Chem. Mater. **1996,** *8,* 1333−1340

Synthesis, Characterization, and Amine Intercalation Behavior of Zirconium *N*-(Phosphonomethyl)iminodiacetic Acid Layered Compounds

Baolong Zhang, Damodara M. Poojary, and Abraham Clearfield*

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

Guangzhi Peng

Qinghai Institute of Salt Lake, Xining, Qinghai, People's Republic of China

Received December 18, 1995. Revised Manuscript Received March 25, 1996[⊗]

New types of zirconium layered compounds containing the *N*-(phosphonomethyl)iminodiacetic acid group ($PMIDAH_2$) have been synthesized and characterized. A mixed phosphate/phosphonate compound, $Zr_2(PO_4)(O_3PCH_2N\{CH_2COOH\}_2)(O_3PCH_2N\{CH_2COOHCH_2COO^-\})(H_2O)_2$ (I) was obtained when a mixture of phosphoric acid and diacetatoiminophosphonic acid ($H_2PMIDAH_2$) solution in the ratio of 1:1 was heated with the zirconyl chloride in the presence of HF. The layer structure of this compound is different from that of any known layered zirconium phosphonate compounds. The bridging of metal atoms by the phosphate groups within the layer is similar to that found in γ-ZrP, while the mode of phosphonate binding is similar to that found for α-ZrP. When the above reaction was carried out with additional phosphoric acid, a similar layered structure but with composition $Zr_2(PO_4)(O_3PC_5H_7O_4N)(O_3PC_5H_8O_4N)_x(HPO_4)_{1-x}(H_2O)_2$ (II) was obtained. In this compound some of the phosphonate groups are replaced by the HPO_4^{2-} groups. When the ratio of phosphoric acid to $H_2PMIDAH_2$ was 4, the compound obtained has the maximum replacement. The value of x for this compound in the above formula is 0.5. Further addition of phosphonic acid yields a new phase with composition $Zr(O_3PC_5H_8O_4N)_x(HPO_4)_{1-x}$ (III). ^{31}P solid-state MAS NMR and XRD patterns suggest that this new phase is structurally similar to α-ZrP. Intercalation reactions with primary alkylamines, $C_nH_{2n+1}NH_2$ ($n = 3-8$), were carried out with all these phases. The results show that 2 mol of amines were taken up by compound I to form $[Zr_2(PO_4)(PMIDAH_2)(PMIDAH)(H_2O)_2]\cdot 2RNH_2$, while 1.5 mol of amine was intercalated into compound III, forming $Zr(PMIDAH_2)_x(HPO_4)_{1-x}\cdot 1.5RNH_2$. In both compounds the amines appear to pack as double layers. The ion-exchange behavior of these compounds is also discussed.

Introduction

The field of metal phosphonate chemistry is undergoing rapid expansion.[1] These phosphonate compounds are often layered hybrid organic−inorganic compounds in which the inorganic portion forms the central portion of the layer with pendent organic groups on both sides of this central layer.[2,3] The nature of the interlayer region may be shaped by the choice of metal and organic and additional functionality may be introduced by choice of the organic group. For example, zirconium phenylphosphonate, $Zr(O_3PC_6H_5)_2$, may be sulfonated[4] to produce $Zr(O_3PC_6H_4SO_3H)_2$, a compound that behaves as an ion exchanger[5] and a fast proton conductor.[6] Porous materials may be synthesized intact[7] or prepared by design.[1a,8−10] Metal phosphonates also lend themselves to supramolecular assembly procedures. Thus, a variety of thin films similar to the Langmuir−Blodgett type have been synthesized[1a] as well as interstratified structures by spontaneous assembly procedures. Continued synthesis of these compounds seems to always reward the investigator with new structure types.

---

[*] To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

(1) (a) Cao, G.; Hong, H.-G.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420. (b) Thompson, M. E. *Chem. Mater.* **1994**, *6*, 1168. (c) Clearfield, A. In *Design of New Materials*; Plenum: New York, 1986; p 121.

(2) Alberti, G.; Costantino, U.; Allulli, S.; Tomassini, N. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113.

(3) Poojary, M. D.; Hu, H. L.; Campbell, F. L.; Clearfield, A. *Acta Crystallogr.* **1993**, *B49*, 996.

(4) Yang, C. Y.; Clearfield, A. *React. Polym.* **1987**, *5*, 13.

(5) Kullberg, L.; Clearfield, A. *Solvent Extr. Ion Exch.* **1989**, *7*, 527.

(6) (a) Stein, E. W.; Clearfield, A.; Subramanian, M. A. *Solid State Ionics* **1996**, *83*, 113. (b) Stein, E. W.; Bhardwaj, C.; Ortiz-Avila, C. Y.; Clearfield, A.; Subramanian, M. A. *Materials Science Forum*; Trans Tech. Publications: Aedermannsdorf, Switzerland, 1994; p 115.

(7) (a) Maeda, K.; Kiyoyumi, Y.; Miyukami, F. *Angew. Chem.* **1994**, *106*, 2427; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2335. (b) Bideau, J. L.; Payen, C.; Palvadeau, P.; Bujoli, B. *Inorg. Chem.* **1994**, *33*, 4885. (c) Poojary, D. M.; Grohol, D.; Clearfield, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1508.

(8) Dines, M. B.; Digiacomo, P.; Callahan, K. P.; Griffith, P. C.; Lane, R.; Cooksey, R. E. In *Chemically Modified Surfaces in Catalysis and Electrocatalysis*; Miller, J., Ed.; ACS Symposium Series 192; American Chemical Society: Washington DC, 1982; p 223.

(9) (a) Alberti, G.; Marmottini, F.; Murcia-Mascaros, S.; Vivani, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1594. (b) Alberti, G.; Costantino, V.; Marmottini, F.; Vivani, R.; Zappelli, P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1357. (c) Alberti, G.; Costantino, V.; Vivani, R.; Zappelli, P. *Mater. Res. Soc. Symp. Proc.* **1991**, *223*, 101.

(10) Vermeulen, L.; Thompson, M. E. *Chem. Mater.* **1994**, *6*, 77.

S0897-4756(95)00601-6 CCC: $12.00

In the present study we have used *N*-(phosphonomethyl)iminodiacetic acid, $H_2PO_3CH_2N(CH_2COOH)_2$-($H_2PMIDAH_2$), to prepare zirconium phosphonate compounds particularly because its functional group, $-N(CH_2COOH)_2$, is itself a complexant similar to the chelating agent EDTA. It is of interest to see the influence of this chelating group on the structure of zirconium phosphonate compounds thus formed. The primary objective of this study, however, is to prepare mixed phosphate/phosphonate compounds and study their structures and reactivities in relation to metal phosphates and metal phosphonates. The phosphate groups serve to space the layer phosphonate groups creating microporosity.[8-10] In this paper, we report the reaction products formed by $H_2PMIDAH_2$ and a zirconium salt in the presence of H_3PO_4, under varied conditions, and their intercalation properties. A preliminary account of the structure of I has been published.[11]

Experimental Section

Materials and Methods. Chemicals were from commercial sources and used without further purification. X-ray powder diffraction patterns were taken on a Seifert-Scintag PAD V diffractometer (no internal standard) using nickel-filtered Cu Kα radiation. ^{31}P solid NMR spectra were obtained on a Bruker MSL-300. TGA data were recorded on a DuPont thermal analyst 950 unit at a heating rate of 10 °C/min under a flow by of oxygen. Infrared spectra were performed with a BIO-RAD FTS-40 spectrometer by KBr disk method. Elemental (C, H, N) analysis data were obtained from Desert Analytical in Arizona.

Synthesis of $Zr_2(PO_4)(O_3PC_5H_8O_4N)(O_3PC_5H_7O_4N)(H_2O)_2$ (I). Compound I was prepared by heating a mixture of H_2-PMIDAH$_2$ and phosphoric acid ($H_2PMIDAH_2/H_3PO_4 = 1:1$) with zirconyl chloride in HF at 60 °C for 5−6 days as reported elsewhere.[11] Elemental analysis for compound I: C, 14.46%; H, 2.43%; N, 3.44%. Calculated for compound I: C, 15.74%; H, 2.49%, and N, 3.67%.

Synthesis of $Zr_2(PO_4)(O_3PC_5H_7O_4N)(O_3PC_5H_8O_4N)_x$-$(HPO_4)_{1-x}(H_2O)_2$ (II). The synthesis procedure of compound **II** is similar to that for compound **I**, but the ratio of phosphoric acid to $H_2PMIDAH_2$ varies from 2 to 4. When this ratio is 4, the compound obtained has the maximum amount of phosphate groups. The composition of this compound is $Zr_2(PO_4)$-$(O_3PC_5H_7O_4N)(O_3PC_5H_8O_4N)_{0.5}(HPO_4)_{0.5}(H_2O)_2$. Elemental analysis: C, 12.37%; H, 2.37%, N, 3.01%. Calculated: C, 12.89%; H, 2.22%; N; 3.01%.

Synthesis of $Zr(O_3PC_5H_8O_4N)(HPO_4)_{1-x}$ (III). The synthesis procedure was similar to that employed above for the parent phosphonate, except that the ratio of phosphoric acid to $H_2PMIDAH_2$ was more than 5. The composition of III showed only a slight change on varying the ratio of H_3PO_4 to $H_2PMIDAH_2$ from 6 to 9. With a ratio of 6, we obtained a compound with composition $Zr(O_3PC_5H_8O_4N)_{0.5}(HPO_4)_{1.5}\cdot H_2O$. Elemental analysis found: C, 8.71%; H, 2.15%; N, 2.08%. Calculated: C, 8.20%; H, 2.05%; N, 1.91%.

Amine Intercalation Reactions. The intercalation reactions were carried out by both the gas−solid and liquid−solid methods. Prior to the reaction, the samples were preheated to 100 °C for about a day. In the case of the gas−solid method, 0.20 g of zirconium phosphonate/phosphate was placed in a flask which was connected to another flask containing *n*-alkylamine through a U-shaped tube. Both flasks were placed in a mineral oil bath. The oil temperature of the bath containing the *n*-alkylamine flask was kept at a temperature slightly below the boiling point of the selected *n*-alkylamine. The temperature of the flask containing the host compound was maintained at about 5 °C below the first one. The intercalation reaction required about 1−3 days for completion depending upon the amine used. The higher *n*-alkylamine required longer reaction times. It was found that in the case of the higher alkylamines the liquid−solid method was more effective than the gas−liquid method. For the liquid−solid method, a general procedure was to stir 50 mL of 0.1 N alkylamine solution with 0.1 g of phosphonate/phosphate at room temperature for 2 days. The solid was collected after filtration and rinsed with deionized distilled water. The samples were then dried in air for 1 day.

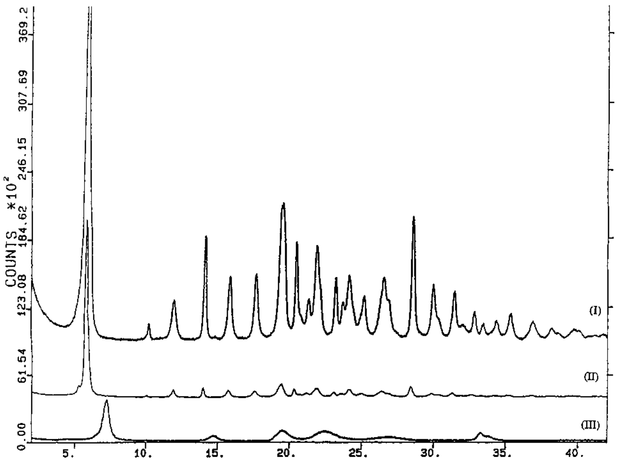

Figure 1. X-ray powder patterns of compounds I (top), II (middle), and III (bottom).

Measurement of K_d Values. K_d values for selected cations were determined by contacting a weighed amount of the particular PMIDA complex (~50 mg) with 10 mL of a 10^{-3} M solution of the ion. Equilibration times were 3 days with intermittent shaking. The solid was then filtered off and the filtrate analyzed for the amount of ion remaining in solution by either AA or DCP (direct current plasma) analysis. The K_d was then calculated from

$$K_d = \left(\frac{C_0 - C_e}{C_e}\right) V/m \qquad (1)$$

where C_0 is the initial ion concentration, C_e is the equilibrium ion concentration, and V/m is the volume-to-solid exchanger ratio. The units of K_d are mL/g.

Results

Figure 1 shows the X-ray powder patterns of compounds I−III. The X-ray patterns of compounds I and II are basically the same except for the changes in intensities of some reflections, indicating that the structural skeleton of compound I remains intact, while in compound II some of the phosphonate groups are replaced by phosphate groups. This replacement, however, causes phase disorder, resulting in peak broadening. The X-ray powder pattern of compound III, on the other hand, is significantly different from that of the compound I. Although the pattern does not contain enough reflections for indexing, some characteristic peaks (4.55, 3.96, and 2.70 Å) suggest that compound III has an α-ZrP type layer structure with $d_{001} = 11.9$ Å.[12] None of these compounds could be obtained as single crystals. However, compound I gave highly crystalline powder samples which allowed the determination of its three dimensional structure ab initio by the use of laboratory and synchrotron powder diffraction

---

(11) Poojary, M. D.; Zhang, B.; Clearfield, A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2324.

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

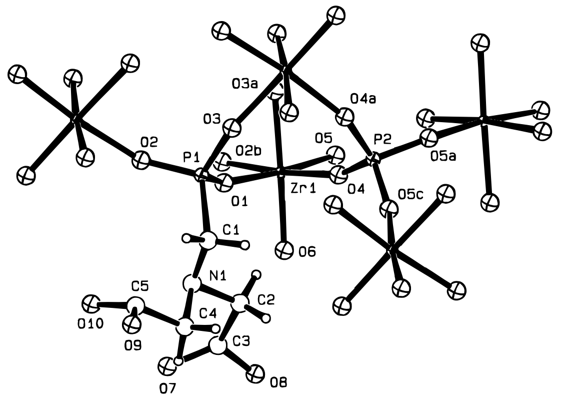

Figure 2. Portion of the structure of I showing the coordination about the zirconium atoms and the bridging nature of phosphate and phosphonate groups.

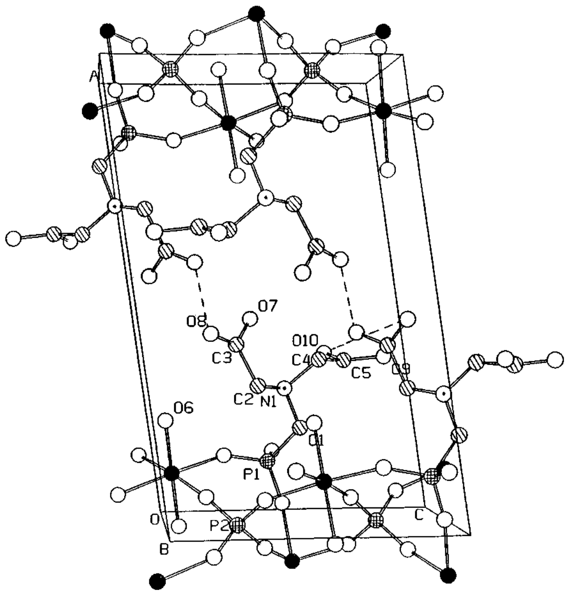

Figure 3. Projection of the structure down the *b* axis showing the layer arrangement.

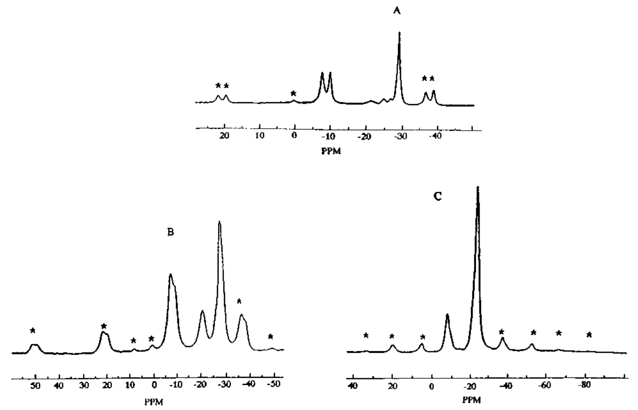

Figure 4. Solid-state MAS ^{31}P NMR for compound I (A), compound II (B), and compound III (C). The spinning side bands are indicated by asterisks.

data. Details regarding the data collection and structure solution have been given in the earlier publication.[11]

The structural study revealed that compound I has a new type of layer arrangement that is different from any of the zirconium layered compounds studied thus far. The binding of phosphonate to three different metal atoms through O1, O2, and O3 and bridging of four metals by the phosphate group (O4, O4a, O5a, and O5c) are shown in Figure 2, while the layer arrangement is shown in Figure 3. The bonding nature of phosphonate in this compound is similar to that found for the orthophosphate groups in α-zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$. However, the phosphate groups use all four oxygens in binding to metal atoms as in γ-ZrP. The octahedral coordination of the metal atoms comprises three oxygens from three different phosphonate groups, two oxygens from phosphate groups, and an oxygen from the water molecule. The carboxylate groups of the phosphonate are linked to each other through a network of hydrogen bonds. One carboxyl group (O7−C3−O8) points away from the layer and toward a similar group in the adjacent layer, forming a short hydrogen bond (O8- - -O8′ = 2.54 Å) that links the layers together. The second carboxyl group (O9−C5−O10) of the phosphonate lies parallel to the layer and forms an H bond (O10- - -O7 = 2.83 Å) with an adjacent phosphonate group in the same layer. Finally there is a short contact (2.96 Å) between O9 and the water coordinated to the zirconium atom. The two O8 atoms which are involved in interlayer hydrogen bonding are related by a 2-fold axis at $^1/_2$, *y*, $^1/_4$, suggesting that they share a proton. On the basis of this result and the overall charge requirement for the compound, the formula of the compound I may be written as $Zr_2(PO_4)(O_3PCH_2N\{CH_2CO_2H\}_2)(O_3PCH_2N\{CH_2CO_2H\}\{CH_2CO_2\})(H_2O)_2$. This composition can be explained as follows: The structure, in fact, contains two types of phosphonate groups, one for which both the carboxylates are protonated which is represented as $PMIDAH_2$. The two carboxylates of the other phosphonate exist as deprotonated and protonated species, respectively. The crystal structure presented here, however, contains only one type of phosphorus atom because the structure was solved and refined in the space group *P*2/*c*. The above explanation of the formula may be realized if one reduces the crystal symmetry to *Pc*. Attempts were made to refine the structure in this low-symmetry space group but were not successful due to the large number of refinable parameters against a limited number of powder diffraction data. The overall structural features should be very similar in both of these space groups, since a satisfactory refinement was obtained in the space group *P*2/*c*.

Spectroscopic Results. The ^{31}P MAS NMR spectrum of compound I contains three major peaks at −28, −9, and −7 ppm corresponding to the presence of the PO_4^{3-}, the protonated carboxyl group of one phosphonate group, and deprotonated phosphonates, respectively. There is also a small peak at −20 ppm, which is close to the chemical shift observed for the HPO_4^{2-} group of the α-ZrP indicating that a small number of phosphate groups have substituted for the phosphonate groups in the structure.[13] When the ratio of phosphoric acid to $H_2PMIDAH_2$ increases in the reaction mixture, this small peak at −20 ppm increases in intensity and at the same time the two phosphonate peaks at −7 and −9 ppm become nonequivalent in their intensity (see Figure 4B). In addition, the integration result shows that the total amount of phosphorus at these three chemical shifts (−7, −9, and −20 ppm) is twice as much as the amount of phosphorus resonating at −28 ppm.

---

[13] Clayden, N. *J. Chem. Soc., Dalton Trans.* **1987**, *8*, 1877.

These results suggest that the HPO_4^{2-} groups selectively replace an equal number of the phosphonate groups bonded to the zirconium atoms. The maximum amount of phosphate replacement appears to be taking place when the phosphoric acid/phosphonic acid ratio is 4. Further increase in the amount of phosphoric acid in the reaction mixture results in the formation of a new product, phase III. The ^{31}P MAS NMR of this new phase is shown in Figure 4C. In place of the peak at −28 ppm in compounds I and II, compound III shows a strong peak at −22 ppm. The resonances due to the phosphonate groups are present but with reduced intensity. This indicates that the new phase has a layer structure very similar to that of α-zirconium phosphate. The ratio of the intensity of the phosphorus peak at −22 ppm to that at −7.5 ppm is about 3. For comparison purposes we note that the resonance of the monohydrogen phosphate group in α-ZrP occurs at −19 ppm.[13] This result together with the C, H, N analysis data, shown in the Experimental Section, indicates that there are approximately three monohydrogen phosphate groups for each of the phosphonate groups. This increase in the amount of HPO_4^{2-} groups leads to a more open structure on either side of the layers so that the zirconium phosphate network can form an α-ZrP type layer.

IR spectra of compounds I and II are shown in Figure 5A,B and for compound III in Figure 6B. The two sharp bands at 3549 and 3488 cm^{-1} in Figure 5A are due to asymmetric OH stretching vibrations of the lattice water.[14] The symmetric stretching vibration and the bending vibration of the lattice water are seen at 3178 and at 1628 cm^{-1}, respectively. Since there is strong hydrogen bonding between carboxlic acids, the CO−H stretching vibration becomes broad in the region 3100−2800 cm^{-1}. The C−H stretching bands are seen superimposed upon the broad CO−H band. The C=O stretching modes of the carboxylate groups are split into two peaks and are seen at 1747 and 1730 cm^{-1}. This result is in agreement with the ^{31}P NMR and crystallography results that show that there exist two kinds of phosphonates in the structure. Since there are no P−OH groups in the compound, the two strong peaks at 1246 and 1048 cm^{-1} are due to the PO_4^{3-} out-of-plane stretching and the band at 1080 cm^{-1} is attributed to $R-PO_3^{2-}$ phosphonate stretching vibrations. The IR spectrum of compound II is very similar to that of compound I, which provides further evidence for the contention that both compounds have the same skeleton structure. The broadening of the peak around 1100 cm^{-1} and appearance of a small peak at 970 cm^{-1} indicate that the structure of compound II indeed contains free P−OH groups as a result of the replacement of some of the phosphonates by phosphate groups. A strong and broad peak in the region 1000−1100 cm^{-1} seen in the IR spectrum of compound III (Figure 6B) is due to the P−O stretching vibration of the PO_3^{2-} group, similar to that observed for α-type zirconium phosphate compounds.[15] The broad O−H stretching vibration around 3500 cm^{-1} indicates that this group is involved in strong hydrogen-bonding interactions. When compared to compound I, the C=O stretching vibration in compound III changes in intensity and also the peak at 1747 cm^{-1} shifts to a lower frequency.

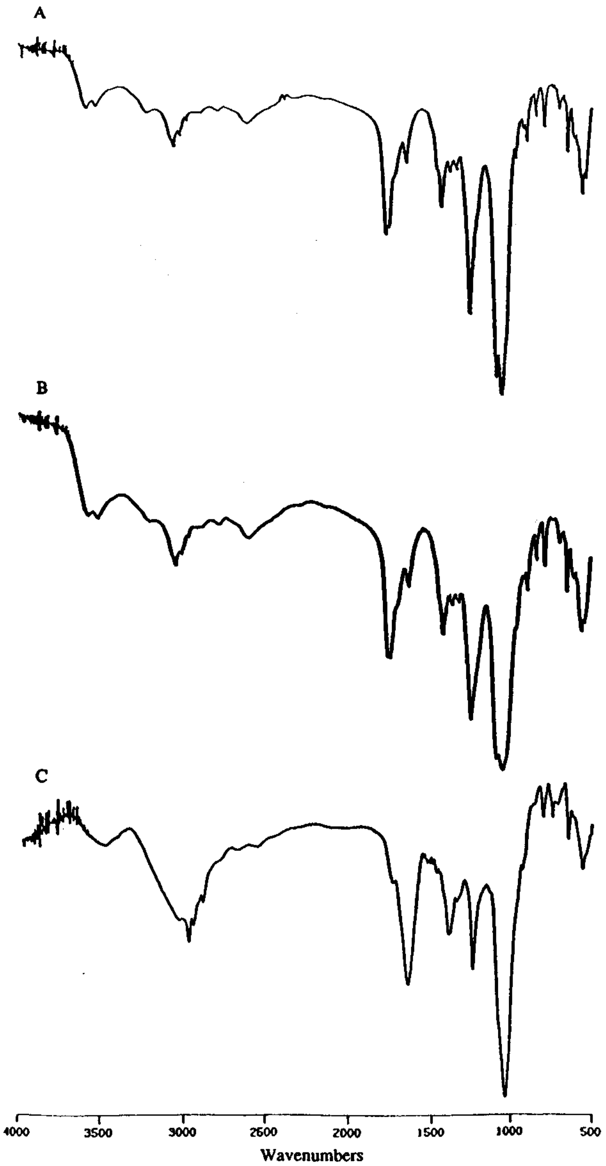

Figure 5. Infrared spectra of compounds I (A), II (B), and the intercalation product of I (C).

Thermogravimetric Study. Compound I contains 2 mol of water molecules. The TGA curve shows that these water molecules are lost below 140 °C (theoretical 4.72%, found 3.18%). Due to the presence of carboxylate groups, this compound is not very stable as compared to other zirconium aliphatic or aryl phosphonates.[16,17] The weight loss due to the decomposition of organic groups starts around 140 °C. Careful analysis of the TGA curve of compound I (Figure 7A) shows that the decomposition is rather regular. The second weight loss of 5.63% corresponds to the loss of 1 mol of CO_2, suggesting that the compound decomposes initially through the loss of a CO_2 molecule. The third weight loss (11.44%) corresponds to the release of 2 mol of CO_2 (calcd 11.54%). Weight loss beyond this temperature is due to the release of the remaining part of the organic groups. The total measured weight loss was 37.68%.

---

(14) Maclachan, D. J.; Morgan, K. R. *J. Phys. Chem.* **1992**, *96*, 3458.

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

(16) Dines, M. B.; Digiacomo, P. M. *Inorg. Chem.* **1981**, *20*, 92.

(17) Cheng, S.; Peng, G.-Z.; Clearfield, A. *Ind. Eng. Chem. Prod. Res. Dev.* **1984**, *23*, 2.

Figure 6. Infrared spectra of compound III (B) along with its intercalation product (A).

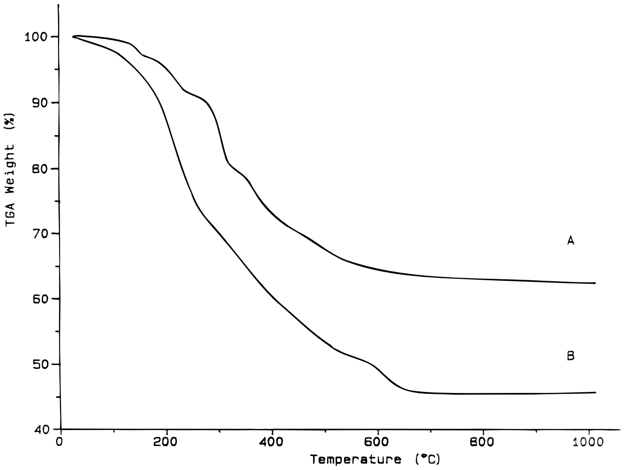

Figure 7. TGA trace of compound I shown in (A) and its octylamine intercalation product (B).

On the basis of these data, the decomposition sequence for compound I may be as follows. This sequence of reactions requires a total weight loss of 38.56%:

$$\mathrm{Zr_2(PO_4)\{O_3PCH_2N(CH_2CO_2H)_2\}\{O_3PCH_2N(CH_2CO_2H)(CH_2CO_2)\}(H_2O)_2 \xrightarrow{140\ ^\circ C,\ -2H_2O}}$$

$$\mathrm{Zr_2(PO_4)\{O_3PCH_2N(CH_2CO_2H)_2\}\{O_3PCH_2N(CH_2CO_2H)(CH_2CO_2)\} \xrightarrow{223\ ^\circ C,\ -CO_2}}$$

$$\mathrm{Zr_2(PO_4)\{O_3PCH_2N(CH_2CO_2H)_2\}\{O_3PCH_2N(CH_2CO_2)(CH_3)\} \xrightarrow{290\ ^\circ C,\ -2CO_2} Zr_2(PO_4)\{O_3PCH_2N(CH_3)_2\}\{O_3PCH_2N(CH_2CO_2)(CH_3)\} \xrightarrow{398\ ^\circ C}}$$

$$\mathrm{HZr_2(PO_4)_3 \xrightarrow{>600\ ^\circ C} 1.5ZrP_2O_7 + 0.5ZrO_2}$$

The TGA curve of the compound III is shown in Figure 8A. The first weight loss occurs below 163 °C and accounts for 5.57% of the mass due to the release of lattice water in the compound (theoretical 4.92%). The second and third steps described above may be seen as a single step, in this case indicating the release of both the CO_2 molecules at around the same temperature unlike that observed for compound I. The total weight loss up to 1000 °C was 25.40%. Assuming that the final decomposition product is ZrP_2O_7, the calculated weight loss for this process is 25.29%.

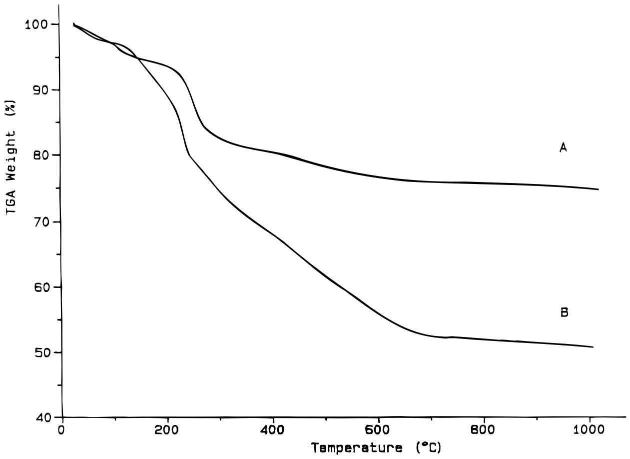

Figure 8. TGA trace of compound III (A) and its octylamine intercalation product (B).

Table 1. *d* Spacings and TGA Weight Losses of Compounds I and III and Their Intercalation Products

	compound I			compound III		
	d spacing (Å)	TGA weight loss		*d* spacing (Å)	TGA weight loss	
		obsd	calcd		obsd	calcd
host	15.2	37.68	38.56	11.9	25.40	25.29
$C_3H_7NH_2$[a]	21.3	49.00	49.00	19.6	40.64	39.85
$C_4H_9NH_2$	23.9	48.27	48.54	21.8	43.14	42.50
$C_5H_{11}NH_2$	25.4	48.17	50.09	23.2	38.01	44.94
$C_6H_{13}NH_2$	27.4	49.78	51.54	26.0	43.97	47.17
$C_7H_{15}NH_2$	30.6	50.95	52.90	27.4	48.15	49.24
$C_8H_{17}NH_2$	33.4	54.55	54.20	31.1	49.34	51.14

[a] This compound contains two additional water molecules as seen in the TGA curve.

Amine Intercalation. Layered metal phosphates are solid acids and thus can be intercalated and ion exchanged by a variety of compounds such as alcohols,[18] alkyamines,[19] and metal keggin ion moieties.[20] A considerable amount of data has been accumulated toward the intercalation behavior of layered phosphonates with alkylamines.[21,22] For divalent metal phosphonates, intercalation occurs by coordination to the metal.[21,23] However, for tetravalent metal phosphonates, intercalation can occur only if a proper functional group is present in the phosphonate. Therefore, it is interesting to compare these results with those obtained by the intercalation of alkylamine into the host layer of compounds I and III. Table 1 lists the interlayer *d* spacings for compounds I and III as well as their

---

(18) Costantino, U. *J. Chem. Soc., Dalton Trans.* **1979**, 402.

(19) Clearfield, A.; Tindwa, R. M. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1057.

(20) Clearfield, A; Roberts, B. D. *Inorg. Chem.* **1988**, *27*, 3237.

(21) Frink, K. J.; Wang, R.; Colon, J. L.; Clearfield, A. *Inorg. Chem.* **1991**, *30*, 1438. Zhang, Y.; Scott, K. J.; Clearfield, A. *Chem. Mater.* **1993**, *5*, 495.

(22) Alberti, G.; Costantino, U.; Vivani, R.; Biswas, R. K. *React. Polym.* **1992**, *17*, 245.

(23) Cao, G.; Lee, H.; Lynch, V. M.; Mallouk, T. E. *Inorg. Chem.* **1988**, *27*, 2781.

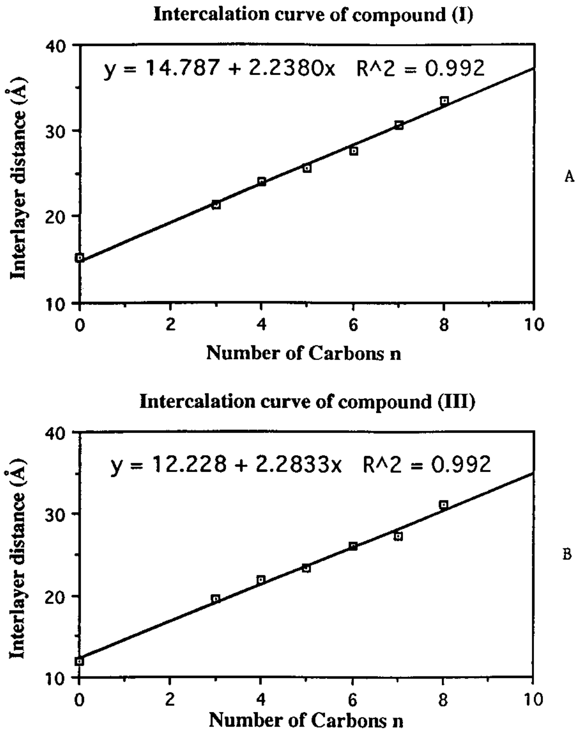

Figure 9. Plot of interlayer distance vs number of carbon atoms in the alkyl chain for compounds I (A) and III (B).

intercalates with primary alkylamines. The plot of interlayer distance versus number of carbon atoms in the alkylamine chain is shown in Figure 9. The slopes of the lines are 2.24 and 2.28 for compounds I and III, respectively. These values are significantly higher than the ideal value of 1.27 Å/CH_2, the maximum increase possible in interlayer distance per carbon atom if one assumes an interdigitated monolayer arrangement of fully extended *trans*-alkyl chains.[23] The values of the slopes are, however, close to a value 2.21, observed for zirconium phosphate intercalates of primary alkylamines.[24] Therefore in the present case the alkyl chains are packed as bilayers, as in the case of α-ZrP intercalates, with a tilt angle of about 62–64° with respect to the mean plane of the layer.

Figure 7B shows the TGA curve for the octylamine intercalated product of compound I. Up to 124 °C, the compound loses 2.57% of its weight corresponding to the release of the coordinated water molecules (calculated 3.53%). The total weight loss up to 1000 °C is 54.55%, which agrees well with the expected weight loss (54.2%) for 2 mol of intercalated octylamines. It is reported[25] that $Zr(O_3PCH_2CH_2COOH)_2$, like α-ZrP, readily intercalates *n*-alkylamines in a Bronsted acid/base reaction to form $Zr(O_3PCH_2CH_2COO^-RNH_3^+)_2$. In compound I, since one carboxylate group has already been deprotonated in the parent compound, it is most likely that the amine close to it interacts through hydrogen bonding. The other amine molecule would then extract a proton from the COOH group forming the $COO^-NH_4^+$ ion pair. The formula for the intercalate is therefore $Zr_2(PO_4)(O_3PC_5H_7O_4N)_2(H_2O)_2RNH_3^+RNH_2$. Evidence for this type of intercalation product comes from the IR spectra. In the parent compound the carbonyl stretching frequency can be seen as a strong peak at 1747 cm^{-1} associated with a shoulder at 1730 cm^{-1}. On intercalation these two peaks merge to give a single peak at 1642 cm^{-1}, suggesting that both of the carboxylates of the two phosphonate groups exist as CO_2^- in the intercalate. TGA results show that in the case of compound III (see Figure 8B) only 1.5 mol of *n*-alkylamine is intercalated. For instance, in the octylamine intercalate of compound III, the total weight loss is 49.33%. Considering that there is only 0.5 mol of $PMIDAH_2$ in compound III, the expected weight loss for a 1.5 mol amine loss is 51.14%.

The C=O stretching vibrations of the carboxylate group, in the intercalates of compound I (Figure 5C) and compound III (Figure 6A), have shifted to lower frequency, 1642 cm^{-1}, indicating their strong H-bonding interaction with the *n*-alkylamines. The peak due to RPO_3^{2-} in compound I shifts about 50 cm^{-1} and merges with that of the PO_4^{3-} stretching vibration to give a single broad peak at 1032 cm^{-1}. In compound III, the peak due to RPO_3^{2-} shifts from 1057 to 988 cm^{-1}, while that due to the PO_3H group remains almost unchanged.

To study the selectivity of compounds I–III to metal ions, the distribution coefficients of some metal ions were determined. The results shows that all the K_d values of compound I are less than 100 mL/g. These measurements were carried out at pH = 2.0. This suggests steric hindrance and strong hydrogen bonding between layers preventing metal ions from diffusing into the layer. The K_d values of compound II and compound III for most of the metal ions are significantly higher than those observed for compound I. This is due to the formation of free open space between the layers for more metal ions to diffuse. Transition-metal ions, especially lanthanides, have larger K_d values with compound II and compound III. For instance, the K_d of La^{3+} for compounds II and III are 11 134 and 25 548 mL/g, respectively.

The low K_d values in the case of compound I for most of the metal ions may be attributed to the weak acidity of the carboxylic acid of the phosphonate group. However, significantly higher K_d values were obtained when the compounds were converted to their sodium forms. For example, compounds II and III when titrated with 0.1 N NaOH up to a pH value of 5.0, showed K_d values of 80 640 and 188 100 mL/g, respectively, for strontium ion. The K_d values for the untitrated compounds were 645 and 769 mL/g for compounds II and III, respectively.

Discussion

There are two main types of layered zirconium phosphates, the α-phase[26] and the γ-phase.[27] In the former compound the Zr atoms lie slightly above and below a mean plane and are bridged by phosphate groups located alternately above and below the plane. These oxygens of each HPO_4^{2-} group bond to three different metal atoms, leaving an OH group pointing into the interlamellar space. The Zr atoms are all octahedrally coordinated to six oxygens from six different phosphate groups.[12]

γ-zirconium phosphate is correctly represented as $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$.[13] The structure has now been

---

(24) Michel, E.; Weiss, A. *Z. Naturforsch.* **1965**, *20B*, 1307.

(25) Kornyei, J.; Szirtes, L.; Costantino, U. *J. Radio. Nucl. Chem.* **1985**, *89/2*, 331.

(26) Clearfield, A.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1963**, *26*, 117.

(27) Clearfield, A.; Blessing, R. H.; Stynes, J. A. *J. Inorg. Nucl. Chem.* **1968**, *30*, 2249.

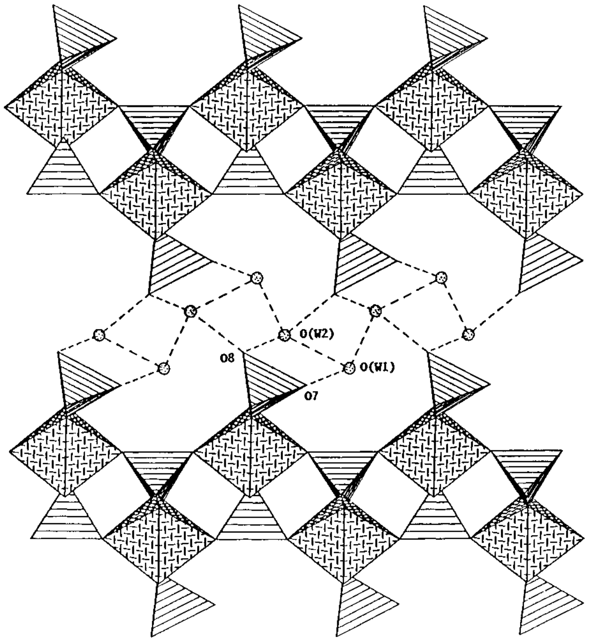

Figure 10. Polyhedral representation of γ-ZrP down the *a* axis. Hydrogen bonds involving the water molecules and hydroxyl groups are marked. The *c* axis is vertical and the *b* axis is horizontal.

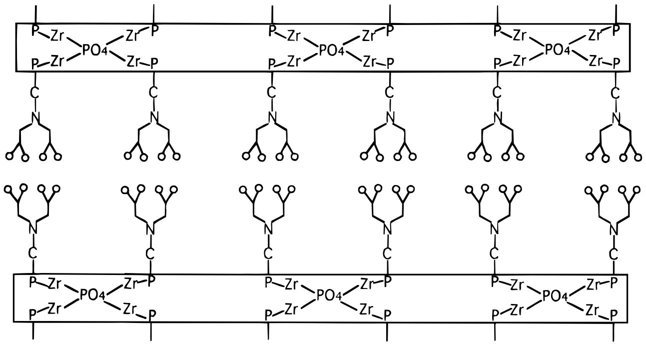

Figure 11. Schematic representation of the interlayer arrangement of compound I. Oxygen atoms are represented by small circles.

completely solved from powder X-ray data.[28] A polyhedral representation of γ-ZrP is shown in Figure 10. The Zr atoms are octahedrally coordinated as shown and lie alternately above and below a mean plane. The zirconium atoms are bridged by the orthophosphate groups to accord to the tetrahedral arrangement of oxygens in these groups. This places the metal atoms in rows parallel to the *a* axis and the alternate up–down arrangement of the rows arises from a 2_1 axis along the *b* direction. The dihydrogen phosphate group connects two adjacent Zr atoms in the same row in the *a* direction. This leaves the two P–OH groups to point into the interlamellar space and hydrogen bond to water as shown in Figure 10. A schematic representation of the structures of compounds I–III is presented in Figures 11–13. The scheme for the structure of I is drawn on the basis of its determined crystal structure (Figure 11). The structure of compound II (Figure 12) is derived from that of I by substituting a monohydrogen phosphate group for some of the phosphonate groups. On the basis of the spectroscopic, thermal, and chemical data shown above, it can be shown that this compound contains three phosphonate groups for each of the monohydrogen phosphate groups on either side of the layers. Since compound II has the same interlayer *d* spacing as that of compound I, it is logical to place the phosphonate groups in a manner shown in Figure 12. Compound III, shown in Figure 13, has the α-type layer structure and contains one phosphonate group for three monohydrogen phosphate groups. Apparently, the presence of the large number of HPO_4 groups forces the layer to adopt an α-ZrP type structure.

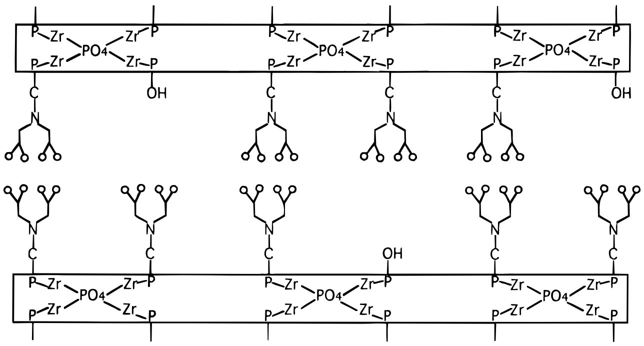

Figure 12. Schematic representation of the interlayer arrangement of compound II. Oxygen atoms are represented by small circles.

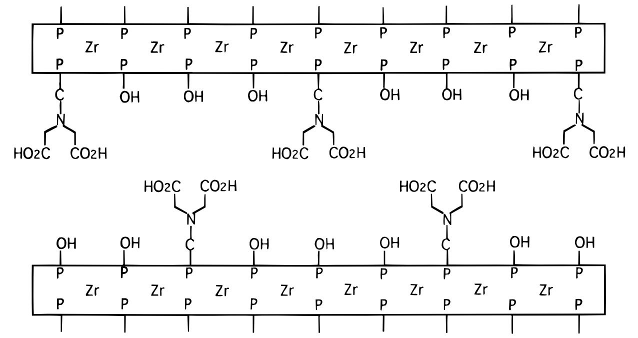

Figure 13. Schematic representation of the interlayer arrangement of compound III.

The formation of the new type of layer structures as described above may be primarily attributed to the bulkiness of the phosphonate group. The large functional groups of the $PMIDAH_2$ cannot fit in the interlayer space if the phosphonate groups were to bond the metal atoms in a fashion similar to the orthophosphates in α-zirconium phosphate. The α-ZrP layer requires the pendant group to occupy a cross-sectional area no more than 24 Å^2. In fact when the reaction was carried out with a zirconium salt and $H_2PMIDAH_2$ alone, a linear chain compound rather than a layered compound was formed.[29] The chains, in the linear chain compound, consist of metal atoms bridged by phosphonate oxygens. Only two oxygens of each phosphonate groups are involved in metal binding, while the third is bonded to a proton. The metal atoms are octahedrally coordinated since the remaining two coordination sites are occupied by fluoride ions. The carboxylate groups are not involved in metal binding similar to that observed in the case of compound I. These groups from adjacent chains

---

(28) (a) Christensen, N.; Andersen, E. K.; Andersen, I. G.; Alberti, G.; Nielsen, M.; Lehmann, M. S. *Acta. Chem. Scand.* **1990**, *44*, 865. (b) Poojary, D. H.; Shpeizer, B.; Clearfield, A. *J. Chem. Soc., Dalton Trans.* **1995**, 111.

(29) Zhang, B.; Poojary, D. M.; Clearfield, A., in preparation.

are projected toward the interchain region. On the other hand, when phosphate is present in addition to $H_2PMIDAH_2$ as in the case of compound I, the phosphate lies in the layer and bridges the metal atoms. This bridging of phosphate creates a large enough space on either side of the layers for the phosphonate molecules to bind in a manner similar to orthophosphate binding in α-ZrP.

Recently we have determined the structure of another mixed phosphate/phosphonate compound, $Zr_2(PO_4)PVF_3 \cdot 3H_2O$,[30] containing a viologen diphosphonate (PV). Interestingly it is found that this compound also has the same type of layer arrangement as described for compound I. In this viologen compound, the phosphate bridges zirconium atoms in a fashion similar to that in compound I, while the viologen diphosphonate group links the inorganic lamellae to form a crisscross stack in order to minimize the electrostatic repulsions of adjacent viologen groups. Another difference in bonding in the inorganic networks of $Zr_2(PO_4)PVF_3 \cdot 3H_2O$ and that of compound I is that in the latter compound, the sixth coordination site on Zr is occupied by a water molecule and not by a fluoride ion as in the former compound. Again, in the absence of phosphate groups in the reaction mixture, the zirconium viologen phosphonate compound formed was not layered; instead it has a double-chain arrangement.[31] These two mixed phosphate/phosphonate compounds thus clearly demonstrate that the organic moieties have a significant influence on the formation of a particular type of metal phosphonate structure. The role of phosphate groups in these mixed compounds clearly is to space the metal atoms in the layer in order to accommodate the bulky phosphonate groups in the interlayer space. Further, these studies show the diversity of metal phosphate and metal phosphonate linkages in tetravalent metal layered compounds which were traditionally thought to have α- *o*r γ-types of layer structures. It is also worth mentioning here another zirconium layered compound, $Zr(PO_4)F(OSMe_2)$,[32] whose layer structure is different from any of the above-mentioned types. The phosphate group bonds to four Zr atoms, forming intersecting chains at right angles to each other such that $a = b \simeq 6.61$ Å. The axial positions are occupied by the fluoride ion and the dimethyl sulfoxide oxygen which alternate up and down in adjacent chains. Finally, it may be remarked that in thin films prepared layer by layer, the use of phosphonates whose cross-sectional area is greater than 24 Å^2 [33] results in films that have Zr/P ratios of greater than 0.5.[34] Until now it has been assumed that the films have α-type structures. However, the discovery of zirconium-rich layered compounds such as described here indicates that the films may also exhibit new layer structure types.

Acknowledgment. This work was supported by the National Science Foundation under Grant DMR-907715 and Robert A. Welch Foundation under Grant A673, for which grateful acknowledgement is made.

CM9506013

---

(30) Byrd, H.; Reis, K. P.; Thompson, M. E.; Poojary, D. M.; Clearfield, A. *Chem. Mater.*, submitted.

(31) Poojary, D. M.; Vermeulen, L. A.; Vicenzi, E.; Clearfield, A.; Thompson, M. E. *Chem. Mater.* **1994**, *6,* 1845.

(32) Poojary, D. M.; Zhang, B.; Clearfield, A. *J. Chem. Soc., Dalton Trans.* **1994**, 2453.

(33) Ungashe, S. B.; Wilson, W. L.; Katz, H. E.; Scheller, G. R.; Putvinski, T. M. *J. Am. Chem. Soc.* **1992**, *114,* 8717. Katz, H. E.; Shilling, M. L.; Chidsey, C. E. D.; Putvinski, T. M.; Hutton, R. S. *Chem. Mater.* **1991**, *3,* 699.

(34) Byrd, H.; Pike, J. K.; Talham, D. R. *Chem. Mater.* **1993**, *5,* 709. Byrd, H.; Whipps, S.; Pike, J. K.; Ma, J.; Nagler, S. E.; Talham, D. R. *J. Am. Chem. Soc.* **1994**, *116,* 295.