Inorganic Chemistry

Zirconium Arene-Phosphonates: Chemical and Structural Characterization of 2-Naphthyl- and 2-Anthracenylphosphonate Systems

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Several new zirconium phosphonates incorporating naphthalene and anthracene ring systems and having the general formula $Zr(O_3PR)_1(O_3PR')_1$ [R and R' = $-C_{10}H_7$, $-C_{14}H_9$, $-OC_4H_9$, and $-OC_2H_5$] have been synthesized. These compounds were chemically characterized using thermal gravimetric analysis (percentage of organic content), infrared spectroscopy (presence of the desired organic functional groups), and solid-state ^{31}P NMR (phosphorus environments), while the structural parameters were determined using X-ray powder diffraction (interlayer *d* spacings). The *d* spacings of the zirconium bis(phosphonates) correlate well with a simple predictive model based on the effective length of the organic functional group. The zirconium mixed phosphonates examined are single-phase structures with random mixtures of the organic moieties within the interlayer and possess *d* spacings that are between those of the two parent zirconium bis(phosphonates).

1. Introduction

α-Zirconium phosphate, $Zr(O_3POH)_2 \cdot H_2O$, is a layered solid whose structure was first determined[1] by Clearfield and Smith and found to consist of planes of zirconium(IV) atoms linked by phosphate groups above and below the plane, in a two-dimensional network. Hydrogen-bonding interactions between the phosphate hydroxyl groups and the intercalated water cause the two-dimensional layers to stack upon one another, forming the three-dimensional structure. Alberti and co-workers[2] and Dines and DiGiacomo[3] later demonstrated that a related family of compounds known as zirconium phosphonates, $Zr(O_3PR)_2$, which also possess a layered structure similar to that of zirconium phosphate, can be synthesized using phosphonic acids instead of phosphoric acid. In these materials, it is now the attractive interactions of the R groups that project into the interlayer region that are responsible for stacking the zirconium planes.

It was subsequently shown that mixed zirconium phosphonates, $Zr(O_3PR)_x(O_3PR')_{2-x}$, can be formed by coprecipitation of zirconium(IV) in the presence of two different phosphonic acids.[4-7] If the two organic groups on the phosphonic acids are sufficiently different in size or physical properties, a material possessing interesting structural features may result. These mixed compounds generally contain a random mixture of the organic groups, i.e., a "solid solution" with all layers at identical stoichiometry. Although less likely, structures in which the different organic groups segregate into adjacent layers, known as "staging", have also been observed.[6,8-11]

Zirconium phosph(on)ates are showing promise as useful new materials with applications in a variety of areas such as catalysis,[12,13] ion exchange,[14-16] and photophysics.[17] A

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thorough review of metal phosphonate chemistry has been written by Clearfield[18] and attests to the growth of this field of solid-state inorganic chemistry.

The present work describes a chemical and structural investigation of zirconium phosphonates containing naphthalene or anthracene rings as the primary organic pendant groups. The compounds can generally be organized into two categories: (a) zirconium bis(phosphonates) containing the arene rings mentioned above and (b) zirconium mixed phosphonates containing naphthalene rings mixed with alkoxy chains. The motivation for synthesizing and thoroughly examining the chemical and structural aspects of these materials is twofold: (i) to our knowledge, there are no reports in the chemical literature regarding zirconium phosphonates containing naphthalene or anthracene ring systems, and (ii) it is believed that the zirconium phosphate crystal lattice structure provides a unique environment for the examination of the photophysics of these aromatic pendant groups. In fact, in our earlier report concerning the emission spectra of the two zirconium bis(arenephosphonates) described in this paper (those with naphthalene and with anthracene rings), we observed some very interesting photophysical behavior.[19] It was found that both of the zirconium bis(arenephosphonates) displayed prominent excimer emission but that the ratio of excimer to monomer emission intensities in these systems was drastically different; the anthracene system displays almost no monomer emission, whereas the naphthalene system displays comparable intensities of excimer and monomer fluorescence. We attributed this to the amount of π overlap in these ring systems, with the former having a larger degree of overlap, thus leading to increased excimer formation.

These interesting results led us to the idea of tuning the amount of excimer formation in these systems statistically by introducing alkyl spacer groups, which would in effect dilute the chromophores and decrease the amount of excimer formation. Additionally, by varying the size of the spacer groups, the volume available to a chromophore for exploring its conformational degrees of freedom is varied, in turn modulating the amount of excimer formation further. Results of the photophysical investigations will be presented in a forthcoming paper.[20]

Thus, we hereby report data on the following compounds within the $Zr(O_3PR)_x(O_3PR')_{2-x}$ motif: (i) R = R' = naphthalene; (ii) R = R' = anthracene; (iii) R = naphthalene, R' = butoxy; (iv) R = naphthalene, R' = ethoxy; (v) R = R' = butoxy; and (vi) R = R' = ethoxy.

2. Experimental Procedures

Materials and Synthetic Methodologies. The above-mentioned novel zirconium phosphonates have been synthesized, and in many instances, the phosphonic acids and precursors to the phosphonic acids were also synthesized. Because the syntheses for the zirconium phosphonates are very similar (mixing of a zirconyl chloride solution in HF with a solution of the stoichiometric amounts of the appropriate phosphonic acid(s), followed by refluxing for several days, and then filtering and drying), only one synthetic methodology is given in detail here. The synthetic methodologies for all other zirconium phosphonates, as well as for all phosphonic acids and all phosphonic acid precursors synthesized, are given in the Supporting Information.

Purchased chemicals were used as received. Hydrofluoric acid was purchased from J. T. Baker, Inc.; CDCl$_3$ and acetone-d_6 were purchased from Cambridge Isotope Labs, Inc.; zirconyl chloride was purchased from Aldrich Chemical Co. Naphthylphosphonic acid was synthesized as described in the Supporting Information. Solvents used for UV–vis spectroscopy were HPLC or spectroscopy grades.

All precursor compounds were characterized by melting point or boiling point, mass spectrometry, NMR (^{1}H, ^{13}C, and ^{31}P), and IR and UV–vis spectroscopies. All zirconium phosphonate materials were fully characterized by thermal gravimetric analysis (TGA) and IR, UV–vis, and solid-state ^{31}P NMR spectroscopies. Structural parameters (i.e., d spacings) of the zirconium phosphonates were determined using X-ray powder diffraction (XRD).

Zirconium Bis(2-naphthylphosphonate), $Zr(O_3PC_{10}H_7)_2$, Zr-(Nap)$_2$. To a solution of zirconyl chloride (0.152 g, 0.473 mmol) in 17.0 mL of water was added 0.93 mL of 2.04 M HF (1.90 mmol). This was added dropwise to a solution of 2-naphthylphosphonic acid (0.198 g, 0.952 mmol) in 19.0 mL of 0.037 M NaOH with stirring, and the mixture was refluxed for 5 days under nitrogen. The solution was cooled to room temperature and centrifuged to collect the solid, after which the solid was successively washed with water, acetone, and diethyl ether and air-dried to afford Zr-(Nap)$_2$ as a white solid (0.153 g, 64.2% yield): ^{31}P NMR (500 MHz, solid state) δ −4.8. XRD d_{001} (Å) 19.1. IR (KBr, cm^{-1}) 3053, 3021, 1628, 1594, 1574, 1501, 1469, 1384, 1366, 1346, 1275, 1246, 1163, 1149, 1117, 1053, 1039, 969, 949, 914, 862, 824, 740, 664, 645, 616, 566, 535, 477, and 411. TGA (150−1000 °C, Zr(Nap)$_2$ → ZrP$_2$O$_7$) percent weight loss: experimental (calculated)[1] 46.7 (47.3). UV (glycerol mull, nm) λ_{max} 230, 276, 283, 292, 309, 316, and 325.

Instrumental Methods. X-ray powder diffraction patterns were obtained with either a Scintag X1 or a Philips PW1877 automated powder diffractometer, using Cu Kα radiation and an internal silicon powder standard with all samples. Patterns were generally measured between 1.00° and 35.00° (2θ), with a step size of 0.02° and X-ray tube settings of 45 kV and 40 mA. The average error in the d-space values for all synthesized zirconium phosphonates is estimated to be ±0.3 Å. Infrared spectra were recorded on a Perkin−Elmer System 2000 FT-IR instrument as KBr pellets for solids and on NaCl plates for neat liquids, using 4 cm^{-1} resolution. Spectral data handling was performed using Gramms Analyst 2000 version 3.01 in the Microsoft Windows environment. TGA runs were performed on a Perkin−Elmer TGS-2 Thermogravimetric Analyzer interfaced to a System 7/4 console and a model 3600 Data Station. All TGA scans were obtained on 10−15 mg of solid, with flowing compressed air, and a 10 °C/min heating rate. The experimental reproducibility of percent weight loss values for the zirconium phophonates synthesized was determined to be ±0.2%. All NMR spectra were acquired on a Bruker ARX 500-MHz spectrometer and using Bruker UXNMR software. Spectrometer operating frequencies were 500.13, 125.76, and 202.40 MHz for ^{1}H, ^{13}C, and ^{31}P nuclei, respectively. For ^{1}H and ^{13}C spectra, either tetrameth-

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ylsilane or the resonance of the deuterated solvent was used as an internal reference, while for ^{31}P spectra, 85% H_3PO_4 was used as an external reference. Spectra of ^{31}P and ^{13}C nuclei were obtained with ^1H decoupling, using standard Bruker pulse sequences. Solid-state ^{31}P NMR spectra were obtained using 7 mm zirconia rotors, Delrin caps, and magic-angle spinning (MAS) at 4 kHz. The average error in the solid-state ^{31}P chemical shifts was estimated to be ±0.2 ppm. Absorbance spectra were obtained on a Perkin−Elmer Lambda 6 UV−vis spectrometer using PECCS data collection software version 3.21. Spectral processing was achieved using Spectracalc Arithmetic version A2.20. Organic compounds were dissolved in an appropriate HPLC- or spectral-grade solvent, and the absorbance spectrum was measured in a 1-cm path-length quartz cuvette. Zirconium phosphonates were ground to a fine powder and then mixed with glycerol to form a mull or suspension, with "concentrations" generally ranging from 5×10^{-2} mg of zirconium phosphonate/mg of glycerol to 1×10^{-3} mg of zirconium phosphonate/mg of glycerol. The absorbance spectrum of the glycerol mull was obtained by placing the mull between two 0.18 cm thick parallel quartz plates, separated by a 0.12 cm thick plastic spacer, with a rectangular opening in the center (1.1 × 1.9 cm).

3. Chemical Characterization

Thermal Gravimetric Analysis. TGA can be used as an analytical tool for the confirmation of the composition of the organic components of zirconium phosphonates. It was shown by Costantino[21] and Alberti et al.[6] that heating zirconium phosphonates in the presence of oxygen or air to temperatures between 1000 and 1200 °C converts the compounds to zirconium pyrophosphate, ZrP_2O_7, in either the α-layered ($d_{001} = 6.1$ Å) or cubic ($d_{001} = 4.8$ Å) structure. Therefore, knowing the final composition of the pyrolysis product, the experimental percent weight loss determined can be compared to the theoretical percent weight loss that is calculated using eq 1.

$$\text{percent weight loss} = \frac{\text{FW of } Zr(O_3PR)_x(O_3PR')_{2-x} - \text{FW of } ZrP_2O_7}{\text{FW of } Zr(O_3PR)x(O_3PR')_{2-x}} \times 100 \quad (1)$$

In general, the TGA traces of the zirconium phosphonates examined show the loss of surface-bound or intercalated water below 150 °C, followed by volatilization of the organic fragments between 300 and 700 °C. As examples, the TGA traces of zirconium bis(2-naphthylphosphonate) [$Zr(Nap)_2$], zirconium 2-naphthylphosphonate ethyl phosphate [$Zr(Nap)_1$-$(OEt)_1$], and zirconium bis(ethyl phosphate) [$Zr(OEt)_2$] are displayed in Figure 1. The TGA traces of zirconium bis(2-anthracenylphosphonate)[$Zr(Anth)_2$], zirconium bis(butyl phosphate) [$Zr(OBut)_2$], and zirconium 2-naphthylphosphonate butyl phosphate [$Zr(Nap)_1(OBut)_1$] are given in Figure 1S in the Supporting Information.

As can be observed in Figure 1, the trace of $Zr(Nap)_2$ displays a larger percent weight loss than the trace of Zr-$(OEt)_2$ and the percent weight loss of $Zr(Nap)_1(OEt)_1$ is between the values of the two bis(phosphonate) compounds. This is in accordance with the difference in the masses of the organic components in these compounds. It is also evident
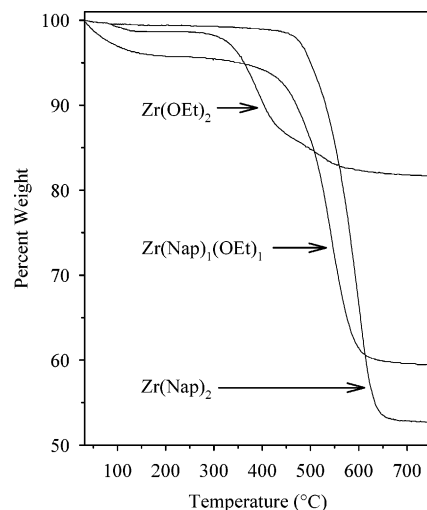

Figure 1. Thermal gravimetric analysis curves of $Zr(OEt)_2$, $Zr(Nap)_1$-$(OEt)_1$, and $Zr(Nap)_2$.

Table 1. TGA Data for the Zirconium Bis(phosphonates), $Zr(O_3PR)_2$, and Zirconium Mixed Phosphonates, $Zr(O_3PR)_1(O_3PR')_1$

compound	T_{loss} (°C)	exptl percent weight loss	calcd percent weight loss	percent difference
$Zr(Anth)_2$	550	55.9	56.1	0.4
$Zr(Nap)_2$	600	46.7	47.3	1.3
$Zr(OBut)_2$	350	29.9	32.9	9.1
$Zr(OEt)_2$	450	17.4	21.8	20.2
$Zr(Nap)_1(OBut)_1$	500	40.9	41.0	0.2
$Zr(Nap)_1(OEt)_1$	550	36.3	37.1	2.2

from Figure 1 that the organic fragments of $Zr(OEt)_2$ begin to volatilize at a lower temperature (∼300 °C) as compared to those of $Zr(Nap)_2$ (∼450 °C), which reflects the greater thermal stability of the arene ring connected via its P−C bond. Table 1 lists the experimentally determined and theoretically calculated percent weight loss values for the zirconium phosphonates synthesized. Although the range of temperatures over which the pendant-group loss occurs varies widely (see Figures 1 and 1S), an approximate midpoint of the organic-loss temperature range is indicated. The agreement between the experimental and calculated values is very good, except for $Zr(OBut)_2$ and $Zr(OEt)_2$, with the experimental values being generally lower than the calculated values. The systematic discrepancy toward lower values is attributed to the incomplete combustion of the organic groups and the subsequent trapping or surface deposition of some of the organic fragments, as evidenced by a slight grayish color of the final solid after TGA analysis.[6,22]

Figure 1 also shows that the organic functional groups of $Zr(Nap)_1(OEt)_1$ did not volatilize distinctly from one another, and therefore, the TGA of this compound does not directly yield the relative stoichiometry. If the stoichiometric parameter x (which is defined as the number of moles of H_2O_3PR incorporated into the zirconium mixed phosphonate) is known, the TGA trace can be used to compare the experimentally determined percent weight loss to the theoretically calculated percent weight loss, and this is what is presented in Table 1, assuming $x = 1.0$ for both mixed compounds. In

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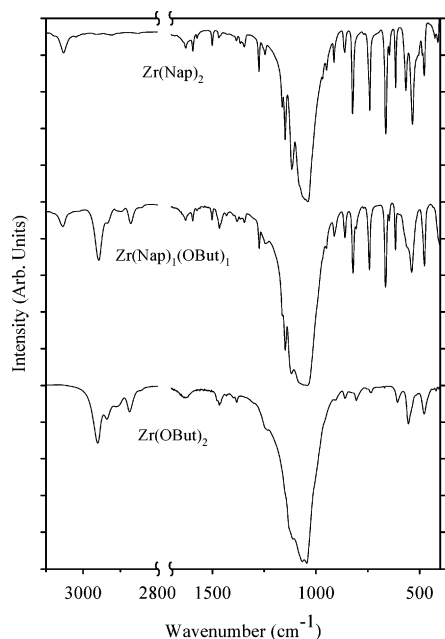(22) Yang, C. Y. Ph.D. Dissertation, Texas A&M University, 1986.

Figure 2. Infrared spectra of Zr(Nap)$_2$, Zr(Nap)$_1$(OBut)$_1$, and Zr(OBut)$_2$ as KBr pellets in the 3100 to 2800 cm^{-1} and 1700 to 400 cm^{-1} spectral regions.

a reverse approach, the value of x can be estimated using eq 2,[6] where W_{150} and W_{1000} are the percent weight loss values

$$\Delta W = \frac{W_{150} - W_{1000}}{W_{150}} = \frac{xR + (2-x)R' - \frac{1}{2}O_2}{ZrP_2O_6 + xR + (2-x)R'} \quad (2)$$

at 150 °C (chosen to represent a state without water content) and 1000 °C, respectively, R and R′ are the formula weights of the different organic fragments, and formulas ZrP$_2$O$_6$ and O$_2$ also represent their formula weights. Using the weights represented in Figure 1 and inserting these into eq 2 yields values of $x = 0.91$ and 1.06 for Zr(Nap)$_1$(OBut)$_1$ and Zr-(Nap)$_1$(OEt)$_1$, respectively, demonstrating that these compounds are indeed comprised of an approximately equal mole ratio of the two functional groups.

Regarding the TGA results of Zr(OBut)$_2$ and Zr(OEt)$_2$, we have also observed such uncharacteristically low values for several other zirconium organophosphates,[23] and these results appear to indicate that there is an additional systematic anomaly in the pyrolysis of these compounds, possibly associated with the availability of a source of oxygen atoms. If, upon pyrolysis of compounds of this type, the product were not ZrP$_2$O$_7$ but materials having additional oxygen content, then the experimental percent weight loss would be lower compared to the theoretical percent weight loss.

Infrared Spectroscopy. The observed IR vibrational frequencies for each of the zirconium phosphonates investigated are listed at the end of each synthetic description, and as examples, the IR spectra of Zr(Nap)$_2$, Zr(Nap)$_1$-(OBut)$_1$, and Zr(OBut)$_2$ are shown in Figure 2. The IR spectra of Zr(Anth)$_2$, Zr(OEt)$_2$, and Zr(Nap)$_1$(OEt)$_1$ are given in Figure 2S in the Supporting Information. For all zirconium

Table 2. Solid-State ^{31}P NMR Isotropic Chemical Shifts for the Zirconium Bis(phosphonates), Zr(O$_3$PR)$_2$, and Zirconium Mixed Phosphonates, Zr(O$_3$PR)$_1$(O$_3$PR′)$_1$

compound	δ_{arene} (ppm)	δ_{alkyl} (ppm)
Zr(Anth)$_2$	−4.0	
Zr(Nap)$_2$	−4.8	
Zr(OBut)$_2$		−21.0, −21.7, −22.4
Zr(OEt)$_2$		−19.8, −20.8, −21.8
Zr(Nap)$_1$(OBut)$_1$	−5.2	−20.9
Zr(Nap)$_1$(OEt)$_1$	−5.2	−20.9

phosphonates, strong absorptions between 1100 and 900 cm^{-1} assigned to the stretching modes of the −PO$_3$ group and weaker absorptions between 600 and 400 cm^{-1} corresponding to the bending modes of the −PO$_3$ group are observed.[24,25] For the compounds containing naphthalene and anthracene rings, the IR spectra display absorptions for the aromatic C−H stretching modes (3100−3000 cm^{-1}), the aromatic carbon−carbon ring stretching modes (1600−1400 cm^{-1}), the in-plane C−H bending modes (1300−1000 cm^{-1}), and the out-of-plane C−H ring bending modes (900−675 cm^{-1}).[2] Compounds containing the alkyl groups possess absorptions for the asymmetric and symmetric C−H stretching modes between 3000 and 2700 cm^{-1}, bands for the asymmetric and symmetric methyl bending modes, near 1450 and 1375 cm^{-1}, respectively, and an absorption for the methylene scissoring mode close to the value of 1465 cm^{-1}.[26] It should be noted that the asymmetric methyl bending peak can sometimes be obscured by the methylene scissoring band.

As can be seen in Figure 2, the IR spectra of Zr(Nap)$_2$ and Zr(OBut)$_2$ display absorptions that are attributable to the respective functional group vibrations described above, confirming that the desired organic groups are intact and present in these compounds. Similar results are observed for Zr(Anth)$_2$ and Zr(OEt)$_2$. Figure 2 also shows that the mixed compound, Zr(Nap)$_1$(OBut)$_1$, does indeed possess both functional group types, as evidenced by the clear presence of distinct vibrations because of the naphthyl ring and the alkyl group. A similar analysis involving its distinct functional group vibrations also held for Zr(Nap)$_1$(OEt)$_1$.

Solid-State ^{31}P NMR. Because phosphorus 31 is an NMR-active nucleus, solid-state ^{31}P NMR spectroscopy can be used to determine the magnetic and chemical environment of the phosphorus atoms in zirconium bis(phosphonate) compounds and to confirm the presence of chemically distinct phosphorus sites in zirconium mixed phosphonates. The isotropic ^{31}P chemical shifts for the zirconium phosphonates studied are given in Table 2, and as examples, the ^{31}P NMR spectra of Zr(Nap)$_2$, Zr(Nap)$_1$(OEt)$_1$, and Zr(OEt)$_2$ are displayed in Figure 3. The solid-state ^{31}P NMR spectra of Zr(Anth)$_2$, Zr-(OBut)$_2$, and Zr(Nap)$_1$(OBut)$_1$ are given in Figure 3S in the Supporting Information.

As can be seen from Table 2, the isotropic ^{31}P chemical shifts for Zr(Anth)$_2$ and Zr(Nap)$_2$, in which the phosphorus

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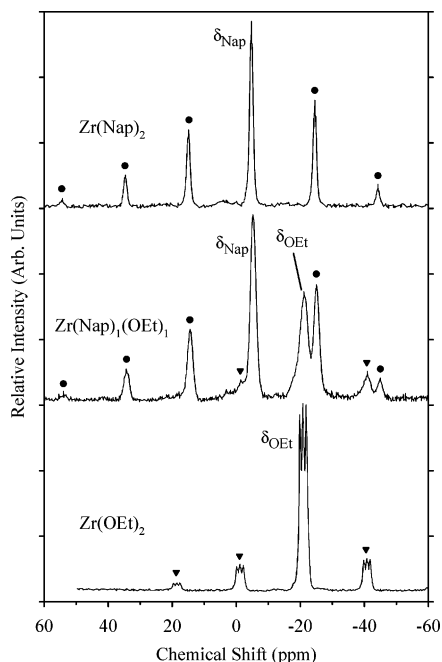
Figure 3. Solid-state ^{31}P NMR spectrum of $Zr(Nap)_2$, $Zr(Nap)_1(OEt)_1$, and $Zr(OEt)_2$. The peaks marked with an asterisk are spinning sidebands. The isotropic resonances associated with the naphthylphosphonate groups are marked with δ_{Nap}, while the isotropic resonances associated with the ethyl phosphate groups are marked with δ_{OEt}.

Table 3. Experimental and Predicted Interlayer Spacings of the Zirconium Bis(phosphonates), $Zr(O_3PR)_2$, and Zirconium Mixed Phosphonates, $Zr(O_3PR)_1(O_3PR')_1$

compound	d_{001} (Å) experimental	d_{001} (Å) predicted[a]
$Zr(Anth)_2$	23.2	23.7
$Zr(Nap)_2$	19.1	19.5
$Zr(OBut)_2$	15.8	16.0
$Zr(OEt)_2$	11.6	11.9
$Zr(Nap)_1(OBut)_1$	18.3	17.8 or 19.1[b]
$Zr(Nap)_1(OEt)_1$	18.2	15.7 or 19.1[b]

[a] Predicted values based on the simple geometrical model described in the text. [b] Predicted values based on propping up of layers to maximum possible distance.

atom is directly attached to the aromatic ring, occur at -4.0 and -4.8 ppm, respectively. The small, upfield shift of the resonance for $Zr(Nap)_2$ as compared to that of $Zr(Anth)_2$ suggests that there is slightly more electron density on the 2-position carbon in $Zr(Nap)_2$, even though the total number of π-electrons is larger in $Zr(Anth)_2$. The spectra of these zirconium bis(phosphonates) are typical, in that each displays a single isotropic resonance along with multiple, lower intensity spinning sidebands.

In contrast, the ^{31}P NMR spectra of both $Zr(OEt)_2$ and $Zr(OBut)_2$ display an unusual and unique result: three isotropic resonances, with chemical shifts between -19 and -23 ppm. It is not believed that these resonances are spin triplets based on two considerations. First of all, the intensity ratios of the peaks are 1.0:1.0:1.0 for $Zr(OEt)_2$ and 1.0:1.2:1.0 for $Zr(OBut)_2$ and not 1:2:1 as would be expected for true spin triplets. Second, the only nuclei that are NMR active and spatially close to the phosphorus are the alkyl group hydrogens, and typical phosphorus–hydrogen coupling constants are on the order of $10-15$ Hz,[26] whereas the separations between the observed peaks are 144 and 136 Hz for $Zr(OBut)_2$ and 202 and 199 Hz for $Zr(OEt)_2$. Rather, these are most likely caused by "locked-in" conformations of the organic chains (presumably similar to the staggered and gauche conformations of butane), which give rise to inequivalent magnetic phosphorus environments in these zirconium bis(phosphonates). Our hypothesis is supported by the fact that this type of magnetic inequivalence because of distinct conformations of the organic groups has also been observed in a zirconium bis(phosphonate) containing 2-naphthylmethylphosphonate groups.[23] However, theoretical mod-

eling studies need to be carried out to unambiguously understand the "multiplet" of resonances for these compounds.

For the mixed systems, $Zr(Nap)_1(OEt)_1$ and $Zr(Nap)_1(OBut)_1$, the ^{31}P resonances are sufficiently resolved that identification and confirmation of the two chemically distinct phosphorus atoms were possible. It should be noted that the resonances for the naphthylphosphonate phosphorus atoms in the mixed compounds are slightly shifted with respect to the resonances of $Zr(Nap)_2$. This is believed to be due to slight perturbations in the magnetic environment of the phosphorus atoms in the mixed compounds, which now have different neighboring groups as compared to that of $Zr(Nap)_2$. Also, the three alkyl phosphate resonances in the mixed compounds have now collapsed into a single isotropic resonance. This is presumably due to restricted conformational freedom of the alkyl chains as a result of the presence of the large, bulky naphthalene rings within the interlayer.

4. Structural Investigations

X-ray Diffraction Patterns. For crystalline zirconium phosphonates, the interlayer distance or d spacing of the zirconium planes can be determined from the $00n$ peaks in the powder XRD pattern (via the Bragg equation, $n\lambda = 2d \sin\theta$). The d-space values for the zirconium phosphonate compounds synthesized in this study are given in Table 3. The XRD patterns of $Zr(Nap)_2$, $Zr(Nap)_1(OBut)_1$, and $Zr(OBut)_2$ are shown in Figure 4, while the XRD patterns for $Zr(Anth)_2$, $Zr(OEt)_2$, and $Zr(Nap)_1(OEt)_1$ are given in Figure 4S in the Supporting Information. As can be seen from Figure 4, all three XRD patterns display a strong 001 peak (the lowest-angle diffraction peak in the pattern) followed by higher order $00n$ peaks at larger angles and lower intensities. The remainder of the XRD pattern consists of lower intensity, unresolved peaks, which are not shown in Figure 4. It should be noted that the interlayer spacings of $Zr(OEt)_2$ and $Zr(OBut)_2$ have been determined previously (11.7 Å[2] and 15.9 Å,[27] respectively) and the present experimental values are in excellent agreement with these.

Bis(phosphonates). For the zirconium bis(phosphonates), the variation of the interlayer spacing is consistent with a layered structure and the observed d-space values can be reconciled with predictions from a somewhat primitive modeling method, which is shown in Figure 5 for $Zr(Anth)_2$

(27) Maya, L. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 207.

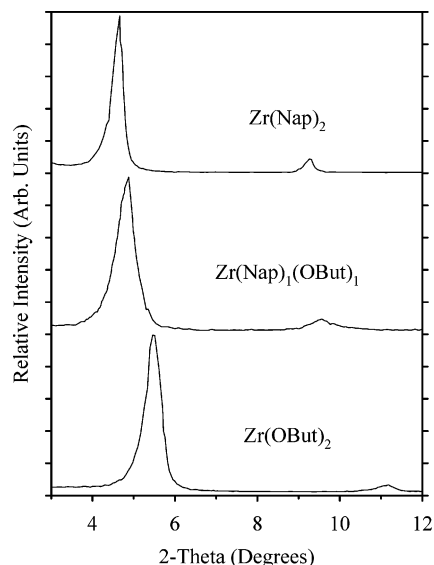**Figure 4.** X-ray diffraction patterns displaying the 00n peaks of Zr(Nap)$_2$, Zr(Nap)$_1$(OBut)$_1$, and Zr(OBut)$_2$.
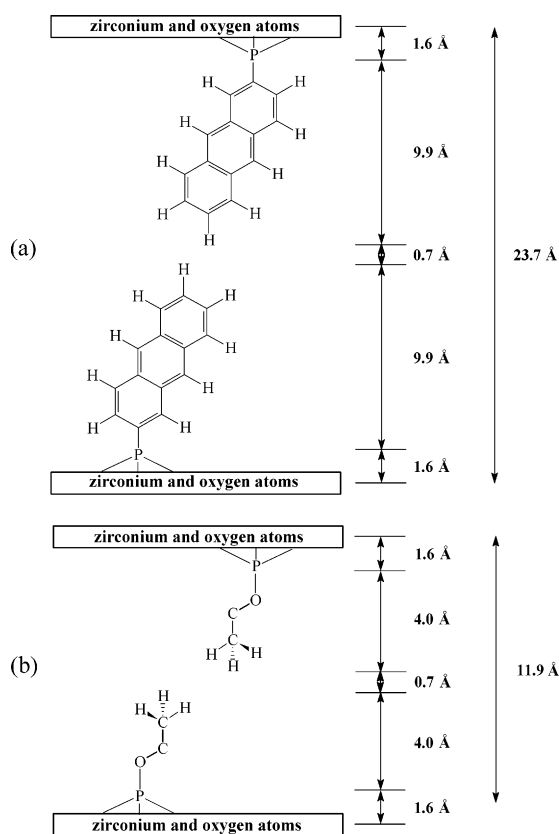

Figure 5. Idealized structural representations of (a) Zr(Anth)$_2$ and (b) Zr-(OEt)$_2$, illustrating the predicted d spaces based on the zirconium phosphate layer thickness and the idealized length of the organic functional groups.

and Zr(OEt)$_2$. The predicted d-space values are obtained by a summation of the zirconium phosphate layer thickness of 3.2 Å,[1,2] plus twice the normal distance (projection along the P−C or P−O bond axis) from the phosphorus atom to the farthest hydrogen atom in the organic functional group, plus twice the value of the hydrogen atomic radius (0.35 Å).[28] Using Zr(OEt)$_2$ as an illustration, Figure 5b represents the idealized, fully extended chain geometry, and as evi-

denced and discussed above (^{31}P NMR spectra), the actual structure most likely includes other conformations of the organic chain not depicted in the figure. At any rate, it is believed that a sufficient number of chains find themselves in this idealized conformation to give rise to the experimentally observed d spacing.

Table 3 reveals that these simply predicted d spacings are in very good agreement with the experimentally determined values, although the predicted values are systematically somewhat higher than the experimental values. This small, regular deviation is most likely due to two assumptions inherent in this simple model: (i) that the P−C or P−O bonds are normal to the zirconium phosphate layer and (ii) that the contact between organic groups in adjacent layers is "end to end". In regards to the first assumption, experimental observations from the Rietveld refinement of the structure of zirconium bis(phenylphosphonate)[29] and molecular mechanics structural calculations for zirconium p-aminobenzylphosphonates[30] both show that this bond is not normal to the layer and is in fact tilted by approximately 30°. Concerning the second assumption, because of the monoclinic nature of the zirconium phosphate unit cell,[1] the organic moieties are actually displaced from being directly above one another, and therefore, the 0.7 Å H−H contact distance is effectively reduced. Thus, both of these assumptions would tend to increase the predicted d spacing as compared to the experimental value.

Mixed Phosphonates. For a zirconium mixed phosphonate, there are generally three different structural possibilities for the arrangement of the organic moieties: (i) a random distribution within the interlayer (all layers therefore equivalent), (ii) an ordered segregation or staging of the functional groups in an alternating fashion (adjacent layers not equivalent), and (iii) precipitation into cocrystallites or domains of the bis(phosphonates), in other words two individual phases.

Each of these situations will give rise to distinct behavior, which will be evident in the XRD powder patterns. The randomly distributed structure will show a single 001 peak at a d-space value equal to or between those of the two parent zirconium bis(phosphonates). The ordered, segregated structure, on the other hand, will display a 001 peak, whose d spacing is that of a sum of the two parent zirconium bis-(phosphonates). The third possibility, distinct cocrystallites, will give rise to an XRD pattern that contains two 001 peaks, one peak at the d spacing for one of the parent zirconium bis(phosphonates) and the other peak at the value for the other parent zirconium bis(phosphonate), as if for a simple physical mixture of the two compounds.

As can be seen from an inspection of Table 3, the d spacings of Zr(Nap)$_1$(OEt)$_1$ and Zr(Nap)$_1$(OBut)$_1$ are between the d-space values of their parent zirconium bis(phosphonates), indicative of single phase, randomly mixed structures

(28) Distances and angles used in the idealized structures were the standard values given in the *CRC Handbook of Chemistry and Physics*, 70th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1989; pp F-188−F-192.
(29) Poojary, D. M.; Hu, H. L.; Campbell, F. L., III; Clearfield, A. *Acta Crystallogr., Sect. B* **1993**, *49*, 996.
(30) Leenstra, W. R.; Amicangelo, J. C. *Inorg. Chem.* **1998**, *37*, 5317.

for both of these compounds. It can also be said that the degree of crystallinity of the two mixed compounds is lower than that of the respective parent bis(phosphonates), as determined from the widths of the 001 XRD peaks. For example, the fwhm line widths of the 001 peaks for $Zr(Nap)_2$, $Zr(Nap)_1(OBut)_1$, and $Zr(OBut)_2$ are 0.27°, 0.52°, and 0.46°, respectively. Therefore, the order of the degree of crystallinity is as follows: $Zr(Nap)_2 > Zr(OBut)_2 > Zr(Nap)_1(OBut)_1$. This is as expected because the packing efficiency should be greater when all of the organic functional groups are identical, although this is not always the case because crystallinity also depends on the refluxing time and amount of HF used.

For the purpose of calculating the interlayer spacings, we employed the same type of primitive predictive model that was used to estimate the interlayer spacings of the zirconium bis(phosphonates). That is, it is presumed that the naphthalene rings are opposite alkoxy groups allowing a "collapse" of the "scaffolded" structure. Under these assumptions, one obtains estimated d-space values of 15.7 and 17.8 Å for $Zr(Nap)_1(OEt)_1$ and $Zr(Nap)_1(OBut)_1$, respectively. However, the experimental interlayer spacings of these compounds are clearly higher and essentially equivalent to one another within the error limits of ±0.3 Å. They are also in direct contrast to the deviations (observed versus calculated) seen for the bis(phosphonates). A more plausible explanation is that, with a stoichiometrically equal number of naphthalene rings and alkoxy chains, i.e., $x = 1$, there are a sufficient number of naphthalene rings that are in contact with a naphthalene ring from the opposite layer, essentially "propping up" the interlayer distance up to a value near that of $Zr(Nap)_2$ at 19.1 Å (listed as such in Table 3). The small decrease (0.8–0.9 Å) in the d spacing of these mixed compounds as compared to the 19.1 Å of $Zr(Nap)_2$ is most likely due to a small amount of interpenetration of the naphthalene rings from the opposite layers.

It is interesting to note that these mixed compounds lack the rotational freedom that would allow a significant "folding over" of the aromatic rings toward their own attachment layer, as was predicted to be occurring in our previous study of a zirconium mixed phosphonate series containing *p*-aminobenzyl and methyl groups.[30] Thus, although zirconium mixed arene-alkoxy phosphonates with x values $\ll 1$ (i.e., a preponderance of the smaller pendant groups) were not synthesized for the present series of compounds, it is envisioned that d-space values for such stoichiometries would indeed be close to the primitive predictions discussed above.

5. Conclusions

Four novel zirconium phosphonates incorporating arene rings have been synthesized, chemically characterized, and structurally examined: two zirconium bis(phosphonates), $Zr(Nap)_2$ and $Zr(Anth)_2$, and two zirconium mixed phosphonates, $Zr(Nap)_1(OEt)_1$ and $Zr(Nap)_1(OBut)_1$.

Chemically, the compositions of all compounds synthesized and studied were confirmed by TGA. The presence of the desired functional groups in all of the compounds was determined by IR spectroscopy. Solid-state ^{31}P NMR spectroscopy was instrumental in revealing the presence of magnetically inequivalent phosphorus environments (multiple resonances) for $Zr(OBut)_2$ and $Zr(OEt)_2$, which were attributed to the presence of distinct, "locked-in" conformations of the alkyl chains, whereas $Zr(Nap)_2$ and $Zr(Anth)_2$ only displayed one dominant phosphorus environment (single resonances), as expected for zirconium bis(phosphonates). Solid-state ^{31}P NMR spectroscopy was also used to confirm the presence of two chemically distinct phosphorus environments for $Zr(Nap)_1(OEt)_1$ and $Zr(Nap)_1(OBut)_1$.

Structurally, the interlayer spacings of $Zr(Nap)_2$ and $Zr(Anth)_2$ were found to vary in accordance with the size of the organic pendant groups, in a simple and predictable manner. Both $Zr(Nap)_1(OEt)_1$ and $Zr(Nap)_1(OBut)_1$ were determined to be single-phase compounds that possess structures with random distributions of the two organic pendant groups within the interlayer. The d spacings of these mixed compounds were found to be very close to that of $Zr(Nap)_2$, and it was concluded that this was a result of a sufficient number of naphthalene rings whose nearest neighbors in the opposite layer are also naphthalene rings, resulting in a "propping up" of the interlayer spacing.

Supporting Information Available: Synthetic methodologies for zirconium bis(phosphonates) and zirconium mixed phosphonates, phosphonic acids, and precursors to phosphonic acids, not specifically described in the paper. Sets of TGA traces, IR spectra, solid-state ^{31}P NMR spectra, and XRD patterns for compounds examined but not explicitly displayed in the paper, given as Figures 1S−4S, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0400282