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1. Introduction

 α -Zirconium phosphate, Zr(O₃POH)₂·H₂O, is a layered solid material, whose crystal structure was first determined by Clearfield and Smith.¹ The structure is found to be comprised of two-dimensional planes of zirconium(IV) atoms covalently bonded to phosphate groups above and below the planes, giving rise to the layers, and the three-dimensional structure is formed by stacking the two-dimensional layers upon one another, with no covalent bonding between the

Structural variability of pendant groups within the interlayer region of zirconium arene-phosph(on)ates: chemical and structural characterization of oxyand methyl-linked 2-naphthyl phosphonates, and mixed oxy-linked derivatives[†]

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Several new zirconium phosphonates incorporating the naphthalene ring and having the general formula $Zr(O_3PR)_1(O_3PR')_1$ [R and R' = $-CH_2C_{10}H_7$, $-OC_{10}H_7$, $-CH_3$, $-OC_2H_5$, -OH] have been synthesized. These materials were chemically characterized using thermal gravimetric analysis (percentage of organic content), infrared spectroscopy (presence of the desired organic functional groups), and solid-state ³¹P NMR (phosphorus environments), while the structural parameters were determined using X-ray powder diffraction (interlayer d spacings). The two new zirconium bis(phosphonates), $Zr(O_3PC_{10}H_7)_2$ and $Zr(O_3PCH_2C_{10}H_7)_2$, were found to have *d* spacings of 19.6 and 20.0 Å, respectively. Three of the four zirconium mixed phosphonates examined are found to be single-phase structures with random mixtures of the organic moieties within the interlayer, and possess d spacings (14.3, 15.3, and 16.1 Å) that are between those of the two parent zirconium bis(phosphonates). The fourth is found to be a staged or segregated structure and possesses a d spacing that is approximately a sum of the two parent zirconium bis(phosphonates), with a d spacing of 28.2 Å. Solid-state 31 P NMR of Zr(O₃PCH₂C₁₀H₇)₂ revealed the presence of two isotropic resonances, which is interpreted in terms of two distinct, "locked-in" conformations of the $-CH_2C_{10}H_7$ group. The experimental d spacings of the zirconium bis(phosphonates) correlate well with a simple predictive model based on the effective length and predominant conformation of the organic functional group.

layers. Each zirconium is bonded to six oxygen atoms from six different phosphate groups, giving it an octahedral bonding environment, and each phosphate group is bonded to three different zirconium atoms. The fourth oxygen atom of each phosphate group is pointing into the region between the layers, known as the interlayer region, and has a hydrogen atom attached to it. The interactions between the layers of α -zirconium phosphate is dominated by hydrogen bonding between the layers and with an intercalated water molecule.^{2–4}

It was demonstrated by Alberti and co-workers,⁵ Maya,⁶ and Dines and DiGiacomo⁷ that by using phosphonic acids (H_2O_3PR) rather than phosphoric acid (H_3PO_4) , where R is an organic functional group, a series of new compounds known as zirconium phosphonates, $Zr(O_3PR)_2$, or more precisely as zirconium bis(phosphonates), could be synthesized. Zirconium bis(phosphonates) possess a layered structure similar to that of zirconium phosphate, but with the organic functional groups now projecting into the interlayer region. For these materials, the principal interactions between the layers are the van der Waals forces between the interlayer func-



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[†]Electronic supplementary information (ESI) available: Synthetic methodologies for Zr(ONap)₂, Zr(ONap)₁(Me)₁, 2-napthylmethylphosphonic acid, and its precursor diethyl 2-napthylmethylphosphonate. Sets of TGA traces, IR spectra, solidstate ³¹P NMR spectra, and XRD patterns for zirconium phosph(on)ate compounds examined but not explicitly displayed in the paper are given as Fig. 1S through 4S, respectively. See DOI: 10.1039/c9dt03875b

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tional groups. One of the key structural parameters used to characterize these materials is the interlayer spacing or d spacing, which is the distance between the adjacent zirconium planes, and it was found that the interlayer spacing varied in accordance with the size of the organic functional group. Since those initial reports, a large number of zirconium bis(phosphonates) have been synthesized, with a variety of organic functional groups, such as alkyl chains, functionalized alkyl groups, and various rings of both the aromatic and non-aromatic type.⁸⁻¹⁰

By co-precipitating the zirconium(IV) with two different phosphonic acids, H2O3PR and H2O3PR', mixed zirconium phosphonates having the general formula $Zr(O_3PR)_x(O_3PR')_{2-x}$ have been synthesized.¹¹⁻¹⁴ Typically, the observed interlayer spacing for the mixed zirconium phosphonate, $Zr(O_3PR)_x(O_3PR')_{2-x}$, is found to be intermediate between the two zirconium bis(phosphonates), $Zr(O_3PR)_2$ and $Zr(O_3PR')_2$, which is generally taken to indicate that the mixed compounds contain a random mixture of the organic groups, *i.e.*, a "solid solution" with all layers at identical stoichiometry. This is pictorially shown in Fig. 1(a), with the different organic functional groups represented by the long and short columns. Note that the structure shown in Fig. 1(a) is an idealized case of a 1:1 mixture in which each long functional group is opposite a short functional group. In that case, the arrangement gives rise to an interlayer spacing that is intermediate between the interlayer spacings of the two zirconium bis(phosphonates), for which the two interlayer structures are represented in Fig. 1(c). It is reasonable to propose such an arrangement as the extended network seeks a global energy minumum by maximizing van der Waals internactions.



Fig. 1 Schematic representations of the three general structural possibilities for a zirconium mixed phosph(on)ates, $Zr(O_3PR)_x(O_3PR')_{2-x}$, with two different organic functional groups, represented by the large and small columns, where (a) the functional groups are randomly dispersed, (b) the functional groups are segregated or staged, and (c) the functional groups precipitate into distinct co-crystallites.

In some cases, particularly if the two organic groups are of significantly different size or possess different types of intermolecular interactions (hydrophilic versus hydrophobic for example), structures in which the different organic groups segregate into adjacent layers, known as "staging", have also been observed.^{9,10,13,15-18} For a system with a staged structure, the observed interlayer spacing is found to be larger than the interlayer spacings of either of the two individual zirconium bis (phosphonate) compounds and often is found to be an approximate sum of the interlayer spacings of the two individual zirconium bis(phosphonates), as is depicted in Fig. 1(b). The structure displayed in Fig. 1(b) is an idealized situation in which the long functional groups are all segregated into the lower layer and the short functional groups all segregated into the upper layer. Within the possible structural arrangments for staged zirconium phosph(on)ates, there are some other more subtle functional group arrangements that include some mixing of functional groups within one of the layers (for example, see Fig. 1 of ref. 13 or Fig. 4(c) of ref. 18) and alternate arrangments of adjacent functional groups (for example, see Scheme 3 of ref. 16). These tend to be more rare than the basic structure presented in Fig. 1(b) and were not observed for the materials presented in the current work.

Zirconium phosph(on)ates are a class of materials that have several potential practical applications in a variety of areas such as catalysis,¹⁹ ion exchange,^{20–22} photophysics,²³ nuclearwaste remediation,^{24,25} biotechnology,²⁶ and drug delivery,^{27,28} for example. Several reviews of zirconium phosph(on)ate chemistry have appeared in the literature^{8–10} and demonstrate the growth of this field of solid-state inorganic chemistry.

The present work describes a chemical and structural investigation of zirconium phosph(on)ates containing methylnaphthalene or oxynaphthalene rings as the primary organic pendant groups. The materials can be generally organized into two categories: (a) zirconium bis(phosph(on)ates) containing the naphthalene ring systems mentioned above and (b) zirconium mixed phosph(on)ates containing the naphthalene ring systems mixed with alkyl or alkoxy chains. The motivation for synthesizing and thoroughly examining the chemical and structural aspects of the present materials stems from our general interest in chromophore-containing layered materials – zirconium phosph(on)ates containing methylnaphthalene or oxynaphthalene ring systems have, to date, not been investigated.

We have found 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 two zirconium bis(arenephosphonates) with naphthalene and anthracene rings, we observed 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.²⁹ Specifically, the anthracene system displays almost no monomer emission, whereas the naphthalene system displays comparable excimer and monomer fluorescence intensities. We attributed this effect to the differing amounts of π -overlap within these ring systems, with the former having a larger degree of overlap of neighboring chromophores, 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 (a) by introducing alkyl spacer groups, in effect diluting the chromophores and decreasing the amount of excimer formation, and (b) by varying the size of the spacer groups (i.e., the volume available to a chromophore for exploring its conformational degrees of freedom is varied) in turn modulating the amount of excimer formation further. Our initial chemical and structural investigation of mixed arene/alkoxy zirconium phoshp(on)ates was concerned with materials of the type $Zr(O_3PC_{10}H_7)_1(O_3PR)_1$, where R = OC_2H_5 and OC_4H_9 .³⁰ In the present paper, we follow up on our initial chemical and structural investigations and present data on a number of additional materials within the $Zr(O_3PR)_x(O_3PR')_{2-x}$ motif in which an additional linking moiety is inserted between the naphthalene ring and the phosphorus atom: (i) R = R' = $CH_2C_{10}H_7$; (ii) $R = R' = OC_{10}H_7$; (iii) $R = OC_{10}H_7$, $R' = CH_3$; (iv) $R = OC_{10}H_7$, $R' = OC_2H_5$, and (v) $R = OC_{10}H_7$, R' = OH (random and staged). The chemical characterization of these new materials using thermal gravimetric analysis (percentage of organic content), infrared spectroscopy (presence of the desired organic functional groups), and solid-state ³¹P NMR (phosphorus environments) is discussed in section 3.1, while the characterization of the primary structural parameter (interlayer d spacing) using X-ray powder diffraction is discussed in section 3.2. Two of the key/novel findings of our study are the formation of a "staged" structure for a mixed zirconium phosphate involving the OC10H7 and OH functional groups, and the presence of two distinct conformations of the functional group for the zirconium bis(phosphonate) with the $CH_2C_{10}H_7$ functional group. A photophysics-oriented investigation of the subject materials will be attempted in the future.

2. Experimental section

2.1 Materials and procedures

Several novel zirconium phosph(on)ates containing naphthalene rings have been synthesized, and in one case (R = $CH_2C_{10}H_7$), the phosphonic acid and its diethyl phosphonate precursor were also synthesized. The materials studied include zirconium phosph(on)ates with one type of functional group [$Zr(O_3PR)_2$, zirconium bis(phosph(on)ates)] as well as materials containing two different functional groups [$Zr(O_3PR)_x(O_3PR')_{2-x}$, zirconium mixed phosph(on)ates]. Because the syntheses for the zirconium phosph(on)ates are very similar (mixing of a zirconyl chloride solution in HF with a solution of the stoichiometric amounts of the appropriate phosphonic acid(s) or phosphates followed by refluxing for several days, then filtering or centrifuging and drying), only the representative synthetic particulars are detailed here. The synthetic methodologies for the other zirconium phosph(on) ates, as well as for the one phosphonic acid and its precursor, are provided as ESI.†

Purchased chemicals were used as received. Hydrofluoric acid was purchased from J.T. Baker, Inc.; CDCl₃ was purchased from Cambridge Isotope Labs, Inc.; zirconyl chloride, ethanol, acetone, and diethyl ether were purchased from Aldrich Chemical Co. 2-Naphthyl phosphate monosodium salt was purchased from Lancaster Synthesis; 2-napthylmethyl-phosphonic acid was synthesized as described in the ESI.† Ethyl phosphate was purchased from TCI America as a mixture of the monoethyl and diethyl forms, and monoethyl phosphate was isolated from the mixture by an extraction procedure similar to that described by Stewart and Crandall.³¹ Solvents used for UV-vis measurements were HPLC or spectroscopy grades.

2-Napthylmethylphosphonic acid and its diethyl phosphonate precursor compound were characterized by melting point or boiling point, mass spectrometry, NMR (¹H, ¹³C, and ³¹P), IR and UV-vis spectroscopies. All zirconium phosph(on)ate materials were fully characterized by thermal gravimetric analysis (TGA) and IR, UV-vis, and solid-state ³¹P NMR spectroscopies. Structural parameters of the zirconium phosph(on)ates (*d*-spacings) were determined using X-ray powder diffraction (XRD).

Zirconium bis(2-naphthylmethylphosphonate), Zr(O₃PCH₂C₁₀H₇)₂, [Zr(CH₂Nap)₂]

To a solution of zirconyl chloride (0.206 g, 0.639 mmol) in 24.0 mL of 75% ethanol/H₂O was added 1.25 mL of 2.04 M HF (2.57 mmol). This solution was added dropwise to a solution of 2-napthylmethylphosphonic acid (0.284 g, 1.277 mmol) in 25.0 mL of 75% ethanol/H₂O with stirring. Afterwards, 5.0 mL of 75% ethanol/H2O was used to rinse the zirconyl chloride flask and the entire mixture was refluxed under nitrogen for six days. The solution was cooled to room temperature, the solid collected by centrifugation and washed successively with 75% ethanol/H2O, acetone, diethyl ether and air dried to yield Zr(CH₂Nap)₂ as a white solid (0.302 g, 89%): ³¹P NMR (500 MHz, solid state) δ 5.2, 2.1; XRD d_{001} (Å) 20.0; IR (KBr, cm⁻¹) 3442, 3055, 3023, 2921, 2911, 2892, 2853, 1632, 1600, 1540, 1510, 1440, 1403, 1384, 1364, 1264, 1248, 1209, 1168, 1145, 1089, 1035, 956, 906, 865, 834, 816, 802, 766, 746, 725, 669, 642, 620, 600, 521, 506, 478; TGA (150 °C to 1000 °C, Zr $(CH_2Nap)_2 \rightarrow ZrP_2O_7)$ % Wt loss: Exptl (calcd) 49.1 (50.1); UV (glycerol mull, nm) λ_{max} 225, 279, 291, 298, 322.

Zirconium 2-naphthyl phosphate ethyl phosphate, Zr (O₃POC₁₀H₇)₁(O₃POC₂H₅)₁ [Zr(ONap)₁(OEt)₁]

A solution comprised of zirconyl chloride (0.173 g, 0.537 mmol) in 19.0 mL of water with 1.08 mL of 1.98 M HF (2.14 mmol) was added dropwise to a solution of 2-naphthyl phosphate monosodium salt (0.132 g, 0.537 mmol) and monoethyl phosphate (0.070 g, 0.537 mmol) in 20.0 mL of water with stirring, 5.0 mL of water was used to rinse the zirconyl chloride flask and the entire mixture was refluxed under nitrogen for 18 hours. After cooling to room temperature, the solid

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was collected by filtration, washed successively with water, acetone, diethyl ether and air dried to afford $Zr(ONap)_1(OEt)_1$ as a white solid (0.205 g, 87.3%): ³¹P NMR (500 MHz, solid state) δ –22.8, –29.1; XRD d_{001} (Å) 16.1; IR (KBr, cm⁻¹) 3058, 3027, 2981, 2931, 2909, 2869, 1632, 1601, 1580, 1548, 1512, 1467, 1442, 1384, 1366, 1357, 1252, 1220, 1169, 1120, 1068, 988, 943, 878, 851, 807, 789, 744, 702, 646, 606, 539, 513, 475; TGA (150 °C to 1000 °C, $Zr(ONap)_1(OEt)_1 \rightarrow ZrP_2O_7)$ % Wt Loss: Exptl (Calcd) 36.1 (39.4); UV (glycerol mull, nm) λ_{max} 226, 229, 282, 292, 309, 316, 325.

Zirconium 2-naphthyl phosphate phosphate, Zr(O₃POC₁₀H₇)₁(O₃POH)₁ [Zr(ONap)₁(OH)₁]

A sample of $Zr(ONap)_1(OEt)_1$ (34.7 mg) was heated in a tube furnace for 24 hours at 270 °C with flowing oxygen. The temperature was then raised to 350 °C and the solid heated six hours with flowing oxygen, after which $Zr(ONap)_1(OH)_1$ was obtained as a brown solid: XRD d_{001} (Å) 14.3; IR (KBr, cm⁻¹) 3056, 1850, 1777, 1719, 1625, 1605, 1584, 1510, 1482, 1466, 1446, 1426, 1384, 1366, 1351, 1249, 1216, 1059, 748, 609, 522, 482; TGA (150 °C to 1000 °C, $Zr(ONap)_1(OH)_1 \rightarrow ZrP_2O_7)$ % Wt Loss: Exptl (Calcd) 28.3 (35.2).

Staged zirconium 2-naphthyl phosphate phosphate, Zr(O₃POC₁₀H₇)₁(O₃POH)₁ [*stg* Zr(ONap)₁(OH)₁]

To a solution of 2-naphthyl phosphate monosodium salt (0.190 g, 0.772 mmol) in 10.0 mL of water was added 1.48 mL of 0.522 M phosphoric acid (0.772 mmol). Zirconyl chloride (0.249 g, 0.772 mmol) was then added to this mixture with stirring followed by 0.40 mL of 2.04 M HF (0.816 mmol). The entire mixture was refluxed under nitrogen for six days. The suspension was cooled to room temperature, 20 mL of absolute ethanol added and the mixture placed in a freezer for two hours. The solid was collected by filtration and washed succesively with water, acetone, diethyl ether and air dried to afford stg $Zr(ONap)_1(OH)_1$ as a white solid (0.271 g, 85.7%): ³¹P NMR (500 MHz, solid state) δ -21.6, -30.0; XRD d_{001} (Å) 28.2; IR (KBr, cm⁻¹) 3051, 1635, 1600, 1578, 1559, 1540, 1510, 1467, 1441, 1419, 1383, 1356, 1253, 1222, 1172, 1081, 1060, 1001, 959, 878, 853, 804, 770, 760, 739, 699, 648, 636, 618, 608, 597, 563, 531, 483, 435; TGA (150 °C to 1000 °C, $Zr(ONap)_1(OH)_1 \rightarrow$ ZrP₂O₇) % Wt Loss: Exptl (Calcd) 31.9 (35.2).

2.2 Instrumental methods

X-ray powder diffraction patterns were obtained with either a Scintag X1 or a Philips PW1877 automated powder diffractometer, using Cu K α radiation and an internal silicon powder standard with all samples. Patterns were generally measured between 1.00° and 35.00° (2 θ), 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 phosph(on) ates is estimated to be ±0.3 Å. Infrared spectra were recorded on a PerkinElmer System 2000 FT-IR instrument, as KBr pellets for solids and on NaCl plates for neat liquids, using 4 cm⁻¹ resolution. TGA scans were performed on a PerkinElmer TGS-2 Thermogravimetric Analyzer interfaced to

a System 7/4 console and a model 3600 Data Station. All TGA scans were obtained on 10 to 15 mg of solid, with flowing compressed air, and a 10 °C min⁻¹ heating rate. The experimental reproducibility of % 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 interfaced with an Aspect Station computer system and using Bruker UXNMR software. Spectrometer operating frequencies were 500.13 MHz, 125.76 MHz, and 202.40 MHz for ¹H, ¹³C, and ³¹P nuclei, respectively. For ¹H and ¹³C NMR spectra, either tetramethylsilane or the resonance of the deuterated solvent was used as an internal reference, while for ³¹P NMR spectra, 85% H₃PO₄ was used as an external reference, unless otherwise noted. Spectra of ³¹P and ¹³C nuclei were obtained with ¹H decoupling, using standard Bruker pulse sequences. Solid-state ³¹P NMR was performed using 7 mm zirconia rotors, Delrin caps, and magic-angle spinning (MAS) at 4 kHz. The average error in the solid-state ³¹P NMR chemical shifts was estimated to be ± 0.2 ppm. Absorbance spectra were obtained on a PerkinElmer Lambda 6 UV-vis spectrometer. Precursor compounds were dissolved in an appropriate HPLC or spectral grade solvent and the absorbance spectrum measured in a 1 cm pathlength 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 zirconium phosph(on)ate per mg glycerol to 1×10^{-3} mg zirconium phosph(on)ate per mg glycerol. The absorbance spectrum of the glycerol mull was obtained by placing the mull between two 0.18 cm thick quartz plates, separated by a 0.12 cm thick plastic spacer, with a rectangular opening in the center $(1.1 \text{ cm} \times 1.9 \text{ cm}).$

Results and discussion

3.1 Chemical characterization

3.1.1 Thermal gravimetric analysis. 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 Costantino³² and by Alberti¹³ that heating zirconium phosphonates in the presence of oxygen or air to temperatures between 1000 °C and 1200 °C converted the compounds to zirconium pyrophosphate, ZrP_2O_7 , in either the α -layered ($d_{001} = 6.1$ Å) or the cubic ($d_{001} = 4.8$ Å) structure. Therefore knowing the final composition of the pyrolysis product, the experimental % weight loss determined can be compared to the theoretical % weight loss (calculated based on the eqn (1) shown below).

% weight loss =
$$\frac{FW Zr(O_3 PR)_x (O_3 PR')_{2-x} - FW ZrP_2 O_7}{FW Zr(O_3 PR)_x (O_3 PR')_{2-x}} \times 100$$
(1)

In general, the TGA traces of zirconium phosph(on)ates examined show loss of surface-bound or intercalated water below 150 °C, followed by volatilization of the organic frag-

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ments between 400 °C and 800 °C. As examples, the TGA traces of zirconium bis(2-naphthyl phosphate) $[Zr(ONap)_2]$, zirconium 2-naphthyl phosphate ethyl phosphate $[Zr(ONap)_1(OEt)_1]$, and zirconium bis(ethyl phosphate) $[Zr(OEt)_2]$ are displayed in Fig. 2. The TGA traces of zirconium bis(2-naphthylmethylphosphonate)[Zr(CH₂Nap)₂], zirconium 2-naphthyl phosphate methylphosphonate $[Zr(ONap)_1(Me)_1]$, zirconium 2-naphthyl phosphate phosphate [Zr(ONap)₁(OH)₁], and staged zirconium 2-naphthyl phosphate phosphate [stg $Zr(ONap)_1(OH)_1$ are given as Fig. 1S in the ESI.[†] Note that the compound referred to as stg Zr(ONap)₁(OH)₁ was determined to possess a segregated or staged interlayer structure from the X-ray diffraction analysis (vide infra).

As can be observed in Fig. 2, the trace of $Zr(ONap)_2$ displays a larger % weight loss than the trace of $Zr(OEt)_2$ and the %



Fig. 2 Thermal gravimetric analysis curves of $Zr(OEt)_2$, $Zr(ONap)_1(OEt)_1$, and $Zr(ONap)_2$.

weight loss of Zr(ONap)₁(OEt)₁ is between the values of the two bis(phosphate) compounds. This is in accordance with the difference in the masses of the organic components in these compounds. It is evident from Fig. 2 that the organic fragments of Zr(OEt)₂ begin to volatilize at a lower temperature (~300 °C) as compared to those of $Zr(ONap)_2$ (~450 °C), which reflects the greater thermal stability of the arene ring. Table 1 lists the experimentally determined and theoretically calculated % weight loss values for the zirconium phosph(on)ates synthesized. Also listed in Table 1 are the % weight loss values for zirconium bis(ethyl phosphate) [Zr(OEt)2],³⁰ zirconium bis (methylphosphonate) $[Zr(Me)_2]^{33,34}$ and α -zirconium phosphate [Zr(OH)₂]³⁵ for comparison with the zirconium mixed phosph(on)ates. Although the range of temperatures over which the pendant-group loss varies (see Fig. 2 and 1S[†]), an approximate midpoint of the temperature loss range is indicated in Table 1. The agreement between the experimentally determined and the theoretically calculated weight-loss values are generally very good, except for Zr(ONap)₂, Zr(OEt)₂, and $Zr(ONap)_1(OH)_1$, with the experimental values for these latter three being lower than their theoretically calculated values, on the order of 14-20%. This systematic discrepancy toward lower values has been discussed in our previous chemical and structural report on mixed arene/alkoxy zirconium phoshp(on)ates, as well as other studies, and is attributed to the incomplete combustion of the organo-phosphate groups and the subsequent trapping or surface deposition of carbon from the organic fragments, as evidenced by a slight grayish color of the final solid after TGA analysis.^{13,30,34,36} This results in an artificial increase in the amount of solid that remains, thereby artificially lowering the weight-loss values.

Fig. 2 also shows that the organic functional groups of $Zr(ONap)_1(OEt)_1$ do volatilize at noticeably different temperatures from one another and therefore the TGA of this compound could theoretically yield the relative stoichiometry directly, however, the volatilization regions are not sufficiently well separated to allow for an accurate determination. For the other mixed compounds studied, the two functional groups did not volatilize separately and therefore the TGA curves of these compounds will not directly yield the relative stoichiometry. However, even with the lack of distinct volatilization, the stoi-

 $\label{eq:table_$

-	rloss °C)	Exptl percent	Theor percent	Percent	
Compound (weight loss	weight loss	difference	x ^a
$Zr(CH_2Nap)_2$ 5	525	49.1	50.1	2.0	
$Zr(ONap)_2$ 6	500	43.5	50.5	13.9	
$Zr(OEt)_2^b$ 4	150	17.4	21.8	20.2	
$Zr(Me)_2^c$ 6	550	4.9	5.0	2.0	
$Zr(OH)_2^d$		12.0	12.0	0.0	
$Zr(ONap)_1(Me)_1$ 5	575	33.6	34.9	3.7	0.94
$Zr(ONap)_1(OEt)_1$ 5	575	36.1	39.4	8.4	0.78
$Zr(ONap)_1(OH)_1$ 5	550	28.3	35.2	19.6	0.75
$stg \operatorname{Zr}(\operatorname{ONap})_1(\operatorname{OH})_1^e$ 5	550	31.9	35.2	9.4	0.90

^{*a*} Calculated for the mixed compounds using eqn (2) as described in the text. ^{*b*} Taken from ref. 30. ^{*c*} Taken from ref. 33 and 34. ^{*d*} Taken from ref. 35. ^{*e*} Stg refers to the structural classification of a staged compound.

chiometric parameter *x*, which is defined as the number of moles of H_2O_3PR incorporated into the zirconium mixed phosph(on)ate, can be estimated using eqn (2),¹³

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

where W_{150} and W_{1000} are the % weight loss values at 150 °C (chosen to represent a state without water content) and at 1000 °C, respectively; R and R' are the formula weights of the different organic fragments; and formulas ZrP₂O₆ and O₂ also represent their formula weights. Using the appropriate weights for the mixed compounds, and inserting these into eqn (2), yields values of x listed in Table 1. The values of x determined this way for $Zr(ONap)_1(Me)_1$ and stg $Zr(ONap)_1(OH)_1$ are close to unity, demonstrating that these compounds are indeed comprised of an approximately equal mole ratio of the two functional groups. The deviations of the calculated values of xfor $Zr(ONap)_1(OEt)_1$ and $Zr(ONap)_1(OH)_1$ from unity are slightly larger, however, we believe that these compounds are also comprised of approximately equimolar compositions of the two functional groups, and that the discrepancies are primarily caused by incomplete combustion or surface deposition of carbon from the organic fragments, as mentioned above.

3.1.2 Infrared spectroscopy. We chose to use IR spectroscopy to confirm the presence of the desired functional groups in all of the materials and for a qualitative confirmation of the thermal analysis measurements. The observed IR vibrational frequencies for each of the zirconium phosph (on)ates synthesized are listed at the end of each synthesis description and, as examples, the IR spectra of Zr(ONap)₂, $Zr(ONap)_1(OEt)_1$ and $Zr(OEt)_2$ are shown in Fig. 3. The IR spectra of Zr(CH₂Nap)₂, Zr(ONap)₁(Me)₁, Zr(ONap)₁(OH)₁, and stg Zr(ONap)₁(OH)₁ are given as Fig. 2S in the ESI.[†] For all the zirconium phosph(on)ates, strong absorptions between 1100 cm⁻¹ and 900 cm^{-1} due to the stretching modes of the -PO₃ group and weaker absorptions between 600 \mbox{cm}^{-1} and 400 \mbox{cm}^{-1} corresponding to the bending modes of the -PO₃ group are observed.^{37,38} For the compounds containing arene rings, the IR spectra display absorptions for the aromatic C-H stretching modes (3100 cm^{-1} to 3000 cm^{-1}), the aromatic -C=C-ringstretching modes (1600 cm⁻¹ to 1400 cm⁻¹), the in-plane C-H bending modes (1300 cm⁻¹ to 1000 cm⁻¹), and the out-ofplane C-H ring bending modes (900 cm⁻¹ to 675 cm⁻¹).³⁹ Materials containing the alkyl groups possess absorptions for the asymmetric and symmetric C-H stretching modes between 3000 cm⁻¹ and 2800 cm⁻¹; bands for the asymmetric and symmetric methyl bending modes, near 1450 cm⁻¹ and 1375 cm⁻¹, respectively; and an absorption for the methylene scissoring mode close to a value of 1465 cm⁻¹.³⁹ Note that the asymmetric methyl bending peak can sometimes be obscured by the methylene scissoring band.

As can be seen in Fig. 3, the IR spectra of $Zr(ONap)_2$ and $Zr(OEt)_2$ 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



Fig. 3 Infrared spectra of $Zr(ONap)_2$, $Zr(ONap)_1(OEt)_1$, and $Zr(OEt)_2$ as KBr pellets in the 3100 to 2800 cm⁻¹ and 1700 to 400 cm⁻¹ spectral regions.

compounds. Similar results are observed for $Zr(CH_2Nap)_2$. Fig. 3 also shows that the mixed compound, $Zr(ONap)_1(OEt)_1$, does indeed possess both functional group types, as evidenced by the clear presence of distinct vibrations due to the naphthyl ring and the ethyl group. A similar analysis involving its distinct functional group vibrations also held for $Zr(ONap)_1(Me)_1$, $Zr(ONap)_1(OH)_1$ and *stg* $Zr(ONap)_1(OH)_1$.

3.1.3 Solid-state ³¹P NMR. Since phosphorus-31 is an NMR-active nucleus, solid-state ³¹P NMR can be used to determine the magnetic and chemical environment of the phosphorus atoms in zirconium bis(phosph(on)ate) materials and confirm the presence of chemically distinct phosphorus atoms in zirconium mixed phosph(on)ates. The isotropic ³¹P chemical shifts for the zirconium phosph(on)ates studied are given in Table 2. Also listed are the known isotropic ³¹P chemical shifts for zirconium bis(ethyl phosphate) [Zr(OEt)₂],³⁰ zirconium bis(methylphosphonate) [Zr(Me)₂],^{33,34} and α-zirconium phosphate [Zr(OH)₂]⁴⁰ for comparison with the zirconium mixed phosph(on)ates. As examples, the solid-state ³¹P NMR spectra of Zr(CH₂Nap)₂, Zr(ONap)₂, and Zr(ONap)₁(OEt)₁ are shown in Fig. 4. The solid-state ³¹P NMR spectra of Zr(ONap)₁(Me)₁ and *stg* Zr(ONap)₁(OH)₁ are shown in Fig. 3S.†

Table 2 Solid-state ³¹P NMR isotropic chemical shifts for the zirconium bis(phosph(on)ates), Zr(O3PR)2, and zirconium mixed phosph(on)ates, Zr(O₃PR)₁ (O₃PR')₁

$\delta_{\text{arene}} \left(\text{ppm} \right)$	$\delta_{\mathrm{alkyl}} (\mathrm{ppm})$
5.2, 2.1	
-29.5	
	-19.8, -20.8, -21.8
	6.9
	-18.7
-28.1	7.0
-29.1	-22.8
-30.0	-21.6
	δ _{arene} (ppm) 5.2, 2.1 -29.5 -28.1 -29.1 -30.0

^a Take	n from	n ref.	30.	^b Takeı	n from	ref.	33	and	34.	c T	aken	from	ref.	40.
^d Stg r	efers to	o the	stru	ictural	classifi	icati	on d	of a a	stag	ed	comp	ound		

δ_{MNap} Zr(CH₂Nap), δ_{ONap} Zr(ONap), δ_{OEt} ONap Zr(ONap)₁(OEt) 40 20 60 0 -20 -40-60 -80

Fig. 4 Solid-state ³¹P NMR spectrum of Zr(CH₂Nap)₂, Zr(ONap)₂, and Zr (ONap)₁(OEt)₁. The peaks marked with an asterisk are spinning sidebands. The isotropic resonances associated with the methylnaphthylphosphonate, the naphthyl phosphate, and the ethyl phosphate groups, are marked with δ_{MNap} , δ_{ONap} , and δ_{OEt} , respectively.

As can be seen from Table 2 and Fig. 4, the isotropic ³¹P chemical shifts for the two zirconium bis(phosph(on)ate) compounds examined in this study, $Zr(CH_2Nap)_2$ and $Zr(ONap)_2$, indicate very different chemical environments for the phos-

phorus atoms in the two compounds, with the phosphorus atoms in Zr(ONap)₂ being much more shielded than those of $Zr(CH_2Nap)_2$. This is understandable given that in $Zr(ONap)_2$, the phosphorus atoms are connected to an oxygen atom which would increase the shielding due to the lone pairs on the oxygen, as compared to the phosphorus atoms being connected to a CH₂ group in Zr(CH₂Nap)₂. More striking are their peak patterns. For Zr(ONap)2, what is seen in the ³¹P spectrum is typical of that of zirconium bis(phosph(on)ate) compounds, in that a single, high-intensity isotropic resonance (-29.5 ppm) along with multiple, lower-intensity spinning sidebands is observed. In contrast, the ³¹P spectrum of $Zr(CH_2Nap)_2$ is unusual in that two isotropic resonances with unequal intensities are observed at 5.2 ppm and at 2.1 ppm $(\Delta = 635 \text{ Hz})$. We do not believe that these two resonances are due to spin-spin splitting. The hydrogens on the CH₂ group are the nearest NMR-active nuclei, and due to the two hydrogens on the methylene group, a spin triplet would be the expected splitting pattern if these hydrogen atoms were coupling to the phosphorus. Additionally, typical two-bond ³¹P-¹H coupling constants are on the order of 10-20 Hz (ref. 39) and the splitting between the two observed peaks in the spectrum of $Zr(CH_2Nap)_2$ is 635 Hz. Rather, the pair of resonances are believed to be due to the distinct, "locked-in" conformations of the naphthyl rings as displayed in Fig. 5.

The structural models for the multiple conformations of Zr $(CH_2Nap)_2$ shown in Fig. 5 were obtained by consideration of the results of low-level molecular mechanics calculations on corresponding phosphonic acid, 2-naphthylmethylphosphonic acid (2NMPA). The molecular mechanics calculations were performed with the Discover energy minimization and dynamics module within the InsightII v95 software package (Molecular Simulations, Inc., San Diego, CA) using the Central Valences Force Field (CVFF).41 For 2NMPA, molecular mechanics calculations suggest that there are three minimum-energy structures along the C1-C2-Cm-P dihedral angle coordinate, which is one of the primary variable coordinates for this molecule. The lowest-energy minimum is a structure in which the C₁-C₂-C_m-P dihedral angle is 89.2° and the P-Cm-C2 angle is 113.0° (somewhat distorted from a pure sp² conformation). The other two minima are equal in energy to each other, and only 3.5 kcal mol⁻¹ higher than the lowest-energy-minimum structure. These two structures both have a value of 120.2° for the P-C_m-C₂ angle and they differ in that one has a C1-C2-Cm-P dihedral angle of 0.0° while the other has a dihedral angle of 180.0°.

In considering which of these structures might be reasonable models for the conformation of the methylnaphthyl groups in the Zr(CH₂Nap)₂ solid, the structure in which the C₁-C₂-C_m-P dihedral angle is 90.0° was ruled out because of the lateral space restrictions of the neighboring arene molecules which are estimated to be 5.3-5.4 Å apart based on the refined crystal structure of zirconium bis(phenylphosphonate).⁴² The cross-sectional size of a naphthalene ring (distance from H_1 to H_4 or H_5 to H_8 in Fig. 5), is estimated to be approximately 5 Å. Therefore, the structures with $C_1-C_2-C_m-P$ dihedral angles of 0.0° and 180.0° were considered the most

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Fig. 5 Idealized structural conformations of $Zr(CH_2Nap)_2$ using (a) a P- C_m-C_2 angle of 120.0° and a $C_1-C_2-C_m-P$ dihedral angle of 0.0° and (b) a P- C_m-C_2 angle of 120.0° and a $C_1-C_2-C_m-P$ dihedral angle of 180.0°.

reasonable for the distinct, "locked-in" conformations of the methylnaphthyl groups in $Zr(CH_2Nap)_2$.

In order to understand how the presence of these two distinct conformations of the methylnaphthyl groups in Fig. 5 would lead to distinct ³¹P resonances, one has to consider the effect of the aromatic ring in the two conformations on the neighboring phosphorus atoms rather than the effect on the phosphorus atom that the methylnaphthyl group is attached to. Due to the close proximity of the aromatic ring, a phosphorus atom to the left of the methylnaphthyl group pictured in Fig. 5(a) would experience increased shielding due to the aromatic ring current anisotropy and the resonance of this phosphorus atom would be expected to be shifted upfield when compared to the analogously neighboring phosphorus atom in Fig. 5(b), in which the aromatic ring is farther away. This would be a case of magnetically inequivalent but chemically equivalent phosphorus atoms. Based on this argument, the ³¹P resonance at 5.2 ppm can be assigned to phosphorus atoms next to aromatic rings with the conformation shown in Fig. 5(b) and the ³¹P resonance at 2.1 ppm can be assigned to phosphorus atoms next to aromatic rings with the conformation shown in Fig. 5(a). Since the phosphorus environment is chemically equivalent for the two conformations, the relaxation time for the phosphorus atom in each type of conformation would expected to be the same. Therefore, using the relative intensities from the ³¹P solid state NMR, we estimate that the ratio of the two conformations present in the $Zr(CH_2Nap)_2$ solid is approximately 60% that of Fig. 5(b) and 40% that of Fig. 5(a).

This type of structural observation (distinct conformations for one type of organic functional group) has been reported previously for zirconium bis(monochlorophosphonate), $Zr(O_3PCH_2Cl)_2$ ⁴³ Using the Rietveld structure refinement method, Clearfield and co-workers were able to solve the structure of zirconium bis(monochlorophosphonate), Zr(O₃PCH₂Cl)₂, and found that there were two crystallographically distinct chlorine atoms in the structure at the same x and z coordinates but differing in their y coordinates. In other words, they were related by a change in the dihedral angle about the P-C bond. In our previous report on the chemical and structural characterization of mixed arene/alkoxy zirconium phosph(on)ates, we made a similar observation (multiple isotropic resonances) in the ³¹P solid-state NMR of zirconium bis(ethyl phosphate) and zirconium bis(butyl phosphate) that were also attributed to "locked-in" conformations of the alkoxy chains.³⁰ The three isotropic resonances of zirconium bis(ethyl phosphate) are listed in Table 2.

The ³¹P NMR spectrum of Zr(ONap)₂, in contrast to the spectrum of Zr(CH₂Nap)₂, only displays a single isotropic resonance at -29.5 ppm, even though one might expect that $Zr(ONap)_2$ would also possess the two conformations described above for Zr(CH₂Nap)₂. Molecular mechanics performed on the precursor, 2-naphthyl phosphate (2NP), which has an oxygen atom between the phosphorus and 2-position carbon of the ring, predicts that there is only one minimum-energy structure along the C_1 - C_2 -O-P dihedral angle coordinate; a structure in which the dihedral angle has a value of 91.6° and the P-O-C₂ angle is at a value of 116.0°. The modeling calculations clearly point to an absence of structures in which the dihedral angle is at a value of 0.0° or 180.0° by not falling to these local energy minima for the isolated 2NP precursor molecule. This result is most likely due to shorter P-O and $O-C_2$ bond lengths in the minimum-energy structure of 2NP, which are 1.62 Å and 1.38 Å, respectively, as compared to the P-C_m and C_m-C₂ bond lengths of 1.75 Å, and 1.54 Å, respectively, in the minimum-energy structures of 2NMPA. The shorter bond lengths in 2NP apparently cause more steric repulsions at C1-C2-O-P dihedral angles of 0.0° and 180.0° than in 2NMPA and therefore the structures with these dihedral angles are no longer energy minima in the isolated 2NP.

Even though the minimum energy structure for the isolated 2NP possesses a C_1-C_2-O-P dihedral angle of approximately 90.0°, when it is bound to the zirconium layer in $Zr(ONap)_2$, this dihedral angle will no longer be possible due to the lateral space restrictions of 5.3–5.4 Å for the aromatic rings discussed above. Therefore the C_1-C_2-O-P dihedral angle would be

forced to be close to the value of 0.0° or 180.0° . Due to the shorter P–O and O–C₂ bond lengths mentioned above, it is expected that there would be considerable steric repulsions of the ring protons with the zirconium layer oxygen atoms for both the 0.0° or 180.0° conformations of $Zr(ONap)_2$. However, because there would only be one proton interacting with the zirconium layer oxygen atoms for the 180.0° , it is thought that this would be the energetically favored conformation in the interlayer region of $Zr(ONap)_2$ and therefore we believe that all (or nearly all) of the naphthoxy groups exist in a conformation with a dihedral angle close to 180.0° , as in Fig. 5(b) but with an oxygen linkage rather than *via* a methylene group.

This assignment also is most consistent with the experimental d spacing of $Zr(ONap)_2$. The experimental finding that serves as indirect evidence for the idea that there is only one conformation in $Zr(ONap)_2$ is an observed disparity in the FWHM of the 001 XRD peaks (*vide infra*): 0.17° for $Zr(ONap)_2$ and 0.33° for $Zr(CH_2Nap)_2$. Since the crystallinity of zirconium phosph(on)ates, which is reflected by the FWHM of the 001 XRD peak, does change with HF concentration and reflux time, the two syntheses for the FWHM comparison were carried out using identical amounts of HF and reflux times. Therefore the decreased FWHM for $Zr(ONap)_2$ can be taken as an indication of more efficient packing of the organic groups in $Zr(ONap)_2$ as compared to such in $Zr(CH_2Nap)_2$, in line with the one-conformation *vs.* two-conformation hypothesis.

For the mixed systems, $Zr(ONap)_1(Me)_1$, $Zr(ONap)_1(OEt)_1$, and stg Zr(ONap)₁(OH)₁, the ³¹P resonances are sufficiently resolved that identification and confirmation of the two chemically distinct phosphorus atoms was possible. Due to the method of synthesizing the mixed compound Zr $(ONap)_1(OH)_1$, a sufficient amount of this material was not produced to permit a ³¹P solid-state NMR to be obtained. It is worth noting that the resonances for the naphthyl phosphate phosphorus atoms in the mixed compounds are slightly shifted with respect to the resonances of Zr(ONap)₂. We believe this is 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 $Zr(ONap)_2$. Also, the three ethyl phosphate resonances observed for Zr(OEt)₂ have now collapsed into a single isotropic resonance and shifted slightly downfield. This is presumably due to restricted conformational freedom of the ethyl group as a result of the presence of the large, bulky naphthalene ring within the interlayer.

3.2 Structural investigations

For crystalline zirconium phosph(on)ates, the interlayer distance or *d* spacing of the zirconium planes can be determined from the 00*n* peaks in the powder X-ray diffraction (XRD) pattern *via* the Bragg equation, $n\lambda = 2d \sin \theta$. The *d*-space values for the zirconium phosph(on)ate materials synthesized in this study are given in Table 3. The XRD patterns of Zr(ONap)₂, Zr(ONap)₁(OEt)₁, Zr(ONap)₁(OH)₁, and *stg* Zr(ONap)₁(OH)₁ are shown in Fig. 6, while the XRD patterns of Zr(CH₂Nap)₂ and Zr(ONap)₁(Me)₁ are given in Fig. 4S

Table 3Experimental and predicted interlayer spacing of the zirconiumbis(phosph(on)ates), $Zr(O_3PR)_2$, and zirconium mixed phosph(on)ates, $Zr(O_3PR)_1(O_3PR')_1$

Compound	d_{001} (Å) Expt	d_{001} (Å) Pred^{a}
$Zr(CH_2Nap)_2$	20.0	19.7
$Zr(ONap)_2$	19.6	19.1
Zr(OEt) ₂	$11.6^{b}, 11.7^{c}$	11.9
$Zr(Me)_2$	$8.8^d, 8.8^e$	8.4
$Zr(OH)_2$	7.6 ^{<i>f</i>}	7.8
$Zr(ONap)_1(Me)_1$	15.3	13.8
$Zr(ONap)_1(OEt)_1$	16.1	15.5
Zr(ONap) ₁ (OH) ₁	14.3	13.4
$stg Zr(ONap)_1(OH)_1^g$	28.2	27.2^{h}

^{*a*} Predicted value based on the simple geometrical model described in the text. ^{*b*} Taken from ref. 30. ^{*c*} Taken from ref. 5. ^{*d*} Taken from ref. 33. ^{*e*} Taken from ref. 44. ^{*f*} Taken from ref. 1. ^{*g*} Stg refers to the structural classification of a staged compound. ^{*h*} Predicted value based on the sum of the experimental *d* spacings of $Zr(ONap)_2$ [19.6 Å] and $Zr(OH)_2$ [7.6 Å].



Fig. 6 X-ray diffraction patterns displaying the 00*n* peaks of Zr(ONap)₂, Zr(ONap)₁(OEt)₁, Zr(ONap)₁(OH)₁, and *stg* Zr(ONap)₁(OH)₁.

of the ESI.[†] The *d*-space values for zirconium bis(ethyl phosphate) $[Zr(OEt)_2]$,^{5,30} zirconium bis(methylphosphonate) $[Zr(Me)_2]$,^{33,44} and α -zirconium phosphate $[Zr(OH)_2]^1$ have also been included in Table 3 in order to allow a comparison of the *d*-space values for the zirconium mixed phosph(on)ates to the zirconium bis(phosphonates). As can be seen from Fig. 6 and Fig. 4S,[†] most of the XRD patterns display a strong 001 peak

(lowest-angle peak in the pattern) followed by higher order 00n peaks at larger angles and lower intensities. The large-angle region of the XRD patterns, which is not shown in the figures, consist of lower intensity, unresolved peaks.

3.2.1 Bis(phosph(on)ates). The *d* spacings observed for the two zirconium bis(phosphonates) synthesized in this study, Zr(ONap)₂ and Zr(CH₂Nap)₂, are 19.6 and 20.0 Å, respectively. These are similar to the *d* spacing of 19.1 Å we observed for zirconium bis(naphthylphosphonate) in our previous report on the chemical and structural characterization of mixed arene/ alkoxy zirconium phoshp(on)ates, which also contained a naphthalene ring system in the interlayer.30 A simple, idealized geometrical modeling method^{30,45} can be used to obtain predicted d spacings based on twice the zirconium phosphonate layer thickness (3.2 Å),^{1,5} 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 magnitude of the hydrogen atomic radius (0.7 Å). Predicted d-space values can be obtained for both of the structural conformations depicted in Fig. 5 for both $Zr(ONap)_2$ and $Zr(CH_2Nap)_2$ in order to determine which conformational model is most consistent with the observed dspacings. For Zr(CH₂Nap)₂, the conformation displayed in Fig. 5(a) yields a predicted d spacing of 15.5 Å while the conformation displayed in Fig. 5(b) yields a predicted d spacing of 19.7 Å. A similar calculation can be performed for $Zr(ONap)_2$ after replacing the methylene group with an oxygen, adjusting the P-O and C₂-O bond lengths to their standard values,⁴⁵ and using a P-O-C₂ angle of 120.0° to be consistent with the $Zr(CH_2Nap)_2$ calculations. With this analysis, one obtains predicted values of 14.9 Å for the analogous conformation to that depicted in Fig. 5(a) and 19.1 Å for the analogous conformation to that depicted in Fig. 5(b). Based on the comparison of the experimental d spacings with both of the predicted dspacings for Zr(ONap)₂ and Zr(CH₂Nap)₂, the structural model with the conformation displayed in Fig. 5(b) is the one most consistent with the experimental d-space values for each compound. As discussed above in the ³¹P solid-state NMR section, for Zr(CH₂Nap)₂ methylnaphthyl groups in the solid that possess the conformation shown in Fig. 5(a) are present at a 40% abundance. However, the experimental d-space measurements suggest that the 60% presence of conformer Fig. 5(b) is sufficient to exhibit the higher d spacing as the overall value.

3.2.2 Mixed phosph(on)ates. For a zirconium mixed phosph(on)ate, 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 co-crystallites or domains of the bis(phosph(on)ates), in other words two individual phases. These three basic structural possibilities are represented schematically in Fig. 1.

Each of these situations will give rise to distinct behavior which will be evident in the XRD powder patterns. The ran-

domly distributed structure will show a single 001 peak at a *d*-space value equal to or between those of the two parent zirconium bis(phosph(on)ates). The ordered, segregated structure, on the other hand, will display an 001 peak whose *d* spacing is that of a sum of the two parent zirconium bis (phosph(on)ates). The third possibility, distinct co-crystallites, 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 (phosph(on)ates) and the other peak at the value for the other parent zirconium bis(phosph(on)ate), as if for a simple physical mixture of the two compounds.

As can be seen from an inspection of Table 3, the magnitudes of the *d* spacings of $Zr(ONap)_1(Me)_1$, $Zr(ONap)_1(OEt)_1$, and $Zr(ONap)_1(OH)_1$ are between the *d*-space values of their parent zirconium bis(phosph(on)ates), indicative of singlephase, randomly mixed structures for each of these materials. In the case of $Zr(ONap)_1(OH)_1$, it is worth noting that this randomly mixed material was not formed by the direct co-precipitation method but rather was obtained in a circuitous route *via* the pyrolysis of the ethyl groups in the randomly mixed $Zr(ONap)_1(OEt)_1$ material. This was done because, as will be discussed below, direct co-precipitation of the two precursor phosphates with zirconyl chloride leads to a segregated or staged structure for the resulting solid.

For the purpose of calculating the predicted interlayer spacings for these random-structure zirconium mixed (phosph (on)ates), we employed the same type of primitive predictive model that was used to estimate the interlayer spacings of the zirconium bis(phosph(on)ates). Namely, it is presumed that the naphthalene rings are opposite a methyl, ethoxy, and hydroxyl group (depending on the functional group that is being mixed), which would allow a "collapse" of the "scaffolded" structure to a lower d-space value than for the zirconium bis(phosph(on)ates). Under these assumptions, one obtains estimated d-space values of 13.8, 15.5, and 13.4 Å for $Zr(ONap)_1(Me)_1$, $Zr(ONap)_1(OEt)_1$, and $Zr(ONap)_1(OH)_1$ respectively. As can be seen by comparing these predicted d-space values to the experimental values, the predicted values are lower than the experimental values by 0.6-1.5 Å. A likely explanation for the deviations is that with a stoichiometrically equal number of naphthoxy groups and methyl, ethoxy, and hydroxyl groups, *i.e.*, a compound with x = 1, there are a sufficient number of naphthalene rings that are near another naphthalene ring from the opposite layer, essentially "propping up" the interlayer distance up to a slightly larger value than that based on the simple prediction. Although zirconium mixed phosph(on)ates with x values less than 1 (i.e., a preponderance of the smaller pendant groups) were not synthesized for the present series of compounds, we envision that *d*-space values for such stoichiometries would be closer to the primitive predictions.

As mentioned above, direct co-precipitation of Zr^{4+} with naphthyl phosphate (O₃POC₁₀H₇) and phosphate groups (O₃POH) does not lead to a randomly mixed structure in which the 001 diffraction peak is at a *d*-space value equal to or between those of the two parent zirconium bis(phosph(on)



Fig. 7 Idealized structural representation of stg Zr(ONap)₁(OH)₁ showing the predicted sum of *d*-space values for a staged compound.

ates), but rather leads to a structure that produces the XRD pattern labeled stg $Zr(ONap)_1(OH)_1$ in Fig. 6. The *d*-space value for 001 peak of this compound is 28.2 Å, which is clearly larger than the *d*-space values of either $Zr(ONap)_2$ or $Zr(OH)_2$ (19.6 Å and 7.6 Å, respectively). This indicates that this material possesses a staged or segregated structure in which the repeating unit consists of layers of alternating composition; an idealized model of this structure is displayed in Fig. 7. A similar type of staging or segregation to this has been observed previously for a zirconium mixed phosph(on)ate material involving phenyl and hydroxyl moieties.^{16,17} Based on the experimental *d*-space values for $Zr(ONap)_2$ and $Zr(OH)_2$, the expected *d*-space value for the idealized staged structure displayed in Fig. 7 is 27.2 Å, which is close to the experimentally observed value of 28.2 Å. The discrepancy between the two values is thought to be a result of possible incorporation of a layer of coordination water molecules within the hydroxy layer, leading to a slightly larger distance than 7.6 Å for that portion of the structure or slight differences in hydration between this mixed compound and the parent compounds. The reason that the two functional groups segregate into alternate layers when directly precipitated is believed to be due to the radical difference in the nature of the two groups, one being extremely hydrophobic (ONap) and the other (OH) being extremely hydrophilic, therefore giving rise to an "immiscibility" of the two groups within the solid. This property is brought out during the slow-growth, six-day self-assembly process detailed in the Experimental section.

4. Conclusions

Six novel zirconium phosph(on)ates incorporating naphthalene rings have been synthesized, chemically characterized, and structurally examined: two zirconium bis(phosph(on) ates), $Zr(CH_2Nap)_2$ and $Zr(ONap)_2$, and four zirconium mixed phosph(on)ates, $Zr(ONap)_1(Me)_1$, $Zr(ONap)_1(OEt)_1$, $Zr(ONap)_1(OH)_1$, and *stg* $Zr(ONap)_1(OH)_1$.

Chemically, the compositions of all materials synthesized and studied were confirmed by TGA within an acceptable experimental error of 2-20%. The presence of the desired functional groups in all of the materials was determined by IR spectroscopy. Solid-state ³¹P NMR spectroscopy revealed the presence of magnetically inequivalent phosphorus environments (multiple resonances) for Zr(CH₂Nap)₂, which is attributed to the presence of two conformationally distinct, "lockedin" geometries of the methylnaphthyl groups involving the dihedral angle about the CH_2 group (0.0 and 180°), whereas $Zr(ONap)_2$ only displayed one dominant phosphorus environment (single resonance), as expected for zirconium bis (phosph(on)ates). The lack of multiple conformations for $Zr(ONap)_2$ is attributed to increased steric interactions between the naphthalene ring and the zirconium phosphate layer oxygen atoms for the 0.0° conformation, due to the shorter P-O and C-O bonds, thereby giving rise to only one favored conformation (180°) in the interlayer region. Solid-state ³¹P NMR spectroscopy was also used to confirm the presence of two chemically distinct phosphorus environments for $Zr(ONap)_1(Me)_1$, $Zr(ONap)_1(OEt)_1$, $Zr(ONap)_1(OH)_1$, and stg $Zr(ONap)_1(OH)_1$. These results thus indicate a new structural type of layered materials: a mixed zirconium phosph(on)ate in which the homogeneous distribution within the interlayer region refers not to chemical composition, but instead denotes a mix of conformers.

Structurally, the interlayer spacings of $Zr(CH_2Nap)_2$ and Zr(ONap)₂, 19.6 and 20.0 Å, respectively, were found to be consistent with the general size of the naphthalene pendant group when compared to the previously reported interlayer spacing for a similar compound containing naphthalene rings, zirconium bis(naphthylphosphonate).³⁰ Using a simple, idealized geometrical modeling method, predicted d space values were calculated based on the two possible conformations (0.0 and 180°) of the ring systems and we find that the models with the 180° conformations are the most consistent with the experimental d space values for both $Zr(CH_2Nap)_2$ and $Zr(ONap)_2$. For the mixed compounds $Zr(ONap)_1(Me)_1$ and $Zr(ONap)_1(OEt)_1$, both were determined to be single-phase compounds that possess structures with random distributions of the two organic pendant groups within the interlayer, with d-space values of 15.3 and 16.1 Å, respectively. Two different mixed compounds were synthesized that both incorporated the ONap and OH functional groups in approximately equal amounts: $Zr(ONap)_1(OH)_1$ in which the two pendant groups are randomly distributed (synthesized by controlled pyrolysis of $Zr(ONap)_1(OEt)_1$, d-space value of 14.3 Å, and stg $Zr(ONap)_1(OH)_1$ in which the pendant groups are segregated into separate layers (synthesized by direct co-precipitation), d-space value of 28.2 Å. The segregated structure in the latter material is attributed to the "immiscibility" of the two groups within the solid due to the very different hydrophobicities of the two functional groups.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 A. Clearfield and G. D. Smith, *Inorg. Chem.*, 1969, **8**, 431-436.
- 2 J. M. Troup and A. Clearfield, *Inorg. Chem.*, 1977, **16**, 3311–3314.
- 3 J. Albertsson, A. Oskarsson, R. Tellgren and J. O. Thomas, *J. Phys. Chem.*, 1977, **81**, 1574–1578.
- 4 E. R. Losilla, M. A. G. Aranda and S. Bruque, *J. Solid State Chem.*, 1996, **125**, 261–269.
- 5 G. Alberti, U. Costantino, S. Allulli and N. Tomassini, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1113–1117.
- 6 L. Maya, Inorg. Nucl. Chem. Lett., 1979, 15, 207-212.
- 7 M. B. Dines and P. M. DiGiacomo, *Inorg. Chem.*, 1981, 20, 92–97.
- 8 A. Clearfield, in *Progress in Inorganic Chemistry*, ed. K. D. Karlin, John Wiley and Sons, New York, 1998, vol. 47, pp. 371–510.
- 9 A. Clearfield, in *Metal Phosphonate Chemistry: From Synthesis to Applications*, ed. A. Clearfield and K. Demadis, The Royal Society of Chemistry, London, 2011, ch. 1.
- 10 R. Vivani, F. Costantino and M. Taddei, in *Metal Phosphonate Chemistry: From Synthesis to Applications*, ed. A. Clearfield and K. Demadis, The Royal Society of Chemistry, London, 2011, ch. 2.
- 11 M. B. Dines, P. M. DiGiacomo, K. P. Callahan, P. C. Griffith, R. H. Lane and R. E. Cooksey, in *Chemically Modified Surfaces in Catalysis and Electrocatalysis*, ed. J. S. Miller, ACS Symposium Series 192, American Chemical Society, Washington, DC, 1982, ch. 13.
- 12 G. Alberti, U. Costantino and R. Guiletti, *Gazz. Chim. Ital.*, 1983, **113**, 547–552.
- 13 G. Alberti, U. Costantino, J. Kornyei and M. L. Giovagnotti, *React. Polym.*, 1985, 4, 1–10.
- 14 G. Alberti, U. Costantino and G. Perego, *J. Solid State Chem.*, 1986, **63**, 455–460.
- 15 G. Alberti, in Solid-State Supramolecular Chemistry: Twoand Three-Dimensional Inorganic Networks, ed. G. Alberti and T. Bein, Comprehensive Supramolecular Chemistry, vol. 7, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, and J.-M. Lehn, Elsevier Science Ltd., Tarrytown, NY, 1996, ch. 5.

- 16 J. D. Wang, A. Clearfield and G. Z. Peng, Mater. Chem. Phys., 1993, 35, 208–216.
- 17 A. Clearfield, J. D. Wang, Y. Tian, E. Stein and C. Bhardwaj, J. Solid State Chem., 1995, 117, 275–289.
- 18 J. C. Amicangelo and W. R. Leenstra, J. Am. Chem. Soc., 1998, 120, 6181–6182.
- 19 A. Clearfield, J. Mol. Catal., 1984, 27, 251-262.
- 20 G. Alberti, Acc. Chem. Res., 1978, 11, 163-170.
- 21 Inorganic Ion Exchange Materials, ed. A. Clearfield, CRC Press, Boca Raton, FL, 1982, ch. 1–3.
- 22 G. Alberti and U. Costantino, in *Intercalation Chemistry*, ed.
 M. S. Whittingham and A. J. Jacobsen, Academic, New York, 1985, ch. 5.
- 23 L. A. Vermeulen and M. E. Thompson, *Chem. Mater.*, 1994, 6, 77–81.
- 24 J. D. Burns, A. Clearfield, M. Borkowski and D. T. Reed, *Radiochim. Acta*, 2012, **100**, 381–387.
- 25 J. D. Burns, T. C. Shehee, A. Clearfield and D. T. Hobbs, Anal. Chem., 2012, 84, 6930–6932.
- 26 B. Bujoli, P. Janvier and M. Petit, in *Metal Phosphonate Chemistry: From Synthesis to Applications*, ed. A. Clearfield and K. Demadis, The Royal Society of Chemistry, London, 2011, ch. 13.
- A. Díaz, M. L. González, R. J. Pérez, A. David, A. Mukherjee,
 A. Báez, A. Clearfield and J. L. Colón, *Nanoscale*, 2013, 5, 11456–11463.
- 28 J. González-Villegas, Y. Kan, V. I. Bakhmutov, A. García-Vargas, M. Martínez, A. Clearfield and J. L. Colón, *Inorg. Chim. Acta*, 2017, 468, 270–279.
- 29 J. C. Amicangelo and W. R. Leenstra, J. Am. Chem. Soc., 2003, 125, 14698-14699.
- 30 J. C. Amicangelo and W. R. Leenstra, *Inorg. Chem.*, 2005, 44, 2067–2073.
- 31 D. C. Stewart and H. W. Crandall, J. Am. Chem. Soc., 1951, 73, 1377–1378.
- 32 U. Costantino and A. L. Ginestra, *Thermochim. Acta*, 1982, 58, 179–189.
- 33 W. R. Leenstra and J. C. Amicangelo, *Inorg. Chem.*, 1998, 37, 5317–5323.
- 34 J. C. Amicangelo, Ph.D. Dissertation, University of Vermont, 1999.
- 35 A. Clearfield and J. A. Stynes, *J. Inorg. Nucl. Chem.*, 1964, 26, 117–129.
- 36 C. Y. Yang, Ph.D. Dissertation, Texas A&M University, 1986.
- 37 S. E. Horsely, D. V. Nowell and D. T. Stewart, *Spectrochim. Acta, Part A*, 1974, **30**, 535–541.
- 38 X. Mathew and V. U. Nayar, *Infrared Phys.*, 1988, **28**, 189–194.
- 39 R. M. Silverstein, F. X. Webster and D. J. Kiemle, *Spectrometric Identification of Organic Compounds*, John Wiley and Sons, New York, 2005.
- 40 N. J. Clayden, J. Chem. Soc., Dalton Trans., 1987, 1877– 1881.
- 41 (a) S. Lifson, A. T. Hagler and P. Dauber, J. Am. Chem. Soc.,
 1979, 101, 5111-5121; (b) A. T. Hagler, S. Lifson and

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P. Dauber, J. Am. Chem. Soc., 1979, 101, 5122–5130;
(c) A. T. Hagler, P. Dauber and S. Lifson, J. Am. Chem. Soc., 1979, 101, 5131–5141.

- 42 M. D. Poojary, H. L. Hu, F. L. Campbell and A. Clearfield, Acta Crystallogr., Sect. B: Struct. Sci., 1993, **49**, 996–1001.
- 43 D. M. Poojary, C. Bhardwaj and A. Clearfield, *J. Mater. Chem.*, 1995, 5, 171–174.
- 44 M. B. Dines and P. C. Griffith, J. Phys. Chem., 1982, 86, 571-576.
- 45 Except for the specific angles mentioned in the text, all other bond distances and angles used in the idealized structures were the standard values given in the *CRC Handbook of Chemistry and Physics*, ed. R. C. Weast, *CRC Press*, Boca Raton, FL, 70th edn, 1989, pp. F-188– F-192.