Synthesis and Crystal Structure of the Linear Chain Zirconium Organophosphonate $(NH_4)Zr[F_2][H_3\{O_3PCH_2NH(CH_2CO_2)_2\}_2]\cdot 3H_2O\cdot NH_4Cl$

Baolong Zhang, Damodara M. Poojary,[†] and Abraham Clearfield*

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

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The new zirconium phosphonate compound $(NH_4)Zr[F_2][H_3\{O_3PCH_2NH(CH_2CO_2)_2\}_2]\cdot 3H_2O\cdot NH_4Cl$ was obtained from the reaction of zirconyl chloride with *N*-(phosphonomethyl)iminodiacetic acid in the presence of HF. It crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 10.743(2)$ Å, $b = 11.483(2)$ Å, $c = 5.330(1)$ Å, $\alpha = 90.63(2)°$, $\beta = 96.65(2)°$, $\gamma = 97.68(2)°$, and $Z = 1$. The structure consists of linear chains of zirconium atoms linked together by phosphonate oxygens. The zirconium atom is six-coordinated by four phosphonate oxygens and two fluoride ions. The compound represents the first example of a linear chain structure in the zirconium phosphate or phosphonate systems. The formation of such linear chains as opposed to the layered structure normally observed for zirconium phosphonates is attributed to the bulkinesss of the phosphonic acid.

Introduction

Metal phosphonates have attracted a great deal of research activity in recent years. This interest primarily stems from their potential application in the area of catalysis,[1] ion exchange,[2] proton conductivity,[3] intercalation chemistry,[4] photochemistry,[5] and materials chemistry.[6] Most of the compounds studied are layered species in which oxygen atoms bridge metal octahedra to form two-dimensional layers that are separated by the hydrophobic regions of the organic moieties.[6] It is interesting to note that a variety of organic groups with active moieties can be organized between the inorganic layers, a fact that is important in designing materials for specific physical properties. Studies from our group and from others have shown that a variety of metal ions, including group 4 and 14 elements and divalent and trivalent ions, form this type of layered compound.[6−9] In most cases, particularly those of group 4 and 14 elements, the phosphonates have structural similarity to their inorganic phosphates. Our recent studies, however, have also revealed some new types of layer structures in zirconium phosphate/phosphonate compounds.[10] Such compounds usually form when the organic portion of the phosphonic acid is too large to fit the interlamellar space. In order to form the α-zirconium phosphate (α-ZrP) type layer structure, the size of the organic group should not exceed ~24 Å^2. This fact derives from the area occupied by phosphate groups on the α-ZrP type layer.[11]

Earlier, we reported[12] a mixed phosphate phosphonate layered zirconium compound formed with the ligand *N*-(phosphonomethyl)iminodiacetic acid (PMIDA). This compound was prepared from a reaction of a zirconium salt with a mixture of phosphoric acid and PMIDA solutions. When this reaction was carried out in the absence of phosphoric acid, we obtained a different phase that is not layered but instead is a linear chain compound. In this paper, we report the synthesis and structure of this compound. As far as we know, this is the first example of a linear chain structure in the zirconium phosphate or phosphonate systems. We also discuss some of the properties of this compound.

Experimental Section

Materials and Methods. *N*-(Phosphonomethyl)iminodiacetic acid, $H_2PO_3CH_2N(CH_2COOH)_2$ ($H_2PMIDAH_2$), was prepared as reported in the literature.[13] All the other chemicals were of reagent grade quality obtained from commerical 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. The ^{31}P solid MAS NMR spectrum was obtained on a Bruker MSL-300 unit and ^{19}F solid state 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 zirconia rotor. Solution NMR were recorded on a Varian Unity Plus 300 spectrometer. H_3PO_4 (85%) and $CFCl_3$ were used as ^{31}P and ^{19}F standard references, respectively. TGA data were taken on a Dupont thermal analyst 950 unit at a heating rate of 10 °C/min under a flow of oxygen. Elemental analysis data were obtained from Desert Analytics, Tucson, AZ.

Synthesis of $(NH_4)Zr[F_2][H_3\{O_3PCH_2NH(CH_2CO_2)_2\}_2]\cdot 3H_2O\cdot NH_4Cl$ (Zr-PMIDA). A 2.27 g sample of *N*-(phosphonomethyl)-

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* To whom correspondence should be addressed.

[†] Present address: Symyx Technologies, 3100 Central Expressway, Santa Clara, CA.

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

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

(3) Stein, E.; Clearfield, A.; Subramanian, M. A. *Solid State Ionics* **1996**, *83*, 113−124.

(4) Alberti, G.; Costantino, U. In *Comprehensive Supramolecular Chemistry*; Lehn, J. M., Ed.; Pergamon−Elsevier Science Ltd.: London, 1996; p 1.

(5) (a) Vermeulen, L. A.; Thompson, M. E. *Nature* **1992**, *358*, 656. (b) Vermeulen, L. A.; Snover, J. L.; Sapochak, L. S.; Thompson, M. E. *J. Am. Chem. Soc.* **1993**, *115*, 11767.

(6) (a) Cao, G.; Hong, H.; Mallouk, T. E. *Acc. Chem. Res.* **1992**, *25*, 420−427. (b) Clearfield, A. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 268−278.

(7) Thompson, M. E. *Chem. Mater.* **1994**, *6*, 1168.

(8) Alberti, G. In *Comprehensive Supramolecular Chemistry*; Lehn, J. M., Ed.; Pergamon−Elsevier Science Ltd.: London, 1996; p 151.

(9) Clearfield, A. *Prog. Inorg. Chem.*, in press.

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

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

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

(13) Moedritzer, K.; Irani, R. R. *J. Org. Chem.* **1966**, *31*, 1603.

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Table 1. Crystallographic Data for Zr-PMIDA

empirical formula	$ZrP_2O_{17}C_{10}N_4H_{31}F_2Cl$	V (Å^3)	647.0(2)
fw	705.99	Z	1
crystal system	triclinic	space group	$P\bar{1}$ (No. 2)
a (Å)	10.743(2)	d_{cal} (g cm^{-3})	1.812
b (Å)	11.483(2)	λ (Å)	0.710 69
c (Å)	5.330(1)	temp (°C)	−110
α (deg)	90.63(2)	μ (cm^{-1})	7.34
β (deg)	96.65(2)	R^a	0.025
γ (deg)	97.68(2)	$R_w{}^b$	0.035

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o{}^2)]^{1/2}$ where $w = 4F_o{}^2/\sigma^2(F_o{}^2)$.

iminodiacetic acid ($H_2PMIDAH_2$) was dissolved in 30 mL of 5 N ammonium hydroxide, and the pH was lowered to 7.0 by addition of 5 N HCl. A 3.22 g amount of $ZrOCl_2$•$8H_2O$ was dissolved in 20 mL of deionized distilled water and 1.6 mL of HF solution (48%). The reactants were mixed, and the pH was adjusted to 2.5. The mixture was then transferred into a Teflon flask fitted with a Teflon condenser and heated at 90 °C for 3 days. On slow evaporation at room temperature, platelike white crystals were formed. Anal. Found: C, 15.47; H, 4.48; N, 7.85. Calcd for $(NH_4)Zr[F_2][H_3\{O_3PCH_2NH(CH_2CO_2)_2\}_2]$•$3H_2O$•$NH_4Cl$: C, 17.01; H, 4.43; N, 7.93. The low value determined for C may be due to incomplete combustion, which is often the case if an oxidant is not used. TGA analysis shows 7.75% weight loss before 134 °C due to release of lattice water, compared to 7.65% calculated on the basis of the above formula. The compound begins to decompose above 200 °C.

X-ray Structure Analysis. A colorless platelike crystal of the Zr-PMIDA complex, with dimensions 0.30 × 0.25 × 0.15 mm^3, was mounted on a glass fiber. All crystallographic measurements were carried out on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) and a 12 kW rotating-anode generator. Unit cell parameters for data collection were obtained from least-squares refinement of 24 reflections chosen from 8−35° 2θ immediately preceding data collection. Intensity data were collected at −110 ± 1 °C using the $\omega-2\theta$ scan mode in shells to a maximum value of 50° in 2θ. Three intensity standards were measured every 150 reflections to monitor crystal decay. Scans of $(1.63 + 0.3 \tan \theta)°$ were made at a speed of 16°/min in ω. The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of three) for good counting statistics. Of the 2424 reflections that were collected, 2290 were unique ($R_{int} = 0.022$). A total of 2010 reflections were observed with $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization effects. Pertinent crystallographic data are presented in Table 1.

The structure was solved by the Patterson method. The position of the heavy atom was located by deconvolution of the Patterson function. Other non-hydrogen atoms were found in the successive difference Fourier maps. The lattice also contains an ammonium ion, a chloride ion, and two water molecules. The chloride ion and one of the water molecules, OW2, are very close to each other (0.76 Å), and therefore they cannot exist with full occupancy. On the basis of the electron density, a fractional occupancy of 0.5 was initially assigned to each of these positions. The correctness of the Cl and the water oxygen positions was tested by interchanging their scattering factors. In this case, however, the thermal parameter of the originally assigned chlorine site became negative together with an increase in the R factors. All the non-hydrogen atoms were refined anisotropically. A difference Fourier map computed at this stage revealed the positions of all the hydrogen atoms except those bonded to one of the carboxylate groups and the disordered water oxygen. The hydrogen atoms were included in the least-squares refinements as found in the difference map and were not refined. The final cycle of full-matrix refinement was based on 2010 reflections and 178 structural parameters. An empirical absorption correction, based on a ψ plot, was applied which resulted in transmission factors ranging from 0.94 to 1.0. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflections. The maximum and minimum peaks on the final difference map corresponded to 0.64 and −0.41 e/Å^3, respectively. Neutral-atom scattering factors were taken from Cromer and Waber.[14]

Table 2. Positional Parameters and B(eq) Values for Zr-PMIDA

atom	x	y	z	B(eq) (Å^2)
Zr1	0	0	0	0.78(1)
Cl1	0.4559(2)	0.5289(2)	0.2728(4)	3.17(9)^a
P1	0.21344(6)	0.02873(6)	0.5690(1)	0.89(2)
F1	0.0285(2)	0.1710(1)	−0.0542(3)	1.88(2)
O1	0.1292(2)	0.0162(2)	0.3192(3)	1.55(7)
OW1	0.2516(2)	0.3786(2)	0.5403(5)	3.4(1)
O2	−0.1439(2)	0.0269(2)	0.2185(3)	1.29(7)
OW2	0.4118(6)	0.5595(5)	0.181(1)	3.6(3)^a
O3	0.2783(2)	0.1510(2)	0.6267(3)	1.47(7)
O4	0.6116(2)	−0.2189(2)	0.9441(4)	1.78(7)
O5	0.4444(2)	−0.1461(2)	1.0654(4)	1.96(8)
O6	0.1490(2)	−0.3560(2)	0.7789(4)	2.17(8)
O7	0.0633(2)	−0.4241(2)	0.3923(4)	1.92(7)
N1	0.3075(2)	−0.1864(2)	0.6117(5)	1.11(8)
N2	0.1488(3)	0.4038(2)	1.0156(5)	2.9(1)
C1	0.3395(2)	−0.0600(2)	0.5467(5)	1.09(9)
C2	0.4250(3)	−0.2439(2)	0.6653(5)	1.5(1)
C3	0.4946(2)	−0.1975(2)	0.9153(5)	1.3(1)
C4	0.2135(3)	−0.2559(2)	0.4173(5)	1.4(1)
C5	0.1372(3)	−0.3530(2)	0.5483(5)	1.5(1)
H1	0.4093	−0.0265	0.6738	1.3
H2	0.3692	−0.0566	0.3694	1.3
H6	0.2526	−0.2822	0.2903	1.6
H4	0.4711	−0.2260	0.5143	1.9
H5	0.4041	−0.3299	0.6736	1.9
H3	0.2635	−0.1914	0.7552	1.3
H7	0.1630	−0.1989	0.3543	1.6
H8	0.2593	0.2939	0.5606	4.1
H9	0.3410	0.4188	0.5451	4.1
H13	0.1252	0.4692	0.9881	4.0
H14	0.1884	0.3904	0.8805	4.0
H12	0.0933	0.3617	1.0091	4.0
H10	0.1887	0.4034	1.1357	4.0
H15	0	−0.5	0.5	2.3

^{a} Occupancy = 0.5.

Results

Structure of Zr-PMIDA. Positional and thermal parameters of the atoms in this structure are given in Table 2, and selected bond distances and angles are listed in Table 3. The structure of Zr-PMIDA consists of one-dimensional chains running along the c axis. The zirconium atoms are located at the centers of symmetry and are bridged by two phosphonate groups through O1−P1−O2 linkages. The third phosphonate oxygen atom, O3, is not involved in bonding although it is deprotonated. The octahedral coordination of Zr atoms is completed by symmetry-related fluorides that occupy the axial positions (see Figure 1). The carboxylate groups of the phosphonate are not involved in metal bonding and are projected into the interchain space. The phosphonate groups of adjacent chains are linked together by hydrogen bonds involving symmetry-related O7 atoms (Figure 2) by sharing a proton that is located at the center of symmetry. The other carboxylic group bends toward the chain and one of its oxygens (O4) hydrogen-bonds with O3 of the phosphonate group (O3−O4 = 2.515 Å). The chloride ion and one of the water oxygen positions, OW2, are partially occupied (occupancy = 0.5). The ammonium ion site is fully occupied and thus balances the charge of the partially occupied Cl^- ion and the metal phosphonate moiety. We note that the bond angles associated with N1, the imino nitrogen, are close to tetrahedral angles, indicating that N1 is protonated.

Although O3 is not involved in metal bonding, the short distances between O3 and O4 (2.515 Å) and between O3 and OW1 (2.706 Å) indicate that there is hydrogen bonding between

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(14) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table 3. Intramolecular Distances (Å) and Bond Angles (deg) for Zr-PMIDA

Zr1−F1	1.976(2)	O5−C3	1.206(3)
Zr1−O1	2.058(2)	O6−C5	1.223(3)
Zr1−O2	2.092(2)	O7−C5	1.283(3)
P1−O1	1.514(2)	N1−C1	1.500(3)
P1−O2	1.528(2)	N1−C2	1.501(3)
P1−O3	1.494(2)	N1−C4	1.501(3)
P1−C1	1.814(3)	C2−C3	1.506(4)
O4−C3	1.305(3)	C4−C5	1.519(4)

F1−Zr1−F1	180.00	O2−P1−O3	114.6(1)
F1−Zr1−O1	91.74(7)	O2−P1−C1	103.7(1)
F1−Zr1−O1	88.26(7)	O3−P1−C1	105.3(1)
F1−Zr1−O2	88.97(7)	Zr1−O1−P1	174.3(1)
F1−Zr1−O2	91.03(7)	Zr1−O2−P1	141.0(1)
F1−Zr1−O1	88.26(7)	C1−N1−C2	111.0(2)
F1−Zr1−O1	91.74(7)	C1−N1−C4	113.5(2)
F1−Zr1−O2	91.03(7)	C2−N1−C4	111.3(2)
F1−Zr1−O2	88.97(7)	P1−C1−N1	114.6(2)
O1−Zr1−O1	180.00	N1−C2−C3	109.0(2)
O1−Zr1−O2	90.21(7)	O4−C3−O5	125.9(2)
O1−Zr1−O2	89.79(7)	O4−C3−C2	112.3(2)
O1−Zr1−O2	89.79(7)	O5−C3−C2	121.8(2)
O1−Zr1−O2	90.21(7)	N1−C4−C5	108.8(2)
O2−Zr1−O2	180.00	O6−C5−O7	127.2(3)
O1−P1−O2	111.2(1)	O6−C5−C4	120.0(2)
O1−P1−O3	113.4(1)	O7−C5−C4	112.8(2)
O1−P1−C1	107.7(1)		

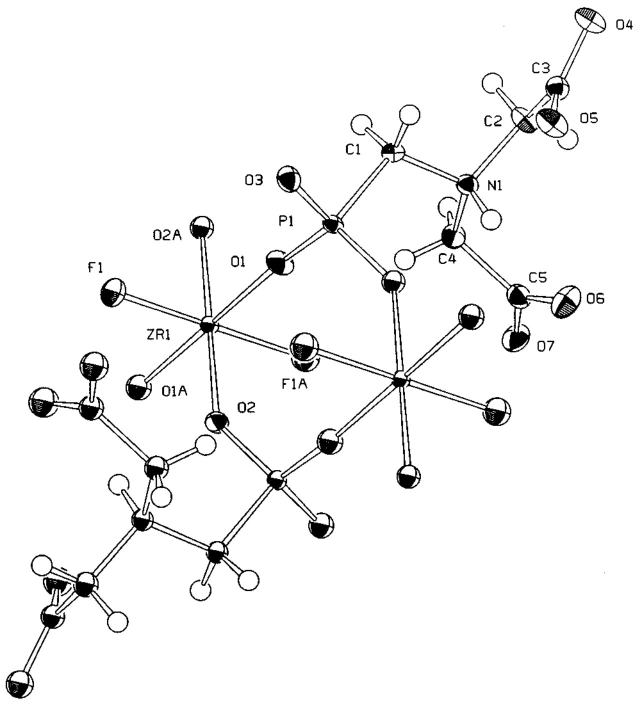

Figure 1. Portion of the structure of Zr-PMIDA showing the coordination about the zirconium atoms and the numbering scheme used in the text.

them. It is interesting to note that there is no bonding interaction between the ammonium and chloride ions (Cl−N2 = 3.53 Å); instead, they are essentially held between interchain space through other hydrogen bondings. The Cl−Cl distance is too close at 2.623 Å, confirming that every other position is unoccupied. However, the chloride ion, in turn, interacts with H_2O (OW1−Cl = 3.09 Å). The other hydrogen bonding involves the ammonium and fluoride ions (N−F = 2.816 Å) and the ammonium ion and water (OW1−N2 = 2.906 Å).

Spectroscopic Study. The ^{31}P MAS solid state NMR spectrum of Zr-PMIDA (see Figure 3) has one peak at −3 ppm, suggesting that there is only one kind of phosphonate. The position of this peak shifts 2 ppm downfield when compared to that of phosphonate, which has the α-type bonding mode, and 5 ppm upfield relative to that of phosphonate in the γ-type structure.[15] This is because one of the oxygens of the phosphonate is not involved in metal bonding. A single peak appears at 31 ppm in the ^{19}F MAS solid state NMR spectrum (see Figure 4), indicating that there is only one kind of fluoride ion in the structure; this is consistent with the crystallographic study result.

Zr-PMIDA shows very little solubility in aqueous solution; however, on heating, it slowly dissolves in water. This property of the compound allowed us to investigate its special properties in solution and compare them to those in the solid state. Its ^{31}P and ^{19}F NMR spectra were recorded in aqueous solution. The ^{31}P NMR spectrum showed a single peak at 8.8 ppm. The ^{19}F spectrum also had only one peak; however, it was shifted upfield 160 ppm compared with its solid state value and fell into the range of the chemical shift of NH_4F. After a few days, the peak in the ^{31}P NMR spectrum was further shifted downfield to 23 ppm and the ^{19}F peak showed no substantial change.

It is interesting to compare the above results with those obtained directly from the reaction solution. The supernate of Zr-PMIDA was taken 1 day after the solid precipitated from solution, and the results are compared in Figures 5 and 6. The ^{31}P spectrum has two peaks at 23 and 8 ppm, and the ^{19}F spectrum has a small broad peak at −13 ppm besides a sharp peak at −130 ppm.

The above results suggest that Zr-PMIDA in solution has a structure different from that in the solid state. In aqueous solution, fluoride ions dissociate from zirconium coordination. This hypothesis is supported by the mass spectrometric study of Zr-PMIDA. Zr-PMIDA was first dissolved in H_2O before taking the mass spectrum. −FAB gave no signal. +FAB showed the highest peak at 541, which corresponded to a mass of the formula $\{ZrH_3[O_3PCH_2NH(CH_2COO)_2]_2\}^+$ (^{90}Zr has the highest isotopic abundance). Since no mass higher than 1000 was observed, this indicated that the linear chain had decomposed to form a monomer.

It is interesting to note that the phase change from solid to solution state is reversible on evaporation. However, to dissolve the solid, thermal energy is necessary in order to break the F−Zr bonding. In solution, the compound exists in more than one form, and accordingly the transition to the solid state may involve several steps, as indicated by the chemical shift of the ^{31}P NMR from 23 to 8 ppm. It is found that the chemical shift of phosphorus depends on the binding mode of phosphate or phosphonate.[15] The extent of upfield shift of the ^{31}P peak is directly proportional to the number of phosphonate oxygen atoms that take part in binding to Zr. Thus, the observed chemical shift of the ^{31}P signal from 23 to 8 ppm upon the phase change apparently involves a bond-making process between phosphonate and zirconium. The chemical shift from −3 ppm in the solid state to 8 ppm in solution involves not only the phase change from polymer to monomer but also the coordination of oxygens of two carboxylic groups because the dissociation of fluoride ions would leave the zirconium in an unfavorable four-coordinated state. The bonding of oxygen of the carboxylic acid has an electron-withdrawing effect from phosphonate to zirconium, resulting in the ^{31}P shift downfield. The bonding between fluoride and zirconium also involves two or more steps as indicated by the chemical shift of fluorine from −130 to −13 ppm and finally to +30 ppm in the solid state.

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(15) Clayden, N. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1877.

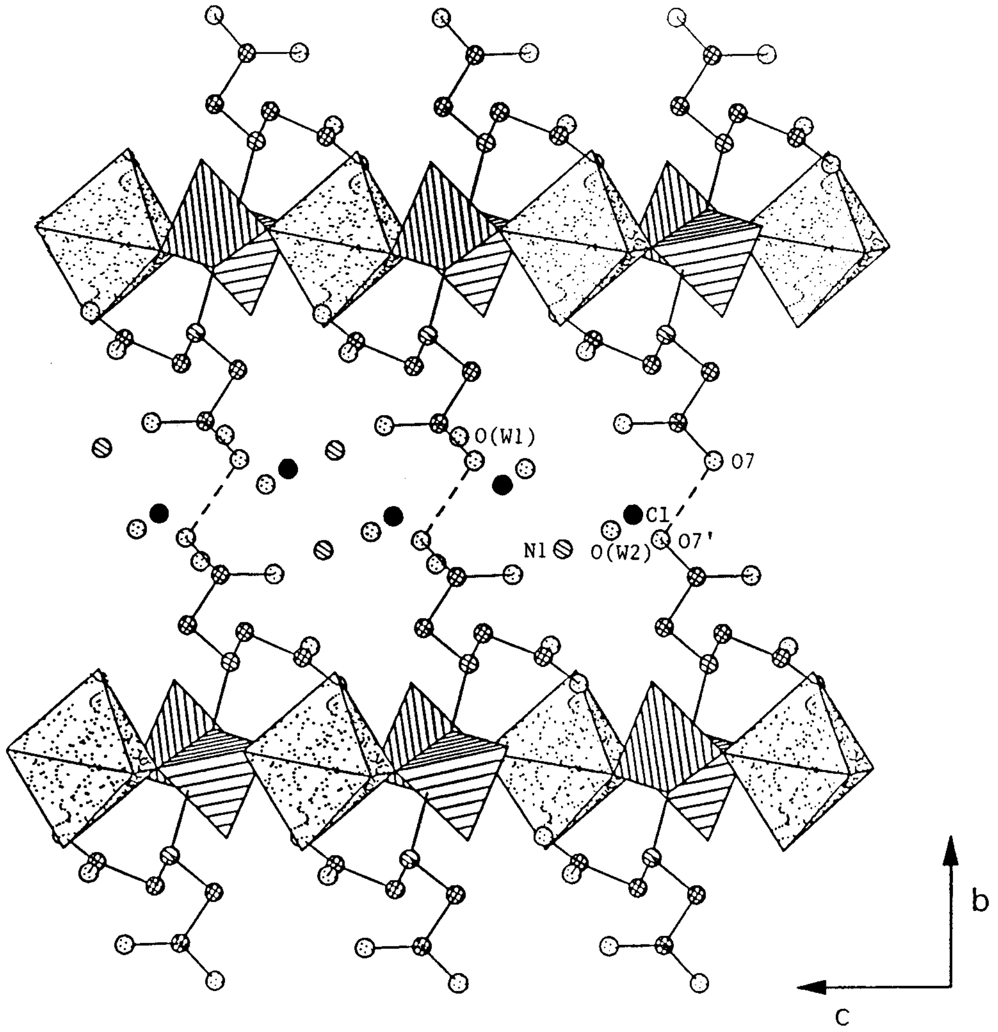

Figure 2. Polyhedral representation of Zr-PMIDA showing linear chains running down the *c* axis. The sketch depicts ZrF_2O_4 as octahedra and PO_3C moieties as tetrahedra. The hydrogen bonding is indicated by - - -.

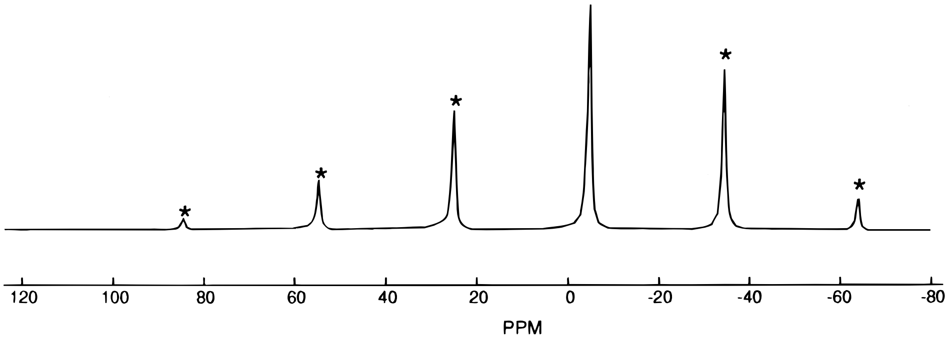

Figure 3. ^{31}P MAS solid state NMR of Zr-PMIDA. The spinning sidebands are indicated by asterisks.

Discussion

Zr-PMIDA is probably the first example of a linear chain zirconium phosphonate that has been structurally characterized. However, two other metal phosphonates with chain structures have been synthesized and characterized. One of them is an iron phenylphosphonate, $HFe(HPO_3PC_6H_5)_4$, reported by Bujoli,[16] and the other one is a uranyl phenylphosphonate, $UO_2(HO_3PC_6H_5)_2{\cdot}2H_2O$, recently synthesized and characterized

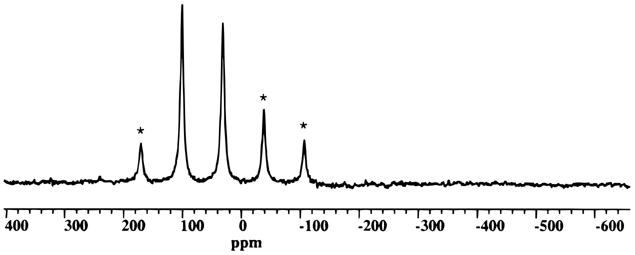

Figure 4. ^{19}F MAS solid state NMR of Zr-PMIDA. The spinning sidebands are indicated by asterisks.

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(16) Bujoli, B.; Palvadeau, P.; Rouxel, J. *C. R. Acad. Sci., Ser. 2* **1990**, *310*, 1213–1220.

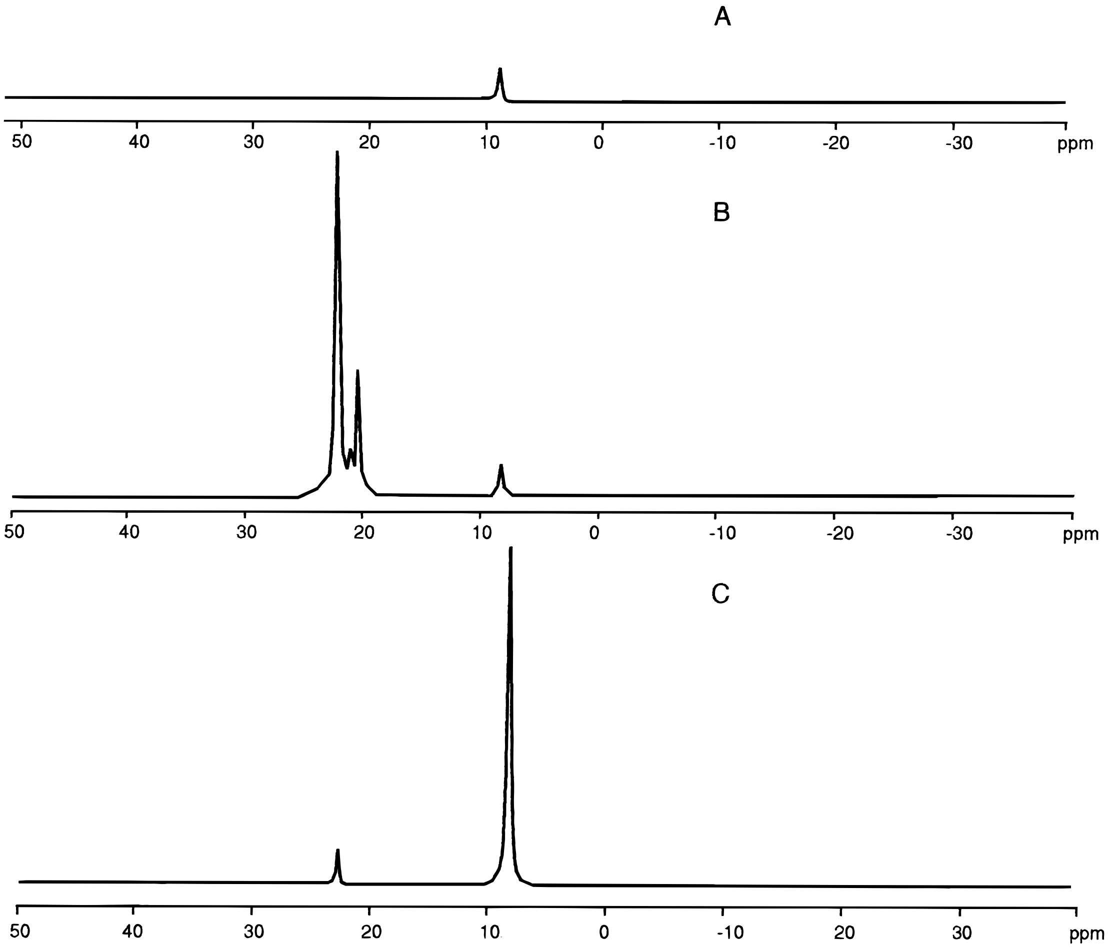

Figure 5. ^{31}P solution NMR of Zr-PMIDA: (A) Zr-PMIDA in D_2O; (B) sample A measured again 4 days later; (C) the supernate of Zr-PMIDA.

by our group.[17] In these compounds, the metals are bridged by phosphonates in a manner similar to that in the zirconium linear structure. However, the axial positions in these two compounds are occupied either by the uranyl oxygens in uranyl phenylphosphonates or by oxygens of a phosphonate group other than the one utilized in chain formation.

The formation of this linear type of zirconium phosphonate may be due to the large size of the phosphonate group.[10] Calculations show that PMIDA is too large to fit into the 24 Å^2 space which is available in the α-type layered structure. Earlier we obtained a new type of layered zirconium compound with PMIDA but in the presence of H_3PO_4.[12] Similar results were obtained for the reaction of zirconium salts with a viologen phosphonate ligand; the Zr–viologen compound that formed had a double-chain arrangement[18] to accommodate the size of viologen. By using phosphoric acid as a spacer molecule, it was possible to obtain a layered compound similar to Zr phosphate/PMIDA.[19] The formation of a new structure type when the ligands are too large to fit the 24 Å^2 requirement of α-ZrP has important implications in the construction of layer by layer thin films based on zirconium bis(phosphonates).[6,20] Katz and co-workers[21] have prepared thin films with large phosphonate ligands. It was tacitly assumed that the films have the α-ZrP layer structure. This may not be the case. The Zr content of such films has been shown to have a higher Zr/P ratio than that required for an α-ZrP type layer. A closer examination of such films is therefore in order to verify the structure type.

Finally, since fluoride and phosphonate dissociate in aqueous solution, this indicates that Zr-PMIDA can be used as an intermediate to prepare other kinds of zirconium phosphonates. Reaction of Zr-PMIDA with an excess of methylphosphonic acid resulted in a new phase with a *d* spacing of 8.9 Å. When the same reaction was carried out in acetone solution, it yielded a more crystalline compound with the same *d* spacing. Since this *d* spacing is the same as the one reported for layered zirconium methylphosphonate,[22] the structure formed is probably a layered one and not a linear chain. This result might have been anticipated because methylphosphonic acid tends to use three oxygens of the phosphonate group to form layered compounds.[22,23] In the present case, the methylphosphonic acid displaced the PMIDA ligand to form a more stable α-type layered compound. Studies of Zr-PMIDA substitution reactions

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(17) Grohol, D.; Subramanian, M. A.; Poojary, D. M.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 5264.

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

(19) Byrd, H.; Clearfield, A.; Poojary, D. M.; Reis, K. P.; Thompson, M. E. *Chem. Mater.* **1996**, *8*, 2239.

(20) Lee, H.; Keply, L. J.; Hong, H.-G.; Mallouk, T. E. *J. Am. Chem. Soc.* **1988**, *110*, 618. Lee, H.; Keply, L. J.; Hong, H.-G.; Akhter, S.; Mallouk, T. E. *J. Phys. Chem.* **1988**, *92*, 2577. Yang, H.-C.; Aoki, K.; Hong, H.-G.; Sackett, D. D.; Arendt, M. F.; Yau, S.-L.; Bell, C. M.; Mallouk, T. E. *J. Am. Chem. Soc.* **1993**, *115*, 11855.

(21) Katz, H. E.; Scheller, G.; Putvinski, T. M.; Schilling, M. L.; Wilson, W. L.; Chidsey, C. E. D. *Science* **1991**, 1485. Katz, H. E.; Shilling, M. L.; Ungashe, S.; Putvinski, T. M.; Chidsey, C. E. In *Supramolecular Architecture*; Bein, T., Ed.; ACS Symposium Series 499; American Chemical Society: Washington, DC, 1992; Chapter 3.

(22) Rosenthal, G. L.; Caruso, J. *J. Solid State Chem.* **1993**, *107*, 497.

(23) Grohol, D.; Gingl, F.; Clearfield, A. Unpublished results for UO_2.

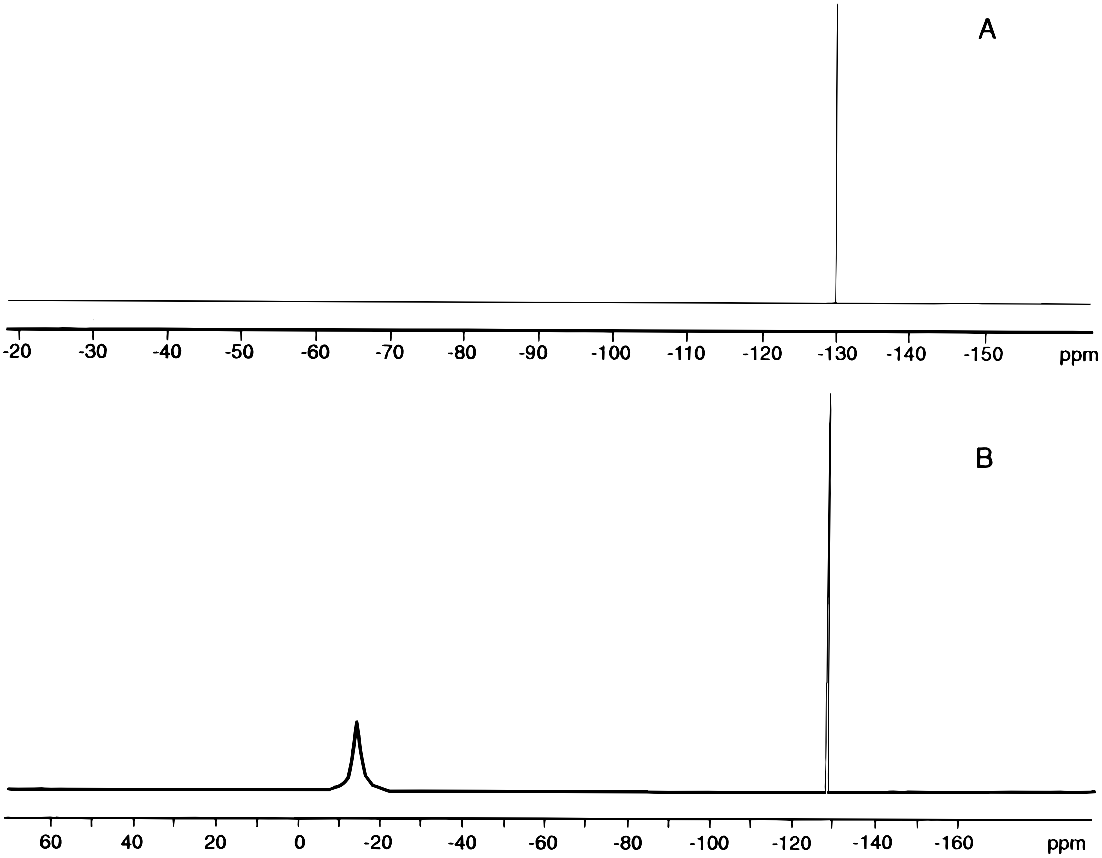

Figure 6. ^{19}F solution NMR of Zr-PMIDA: (A) Zr-PMIDA in D_2O; (B) the supernate of Zr-PMIDA.

with other ligands that attack the vacant or carboxyl-coordinated Zr site are in progress and will be published subsequently.

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Supporting Information Available: Tables providing X-ray experimental details and anisotropic thermal parameters (4 pages). Ordering information is given on any current masthead page.

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