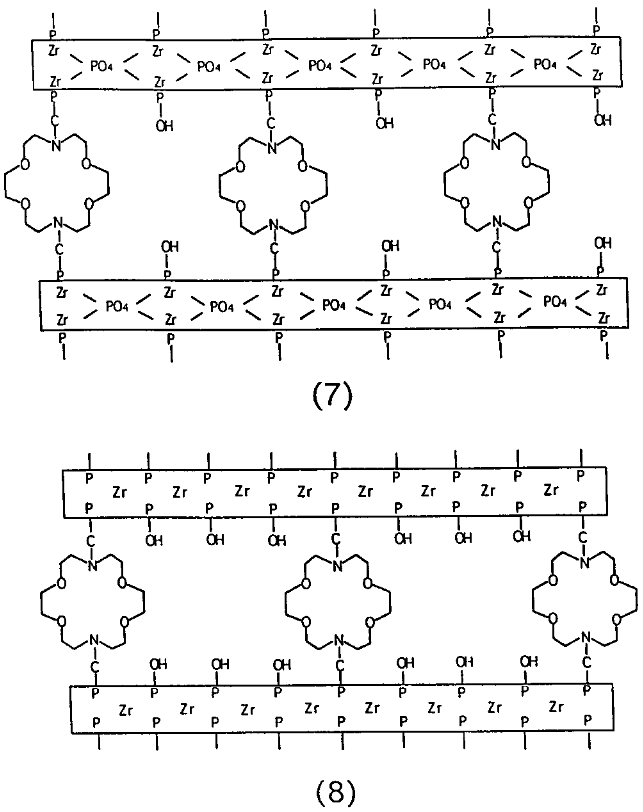

Figure 3. Schematic representation of compound **7**, in which the zirconium atoms are bridged by orthophosphate groups within the layers and O_3P groups with either pendant OH group or cross-linking azacrown phosphonate groups, and compound **8**, which has an α-type $Zr(O_3P)_2$ layer with the azacrown cross-linking phosphonate groups spaced farther apart than those in compound **7**.

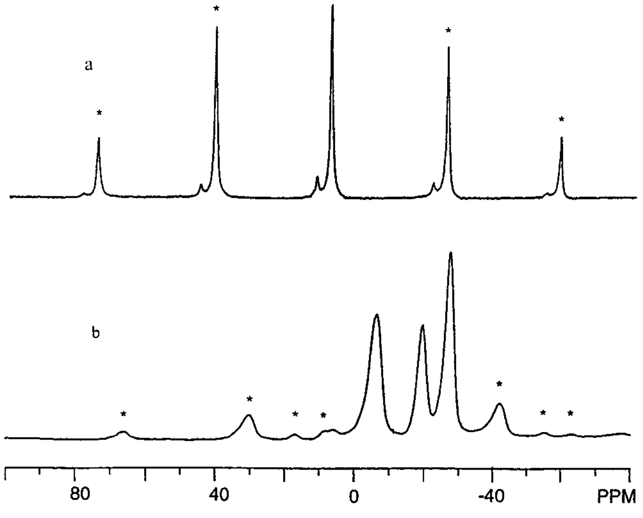

Figure 4. (a) ^{31}P MAS NMR spectrum of *N*,*N*′-(phosphonomethyl)-1,10-diaza-18-crown-6 (compound **6**, Scheme 1) and (b) the diazacrown ether bonded as in compound **7**. Asterisks denote spinning sidebands.

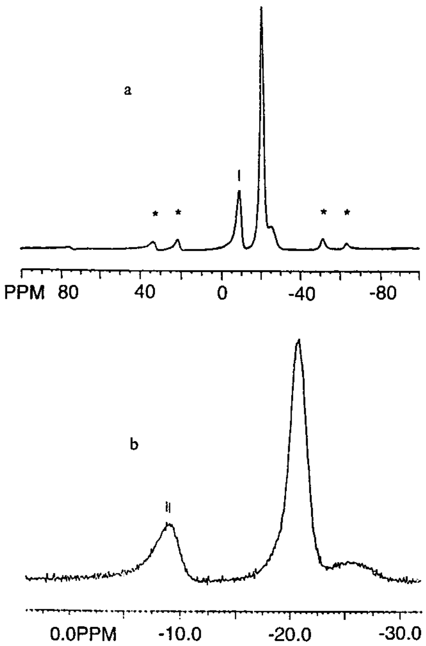

Figure 5. (a) ^{31}P MAS NMR spectrum of compound **8**, Scheme 1, and (b) the same spectrum on an expanded scale and with resolution enhancement. Asterisks denote spinning sidebands.

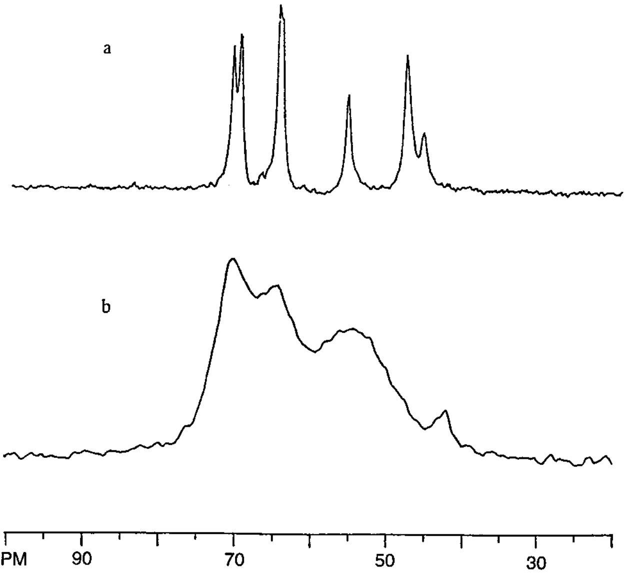

Figure 6. ^{13}C NMR spectrum of (a) the diazacrown phosphonic acid (compound **6**) and (b) the same spectrum of the diazacrown attached at both ends to the layers in compound **7**.

model layer used was of the α-type since it was expected that this would be the layer type, and the interlayer separation, taken from the X-ray powder pattern, was 14.7 Å. It was found that the azacrown ether as determined from its crystal structure could not span the interlayer distance of this magnitude. It was necessary to choose a more elongated conformation, as shown in Figure 7, to span the layers. This model reveals that the conformation of the crown ether is more rectangular than that of the unbonded compound **6**. The elongation may be partly responsible for the line broadening of the NMR peaks for the bound aza crown. Furthermore, the model shows that the crown ether rings overlap slightly, fitting poorly onto the α-type layer, and that the orientation of the cross-links is oblique and not perpendicular as shown in Figure 3. This overlap is reasonable considering that the distance between phosphorus atoms in α-zirconium phosphate is 5.3 Å. Reference to Table 2 shows that the width of the crown ether ring exceeds this value. In adding phosphoric acid to the reaction mix O_3POH groups affix to the layers, allowing sufficient room for the azacrown ring. This was not taken into account in the model. Obviously, a more

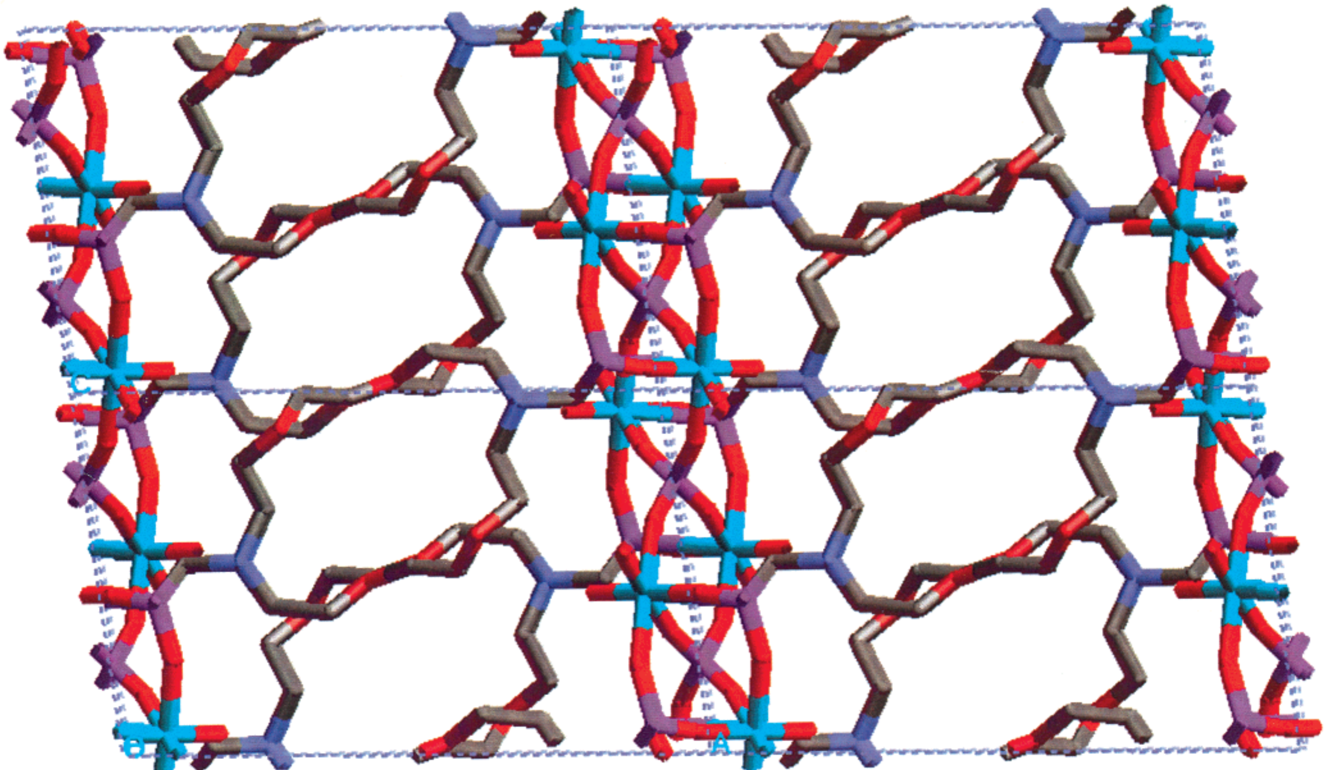

Figure 7. Schematic representation of the crown ether pillared structure with α-zirconium phosphate-type layers as determined by a computer model. The Zr atoms are indicated in blue, oxygen atoms in red, phosphorus atoms in purple, carbon atoms in gray-black, and nitrogen in dark blue.

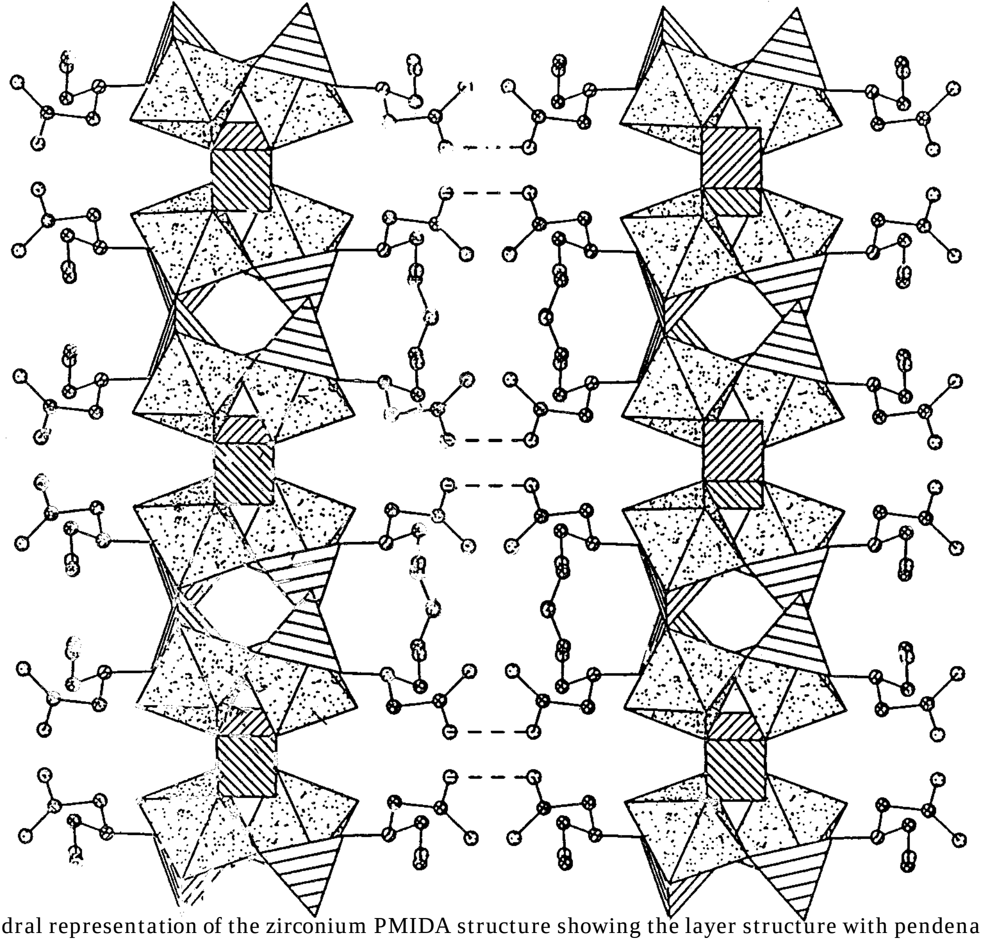

Figure 8. Polyhedral representation of the zirconium PMIDA structure showing the layer structure with pendenant iminodiacetate groups. The cubes with slanted lines represent orthophosphate groups in the middle portion of the layer bonded to Zr to form ZrO_6 octahedra (stippled). The phosphonate tetrahedra to which the PMIDA groups are attached are represented by tetrahedra with slanted lines, which appear as triangles. The pendent iminodiacetate groups have N (threaded circle), C (hatched circle), and O (dotted circle).

detailed model needs to take this into account and the study will include a PMIDA-type layer as well.

Discussion

Two types of zirconium-immobilized azacrown ether phosphonates have been prepared, mono- and bis(phosphonates).[9] The monophosphonates swell in water, allowing easy access of metal compounds to the rings. These compounds will be described in more detail in a subsequent paper. Recently, we prepared a cadmium *N*-phosphonomethyl)-1-aza-15-crown-5 that has a linear chain structure with the crown ether groups stacked as leaves on a twig.[23] The crown ether rings are only 3.5–3.6 Å apart, indicating that cooperative uptake of ion pair species may occur. For the zirconium compounds the evident disorder prevents a complete structure solution but the type of layers formed and their separation are revealed by NMR and X-ray data, respectively. We can now construct more detailed models of the structures based on this information. However, even the simple model presented here based on the α-type layer reveals why initially the PMIDA layer type forms. A polyhedral representation of the Zr PMIDA layer is shown in Figure 8. The placement of the orthophosphate in the central plane of the layers spreads the ZrO_6 octahedra farther apart than that in the α-layers. This relieves the stress on the pendant groups, allowing sufficient room on the layers to avoid close proton–proton approach. As the amount of monohydrogen phosphate groups attached to the layer was increased, the pendant crown ether groups become far enough apart to prevent crowding or proton–proton interactions among neighboring rings and the α-type layer formed. In all cases the nitrogens of the crowns are protonated and this charge requires the presence of free anions for compensation. Anion exchange was demonstrated by washing the solid (**8**) with dilute nitric acid where upon the fluoride ion was replaced by nitrate groups as shown by a lack of ^{19}F resonance in the NMR spectrum.

These crown ether derivatives represent an intriguing new class of supramolecular compounds. The cadmium *N*-phosphonomethyl-18-crown-6 was obtained as single crystals so its structure was precisely determined. This result portends the synthesis of a host of ordered arrays of crown ethers with different arrangements and potential cooperative phenomena relative to ion transport.

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Supporting Information Available: Tables of X-ray positional and thermal parameters (Tables 1S and 2S), torsion angles (Table 3S), and crystallographic data (Table 4S) for compound **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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