Crystal Engineered Supramolecular Metal Phosphonates: Crown Ethers and Iminodiacetates

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Three classes of metal phosphonates will be described in this brief review. First, we describe the zirconium derivatives of *N*-(phosphonomethyl)iminodiacetic acid, $H_2O_3PCH_2N(CH_2COOH)_2$. The acid itself is a zwitterion formed by transfer of a phosphonic acid proton to the nitrogen. Consequently, the acid forms a phosphonic acid dimer (O···O, 2.61 Å). Each carboxyl group then hydrogen bonds with phosphonate oxygens to form a three-dimensional network of short hydrogen bonds. A linear chain compound is formed when the phosphonic acid was combined with Zr(IV), but the addition of phosphoric acid as a spacer molecule results in the formation of layered compounds. When limited amounts of phosphoric acid were added, the layer that formed was of a new type embodying features of both the α- and γ-type zirconium phosphate layers. Increased addition of H_3PO_4 allowed the layers to revert to the α-type. A series of *N*-(phosphonomethyl) aza-crown ethers were prepared and reacted with M(IV) and M(II) ions. With zirconium, the layered compounds have structures similar to those of the *N*-(phosphonomethyl)iminodiacetic acid. However, with the divalent elements and Ce(IV), linear chain compounds resulted. These compounds have been described as macroscopic leaflets since the crown ether portions resemble leaves bound to twigs. The chains are either formed by covalently bonded metal phosphonate bridging or self-assembled hydrogen bonding of phosphonic acid dimers, which in turn are linked by extremely short (2.45 Å) chain-forming hydrogen bonds. These compounds show promise for use in separation science and catalysis and for design of a wide variety of structures with built-in physical properties.

Introduction

During the last 2 decades, we have expended major effort toward metal phosphate chemistry. Our reasons for doing so were ably expressed in a review article by Tom Mallouk and his collaborators.[1] "Metal phosphonates have two endearing properties that have stimulated extensive exploration of their chemistry." First, they are made at low temperatures in which the bonding within the reactant molecules is retained. Thus, the phosphonate moiety may bear functional groups that do not disturb the bonding to the inorganic portion of the molecule. The second attractive feature is their potential for supramolecular assembly.

Crystal engineering is a relatively new field of chemical research concerned with controlling or predicting the type of structures that can be formed from a given ligand. Not only can such techniques be used to generate new materials with specific physical properties, but it can also result in a better understanding of solid-state topochemically governed reactions. Phosphonic acids have been shown, in previous studies by our group, to form extremely strong hydrogen bonds as the basis of their solid-state structures. We have begun to exploit these properties in the formation of layered and linear supramolecular arrays of crown ethers and covalently bonded metal phosphonate polymers. In this short review, we shall emphasize all of these points with illustrations from our most recent work. These include iminodiacetic acid compounds, linear and layered crown ether arrays, and hydrogen-bonded complex metal phosphonates.

Table 1. Hydrogen-Bond Data for *N*-(Phosphonomethyl)iminodiacetic Acid

D−H···A	D···A (Å)	DHA∠ (deg)
(P−)O11−H11···O12	2.607(2)	174
(C−)O21−H21···O13	2.631(2)	174
(C−)O31−H31···O12	2.594(2)	159
N−H···O13	2.761(2)	159

Experimental Results

We will begin our excursion by examining the compounds formed by *N*-(phosphonomethyl)iminodiacetic acid, $H_2O_3PCH_2N(CH_2COOH)_2(H_2PMIDAH_2)$, upon reaction with zirconium(IV). This phosphonic acid was prepared as described by Moerdritzer and Irani.[2] An ORTEP representation of this compound is shown in Figure 1. The important feature of the structure is that the conformation of the molecule is controlled by hydrogen bonding. Hydrogen-bonding data are presented in Table 1. One of the phosphonate protons is transferred to the nitrogen atom, forming a zwitterion. This transfer leaves a negative charge on O12 of the phosphonate group. As a result, dimerization occurs as shown in Figure 1, with the formation of dual O11−H···O12 hydrogen bonds (O···O, 2.61 Å). Each carboxyl group then also forms hydrogen bonds of the type C−O−H···O−P with O12 and O13 of the phosphonic acid groups. This hydrogen-bonding scheme is completed by an N−H···O13 bond between an N−H donor group on one

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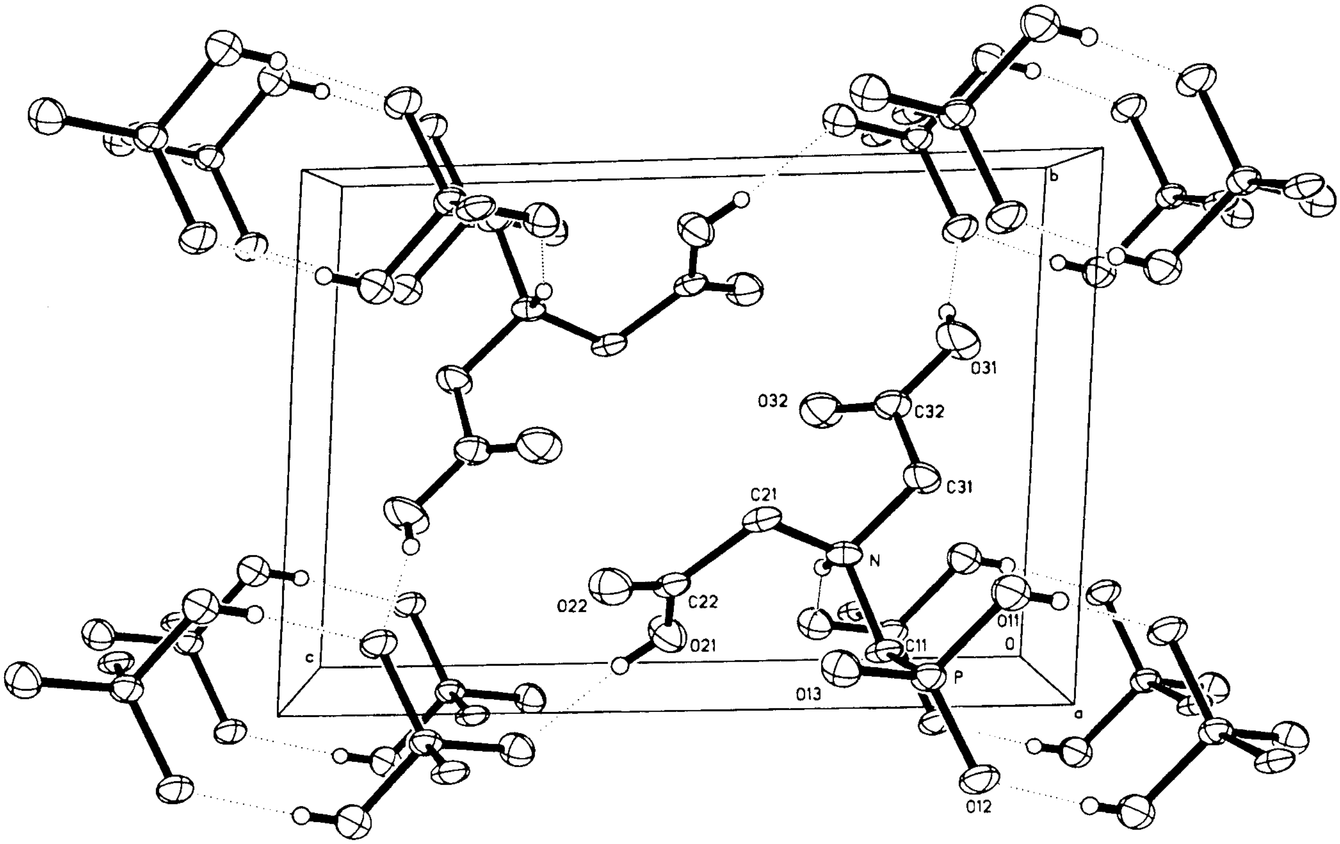


Figure 1. ORTEP drawing of a view down the *a*-axis of $H_2PMIDAH_2$. $a = 5.5962(6)$, $b = 7.4200(6)$, $c = 10.6483(8)$Å, $\alpha = 93.125(6)°$, $\beta = 94.993(7)°$, $\gamma = 90.376(8)°$. Dotted lines indicate hydrogen bonds.

molecule to P−O13 of an adjacent molecule. We note that all the hydrogen bonds are relatively short, and as we shall see, this is a feature of hydrogen bonding in phosphonic acids. The angles about the nitrogen atom are truly tetrahedral, ranging from 108.9° to 114.5°.

Reactions of $H_2PMIDAH_2$ with Zr(IV). Three compounds were obtained by variation of the reaction conditions. In the first, the phosphonic acid was dissolved in ammonia and then added to an HF solution of $ZrOCl_2 \cdot 8H_2O$. Heating to 90 °C, cooling, and allowing the solution to slowly evaporate produced small platelet-like crystals. The resultant compound had the composition $NH_4ZrF_2[H_3\{O_3PCH_2NH(CH_2COO)_2\}_2] \cdot 3H_2O \cdot NH_4Cl$. The compound consists of linear chains of ZrO_4F_2 octahedra and O_3PC tetrahedra, as shown in Figure 2. The fluoride ions occupy the axial positions, while the equatorial positions are filled by phosphonate oxygens. The chains are formed by the bridging of Zr atoms by the phosphonate groups as shown in Figure 2. The third oxygen of each phosphonate group is not involved in bonding, although it is deprotonated. However, the nitrogen atoms are protonated, as evidenced by the observed tetrahedral bond angles C−N−C average 113.9(2)°.

The carboxyl groups are not involved in bonding to zirconium, but are rather projected into the interchain space. One of the carboxyl groups hydrogen bonds to its symmetry-related carboxyl group in an adjacent chain by sharing a proton that is located at the center of symmetry. The O⋯O distance is 2.49 Å. The other carboxyl group bonds toward the metal phosphonate chain and hydrogen bonds to the phosphonate oxygen that is not involved in bonding to Zr. This phosphate oxygen also bonds to a water molecule, (O⋯O, 2.71 Å); ammonium ion and the charge-balancing chloride ion (half-occupancy) are held in the interchain space.

Chain compounds are rare in zirconium phosphate chemistry, although such compounds are known for uranyl phosphonates,[4a,b] molybdenyl phenylphosphonate,[4] and $HFe(O_3PC_6H_5)_4$.[5] Most zirconium phosphonates are layered in nature,[6] with the layers having an α-Zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$, structure (ZrP for short).[7] In this structure, the Zr atoms lie almost in a plane and are bridged by phosphate groups.[7] Three of the phosphate oxygens bond to three different metal atoms and alternate above and below the plane. The fourth oxygen is protonated and points into the interlamellar space forming hydrogen bonds with the water molecule. The interplanar distance is 7.65 Å and the area occupied by the phosphate group is 24 $Å^2$. For a phosphonate ligand to form an α-type layer upon reaction with Zr, the organic group should not exceed this value. However, it is possible to accommodate a larger pendant group by including spacer molecules into the reaction mix. A classic example of this technique was supplied by Alberti et al.[8] They carried out a reaction of 3,5,3′,5′-tetramethylbiphenylene-4,4′-bis(phosphonic acid) with zirconyl chloride using phosphorous acid as a spacer. The biphenyldiphosphonic acid cross links the α-ZrP layers, but with the methyl groups in positions adjacent to the phosphonic acid groups, the ligand extends beyond the 5.3-Å separation of phosphate positions on the α-ZrP layer. By interposing the spacer group, the larger biphenyl pillars occupy every other position on the layer (10.6 Å apart). This alternation of pillar and spacer produces a porous product with a pore size of ≈6 Å and a surface area of over 300 m^2/g (Figure 3).

Being cognizant of the above behavior of phosphonate ligands, we had prior to the preparation of the linear PMIDA complex prepared compounds using phosphate ions as spacers.[9,10] The products obtained were layered, but the layer structure depended upon the ratio of phosphate to phosphonate in the reaction mix.

$-PO_4/-PO_3H_2$ Ratio 1 (Compound I). This layered compound was prepared from a mixture of H_3PO_4 and H_2-$PMIDAH_2$ in a 1:1 ratio added to an aqueous solution of zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$, in aqueous HF. The mixture was heated at 60 °C until a fine, white powder precipitated. The structure was solved, utilizing X-ray powder data obtained at the Synchrotron Light Source, Brookhaven National Laboratory.[9] This compound has a new layer-type structure that contains features of both the α-ZrP layer and γ-zirconium phosphate (γ-ZrP) layers.

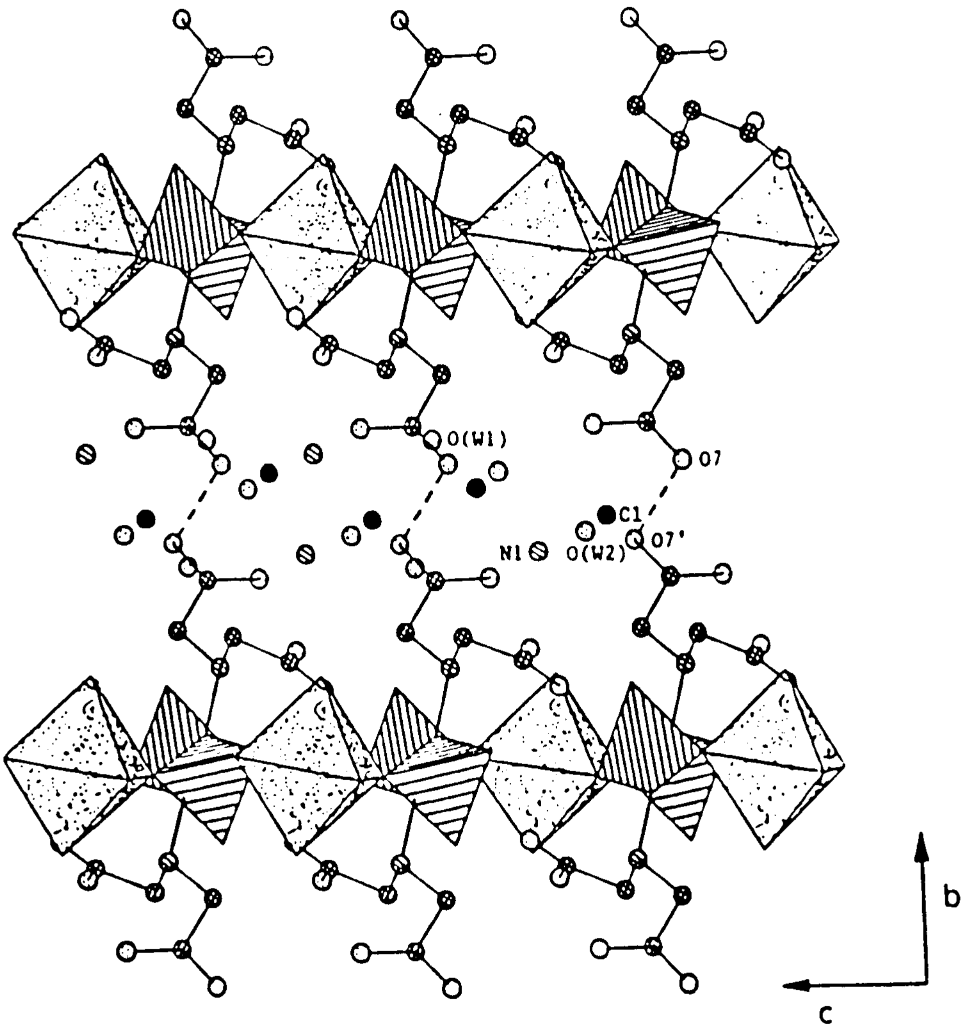


Figure 2. Mixed polyhedral-ball-and-stick representation of Zr−PMIDAH compound showing the linear chains oriented in the *c*-axis direction and the disposition of the iminodiacetic acid phosphonate groups. The stippled octahedra represent ZrO_4F_2 groups, and the striped tetrahedra represent PO_3C moieties.

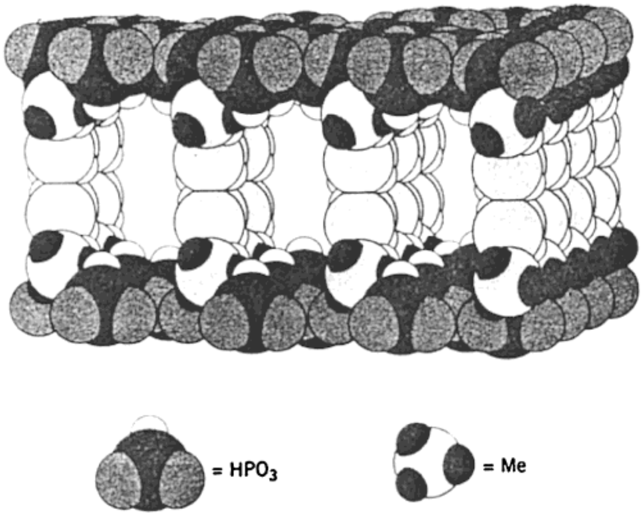


Figure 3. Computer-generated model of the pillared microporous compound of composition $Zr(HPO_3)_{1.34}(O_3PRPO_3)_{0.33}$ where R represents the tetramethylbiphenyl group. Reprinted with permission from reference 8 (Wiley-VCH).

γ-ZrP was first prepared by adding a mixture of ammonium or sodium dihydrogen phosphate to zirconyl chloride in HCl.[11] It has the composition $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$ and an interlayer distance of 12.2 Å. The layer contains both orthophosphate groups that bond to four different Zr atoms and dihydrogen phosphate groups in which two of the phosphate oxygens bridge adjacent Zr atoms and the two hydrogen phosphate groups point into the interlamellar space, as shown in Figure 4.[12]

The 1:1 layered compound has the composition $Zr_2(PO_4)[H\{O_3PCH_2NH(CH_2COO)_2(H_2O)\}_2]$ and represents a new type of layer. The orthophosphate group is situated in the middle of the layer and bonds to four different Zr atoms. This positioning of the phosphonate group is similar to that in the γ-ZrP. The phosphonate groups lie on the outer periphery of the layer and bridge across three Zr atoms through O−P−O type bonds as in α-ZrP. The iminodiacetic acid groups then project into the interlamellar space as shown in Figure 5. The metal coordination is six, two oxygens from two phosphate groups, three oxygens from three phosphonate groups, and the remaining metal site occupied by a water molecule. The carboxyl groups are deprotonated except for one proton that most likely is shared between two carboxylated oxygens as shown by the dashed line in Figure 5. The two oxygens are related by a 2-fold axis at $^1/_2$, y, $^1/_4$. The distance between them is 2.54(1) Å, but with only one proton. Thus, it is postulated that the proton lies on the 2-fold axis equidistant from the two oxygens. A second weak hydrogen bond (O⋯O 2.96 Å) occurs between the coordinated water molecule and an oxygen atom of the carboxyl group not involved in the short interlayer H bond.

This new layer type, by placing an orthophosphate group totally within the layers, increases the distance between metal

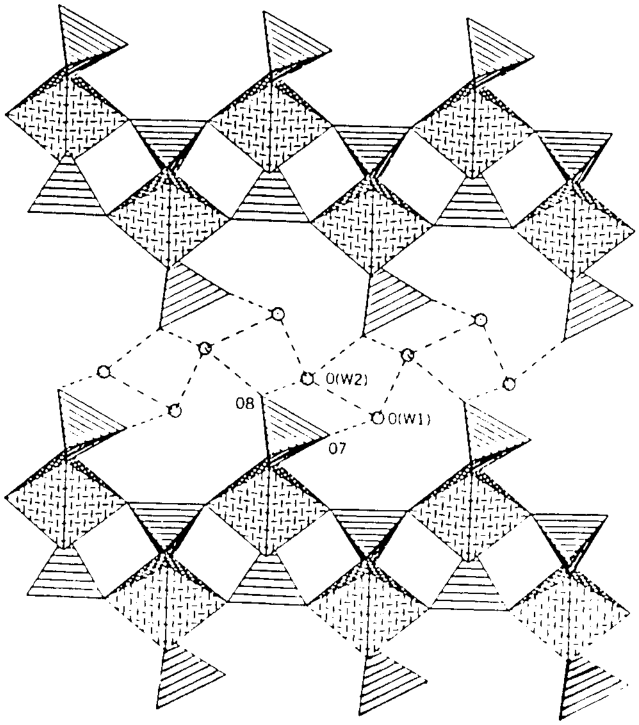


Figure 4. Polyhedral representation of the structure of γ-zirconium phosphate as viewed down the *a* axis. The white squares are the PO_4 groups bonding to four different Zr atoms within the layer and the striped tetrahedra are H_2PO_4 groups showing the hydrogen bonding between the pendant POH groups and the interlayer water molecules.

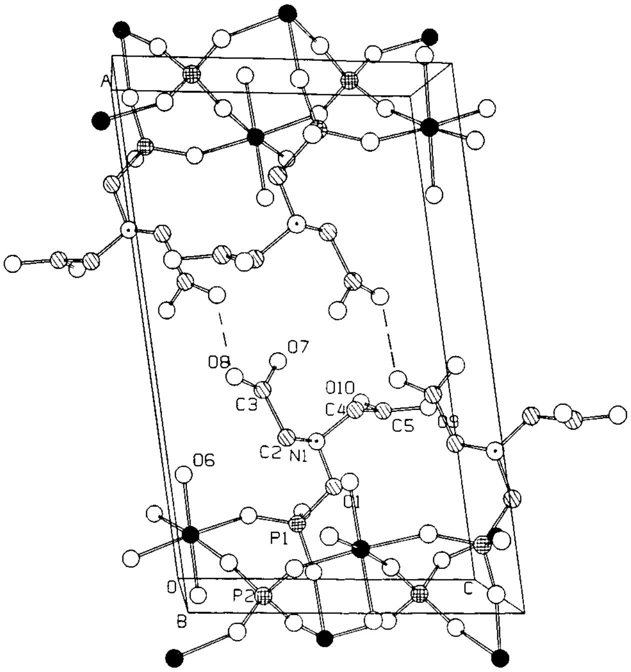


Figure 5. A ball-and-stick representation of the layered compound, $Zr(PO_4)[H\{O_3PCH_2NH(CH_2COO)_2(H_2O)\}_2]$, showing the PO_4 groups bonding to four Zr atoms and the disposition of the iminodiacetic acid groups between the layers. The dashed line represents the strong H bond between layers.

atoms, which increases the surface area by about 16% over the area available in the α-type layer. This increase in area allows the formation of a layered, rather than a linear, complex.

$PO_4/RPO_3H_2 = 2-4$ (Compound II). Increasing the ratio of phosphoric acid to phosphono-iminodiacetic acid in the range of 2−4 produced a series of compounds whose composition may be described by the general formula $Zr_2(PO_4)(HPO_4)_x[H_{1-x}\{O_3PCH_2NH(CH_2COO)_2\}_{2-x}(H_2O)_2]$. At a ratio of 4, $x = 0.5$, and this ratio is the limiting value of *x*. In this series the layer structure is essentially the same as that in compound **I**, but with increasing substitution of monohydrogen phosphate groups for phosphonate groups. This conclusion was drawn from a consideration of the ^{31}P MAS NMR spectra. The spectrum of compound I contained a doublet centered at −8 ppm and a single peak at −28 ppm. This latter resonance is due to the orthophosphate group, as had been shown earlier for γ-ZrP.[13] The doublet is assigned to the phosphonate phosphorus atoms as many spectra of zirconium phosphonates exhibit a peak in this region of the spectrum.[14] The doublet indicates that the two phosphonate groups have slightly different environments and this requires lowering the symmetry from *P*2/*c* to *Pc*, but the powder data did not allow refinement at the lower symmetry.[9]

The compound II series yielded a new peak at −20 ppm, resulting from the presence of the monohydrogen phosphate group.[13] As the ratio of H_3PO_4 to phosphonic acid increased, the peak at −20 ppm increased, while the phosphonate peak decreased in intensity. Integration of the peaks revealed that the total amount of phosphorus at the three resonances, −7, −9, and −20 ppm, was always twice as much as that at −28 ppm as required by the formula. These results are good evidence that the HPO_4^{2-} groups selectively replace an equal number of phosphonate groups bonded to zirconium.

$PO_4/RPO_3 > 4$. When the level of phosphoric acid was increased beyond a ratio of 4, the peak at −28 ppm was no longer present but now the ratio of the resonance at −20 ppm relative to the peak at −8 ppm, now a singlet, increased. This change in spectrum was interpreted as indicating the layer to now be of the α-type as α-ZrP produces a single resonance at −19 ppm arising from the HPO_4^{2-} groups.[13] This spectral type of analysis was required because the crystallinity of the mixed ligand products decreased to the point where X-ray structure determinations were not possible.

Elemental analysis of the α-type complex, termed Compound III, indicated that the ratio of HPO_4^- to iminodiacetic acid ligands was 3:1. This increase in the amount of monohydrogen phosphate groups leads to a more open structure in compound III. The interlayer spacing is ≈11.3 Å which is dictated by the phosphonate groups; with perhaps some interdigitation, the interlayer spacing of both compounds I and II is 15.2 Å. The sum of half the interlayer spacings of α-ZrP and compound I is 11.4 Å, just the value observed for compound III. Thus, the pendant iminodiacetic acid groups are able to align themselves opposite the HPO_4^- groups in the adjacent layer. A schematic representation is shown in Figure 6. There must, of necessity, be strong hydrogen bonding between the layers.

Amine Intercalation and Chemical Considerations. Compounds I−III were found to intercalate amines. Intercalation was effected through both gas−solid and dilute amine solution−solid methods.[10] In both cases, a bilayer of primary amines forms in the interlamellar space. The angle of tilt from the perpendicular position, as determined from the slopes of the interlayer distance versus the number of carbon atoms in the chain, was 28° and 26° for compounds I and II, respectively. These values are close to the value observed for α-ZrP.[15] The question arises as to how the amines are positioned in the interlayer space since there are two carboxyl groups per amine and also the protonated imino-nitrogens, one for each amine. The interlayer spacing of the butylamine intercalate (23.9 Å) represents an 8.7 Å increase over that of the parent compound I. In α-ZrP, this difference in interlayer spacing for butylamine amounts to 10.6 Å, even though the tilt of the amines in both environments is almost identical. It may indicate that the amines find positions between the protonated imino groups and the negatively charged carboxyl groups, thus, shifting them closer to the layers with attendant reduction of the interlayer spacing.

Compound III intercalates 1.4 mol of amine. In this case, the increase in interlayer spacing for the butylamine interca-

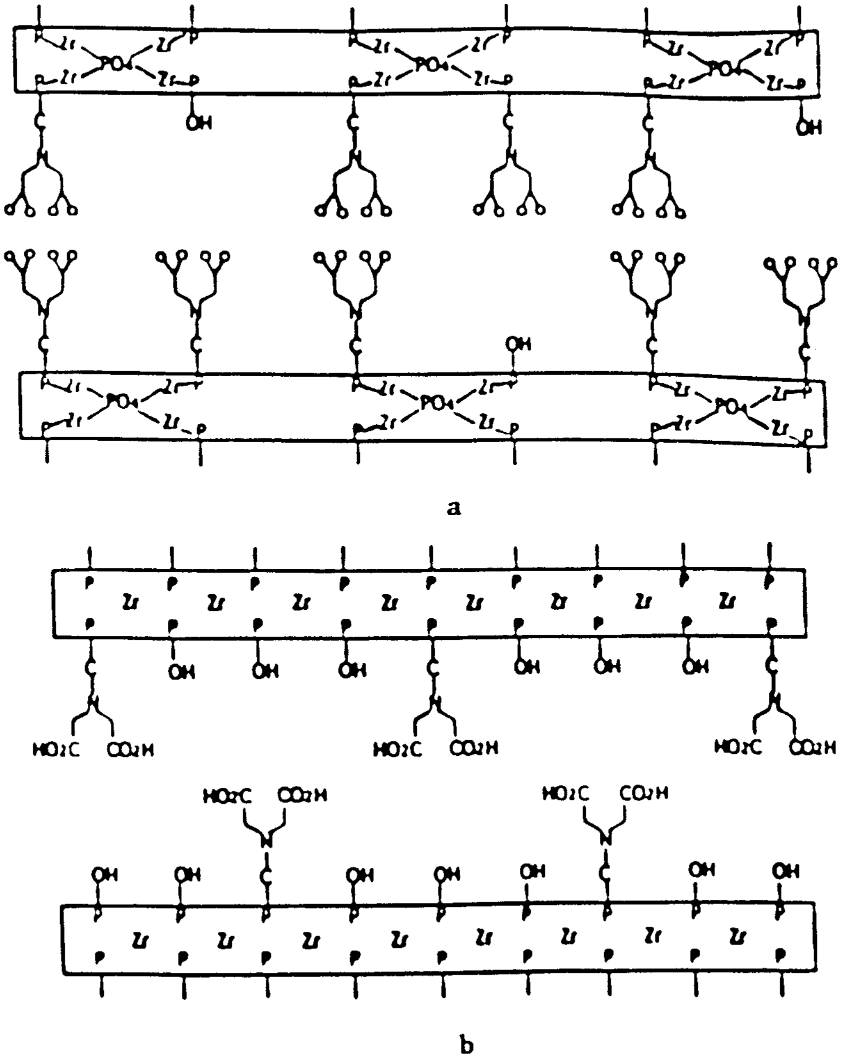


Figure 6. Schematic version of compound II (a) showing the orthophosphate group within the layers and noninterdigitation of the iminodiacetic acid groups. The interlamellar spacing is 15.2 Å. The illustration of compound III(b) positions the iminodiacetic acid groups of one layer over the HPO_4^{2-} groups of an adjacent layer, allowing closer approach of the layers to 11.3 Å. Both the monohydrogen phosphate and the phosphonate groups bridge to three Zr atoms as in α-ZrP.

late is 9.9 Å, indicating that the amines apparently locate close to the monohydrogen phosphate groups. In fact, there is just one amino group per HPO_4^- with the formula of this particular phase being $Zr_2(HPO_4)_3[O_3PCH_2N(CH_2COOH)_2]\cdot 3RNH_2\cdot H_2O$.

It is to be expected that the zirconium iminodiacetic acid phosphonate compounds described in the foregoing should behave as both ion exchangers and complexing agents. However, when the linear chain compound was contacted with aqueous salt solutions, certain chemical changes were observed. This compound yielded a single resonance for ^{31}P at −3 ppm in the solid-state MAS NMR[3] as required by the X-ray symmetry. There was only one peak at 31 ppm in the ^{19}F NMR spectrum representing fluorine in the axial positions of the ZrO_4F_2 octahedra. The linear ZrPMIDA compound is initially insoluble in water. However, when the mixture is warmed, a slow solublization occurs. Once dissolved, the solution showed a shift in the ^{31}P resonance to 8.8 ppm and the ^{19}F peak was shifted upfield by 160 to −130 ppm. This latter position is similar to that obtained for dissolved ammonium fluoride. It is evident that the fluorine was displaced, but the +FAB mass spectrum showed that the highest peak was at a mass of 541. This corresponds to a formula given by $\{ZrH_3[O_3PCH_2NH(CH_2COO)_2]_2\}^+$. Thus, we conclude that depolymerization occurs in solution with loss of NH_4F + HF. The vacated sites occupied by fluoride ions are apparently now occupied by carboxylate oxygens to form a monomer. Additional changes in the ^{31}P NMR spectra indicate a complex mechanism is operative that requires further study to elucidate.

No such complications arise with the layered compounds. Compound I is insoluble and, with a variety of cations, yields a distribution coefficient, K_d, of less than 100 mL/g. The distribution coefficient is defined as

$$K_d = \frac{(C_i - C_f)}{C_f}\left(\frac{V}{m}\right)$$

where C_i is the initial concentration of the solution in contact with the sorbent and C_f is the concentration at equilibrium. V/m is the volume of solution to mass of sorbent ratio. The higher the value of K_d, the more selective the sorbent for the species taken up. Since the pH of the tests was 2, the cations are in competition with the hydronium ion. The low K_d values for Compound I indicate that there is strong hydrogen bonding between layers and perhaps strong repulsion of the cation from the NH^+ groups.

In contrast, compounds II and III exhibited much higher values of K_d toward divalent transition metals and lanthanide cations. For La^{3+}, the K_d values were 11,130 and 25,550 mL/g for compounds II and III, respectively. We should expect higher K_d values in less acidic solutions because of the much lower concentration of protons competing for sites on the carboxylate and phosphate groups. This was actually found to be the case. At pH 5, the K_d values for Sr^{2+} uptake by compounds II and III were 80,640 and 188,000 mL/g, respectively. The comparable values at pH 2 were 645 and 769 mL/g. These prelimi-

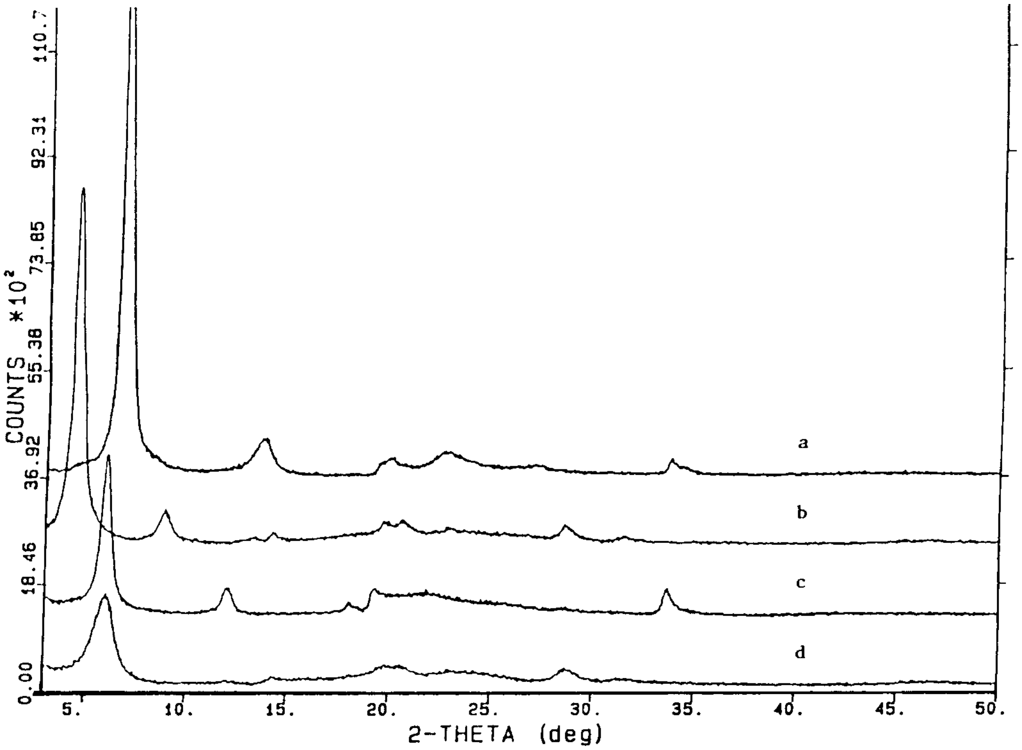


Figure 7. X-ray diffraction patterns of zirconium crown ether compounds. (a) Compound (4), d_{001} = 13.0 Å; (b) compound (3), d_{001} = 20.0 Å; (c) compound (8), d_{001} = 14.7 Å; (d) compound (7), d_{001} = 14.4 Å.

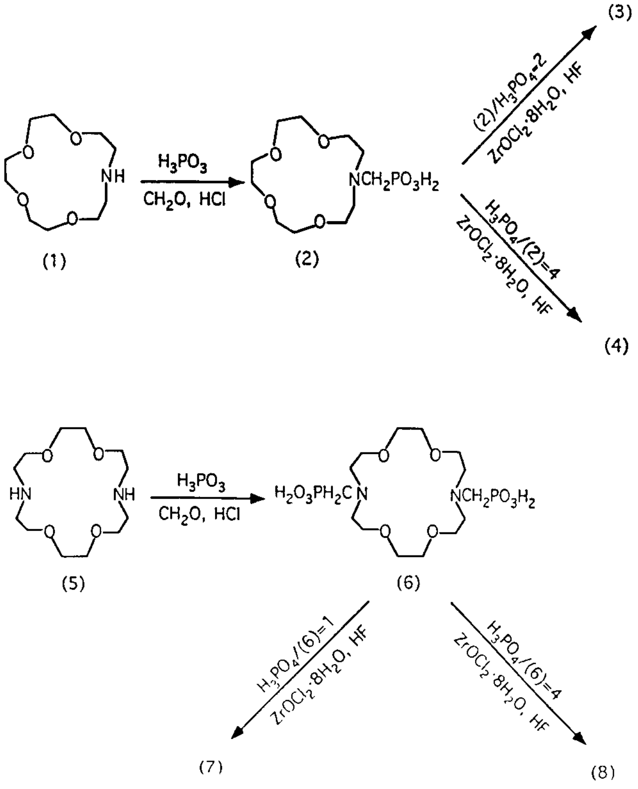
nary studies indicate that the Zr−PMIDA complexes may prove useful for certain separations, especially those based upon cation size and charge.

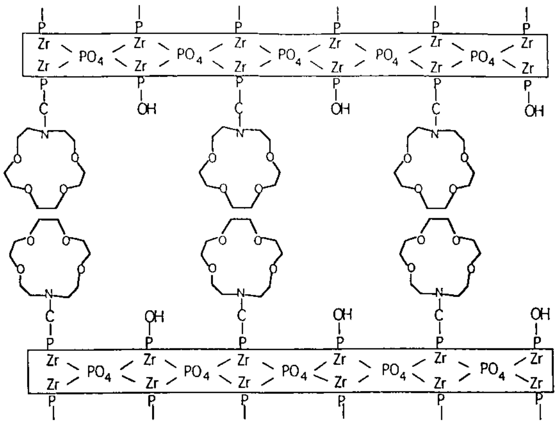
Supramolecular Crown Ether Arrays. Crown ethers have been intensively studied during the past 30 years[16] because of their selective complexation properties[17] and because their study provides for exploration of structural assembly.[17a,18,19] Interest also stems from the chemical and biological potential of these compounds as ion exchangers[20] and possible agents for transporting ionic species in living tissues.[21] Macrocyclic ligands are remarkable for their selective sorption of metal ions, making them excellent choices for separation of these species.[17b] However, the recognition ability of crown ethers is somewhat comprised in aqueous solution by the leveling effect of the solvent. Researchers have attempted and largely succeeded in increasing the selectivity of the host by synthesizing more complex structures.[19a,23] However, one of the major problems in using crown ethers in separations and other processes such as catalysis is the loss of expensive macrocycles in solution resulting from their solubility.[24] One way to overcome this problem is to attach the macrocyclic ligands covalently to a solid support such as a polymer[25] or other solid matrixes.[24,26] In fact, industrial-scale separations require such fixation of the macrocycle to be economically viable. Similarly, bound macrocycles are used in catalysis[27] and phase transfer catalysis.[28]

Another approach that has been more recently examined is the immobilization of crown ethers or azacrown ethers on ordered layered matrixes. Brunet et al.[29] 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.[30a,c] carried out similar ester interchange reactions using the phosphonic acid of benzo-15-crown-5. 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 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.[30b,c]

Recently, we prepared both the *N*-(phosphonomethyl)-aza-15-crown-6, (2), and *N*,*N*′-bis(phosphomethyl)-1,10-diaza-18-crown-6, (6), compounds and synthesized layered zirconium derivatives of these acids by direct reaction with Zr(IV) solutions.[31] Phosphoric acid was added to the reaction mix to produce mixed phosphate−phosphonate groups on the layers. The reactions are outlined in Scheme 1. The resultant compounds were poorly crystalline, as shown by the X-ray patterns

Scheme 1





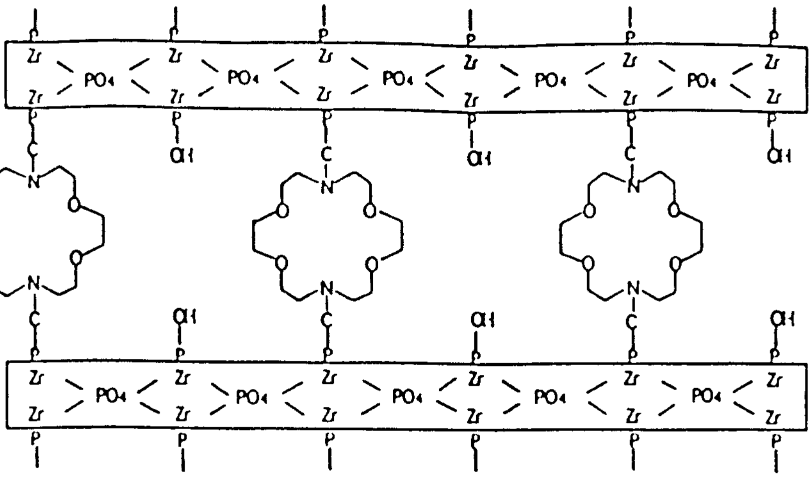
(3)

Figure 8. Schematic drawing of compound (3) depicting the bilayer of crown ethers separated by $HOPO_3$ groups. The orthophosphate groups bonded to four Zr atoms within the layer, whereas the monohydrogen phosphate groups bridge three Zr atoms and project the hydroxyl group into the interlayer space.

in Figure 7. However, the initial peak corresponds to the interlayer spacing. A combination of X-ray, NMR, and elemental analysis was used to determine the structures of the synthesized compounds.

There are two cases to consider, those products prepared from the aza-crown monophosphonic acid, compounds (3) and (4), and those obtained with the diaza-diphosphonic acid, compounds (7) and (8). In compound (3), the ratio of phosphoric acid to phosphonic acid was 0.5, which was increased to 4:1 in compound (4). The solid-state MAS NMR ^{31}P spectra contained two main peaks at −27.2 and −5.98 ppm and a smaller peak at −19 ppm. These resonances are the same as those determined for the layered Zr(PMIDA) derivative compound I and indicated the presence of an almost equal amount of the crown ether phosphonate and orthophosphate and a somewhat lesser amount of HPO_4^{2-}. With the aid of elemental analysis and TGA data, compound (3) was formulated as $Zr_2(O_3PCH_2NHC_{10}H_{20}O_4)_{1.17}(PO_4)(HPO_4)_{0.83}F_2{\cdot}Cl_{0.17}{\cdot}1.7H_2O$. ^{19}F NMR indicated that two types of fluorine were present, a peak at +45 ppm indicative of bonding to zirconium as in the Zr(PMIDA) compound and another at −123 ppm due to free fluoride ion. There was also some Cl^- determined by elemental analysis. We note that the aza-nitrogen is protonated, and apparently, the free F^- and Cl^- are required to neutralize the aza protons. Since the interlayer spacing is 20 Å, there is no interdigitation of crown ether groups. A simplified representation of compound (3) is presented in Figure 8.

In compound (4), the ^{31}P NMR did not contain the peak in the vicinity of −27 to 30 ppm, signifying the absence of the



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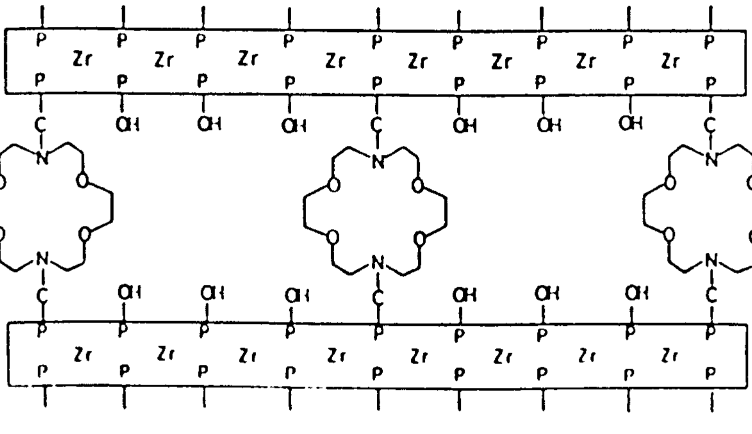


(8)

Figure 9. Schematic representation of cross-linked diaza-18-crown-6 bisphosphonates. Compound (7) has the same layer-type as Compound (3). Compound (8) has an α-type layer in which no orthophosphate is present and both the phosphonate and monohydrogen phosphate groups bond to three Zr atoms and extend into the interlamellar space.

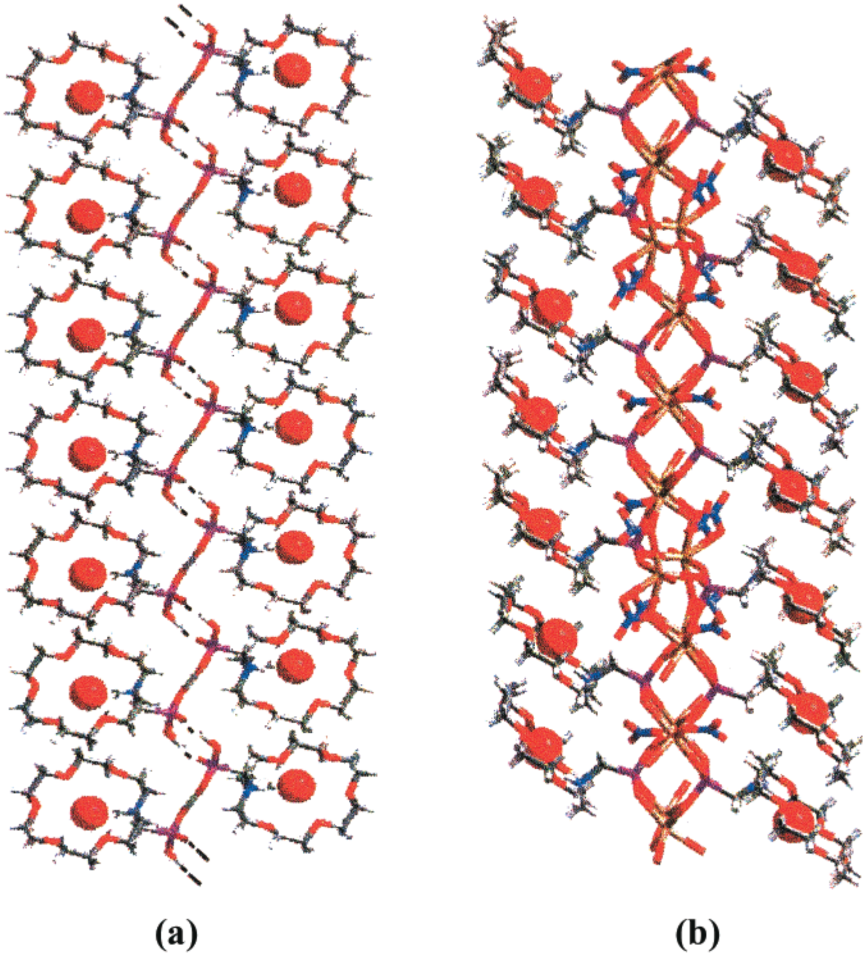
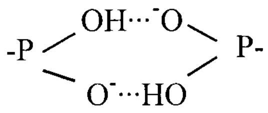


Figure 10. Schematic representation of the macrocyclic leaflets. (a) The self-assembled *N*-(phosphonomethyl)-aza-18-crown-6. The backbone is formed by hydrogen bonding of the phosphonic acid dimers shown by the dashed lines and the O−H−O region indicated by the gray line. Each crown ether ring contains a water molecule. (b) Cd_4 macrocycle, showing the more complex backbone, consisting of four Cd, three phosphonate, four nitrate, and three water groups. Note the difference in orientation of the macrocyclic groups in the two compounds.

orthophosphate group. The observed peaks were at −9.3 ppm (phosphonate) and −21.2 ppm (HPO_4^-). Elemental analysis coupled with thermogravimetric analysis (TGA) were in accord with the formulation of this compound as $Zr(O_3PCH_2NH-C_{10}H_{20}O_4)_{0.22}(HPO_4)_{1.78}F_{0.22}\cdot 1.86H_2O$. The fluorine was all present as free F^- as shown by ^{19}F NMR. The interlayer spacing of ≈13 Å indicates complete interdigitation of the crown ether groups. This formulation is in accord with the fact that there are approximately eight monohydrogen phosphate groups bonded to the layer for each crown ether. It would appear that by close control of the ratio of phosphate to phosphonate, a series of such compounds could be prepared, with the determination point at which the layer changes from the mixed orthophosphate γ,-α-type to pure α-type. It should also be noted that compounds (3) and (4) swell in water, allowing easy access of dissolved species to the crown ether.

In the case of *N,N′*-bis(phosphonomethyl)-1;10-diaza-18-crown-6, $HO_3PCH_2NHC_{12}H_{24}O_4NHCH_2PO_3H$, cross-linking of layers occurs as for other diphosphonic acids.[8,32] The crystal structure of the phosphonic acid revealed that the phosphonic acid groups are trans to each other and that the aza nitrogens are protonated.[33] The compound crystallizes as a tetrahydrate, space group $P\bar{1}$ with $Z = 1$. The center of the azacrown coincides with the center of symmetry. All of the hydrogens were determined experimentally, clearly delineating the hydrogen-bonding scheme. Partial deprotonation of the phosphonic acid groups results in the formation of strong hydrogen bonding with the adjacent phosphonic acid groups of the type



in which the O−H···O distance is 2.553(2) Å.

There are two such short hydrogen bonds at each end of the molecule forming linear chains along the cell diagonal. Extensive hydrogen bonding also occurs between the water molecules and both the phosphonic acid groups and the protonated azo-nitrogens. As we will further demonstrate, removal of a proton from a phosphonic acid group creates a short hydrogen bond because of the added attraction of a negatively charged oxygen.

The two compounds produced by the reaction of zirconyl chloride in aqueous HF with the diphosphonic acid also had different layer structures.[32,33] When the ratio of H_3PO_4 to diphosphonic acid was 1, orthophosphate was incorporated into the layers and monohydrogen groups at the layer periphery, as shown in Figure 9. The composition is represented as $Zr_2(O_3PCH_2NHC_{12}H_{24}O_4NHCH_2PO_3)_{0.75}(PO_4)(HPO_4)_{0.5}F_{2.5}\cdot 4H_2O$. In this compound, and the next one, the fluoride ions are not bonded to Zr but reside in the tunnels formed by the pillaring phosphonate groups.

The second compound, (8), was prepared with an increase in the amount of phosphonic acid (4:1 ratio) and yielded α-type

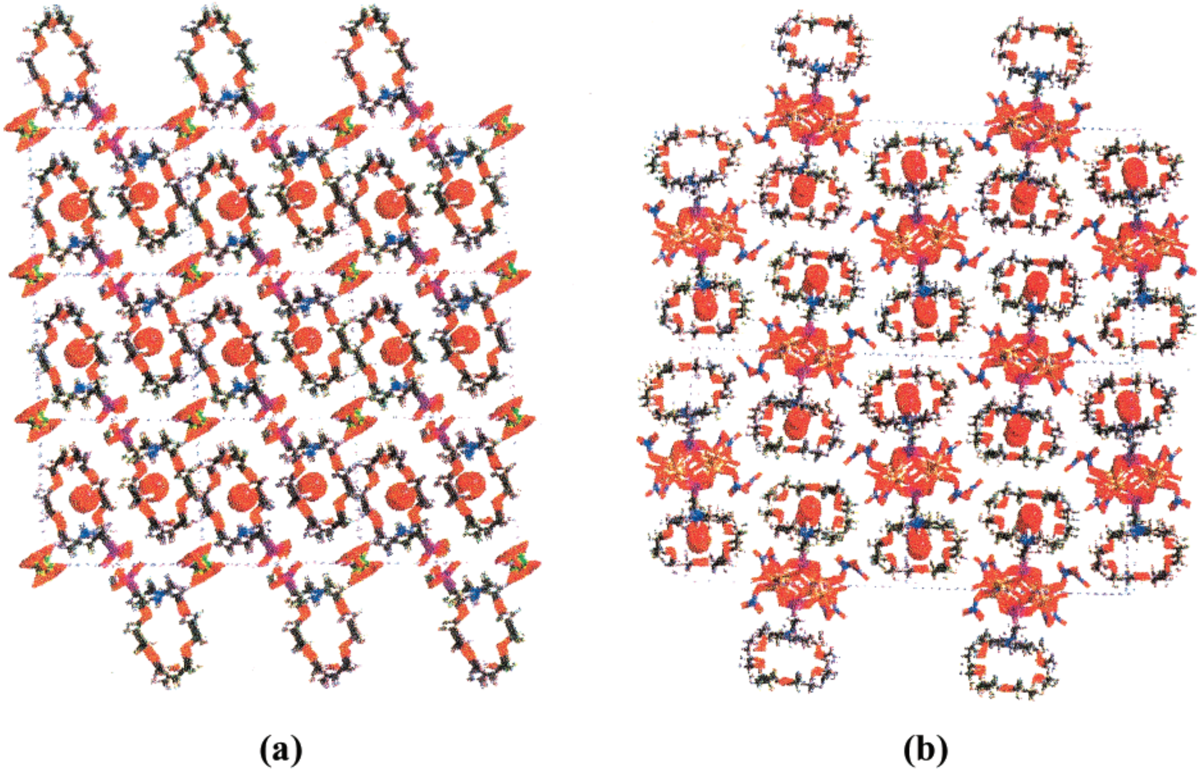


Figure 11. Packing diagrams of the macrocyclic leaflet: chains are oriented perpendicular to the plane of the page. (a) Self-assembled hydrogen-bonded leaflet with disordered perchlorate anions between the chains. (b) Cd_4 compound with nitrate ions between the chains. Note the formation of continuous channels in these compounds, which may facilitate cooperative effects and ion transport.

layers (Figure 9). Its composition is formulated as $Zr(O_3PCH_2NH^+C_{12}H_{24}O_4NHCH_2PO_3)_{0.33}(HPO_4)_{1.34}F_{0.66}\cdot 1.8H_2O$. Both cross-linked products had approximately the same interlayer spacings as would be expected from the size of the cross-linker.

An interesting observation is the fact that the ^{13}C resonances of the diazacrown diphosphonic acid, compound (6), were greatly broadened when it was attached as a layer cross-linking agent.[33] This broadening is thought to be due to the dispersion of local environments of the crown ether rings between the layers. A modeling study was also carried out in which the layer was assumed to have the α-type structure and only the 18-diazacrown-6 molecules were bonded to the layers. It was found[33] that the length of the diphosphonic acid molecule, as determined from its crystal structure, was insufficient to cross link the layers to produce an interlayer spacing of 14.7 Å. It was necessary to elongate the crown ether ring into a more rectangular shape to accomplish the correct layer spacing. Interestingly, the free diphosphonic acid already exhibited a more rectangular ring conformation over the original unphosphonated diaza-8-crown-6. This changed conformation of the ring may well affect their behavior as metal complexing agents and a study is now underway to determine the nature of this effect.

Macrocyclic Leaflets. We have demonstrated in the past, as has Mallouk,[34] that preparation of metal phosphonates of divalent metals generally yields crystalline products whose structures may be solved either from formation of single crystals or from their powder patterns.[32,35] Therefore, we carried out a number of reactions between divalent metals and crown ether phosphonic acids and were able to obtain single crystals for a number of them. For this purpose, we prepared N-(phosphonomethyl)-aza-18-crown-6, $H_2O_3PCH_2NC_{12}H_{24}O_5$, in a fashion similar to that shown in Scheme 1. This compound also exists as a zwitterion with a proton bonded to the aza-nitrogen. In general, an ethanolic solution of the crown ether was layered with the metal salts dissolved in ethanol.[36] In some cases, the solutions were treated hydrothermally to achieve single crystals.

Interestingly, use of cobalt(II) perchlorate hexahydrate did not result in the formation of a cobalt phosphonate. Rather, the phosphonic acid formed linear chains by self-assembly through hydrogen bonding (Figure 10a). The arrangement of the crown ethers on the chain resemble leaves on a twig, hence the title macrocyclic leaflets. The phosphonic acid groups hydrogen bond to form dimers in which the O···O distance is 2.501(3) Å. It turns out that the dimers gain one proton per dimer from the solution. This proton forms a hydrogen bond between the third oxygen of the phosphonate group, not involved in dimer formation, with a similar oxygen on an adjacent dimer (O···O, 2.415(2) Å), thus creating the chains. The closeness of the oxygens involved in this hydrogen bond indicates that they equally share the proton. The inclusion of this proton creates a positive charge of one per dimer and results in inclusion of perchlorate anions in channels between the chains (Figure 11a). The structure is completed by enclosing a water molecule within the crown rings. The encapsulated water forms five H bonds with the ether oxygens with O···O contacts of 2.9−3.0 Å and a shorter H bond with the NH group, N···O, 2.686(3) Å.

The reaction of the phosphonic acid with $Cd(NO_3)_2\cdot 4H_2O$ produced a complex cadmium phosphonate of composition $[Cd_4(O_3PCH_2NHC_{12}H_{24}O_5\cdot H_2O)_3(NO_3)_4(H_2O)_5]NO_3$. Despite this complicated formula, this compound also forms a leaflet-type structure (Figure 10b). The Cd(II) ions are six-coordinate. Each phosphonate group bonds to four cadmiums by forming one Cd−O−P−O−Cd linkage and having the third phosphonate oxygen bridge two other cadmiums. This arrangement of phosphonate groups results in the formation of a one-dimensional polymeric network in which each cadmium bonds to three phosphonate oxygens. The coordination sphere is completed by nitrate anions and water molecules. Half the nitrate ions bridge across metal atoms. The crown ether rings again form a leaflet structure in which the rings encapsulate

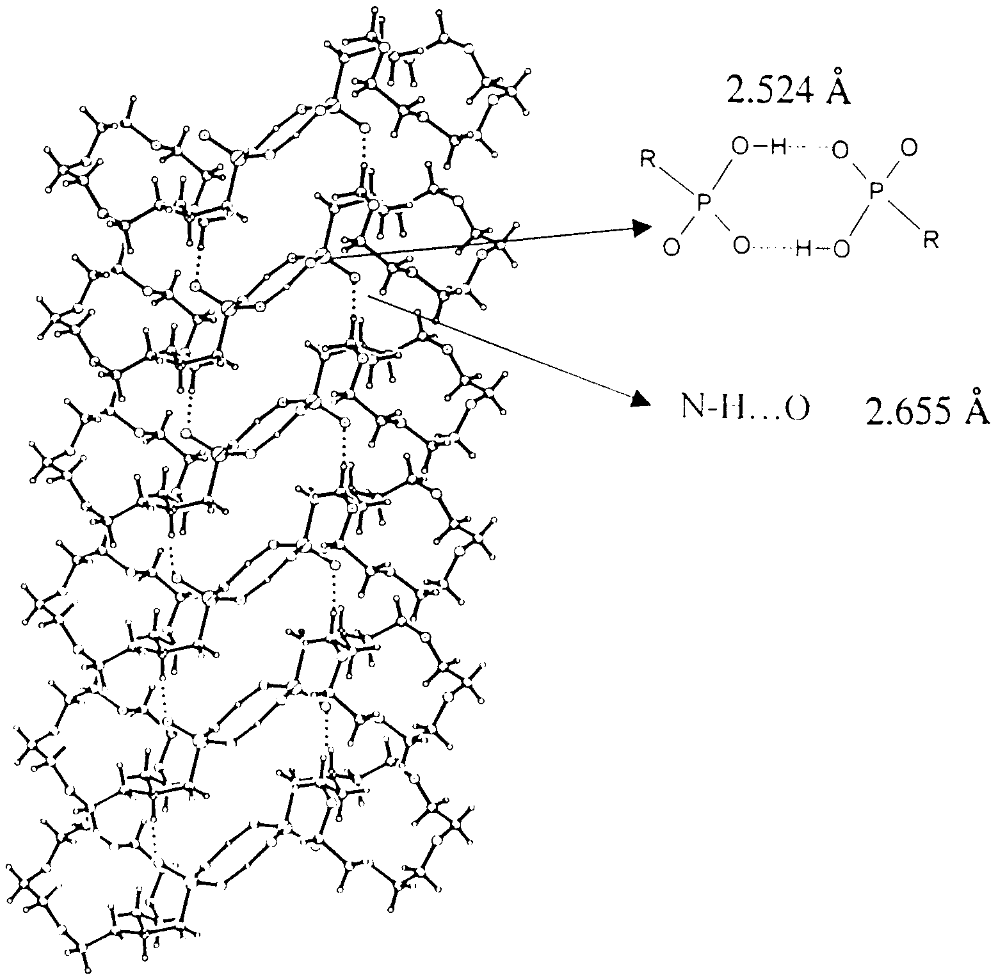
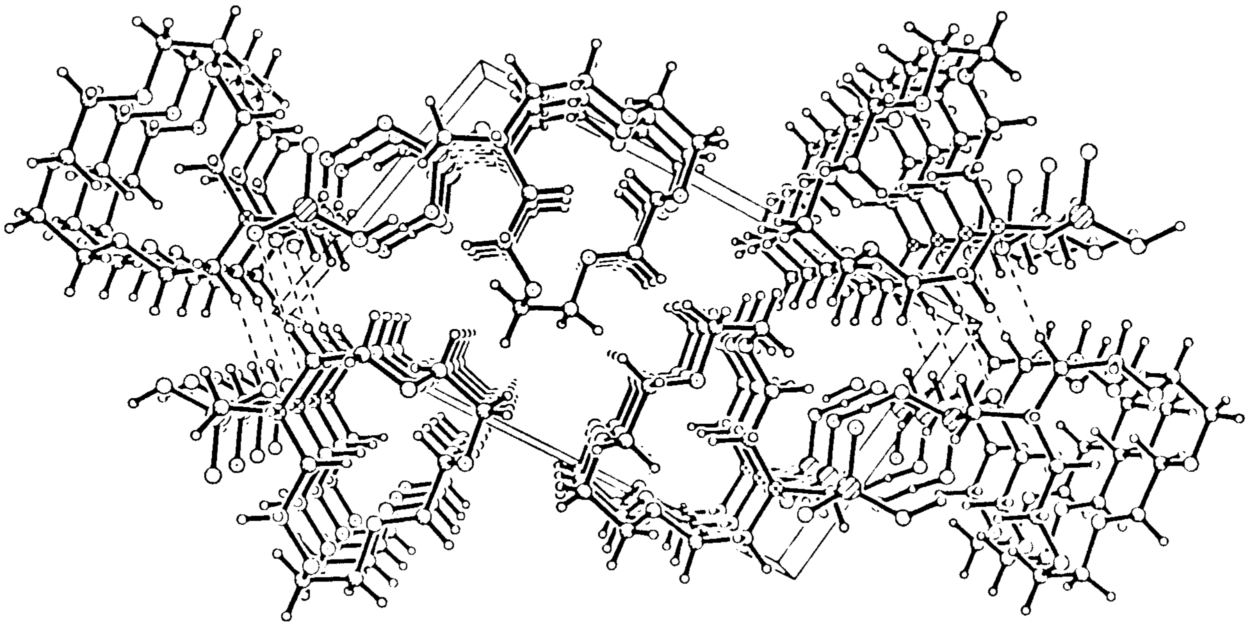


Figure 12. One-dimensional array of self-assembled *N*-(phosphonomethyl)-aza-15-crown-5 through hydrogen bonding.



a = 5.627(1) Å, b = 8.922(1) Å, c = 15.108(2) Å
α = 77.495(2)°, β = 84.520(2)°, γ = 72.537(2)°

Figure 13. Packing diagram of *N*-(phosphonomethyl)-aza-15-crown-5.

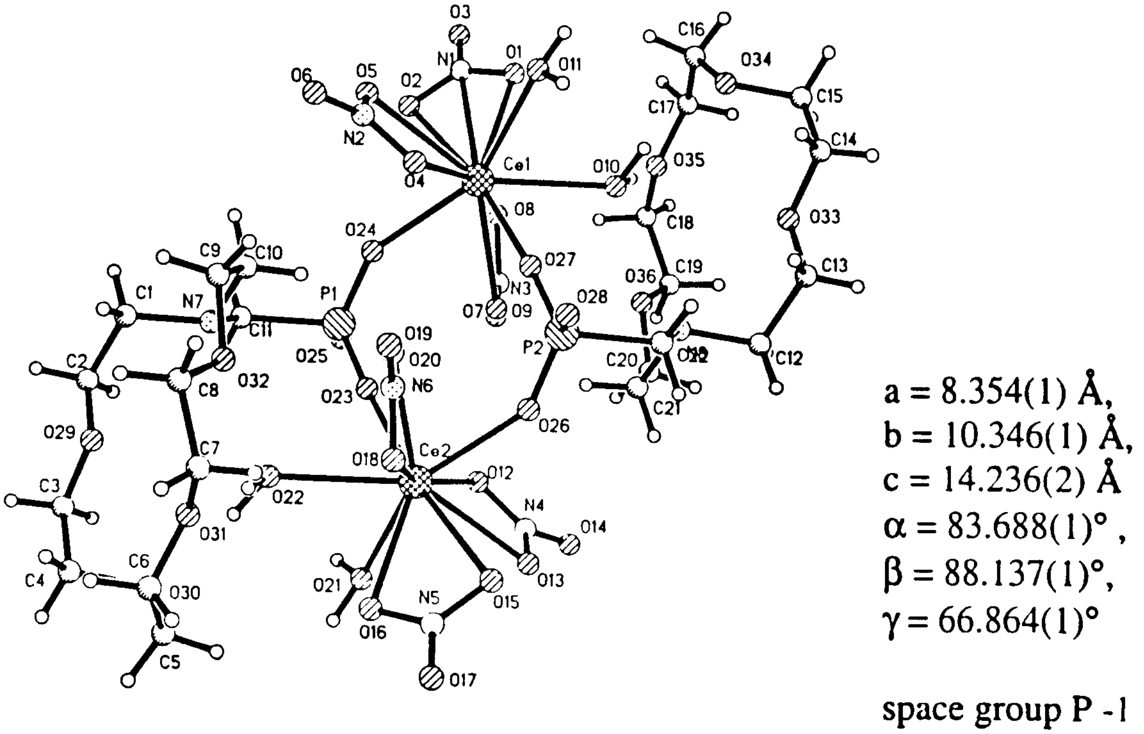


Figure 14. Discrete coordination bonded dimer of formula $[Ce(HO_3PCH_2NHC_{10}H_{20}O_4)(NO_3)_3(H_2O)_2]_2 \cdot H_2O$ formed by the reaction of *N*-(phosphonomethyl)-aza-15-crown-5 with $(NH_4)_2Ce(NO_3)_4 \cdot 2H_2O$.

water molecules. There are no short hydrogen bonds because both phosphonic acid protons have been removed by the metal and aza nitrogen atoms. The N−H···O water hydrogen bonds, of which there are three, and they are almost of the same length (N···O, 2.71(2), 2.72(2), 2.73(2) Å). The chains bear a single positive charge per four Cd(II) units, neutralized by nitrate groups between the stacked linear chains (Figure 11b).

Our experience in obtaining the macrocyclic leaflets with aza-18-crown-6 methylphosphonic acid prompted us to also examine reactions of *N*-(phosphonomethyl)-aza-15-crown-5, $HO_3PCH_2NHC_{10}H_{20}O_4$. This compound consists of phosphonic acid dimers in which the O···O distance is 2.524(4) Å. The dimers are interconnected through hydrogen bonding between NH^+ as the donor and the third phosphate oxygen, which is not involved in dimer formation (N···O, 2.655(4) Å), Figure 12. However, the structural features are not those of a leaflet, probably because the crown ether moieties are puckered and overlap each other so as to form a continuous open channeled structure as shown in its packing diagram (Figure 13).

Two additional metal derivatives of the azacrown were prepared, $Zn[O_3PCH_2NHC_{10}H_{20}O_4)(NO_3)] \cdot {}^1/_2H_2O$ and $Ce(NO_3)_3$-$(H_2O)_2(HO_3PCH_2NHC_{10}H_{20}O_4)$.[38] The cerium compound forms a dimer by covalent bonding to two phosphonate groups that bridge across the Ce. The 10-fold coordination of the cerium atoms is completed by means of three bidentate nitrate ions and two water molecules (Figure 14). The dimers then hydrogen bond to each other, via water as donors and nitrate oxygens as acceptors (O···O 2.698(5), 2.772(5) Å), forming linear chains as illustrated in Figure 15.

The zinc compound is orthorhombic with $a = 9.780(7)$, $b = 17.353(13)$, and $c = 21.118(14)$ Å. The zinc atoms are four-coordinate and bonded to three phosphonate oxygens from three different groups. The coordination sphere is completed by bonding to oxygen of a monodentate nitrate group. The bridging of Zn atoms by the phosphonate groups forms eight-membered rings that are alternately circular and chairlike in conformation. A water molecule occupies the circular ring rather than the crown ether ring. The bridging of zinc atoms is continuous, forming linear chains with the crown ether rings taking leaflet-like positions about the chain (Figure 16). In this case, chain formation is due entirely to covalent bonding, providing an even more robust leaflet structure.

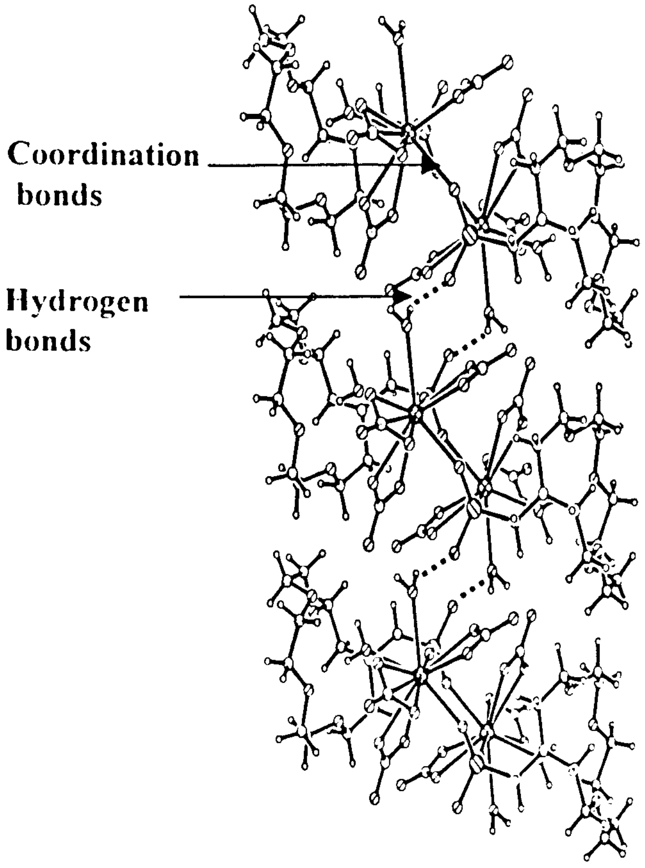


Figure 15. Self-assembly through hydrogen bonding of the cerium phosphonate dimers of Figure 14 to form a macrocyclic leaflet-type structure.

Discussion

The structural features demonstrated by the compounds described in this brief review are of interest from

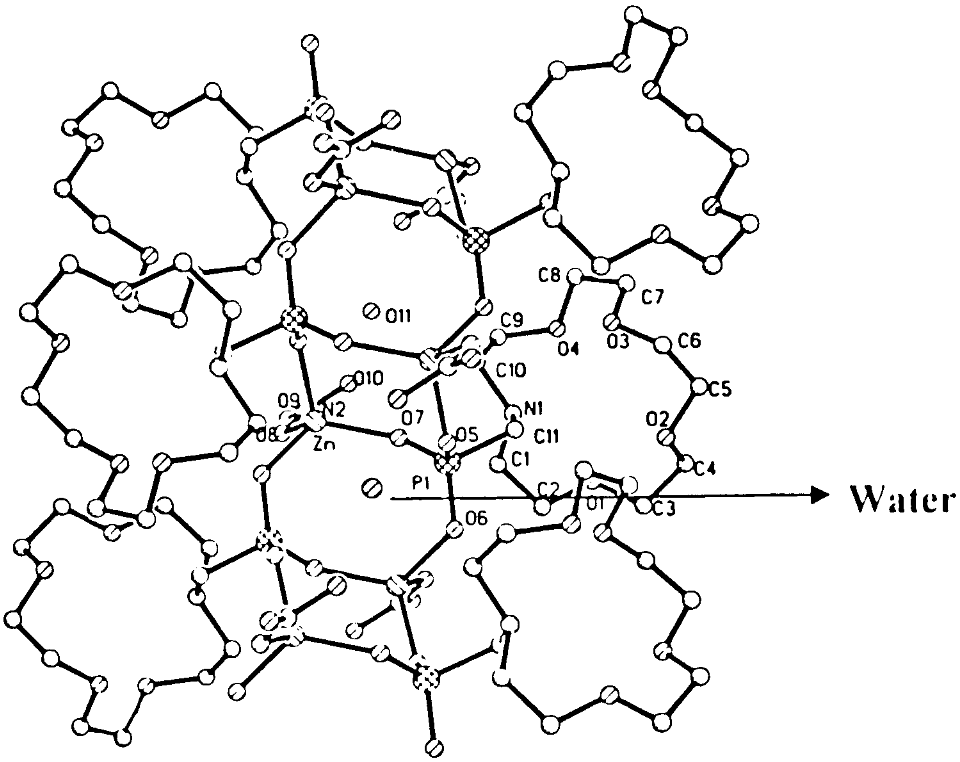
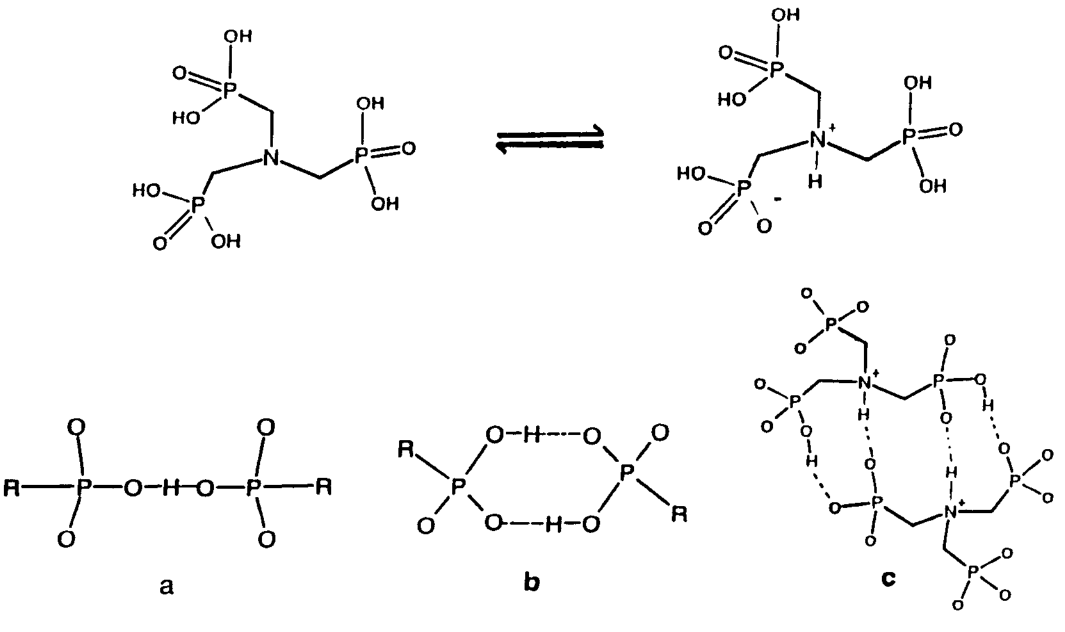


Figure 16. A portion of the linear double-stranded chains formed by reaction of $Zn(NO_3)_2{\cdot}6H_2O$ with *N*-(phosphonomethyl)-aza-15-crown-5.

several points of view. The macrocyclic leaflets are aesthetically appealing and suggest novel supramolecular routes to immobilizing crown ethers into a polymeric matrix. Deprotonation of the organophosphonic acids leads to the formation of linear hydrogen-bonded or covalently bonded chains as opposed to the layered assemblies. Essentially, the self-assembly of the crown ethers is triggered by the partial deprotonation of the phosphonic acid. The favored types of H bonding are shown in Scheme 2a and 2b. An interesting feature of those compounds which do not crystallize well is that they form nanoparticles just a few tens of nanometers in size.

Recently, we prepared novel structures using nitrilotri(methylphosphonic) acid, $N(CH_2PO_3H_2)_3$. This acid acts as a zwitterion in its pure form, as shown in Scheme 2, and reveals a complex three-dimensional structure involving five of its acidic protons.[39] Two types of complexes have been synthesized with this ligand. Reaction with divalent metals doubly deprotonates the acid, yielding trihydrated complexes of composition $M[NH(CH_2PO_3H)_3(H_2O)_3]$ where M = Mn, Co, Ni, Cu, Zn, Cd and mixtures of these ions.[40] The removal of the protons induces a self-assembly process among the phosphonate anions through the H-bonding motif, shown in Scheme 2c. The metal atoms are octahedrally coor-

Scheme 2



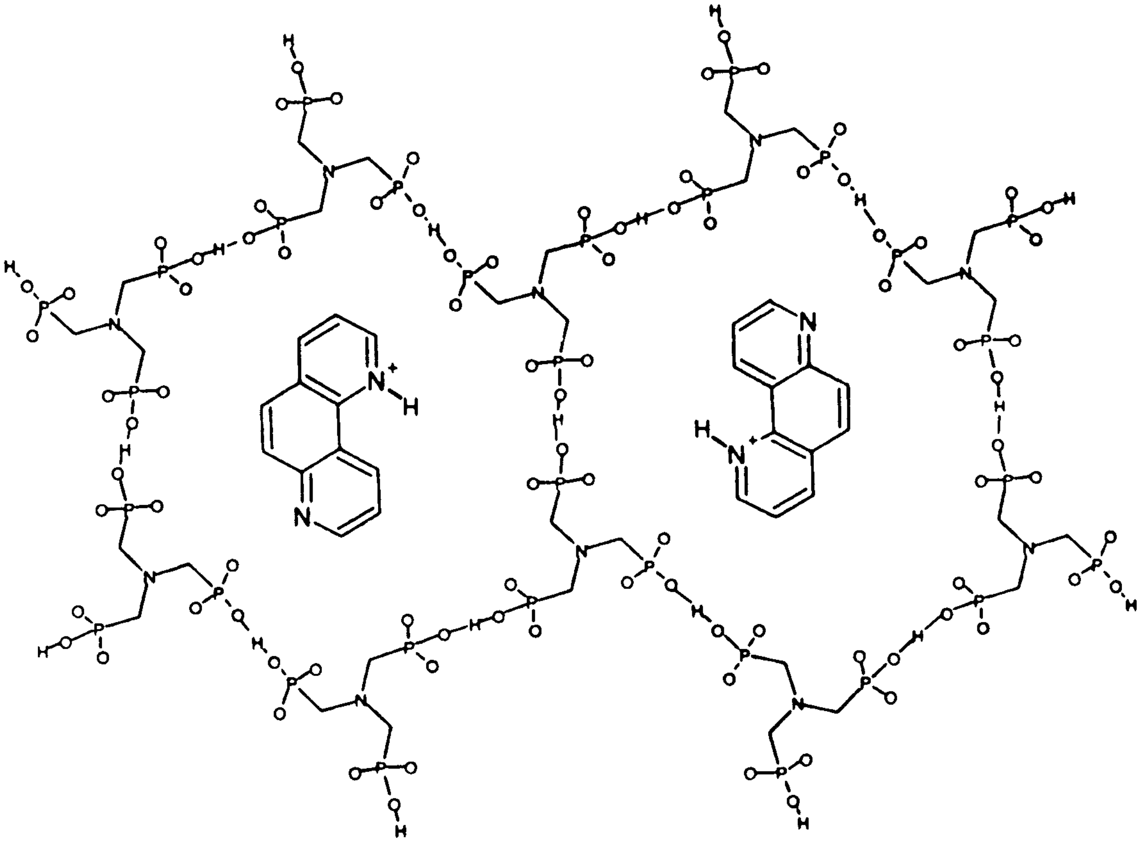


Figure 17. Planar view of the formation of a hexagonal framework based on hydrogen bonding of nitrilotris(methylphosphonic acid) in the presence of phenanthrolines. Additional hydrogen bonding creates a three-dimensional tunnel network.

dinated by three water molecules and three oxygens from two phosphonate anions and the resulting compounds are allisostructural.

Removal of one proton from the nitrilotriphosphonic acid by certain amines, such as phenanthrolines, results in the formation of an open two-dimensional hexagonal network, as shown in Figure 17. In the process, the amines are encapsulated within the rings.[41] These hexagonal two-dimensional structures self-assemble into a three-dimensional framework through additional hydrogen bonds directed at near right angles to the plane of the hexagons. The hydrogen bonds within the hexagonal network are exceedingly strong (O···O 2.45–2.48(1) Å), while the N^+–H···O distance is 2.691(4) Å). The hexagons are linked in the third dimension through a symmetrical hydrogen bond network in which O···O is 2.464(3), 2.455(3) Å. The structures so formed are quite rigid and hydrophilic with water and amine filling the cavities.

Double deprotonation of nitrilotri(methylphosphonic) acid, using 2 mol of amine, leaves one proton on each of the phosphonic acid groups. Consequently, the three-dimensional hydrogen-bonding ability of the anion is lost and only one-dimensional H-bonded chains formed. Three separate motifs were obtained depending on the nature of the amine, which intercalates between the chains.[41]

We have devoted a significant part of this brief review to phosphonates of α-zirconium phosphate structure or a cross between α- and γ-type structures. Comparable literature is available for γ-type phosphonates[42,43] and is recommended to the interested reader.

In summary, we have demonstrated many of the ways that phosphonic acids may be utilized to design organic–inorganic hybrids and/or totally organic crystal engineered structures. There are many ways that these compounds can be exploited for applications in separations science, phase transfer catalysis, and formation pf magnetically interesting structures. The phosphonic acids can be designed with functional groups and in geometries to provide a cornucopia of synthons for engineered structures. The polymeric assemblies of crown ether and other exocyclic functional groups may exhibit distinct selectivities as compared to the monomeric molecule. Further, the polymeric assemblies may exhibit other cooperative effects in metal binding and transport through tubular channels created by the pendant ligands.

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