Chem. Mater. **2004,** *16,* 2463−2470

Heterocyclic Amine Derivatives of Zinc Organophosphonates

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Received January 7, 2004. Revised Manuscript Received April 7, 2004

A series of novel zinc(II) organophosphonates with coordinated 2,2′-bipyridyl (2,2′-bipy, $C_{10}H_8N_2$) and 1,10-phenanthroline (phen, $C_{12}H_8N_2$) ligands (with the proposed formulations: $Zn(O_3PC_6H_5)(C_{12}H_8N_2)$, $Zn_2(O_3PR)_2(C_{12}H_8N_2)$ ($R = C_6H_5CH_2, C_2H_5, CH_3$), and $Zn_2(O_3PR)_2(C_{10}H_8N_2)(H_2O)$ ($R = C_6H_5, C_6H_5CH_2$)) has been prepared and characterized. The amine derivatives have the same 1:1 metal/phosphorus ligand ratio as the parent zinc(II) organophosphonates, and, with the exception of the phen derivative of zinc(II) phenylphosphonate, $Zn(O_3PC_6H_5)(C_{12}H_8N_2)$, all of the amine derivatives were found to possess a metal/phosphorus/amine ratio of 2:2:1 where one amine ligand is coordinated to every two zinc atoms. Elemental analyses, FTIR, TGA, XPS, and solid-state $^{31}P/^{13}C$ MAS NMR data are consistent with the proposed formulations. Powder XRD measurements show $Zn(O_3PC_6H_5)(C_{12}H_8N_2)$ and $Zn_2(O_3PCH_2C_6H_5)_2(C_{12}H_8N_2)$ to be layered, whereas the other complexes are nonlamellar materials. XPS data suggests that the nitrogen atoms of the amine ligands are coordinated to the zinc center in an unsymmetrical manner.

Introduction

Zinc(II) organophosphonates have been investigated extensively.[1−3] Most zinc(II) organophosphonates reported in the literature are lamellar, with an octahedral coordination environment about the Zn(II) ion. Generally, a channel structure is adopted by zinc atoms with *tetrahedral* coordination.[2,3] However, by using a difunctional phosphonate, Hix was able to produce an *octahedral* coordination complex, $[Zn(O_3PCH_2OH)]$, with a channel structure.[4] To further extend the functionality of these materials, and to provide additional opportunities for structural diversification, one strategy has been to investigate the interaction of zinc(II) organophosphonates with amines, by both direct "one-pot" reactions and coordinative intercalation reactions.

The parent organophosphonates can be dehydrated, and Cunningham suggested that this created an open coordination site on the metal and also caused lattice expansion, which increased accessibility to the vacant site.[5] Since then, numerous intercalates of zinc(II) organophosphonates have been reported, where small or linear aliphatic amines react with the zinc complexes. These reactions occur with a high degree of shape selectivity in layered zinc(II) organophosphonates of formula $Zn(O_3PR)$ ($R = CH3, C_6H_5$): both hydrated and anhydrous zinc(II) phenylphosphonate react with primary amines to give $Zn(O_3PR)\cdot R'NH_2$ ($R = CH_3, C_6H_5$; $R' = H$ to $n\text{-}C_8H_{17}$), and as the number of carbons on the amine group increases, so do the interlayer distances.[3,6] However, primary amines with branching in the α-position, and *sec*- and *tert*-butylamine, are excluded from the structure.[6]

Previous attempts to produce amine intercalates by direct "one-pot" methods, and also to incorporate larger amines, include those of Gerbier.[7] Gerbier used an organometallic route involving dimethylzinc in tetrahydrofuran to synthesize the zinc(II) organophosphonates, $Zn(O_3PR)$ (where $R = CH_3$, C_6H_5, 2- and 3-thienyl, thiophen-3-ylmethyl).[7] However, although the presence of an *n*-alkylamine in the reaction mix resulted in the formation of coordinatively intercalated phases of $Zn(O_3PR)\cdot R'NH_2$ (where $R = CH_3$, C_6H_5, $2\text{-}C_4H_3S$, $3\text{-}C_4H_3S$, $CH_2(3\text{-}C_4H_3S)$; $R' =$ butyl, pentyl), the addition of the more bulky cyclohexylamine gave $Zn(O_3PC_6H_5)\cdot(c\text{-}hexNH_2)_2$ with a one-dimensional polymeric chain structure.

Structural studies on complexes of this type have shown that the intercalated molecules are actually coordinated to the metal center,[3] and the present study arose because of interest in this type of complex. A review of the interactions of zinc(II) organophosphonates with aliphatic amines shows that desirable physicochemical properties may be introduced into the material by varying the nature of the organic substituents on the phosphonate or amine groups.[8−11] However, to our

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10.1021/cm049956p CCC: $27.50

knowledge, little work has been conducted on mixed-ligand complexes containing heterocyclic aromatic amines, such as 2,2′-bipyridyl (2,2′-bipy) and 1,10-phenanthroline (phen), that are considerably larger, conjugated systems which often confer interesting conductive and optical properties on the metal center, e.g., $[Fe(phen)_3]^{3+}$ and $[Ru(bipy_3)]^{3+}$.[12a,b] The research presented here describes the synthesis and characterization of a series of novel mixed-ligand zinc(II) organophosphonates, and investigates the effect of aromatic heterocyclic amine ligands on the structure and properties of the complexes.

Experimental Section

Preparation of Zinc(II) 1,10-Phenanthroline Phosphonate Complexes. The zinc(II) compounds **1**−**4** were synthesized from an ethanolic solution of the appropriate organophosphonic acid (phenyl-, benzyl-, ethyl-, and methyl-phosphonic acid, 0.2 mol in 20 mL of ethanol), added to a well-stirred ethanolic solution of zinc(II) acetate dihydrate (0.1 mol, 10 mL) and 1,10-phenanthroline monohydrate (0.2 mol, 20 mL). The zinc(II) complexes began to precipitate immediately at room temperature, and the mixtures were then refluxed for a further 6 h to ensure complete conversion of starting materials to products. The resulting white solids were filtered, washed with cold ethanol, air-dried, and then dried over P_2O_5.

Preparation of Zinc(II) 2,2′-Bipyridyl Phosphonate Complexes. Attempts to synthesize the zinc(II) 2,2′-bipy organophosphonate derivatives, following the methods outlined above for the phen derivatives, were unsuccessful. The only materials isolated were the zinc(II) organophosphonates with no incorporation of 2,2′-bipy into the complexes. Therefore, zinc complexes **5** and **6** were synthesized from an aqueous suspension of the appropriate zinc(II) organophosphonate (phenyl and benzyl derivatives, 0.1 mol, 10 mL, see below) and 2,2′-bipy (0.2 mol, 10 mL). The suspensions were sealed in Teflon-lined stainless steel autoclaves and heated at 160 °C for 72 h under autogenous pressure. The resulting white solids were filtered, washed with cold ethanol to remove any unreacted 2,2′-bipy, air-dried, then dried over P_2O_5. Attempts to synthesize methyl- and ethyl-phosphonate 2,2′-bipy derivatives using analogous methods were unsuccessful: the only materials isolated were the zinc(II) alkylphosphonates with no incorporation of 2,2′-bipy into the complexes.

Preparation of Zinc(II) Organophosphonates. Zinc(II) organophosphonates were prepared following the procedure of Cunningham.[5] Typically, an aqueous solution of the zinc(II) chloride or sulfate (0.1 mol, 50 mL) was mixed with an aqueous solution of the appropriate organophosphonic acid (0.1 mol, 50 mL). The zinc(II) organophosphonate began to precipitate immediately at room temperature and was stirred for a further 5 h to ensure complete conversion of starting materials to products. The resulting solid was filtered off, washed with ethanol, and dried over P_2O_5.

All chemicals were obtained from Aldrich Chemical Co. or BDH Laboratory Supplies and were AR grade. The resulting compounds were characterized by elemental analysis, FTIR, TGA, powder XRD, XPS, and $^{31}P/^{13}C$ MAS NMR. Analyses for Zn and P were performed on a Hewlett-Packard HP 4500 Series 300 Shield Torch System ICP-MS coupled with a quadrupole mass analyzer. The plasma gas (Ar) flow rate was 20 $L\cdot min^{-1}$ with the auxiliary gas (Ar) set to 1 $L\cdot min^{-1}$; the power level of the radio frequency coil was set at 1280 W; and the spray chamber temperature was set at 20 °C. Samples were introduced with a peristaltic pump at an uptake speed of 0.1 rps and an uptake and stabilization time of 50 s. Analyses for C, H, and N were carried out by The Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, Dunedin, New Zealand. Thermogravimetric analyses (TGA) were performed under flowing nitrogen gas in a Perkin-Elmer TGA 7/DX thermogravimetric analyzer. Infrared spectra were obtained on a Perkin-Elmer 2000. Fourier transform infrared spectra were obtained on a Perkin-Elmer FTIR Spectrum 2000 spectrometer with the sample dispersed in a KBr disk. Powder XRD patterns were acquired on a Bruker D8 ADVANCE diffractometer using Cu Ka radiation. Cross-polarization solid-state MAS NMR for ^{13}C and ^{31}P were acquired using a Varian 300 NMR spectrometer at 75.45 MHz for ^{13}C and 121.46 MHz for ^{31}P, with the ^{13}C chemical shifts referenced to TMS (see Supporting Information) and the ^{31}P chemical shifts referenced to potassium dihydrogen orthophosphate.

The elemental analyses for Zn, P, C, H, and N in the 2,2′-bipy and phen derivatives of zinc(II) organophosphonates gave good agreement with the proposed formulations ($C_{10}H_8N_2$ = 2,2′-bipy, $C_{12}H_8N_2$ = phen) as follows.

$Zn(O_3PC_6H_5)(C_{12}H_8N_2)$ (**1**). Found: Zn, 16.7; P, 8.4; C, 53.6; H, 3.5; N, 6.8. Calcd: Zn, 16.3; P, 7.7; C, 53.8; H, 3.3; N, 7.0%.

$Zn_2(O_3PCH_2C_6H_5)(C_{12}H_8N_2)$ (**2**). Found: Zn, 19.7; P, 10.2; C, 47.5; H, 3.6; N, 4.3. Calcd: Zn, 20.1; P, 9.5; C, 48.0; H, 3.4; N, 4.3%.

$Zn_2(O_3PC_2H_5)_2(C_{12}H_8N_2)$ (**3**). Found: Zn, 24.6; P, 12.5; C, 37.2; H, 3.7; N, 5.0. Calcd: Zn, 24.8; P, 11.8; C, 36.5; H, 3.4; N, 5.3%.

$Zn_2(O_3PCH_3)_2(C_{12}H_8N_2)$ (**4**). Found: Zn, 26.7; P, 11.8; C, 33.8; H, 3.0; N, 5.5. Calcd: Zn, 26.2; P, 12.4; C, 33.7; H, 2.8; N, 5.6%.

$Zn_2(O_3PC_6H_5)_2(C_{10}H_6N_2)$ (**5**). Found: Zn, 21.7; P, 10.1; C, 42.9; H, 2.9; N, 4.4. Calcd: Zn, 21.3; P, 10.1; C, 43.0; H, 2.9; N, 4.6%.

$Zn_2(O_3PCH_2C_6H_5)_2(C_{10}H_6N_2)$ (**6**). Found: Zn, 20.7; P, 10.0; C, 44.5; H, 3.7; N, 4.1. Calcd: Zn, 20.3; P, 9.6; C, 44.8; H, 3.5; N, 4.4%.

Results and Discussion

Elemental Analysis. Apart from the phen derivative of zinc(II) phenylphosphonate (**1**), which has a Zn/P/Phen ratio of 1:1:1 and formula $Zn(O_3PR)(phen)$, elemental analyses show a 2:2:1 molar ratio of Zn/P/amine, in agreement with the empirical formula, $Zn(O_3PR)(D)_{0.5}$ (where R = C_6H_5, $CH_2C_6H_5$, C_2H_5, CH_3; D = phen; and R = C_6H_5, $CH_2C_6H_5$, when D = 2,2′-bipy). The parent zinc(II) organophosphonates have the same Zn/P ratio as the amine complexes. All phen derivatives presented here are anhydrous (**1**−**4**), whereas the 2,2′-bipy derivatives are monohydrates (**5** and **6**). These formulations are supported by results from TGA, FTIR, powder XRD, XPS, and solid state $^{31}P/^{13}C$ MAS NMR data.

Thermogravimetric Analysis. Thermogravimetric curves for all materials exhibit stepwise mass losses that are consistent with the suggested formulations. TGA of the parent compound, zinc(II) phenylphosphonate, and the phen, and 2,2′-bipy derivatives are shown in Figure 1.

The TGA of the parent compound contains a mass loss above 500 °C due to phenyl group decomposition.[5,13−17]

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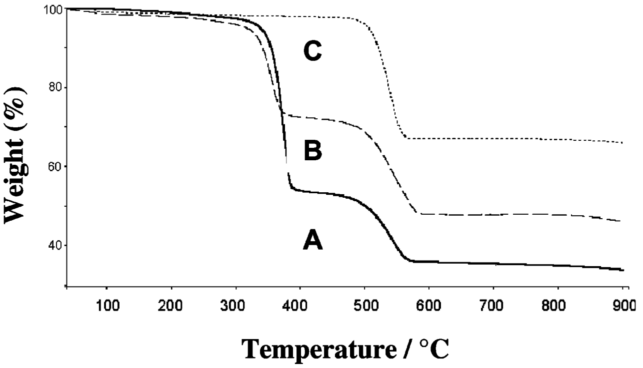

Figure 1. TGA spectra of the phen (**1**) (A) and 2,2′-bipy (**2**) (B) adducts of zinc(II) phenylphosphonate, and the parent compound zinc(II) phenylphosphonate (C).

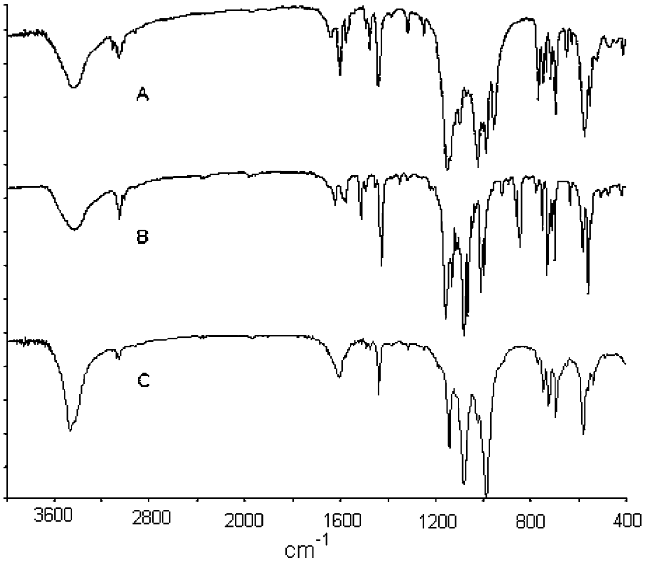

Figure 2. FTIR spectra of the phen (**1**) (A) and 2,2′-bipy (**2**) (B) derivatives of zinc(II) phenylphosphonate and the parent compound zinc(II) phenylphosphonate (C).

The TGA of the phen derivative of zinc(II) phenylphosphonate (**1**) shows two major decompositions: the first between 350 and 450 °C can be attributed to loss of phen (observed 46.1%, calculated 46.8%), and the second between 495 and 750 °C, corresponding to decomposition of the phenyl group on the phosphonate (observed 17.7%, calculated 18.3%), as for the parent compound. Decomposition of the organophosphonate group is often incomplete at 900 °C, as observed in this case, due to only partial breakdown of the organic constituents.[5,13−17] The zinc(II) phen complexes show no sorbed or coordinated solvent.

The two 2,2′-bipy derivatives (**5** and **6**) lose mass between 40 and 100 °C due to loss of water of crystallization. The low temperature at which water is lost suggests that it is held in lattice voids and not bonded to the metal ion. Mass losses between 200 and 400 °C are attributed to the loss of 2,2′-bipy, and a mass loss between 495 and 750 °C is characteristic of the loss of the organic moiety from the phosphonate. The 2,2′-bipy ligand is lost at a much lower temperature than the phen derivative, signifying that the 2,2′-bipy complexes are less thermally stable.

The TGA of the 2,2′-bipy derivative of zinc(II) phenylphosphonate (**5**) exhibits loss of water from 40 to 100 °C (observed 2.8%, calculated 2.8%), loss of 2,2′-bipy from 250 to 400 °C (observed 24.5%, calculated 24.1%), and loss of phenyl group from 450 to 600 °C (observed 23.9%, calculated 23.8%). In a similar fashion, the bidentate 2,2′-bipy group incorporated into a zirconium phosphate system was found to decompose between 330 and 400 °C, consistent with these assignments.[18]

Fourier Transform Infrared Analysis. The FTIR spectra of the zinc(II) compounds are typical of metal organophosphonates,[1−3] and, apart from minor shifts and the splitting of some bands, the fundamental frequencies of the uncoordinated amine ligands are altered little on coordination to zinc ions. The spectrum of the phen derivative of zinc(II) phenylphosphonate (**1**) (Figure 2) contains a group of relatively weak peaks between 3100 and 2900 cm^{-1} due to aromatic CH stretching bands, and a sharp, intense peak due to aromatic CH bending at 1426 cm^{-1}. Similar absorptions are found in zinc(II) phenylphosphonate, as shown in Figure 2c. Absorptions due to the PO_3 group of the phosphonic acid are observed in the region between 900 and 1200 cm^{-1}, and three absorptions due to the out-of-plane CH vibrations of C_6H_5 are located at 752, 731, and 698 cm^{-1}, which are characteristic of phenylphosphonates in general.[14,15] Other absorptions attributed to the phen ligand are seen at 1621, 1576, 1513, and 1490 cm^{-1}, consistent with coordination of the amine to the metal.[19,20]

The phen derivative of zinc(II) benzylphosphonate (**2**) displays similar absorptions, with the only major difference being the presence of a CH_2 bending vibration, at 1495 cm^{-1}, due to the methylene group of the benzylphosphonate. The ethylphosphonate derivative (**3**) contains an ethyl CH_2 absorption at 1457 cm^{-1}, and the methylphosphonate derivative (**4**) contains a methyl CH stretch at 2995 cm^{-1}. The FTIR spectra of the corresponding 2,2′-bipy derivatives are very similar, as shown in Figure 2b. Absorptions attributed to the 2,2′-bipy ligand occur at 1607, 1599, 1577, and 1476 cm^{-1}, consistent with coordination of the amine to the metal.[15] Corresponding peaks are observed at slightly lower frequencies in un-complexed 2,2′-bipy.[18]

Solid State ^{31}P MAS NMR. ^{31}P solid-state NMR spectroscopy has become a powerful tool for providing structural information about the environment of the phosphorus atoms in zinc(II) organophosphonates. For a series of known structures, the connectivity of the RPO_3^{2-} groups (i.e., the number of metal atoms bonded to the three oxygen atoms of the phosphonate units) can be differentiated on the basis of the value of the chemical shift, asymmetry, and anisotropy (Table 1). Massiot[21] has reported that isotropic chemical shifts (δ_{iso}) move downfield as the connectivity of the phosphonate oxygens to the zinc increases. This is due to an increase in the paramagnetic contribution to the nuclear shielding as the oxygen−phosphorus bond strength decreases and the number of zinc atoms

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Table 1. ^{31}P MAS NMR Data for Amine Derivatives of Zinc(II) Organophosphonates, Reference Complexes, and Some Aluminum, Gallium, and Indium Amine Derivatives

complex	δ_1 (ppm)^a	δ_2 (ppm)^a	ref.
$Zn(O_3PC_6H_5)(phen)$	6.0		this work
$Zn_2(O_3PCH_2C_6H_5)_2(phen)$	25.1	17.0	this work
$Zn_2(O_3PC_2H_5)_2(phen)$	34.2	27.2	this work
$Zn_2(O_3PCH_3)_2(phen)$	31.9	25.1	this work
$Zn_2(O_3PC_6H_5)_2(2,2'\text{-bipy})(H_2O)$	21.9	14.6	this work
$Zn_2(O_3PCH_2C_6H_5)_2(2,2'\text{-bipy})(H_2O)$	23.6	14.6	this work
$Zn(O_3PC_6H_5)\cdot H_2O$	23.3		7
$Zn(O_3PC_6H_5)\cdot c\text{-hexNH}_2$	12.4		7
$Zn_2(O_3PC_2H_4CO_2H)_2(C_6H_5NH_2)$	34.4	28.9	2
$Zn(O_3PC_2H_4NH_2)$	27.0		2
$Zn_3(O_3PC_2H_4CO_2)_2$	35.9		10
$Ga(O_3PC_6H_5)(O_2P(OH)C_6H_5)phen\cdot H_2O$	−1.4	4	17
$Ga(O_3PC_6H_5)(O_2P(OH)C_6H_5)2,2'\text{-bipy}$	7	−5	17
$Ga(O_3PCH_2C_6H_5)(O_2P(OH)CH_2C_6H_5)2,2'\text{-bipy}\cdot H_2O$	10	8	17
$Ga(O_3PCH_2C_6H_5)(O_2P(OH)CH_2C_6H_5)phen\cdot H_2O$	10	8	17
$Al(O_3PC_6H_5)(O_2P(OH)C_6H_5)2,2'\text{-bipy}\cdot H_2O$	4	−1	14
$Al(O_3PC_6H_5)(O_2P(OH)C_6H_5)phen\cdot H_2O$	4.5	−0.5	14

[a] δ_1 and δ_2 denote (111) and (112) connectivity, respectively.[21]

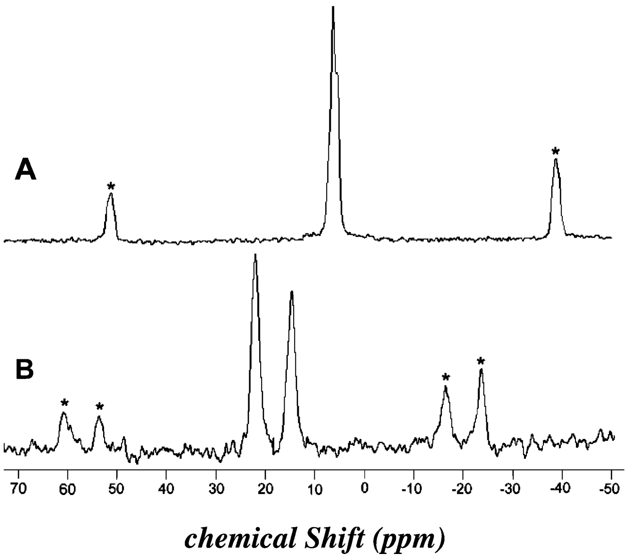

Figure 3. ^{31}P MAS NMR spectra of (A) the phen derivative of zinc(II) phenylphosphonate, $Zn(O_3PC_6H_5)(phen)$ (**1**) (the shoulder on the 6 ppm peak is not believed to be significant; the magnitude of the difference is so small that this may simply be a solid-state effect reflecting subtle differences in the site symmetry for the P atom and the nature of its nearest neighbors); and (B) the 2,2′-bipy derivative of zinc(II) phenylphosphonate, $Zn_2(O_3PC_6H_5)_2(2,2'\text{-bipy})(H_2O)$ (**5**). Spinning sidebands are denoted by an asterisk.

connected to a PO_3^{2-} group increases from two to five. Massiot also used chemical shift asymmetry and anisotropy trends, as calculated from ^{31}P static spectra, to distinguish connectivity.

Typical spectra for the ^{31}P MAS NMR of the phen derivative of zinc(II) phenylphosphonate, $Zn(O_3PC_6H_5)$(phen) (**1**), and the corresponding 2,2′-bipy derivative, $Zn_2(O_3PC_6H_5)_2(2,2'\text{-bipy})(H_2O)$ (**5**), are shown in Figure 3. The phen derivative has one narrow phosphorus resonance, at $\delta = 6.0$ ppm, consistent with one phosphorus site, whereas the corresponding 2,2′-bipy derivative has two phosphorus resonances of equal intensity, at $\delta = 21.9$ ppm and $\delta = 14.6$ ppm. This difference is believed to arise from different bonding modes of the phosphonate ligands, as discussed below. Table 1 compares the zinc complexes prepared in this study to a number of other zinc(II) organophosphonates of known structure.

The phen derivative of zinc(II) phenylphosphonate (**1**) has one signal positioned much further upfield ($\delta_1 = 6.0$ ppm) compared to the other derivatives. It would seem reasonable to conclude that the phosphonate ligand in this compound has a different connectivity to the other derivatives. It may also be that ring current effects from the phen ligand could shield the phosphorus atom in an abnormal way, causing a significant upfield shift of the ^{31}P resonance. This resonance, which, although far removed from other compounds prepared in this work and those reported by others (Table 1), may simply reflect that the resonance positioning of the ^{31}P nucleus is very sensitive to small changes in its spatial environment, for example, the geometry of its surrounding O_3C tetrahedron, bond lengths, MOP dihedral angles, connectivity, and the electron-withdrawing ability of the metal. Thus, the phosphorus is believed to have a (111) connectivity, leading to a five-coordinate geometry for the zinc atom in the phen derivative of zinc(II) phenylphosphonate (**1**) (Figure 6, see below).

In contrast, all other complexes show two resonances, with an approximate 1:1 ratio, suggesting two different phosphorus environments. Because the zinc(II) alkylphosphonate derivatives (**3** and **4**) exhibit characteristics and chemical shifts similar to those observed for $Zn_2(O_3PCH_2CO_2)_2(C_6H_5NH_2)$,[2] which has two types of RPO_3 groups, the alkylphosphonate derivatives reported here are believed to have analogous δ_1(111) and δ_2(112) connectivities (Table 4, see below).[21] Thus, one phosphonate is suggested to be bonded to three zinc atoms through each of its oxygen atoms with (111) connectivity ($\delta = 28.9$ ppm) while another is connected to four zinc atoms with one oxygen bridging two metal atoms and having (112) connectivity ($\delta = 34.4$ ppm).

The phen and 2,2′-bipy derivatives of zinc(II) benzylphosphonate (**2** and **6**), and the 2,2′-bipy derivative of zinc(II) phenylphosphonate (**5**), show similar ^{31}P NMR shifts at $\delta = \sim 15$ ppm and $\delta = \sim 24$ ppm. One phosphorus is thought to be in an environment similar to those of the alkylphosphonates ($\delta = \sim 24$ ppm) and, therefore, has a (111) connectivity. The other phosphorus signal ($\delta = \sim 15$ ppm) probably corresponds to a different connectivity, which may be (011) conforming well to other zinc(II) organophosphonates with similar proposed structures.[21] Alternatively, both resonances

Table 2. N_{1s} Binding Energies of Zinc(II) Complexes and Reference Zinc(II) Compounds with 2,2′-bipy and Phen Ligands

complex	N_1 (eV)	ΔN_1 (eV)[a]	N_2 (eV)	*ΔN_2 (eV)[a]
phen	398.39			
$Zn(O_3PC_6H_5)$(phen) (**1**)	399.09	+0.70		
$Zn_2(O_3PCH_2C_6H_5)_2$(phen) (**2**)	399.68	+1.29	397.78	−0.61
$Zn_2(O_3PC_2H_5)_2$(phen) (**3**)	399.43	+1.04	398.06	−0.33
$Zn_2(O_3PCH_3)_2$(phen) (**4**)	399.38	+0.99	398.82	−0.43
$Zn_2(O_3PC_6H_5)_2$(2,2′-bipy)(H_2O) (**5**)	399.48	+1.09	397.79	−0.60
$Zn_2(O_3PCH_2C_6H_5)_2$(2,2′-bipy)(H_2O) (**6**)	399.56	+1.17	397.64	−0.75

[a] $\Delta N_1 = N_1(\text{complex}) - N_1(\text{phen})$; $\Delta N_2 = N_2(\text{complex}) - N_1(\text{phen})$.

may correspond to (111) connectivity with the peak at $\delta = \sim 15$ ppm being shifted upfield by ring current effects.

The ^{31}P NMR results of a similar study, involving heterocyclic amine interactions with aluminum(III), gallium(III), and indium(III) organophosphonates, are included in Table 1. Like the compounds isolated in the present study, these complexes also show two phosphorus environments. However, unlike the present compounds, it was necessary to formulate them as containing both the mono and dianionic forms of the phosphonic acid to maintain charge balance.[15]

Solid State^{13}C MAS NMR. The ^{13}C MAS NMR of the phen derivative of zinc(II) phenylphosphonate (**1**) contains large peaks at $\delta = 124$ ppm and $\delta = 130$ ppm with smaller shoulders at $\delta = 135$ ppm and $\delta = 149$ ppm, accounting for the aromatic carbons of the phen and the phenylphosphonate which overlap.[1] All phen derivatives show similar aromatic peaks; however, the benzyl derivative (**2**) shows a singlet at $\delta = 33$ ppm due to the methylene group of the phosphonate, the ethyl derivative (**3**) shows two carbon signals for the ethyl group at $\delta = 20$ ppm and $\delta = 6$ ppm, and the methyl derivative (**4**) shows a single methyl peak at $\delta = 12$ ppm.

The 2,2′-bipy derivatives have peaks assigned to the aromatic carbons of 2,2′-bipy and phenylphosphonate at $\delta = 145$ ppm and $\delta = 124$ ppm, and a shoulder at $\delta = 135$ ppm. Those of the benzyl derivative (**6**) are shifted slightly to $\delta = 147$ ppm and $\delta = 125$ ppm, with shoulders at $\delta = 134$ ppm and $\delta = 120$ ppm, comparable to those reported by others.[1] The benzyl derivative also gives a methylene signal at $\delta = 33$ ppm.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectroscopy (XPS) has been used in this instance to verify the coordination of the heterocyclic amine ligand to the metal center. As noted earlier, FTIR peaks of the complexes are observed at slightly higher frequencies compared to those of the free ligands. This is indicative of amine coordination to the metal center, rather than just intercalation or a physical mixture of products. To confirm this, the XPS data of most relevance are the binding energies of electrons in the 1s orbital of nitrogen in the complexes, which are denoted N_1, and if there is another peak, N_2, in Table 2.

From the XPS data of the free ligand (Table 2), it can be seen that phen shows only one type of nitrogen. A comparable measurement could not be obtained for 2,2′-bipy because the sample sublimed during analysis, and so for calculation purposes it was assumed to have the same value. On complexation of amine to the metal center, an increase in binding energy (ΔN_1) of between +0.70 and +1.29 eV is observed. This verifies that the nitrogen in the metal complex is in a different, more strongly bound environment, and denotes metal−nitrogen bonding.[15] If the amine ligands were simply intercalated, the binding energies would not show a significant change from that of the free ligand (0.10−0.15 eV). The zinc(II) complexes all show one nitrogen site, suggesting that the two nitrogen atoms of the ligands are equivalent. Because of the characteristic rigidity of the phen ligand, both nitrogen atoms must be coordinated to the same zinc center.

Table 3. Powder XRD Diffraction Data of the Zinc(II) Organophosphonate Complexes

	complex *d* spacing (Å)	parent *d* spacing (Å)
$Zn(O_3PC_6H_5)$(phen) (**1**)	11.23	14.34
$Zn_2(O_3PCH_2C_6H_5)_2$(phen) (**2**)	16.20	15.60
$Zn_2(O_3PC_2H_5)_2$(phen) (**3**)	nonlayered	
$Zn_2(O_3PCH_3)_2$(phen) (**4**)	nonlayered	
$Zn_2(O_3PC_6H_5)_2$(2,2′-bipy)(H_2O) (**5**)	12.22	14.34
$Zn_2(O_3PCH_2C_6H_5)_2$(2,2′-bipy)(H_2O) (**6**)	15.41	15.60

Powder X-ray Diffraction. Powder XRD patterns for the phen derivatives of zinc(II) phenyl- (**1**) and benzyl-phosphonate (**2**) show these compounds to be lamellar, crystalline materials in the solid state. The strong diffraction from the (001) plane is indicative of a lamellar material and is observed in a number of similar systems;[1] the powder XRDs for previously reported zinc(II) organophosphonates are also consistent with layered solid-state structures.[7] The phen derivative of zinc(II) benzylphosphonate (**2**) shows a *d*(001) layer spacing of 16.20 Å, slightly larger than that of the parent zinc(II) benzylphosphonate (15.60 Å), whereas the corresponding 2,2′-bipy derivative shows a slight decrease (**6**). However, the XRD patterns of the other derivatives show *d*(001) layer spacings which are significantly smaller than those of the parent zinc(II) phenyl- and benzyl-phosphonates (Table 3).

The decrease in spacing of the layered phen and 2,2′-bipy derivatives, relative to the parent zinc(II) phenylphosphonates, suggests that a structural rearrangement of the complex occurs to accommodate the amine in a more favorable coordination. This trend has been observed for several gallium and indium derivatives of bidentate amines.[13−15] In contrast, for the phen and 2,2′-bipy derivatives of zinc(II) benzylphosphonate (**2** and **6**), the amine ligand has a minimal effect on the interlayer distance. This is attributed to the greater flexibility of the benzyl group enabling the metal to accommodate the additional ligand without requiring a change in structure.

The alkylphosphonate derivatives (**3** and **4**), however, are crystalline nonlamellar solids. The XRD patterns do not display strong (001) diffractions, but rather shoulders and small peaks indicative of their nonlamel-

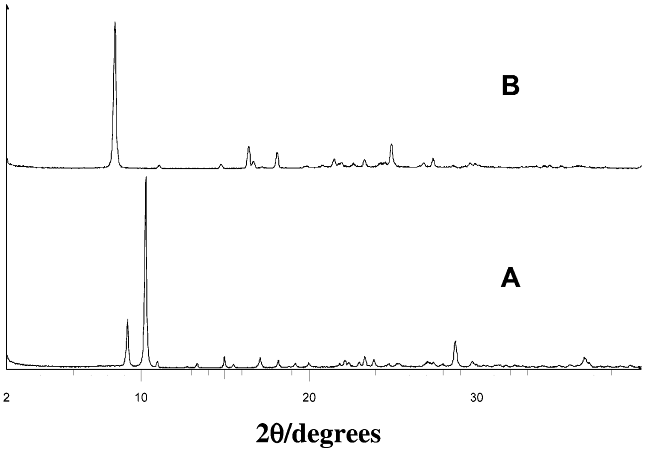

Figure 4. Powder XRD diffraction pattern of the nonlayered phen derivative of zinc(II) methylphosphonate (A) and the layered phenyl derivative (B)

lar nature. Figure 4 compares the XRD pattern of the lamellar phen derivative of zinc(II) phenylphosphonate (**1**) with the nonlayered methyl derivative (**4**).

Suggested Structures. Generally, as discussed in the Introduction, the lamellar nature of zinc(II) organophosphonates is achieved through octahedral coordination around the metal cation, with interconnectivity occurring between the zinc and phosphonate oxygens. In the parent zinc(II) phenylphosphonate, for example, two oxygens of each phosphonate group chelate to a zinc atom (forming a bridge between adjacent zinc atoms), the third oxygen atom bonds to a single zinc atom, the fourth and fifth oxygen atoms are donated from two adjacent phosphonate groups, and a water molecule occupies the final coordination site.[6,22] In the present study, the reaction of zinc acetate, phenylphosphonic acid, and one equivalent of phen produces a lamellar material in the solid state with a decreased interlayer spacing relative to the parent organophosphonate. In the complex, $Zn(O_3PC_6H_5)(phen)$ (**1**), with a Zn/P/phen ratio of 1:1:1, the layers are believed to be made up of five-coordinate ZnN_2O_3. Because of steric restraints, the amine ligand is characteristically bidentate to a single metal center, making it unlikely that it also acts as a bridging ligand between metal atoms. Therefore, the zinc atoms in the layers are thought to be bridged by three oxygen atoms from each phosphonate group giving a structure that consists of two-dimensional polymeric layers. A schematic representation is presented in Figure 5 , and Figure 6 gives a representation of the bonding around the zinc atom.

It is instructive to compare the structure of $Zn(O_3PC_6H_5)(phen)$ (**1**) with a material of similar stoichiometric ratio, $Zn(O_3PC_6H_5)(c\text{-}hexNH_2)_2$, as it appears there are steric constraints induced by the size of the amine ligand. Although we might expect the structure for $Zn(O_3PC_6H_5)(c\text{-}hexNH_2)_2$ to be similar to that of $Zn(O_3PC_6H_5)(phen)$ (**1**), the former actually consists of one-dimensional polymeric chains in a (011) connectivity, rather than a layered structure, due to the bulkiness of the c-hex groups.[7]

However, in this case, the connectivity of the phosphonate group is not in full agreement with that

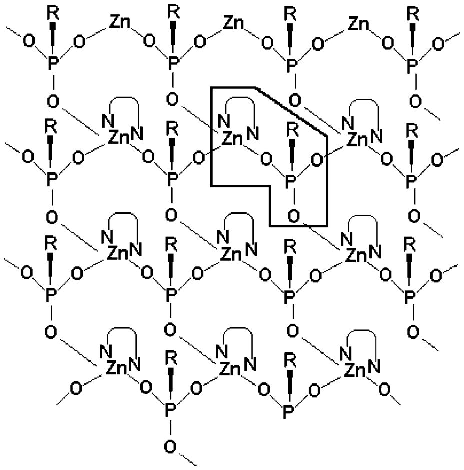

Figure 5. Schematic representation of the layer arrangement of the suggested structure of $Zn(O_3PC_6H_5)(phen)$ (**1**) showing the five-coordinate nature of ZnO_3N_2 and the (111) connectivity of the phosphonate group.

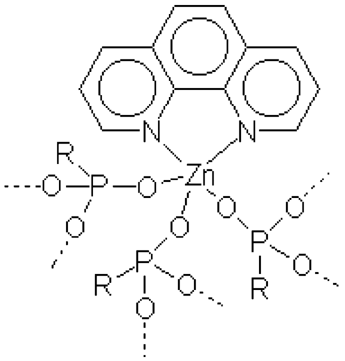

Figure 6. Schematic representation of bonding around the zinc atom in $Zn(O_3PC_6H_5)(phen)$ (**1**).

assigned by Massiot, on the basis of the position of the single resonance on the ^{31}P MAS NMR.[21] The complex needs to adopt at least a (111) connectivity to be a lamellar material; however, the observed ^{31}P MAS NMR chemical shift, $\delta = 6$ ppm, is placed unusually compared with those of the other Zn(II) compounds described in Table 1, and is somewhat upfield from that predicted for similar reference compounds (see Table 4). This irregular behavior may arise from a ring current effect where the phosphorus atom is positioned above or below the plane of the phen ligands and is abnormally shielded. The XPS data and FTIR spectra provide supporting evidence for amine coordination, rather than just insertion (intercalation), of the phen between the zinc(II) organophosphonate layers.

Compared to the $Zn(O_3PC_6H_5)(phen)$ (**1**) compound, the 2,2′-bipy derivative of zinc(II) phenylphosphonate (**5**), and the phen and 2,2′-bipy zinc(II) benzylphosphonate complexes (**2** and **6**), of general formula $Zn_2(O_3PR)_2(D)$ contain one less amine per zinc. Characterization results suggest a slightly different structure, even though they are also lamellar materials in the solid state. The amine is bound to the metal, as evidenced from XPS and FTIR data; however, the XPS data suggest that the nitrogen atoms of the amine ligands are coordinated to the zinc center in an unsymmetrical manner. Two resonances of equal intensity are displayed in the ^{31}P MAS NMR, which also implies two different phosphorus sites, and the shifts correspond

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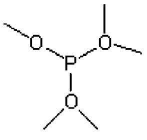
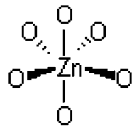
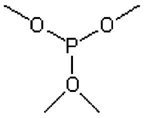
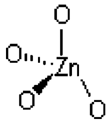
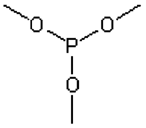
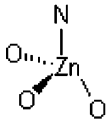
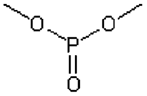
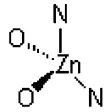
(22) Martin, K.; Squattrito, P.; Clearfield, A. *Inorg. Chim. Acta.* **1989**, *155*, 7.

Table 4. Connectivity of Zinc(II) Organophosphonates of Known Structure Based on ^{31}P NMR Data[21] [a]

COMPLEX	δ_{iso}	CONNECTIVITY[#]		ZINC ENVIRONMENT	REF:
$Zn(O_3PC_2H_5).H_2O$	37.7	122			2
$Zn_3(O_3PC_2H_4CO_2)_2.2H_2O$	32.4	112			1
$Zn(O_3PC_2H_4NH_2)$	27.0	111			10
$Zn(O_3PC_6H_5).(c\text{-}hexNH_2)_2$	13.0	011			7

[a] δ_{iso} = isotropic chemical shift. [#]Connectivity: (011) = one oxygen of phosphonate not bonded and two oxygen atoms are coordinated to two different zinc atoms; (111) = three oxygen atoms of the phosphonate are coordinated to three different zinc atoms; (112) = two oxygens are each bonded to one metal atom and one oxygen is bridging two zinc atoms; (122) = one oxygen is bonded to one metal atom and two bridging oxygens are present.[21]

well to reference compounds that have (011) and (111) connectivities.[21] However, the structure is believed to have (111) connectivity only, with one phosphorus atom being shielded abnormally due to ring current effects. A schematic representation of the suggested monomer unit is presented in Figure 7. The $Zn_2(O_3PR)_2(D)$ complexes have two different zinc atoms both with tetrahedral geometries. The first zinc atom, Zn(1), bonds with two oxygen atoms from two different phosphonate groups, and two nitrogen atoms from a bidentate amine ligand. The secondzinc atom, Zn(2), bonds with four oxygen atoms from four different phosphonate groups. The phosphonate groups are bonded to three zinc atoms through each of their oxygen atoms, in (111) connectivity. This arrangement leads to the formation of two-dimensional layered sheets, as presented in Figure 7b. It is suggested that the bulky phenyl or benzyl groups of the phosphonate restrict the formation of a three-dimensional complex.

The phen derivatives of zinc(II) alkylphosphonates (**3** and **4**) appear to possess a slightly different structure, as they are nonlamellar materials in the solid state. The complexes have a Zn/P/D ratio of 2:2:1 and show FTIR, XPS, and ^{31}P MAS NMR data that are similar to the phen and 2,2′-bipy derivatives of zinc(II) benzylphosphonate (**2** and **6**) and the 2,2′-bipy derivative of zinc(II) phenylphosphonate (**5**). The ^{31}P MAS NMR shows two peaks of equal intensity at $\delta_1 = \sim 33$ ppm and $\delta_2 = \sim 26$ ppm. One peak of the ^{31}P MAS NMR corresponds to a (111) connectivity, observed at a position similar to the equivalent (111) peak in the phen and 2,2′-bipy derivatives of zinc(II) benzylphosphonate, and the 2,2′-

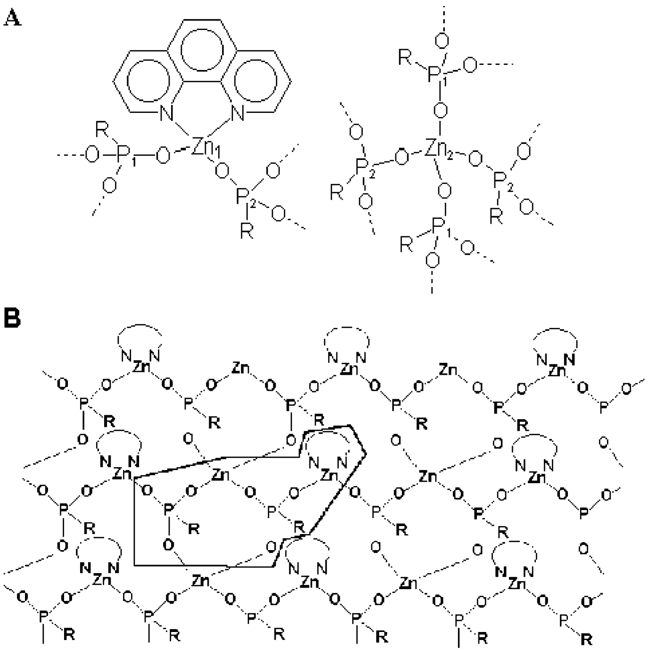


Figure 7. Schematic representation of the bonding around the zinc atoms (A) and layer arrangement (B) of the suggested structure of $Zn_2(O_3PR)_2(D)$ (when R = $CH_2C_6H_5$, D = phen (**2**); when R = C_6H_5 (**5**), $CH_2C_6H_5$ (**6**), D = 2,2′-bipy), showing repeat unit.

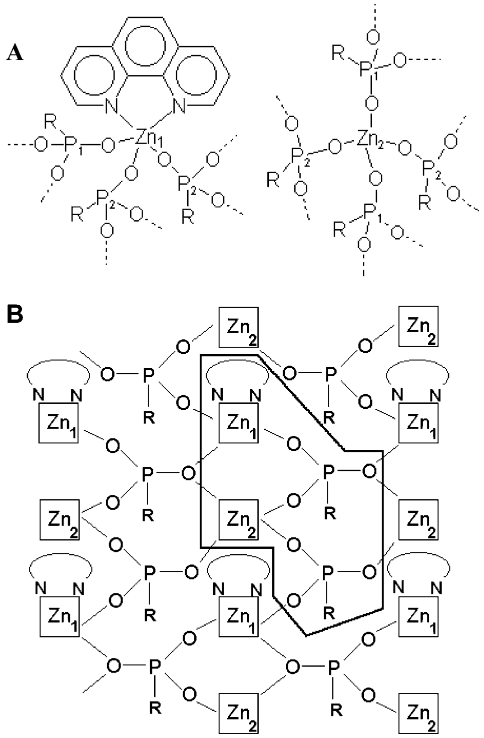


Figure 8. Schematic representation of bonding around the zinc atoms (A) and polymer arrangement (B) of the suggested structure of $Zn_2(O_3PR)_2(phen)$ (R = C_2H_5 (**3**), CH_3 (**4**)).

bipy derivative of zinc(II) phenylphosphonate. The other peak is shifted significantly downfield to $\delta = \sim 33$ ppm, a position similar to the (112) peak observed in reference compounds.[2]

As described earlier, a similar complex, $Zn_2(O_3P(CH_2)_2CO_2H)_2(C_6H_5NH_2)$, has been reported by Drumel[2] which also shows two ^{31}P MAS NMR resonances of equal intensity and similar chemical shifts. A crystal structure of the complex[11] shows zinc atoms with two different tetrahedral geometries. The first has four coordinating phosphonate oxygen atoms, whereas the second has three phosphonate oxygen atoms and a nitrogen atom from aniline.

In the present study, the two peaks seen in the ^{31}P MAS NMR spectrum confirm phosphorus in two different environments. Thus, it is suggested that the first zinc atom has three phosphonate oxygen atoms and two nitrogen atoms from the phen ligand, and the second has four coordinating phosphonate oxygen atoms. In addition, the first phosphonate group is proposed to be bonded to three zinc atoms through each of its oxygen atoms; the second is bonded to four zinc atoms, with one of the oxygens bridging two zinc atoms.

In contrast, the phen alkylphosphonate derivatives (**3** and **4**) are believed to have a three-dimensional structure; the complexes are not layered due to extensive phosphonate connectivity. A schematic representation of the monomer unit is presented in Figure 8. The first zinc atom, Zn(1), is five coordinate, and bonds with three phosphonate oxygen atoms and two nitrogen atoms from the bidentate amine ligand. The second zinc atom, Zn(2), has a tetrahedral geometry with four coordinating phosphonate oxygen atoms. Two of the phosphonate groups are bonded to three zinc atoms through each of their oxygen atoms; the other two phosphonate groups are bonded to four zinc atoms with one of the oxygen atoms on each phosphonate bridging two zincs. All of these suggested structures are consistent with the spectroscopic and analytical data available.

The nonlayered character of $Zn_2(O_3PR)_2(phen)$, where R = C_2H_5 (**3**), CH_3 (**4**), is suggested on the basis that no strong (001) diffraction lines can be observed in the XRD powder pattern (Figure 4). However, if the medium line observed at 8.6 Å for $Zn_2(O_3PCH_3)_2(phen)$ (**4**) is attributed to impurities in the sample, a lamellar structure may be proposed with an arrangement similar to that determined for the lamellar aniline derivative, $Zn(O_3P(CH_2)_2CO_2H)(C_6H_5NH_2)_{0.5}$.[2,11]

Conclusion

A series of heterocyclic amine derivatives of zinc alkyl- and aryl-phosphonic acids have been successfully prepared using "direct" methods. The reaction of zinc acetate with phenylphosphonic acid and phen produced a lamellar material (**1**) which is believed to contain five-coordinate ZnN_2O_3 units. The amine is classically bidentate, and the zinc atoms are bridged by three oxygen atoms from each phosphonate group, producing two-dimensional polymeric layers. The corresponding reaction of zinc acetate with phenylphosphonic acid and 2,2′-bipy (**5**), and with benzylphosphonic acid and phen (**2**) or 2,2′-bipy (**6**), also produced lamellar materials. These $Zn_2(O_3PR)_2(D)$ complexes contain two different zinc atoms, both with tetrahedral geometries: Zn(1) bonds with two oxygen atoms from two different phosphonate groups and two nitrogen atoms from a bidentate amine ligand, and Zn(2) bonds with four oxygen atoms from four different phosphonate groups. The phosphonate groups are bonded to three zinc atoms through each of their oxygen atoms in (111) connectivity. This arrangement leads to the formation of two-dimensional layered sheets. The differences between the structures of **2**, **5**, and **6** and that of **1** may have arisen due to the increased flexibility of the benzyl-phosphonic acid and/or that of 2,2′-bipy.

In contrast, the reaction of zinc acetate with the nonaromatic phosphonic acids (methyl- and ethyl-) and phen produced three-dimensional structures with extensive phosphonate connectivity. These materials contain two zinc sites: Zn(1) which is 5-coordinate and bonds with three phosphonate oxygen atoms and two nitrogen atoms from the bidentate amine ligand; and Zn(2) which has tetrahedral geometry with four coordinating phosphonate oxygen atoms. Two of the phosphonate groups are bonded to three zinc atoms through each of their oxygen atoms; the other two phosphonate groups are bonded to four zinc atoms, with one of the oxygen atoms on each phosphonate bridging two zinc atoms. Attempts to produce 2,2′-bipy analogues of (**3** and **4**) were unsuccessful.

Acknowledgment. We thank the following people for their assistance: Dr. Johan Du Plessis from RMIT for XPS measurements; Mr. Paul Morrison for assistance with ICP analyses; and Assoc. Prof. Frances Separovic from Melbourne University for assistance in recording the MAS NMR spectra.

Supporting Information Available: Reference for MAS NMR data (tif). This material is available free of charge via the Internet at http://pubs.acs.org.

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