

# Syntheses and Crystal Structures of the New Zinc Phosphonates $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{R})(\text{C}_6\text{H}_5)) \cdot x\text{H}_2\text{O}$ , Based on Mixed Phosphonic Acid–Phosphine Oxide Building Blocks

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The two new zinc(II) phosphonates  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2)$  (monoclinic  $P2_1/c$  (No. 14),  $a = 9.961(2)$  Å,  $b = 5.838(1)$  Å,  $c = 24.608(5)$  Å,  $\beta = 101.48(3)^\circ$ ,  $Z = 4$ ) and  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)) \cdot 0.67\text{H}_2\text{O}$  (monoclinic  $P2_1/c$  (No. 14),  $a = 15.879(5)$  Å,  $b = 7.383(2)$  Å,  $c = 10.475(3)$  Å,  $\beta = 105.01(5)^\circ$ ,  $Z = 4$ ) were prepared by reaction of zinc nitrate,  $(\text{R})(\text{C}_6\text{H}_5)\text{P}(\text{O})\text{CH}_2\text{PO}_3\text{H}_2$  [ $\text{R} = \text{C}_6\text{H}_5, \text{CH}_3$ ], and sodium hydroxide in water in an autoclave. For the first compound, a unidimensional arrangement is observed, while for the second, a layered structure is obtained, in relation to the size of the substituents present on the phosphine oxide moiety.

## Introduction

Metal phosphonate chemistry has attracted substantial research interest because of their wide variety of accessible structure types and their potential application in areas such as ion exchange, catalysis, and nonlinear optics.<sup>1</sup> Transition metal phosphonates are usually layered, with an arrangement in the slabs that strongly depends on the nature and oxidation state of the metal. Recently, pillared layered phosphonates (PLP's) were prepared by using bis(phosphonic acid) precursors,  $\text{H}_2\text{O}_3\text{P}-\text{R}-\text{PO}_3\text{H}_2$ .<sup>2</sup> And we have demonstrated that functionalized phosphonic acids  $\text{H}_2\text{O}_3\text{P}-\text{R}-\text{Z}$  ( $\text{Z} = \text{CO}_2\text{H}, \text{NH}_2$ ) are also powerful tools for this purpose.<sup>3</sup> It is possible to manipulate the phosphonate framework of these new PLP's by the choice of the Z functional end, simply by varying the number of its potential binding sites (three oxygen atoms of  $\text{PO}_3\text{H}_2$ , two oxygen atoms of  $\text{CO}_2\text{H}$ , and one nitrogen atom of  $\text{NH}_2$ ) that can participate in the cohesion of the network. All these results have shown that a certain control of the dimensionality of metal phosphonates could be achieved by the suitable choice of the phosphonic acid precursor. Another fundamental aspect that has not been extensively studied<sup>4–6</sup> is the effect of the steric

bulk of the  $\text{RPO}_3\text{H}_2$  starting compound on the structure and dimensionality of metal phosphonates. One example was described by us,<sup>5</sup> showing that cobalt phosphonates having the same formulation but different structures could be obtained simply by changing the size of the organic radical bound to phosphorus. If R is a linear alkyl chain (e.g., *n*-butyl), the layer of  $\text{Co}^{\text{II}}(\text{RPO}_3) \cdot \text{H}_2\text{O}$  is flat and the metal atoms are found in one octahedral environment. However if R is a bulky *tert*-butyl group, the cobalt atoms are present in two tetrahedral sites and one octahedral site, thus leading to corrugated layers to minimize the electrostatic repulsions of adjacent R groups. In fact, one important feature is the comparable distance separating two adjacent  $\text{PO}_3$  groups in layered phosphonates and adjacent  $\text{PO}_3$  and Z groups in PLP's, invariably observed between 5 and 6 Å. Thus, it is reasonable to think that the dimensionality of phosphonates will be directly influenced by the size of the organic chain bound to phosphorus. To check the validity of this concept, we have prepared the phosphonic acids  $\text{H}_2\text{O}_3\text{P}-\text{CH}_2-\text{Z}$ , functionalized by phosphine oxide ligands having different sizes (compound **1**,  $\text{Z} = \text{P}(\text{O})(\text{C}_6\text{H}_5)_2$ ; compound **2**,  $\text{Z} = \text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)$ ). These compounds were then reacted with zinc nitrate in water, under neutral-pH conditions, to yield two new zinc phosphonates:  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2)$  (**A**) and  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)) \cdot 0.67\text{H}_2\text{O}$  (**B**).

## Experimental Section

**Materials and Methods.** All starting materials were purchased from Aldrich Chemical Co. and were used as received. Chemical analyses were performed by the CNRS Analytical Laboratory (Vernaison, France). FTIR spectra were obtained on a Nicolet 20SX FT-IR spectrometer with the usual KBr pellet technique. A Perkin-Elmer TGS2 thermogravimetric analyzer was used to obtain TGA thermograms, which were acquired in air from room temperature to 250 °C at a scan rate of 5 °C/min. <sup>1</sup>H and <sup>31</sup>P NMR spectra recorded in solution were taken on an AC 200 Bruker spectrometer, with TMS (for <sup>1</sup>H) and 85 wt %  $\text{H}_3\text{PO}_4$  (for <sup>31</sup>P) as the reference. Solid state <sup>31</sup>P NMR spectra were recorded on a DSX 300 Bruker spectrometer as previously

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described.<sup>7</sup> Principal components of the chemical shift tensors were measured using the spinning-side band fitting routine<sup>8</sup> under various observation conditions (static and MAS at different spinning rates).

**Synthesis of  $\text{H}_2\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2$ , **1**.** To a solution of diethyl methylphosphonate<sup>9</sup> (64 mmol) in dry THF (120 mL) under nitrogen at  $-78^\circ\text{C}$  was added dropwise 62.5 mmol of *n*-BuLi in hexane. After 15 min, diphenylphosphinyl chloride was added dropwise, and the solution was slowly allowed to warm to  $-35^\circ\text{C}$  in 3 h. Water was then added, and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$ . The extract was dried ( $\text{MgSO}_4$ ) and concentrated under vacuum. Excess diethyl methylphosphonate was removed under vacuum using a Kugelrohr apparatus. The remaining oil (the diethyl ester form of **1**) was purified by chromatography on silica gel, and an ethanol/ethyl acetate (40:60) mixture was used as the eluent (86% yield).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.99 (dd,  $\text{PCH}_2\text{P}$ ,  $^2J(\text{P}^1-\text{H}) = 21$  Hz,  $^2J(\text{P}^2-\text{H}) = 14$  Hz).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.2 ( $\text{PO}_3$ ), 24.2 (PO). This oil was then refluxed in concentrated hydrochloric acid for 2 days. After evaporation of the mixture under reduced pressure, water was added. The aqueous phase was washed twice with ethyl acetate and then evaporated to give compound **1** in quantitative yield.  $^1\text{H}$  NMR (200 MHz, DMSO):  $\delta$  3.04 (dd,  $\text{PCH}_2\text{P}$ ,  $^2J(\text{P}^1-\text{H}) = 20$  Hz,  $^2J(\text{P}^2-\text{H}) = 14$  Hz).  $^{31}\text{P}$  NMR (81 MHz, DMSO):  $\delta$  14.0 ( $\text{PO}_3$ ), 24.2 (PO).

**Synthesis of  $\text{H}_2\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)$ , **2**.** Methylphenylphosphinyl chloride was prepared according to the literature by reaction of the sodium salt of ethyl phenylphosphinate with methyl iodide (85% yield).<sup>10</sup> The resulting ethyl methylphenylphosphinate was treated with phosphorus pentachloride in carbon tetrachloride<sup>11</sup> to give the desired product in 85% yield. Then, a procedure similar to that described for the preparation of **1** was performed with methylphenylphosphinyl chloride, except that *t*-BuLi was used instead of *n*-BuLi. The diethyl ester form of **2** was prepared in 70% yield.  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.99 (d,  $\text{PCH}_3$ ,  $^2J(\text{P}-\text{H}) = 14$  Hz), 2.60 (m,  $\text{PCH}_2\text{P}$ ).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta$  19.3 ( $\text{PO}_3$ ), 29.6 (PO). Compound **2** was then obtained in quantitative yield.  $^1\text{H}$  NMR (200 MHz, DMSO):  $\delta$  1.81 (d,  $\text{PCH}_3$ ,  $^2J(\text{P}-\text{H}) = 14$  Hz), 2.55 (m,  $\text{PCH}_2\text{P}$ ).  $^{31}\text{P}$  NMR (81 MHz, DMSO):  $\delta$  14.4 ( $\text{PO}_3$ ), 32.7 (PO).

**Synthesis of  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2)$ , **A**.** A mixture of zinc nitrate (2 mmol), precursor **1** (1 mmol), and 1 M sodium hydroxide (2 mL) with 10 mL of water was placed in the PTFE cell (23 mL capacity; 50% fill volume) of an autoclave, which was then sealed and kept at  $180^\circ\text{C}$  in a drying oven for 60 h.  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2)$  was obtained as white crystals, used for the X-ray structure determination, in 86% yield. Anal. Calcd for  $\text{ZnP}_2\text{O}_4\text{C}_{13}\text{H}_{12}$ : P, 17.23; C, 43.42; H, 3.36; Zn, 18.19. Found: P, 17.22; C, 43.15; H, 3.37; Zn, 18.36. IR (KBr): 1438 (m), 1145 (s), 1124 (s), 1100 and 1090 (vs), 1003 (m)  $\text{cm}^{-1}$ . TGA (room temperature to  $300^\circ\text{C}$ ): 0%.  $^{31}\text{P}$  MAS NMR (85 wt %  $\text{H}_3\text{PO}_4$ ): 50%  $\text{PO}_3$  [ $\delta_{11} = -43.3$ ,  $\delta_{22} = -14.7$ ,  $\delta_{33} = 93.5$  ppm], 50% PO [ $\delta_{11} = -58.3$ ,  $\delta_{22} = 84.5$ ,  $\delta_{33} = 99.6$  ppm].

**Synthesis of  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5))\cdot 0.67\text{H}_2\text{O}$ , **B**.** The same procedure as above was followed using precursor **2**, except that the reaction was performed at  $100^\circ\text{C}$  for 6 days (60% yield). Anal. Calcd for  $\text{ZnP}_2\text{O}_{4.67}\text{C}_8\text{H}_{11.34}$ : P, 20.01; C, 31.04; H, 3.69; Zn, 21.12. Found: P, 19.71; C, 30.96; H, 3.66; Zn, 21.05. IR (KBr): 3649 (w), 3440 (b w), 1437 (m), 1304 (m), 1157 (s), 1135 (s), 1110 and 1100 (vs), 1015 (m)  $\text{cm}^{-1}$ . TGA (water loss  $35^\circ\text{C}$ ): calcd, 3.90%; found, 3.85%.  $^{31}\text{P}$  MAS NMR (85 wt %  $\text{H}_3\text{PO}_4$ ): 50%  $\text{PO}_3$  [ $\delta_{11} = -40.7$ ,  $\delta_{22} = -14.3$ ,  $\delta_{33} = 85.6$  ppm], 50% PO [ $\delta_{11} = -51.3$ ,  $\delta_{22} = 85.0$ ,  $\delta_{33} = 126.9$  ppm].

**X-ray Structure Analyses.  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2)$ , **A**.** A white needlelike crystal having approximate dimensions  $0.02 \times 0.06 \times 0.15$   $\text{mm}^3$  was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Cell constants and an orientation

**Table 1.** Crystallographic Data for  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2)$  (**A**) and  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5))\cdot 0.67\text{H}_2\text{O}$  (**B**)

	<b>A</b>	<b>B</b>
empirical formula	$\text{ZnP}_2\text{O}_4\text{C}_{13}\text{H}_{12}$	$\text{ZnP}_2\text{O}_{4.67}\text{C}_8\text{H}_{11.34}$
fw	359.57	309.54
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
<i>a</i> , Å	9.961(2)	15.879(5)
<i>b</i> , Å	5.838(1)	7.383(2)
<i>c</i> , Å	24.608(5)	10.475(3)
$\beta$ , deg	101.48(3)	105.01(5)
<i>V</i> , Å <sup>3</sup>	1402.4(8)	1186.1(9)
<i>Z</i>	4	4
$\rho_{\text{calcd}}$ , g $\text{cm}^{-3}$	1.70	1.73
$\rho_{\text{obsd}}$ , g $\text{cm}^{-3}$	1.75	1.69
<i>T</i> , °C	$25 \pm 1$	$25 \pm 1$
$\lambda(\text{Mo K}\alpha)$ , Å	0.7107	0.7107
$\mu$ , $\text{cm}^{-1}$	19.9	23.4
<i>R</i> <sup>a</sup>	0.053	0.048
<i>R</i> <sub>w</sub> <sup>b</sup>	0.060	0.054

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

matrix for data collection were obtained from least-squares refinement of the setting angles of 25 randomly oriented reflections in the range  $10^\circ \leq 2\theta \leq 35^\circ$ , corresponding to a monoclinic cell. To check on crystal and instrument stability, three representative reflections were measured every 60 min, and no decay was observed. An empirical absorption correction based on  $\psi$ -scan measurements was applied, and the data were corrected for Lorentz and polarization effects. The data were collected out to  $60^\circ$  in  $2\theta$  using the  $\omega$ - $2\theta$  scan technique ( $h = -14, 14$ ;  $k = -1, 8$ ;  $l = -1, 34$ ). On the basis of the systematic absences and the successful refinement of the structure, the space group was found to be  $P2_1/c$ . The atomic scattering factors were taken from Cromer and Waber,<sup>12</sup> and anomalous dispersion corrections were taken from Cromer and Ibers.<sup>13</sup> For the data reduction and structure solution and refinement, programs in the SHELXTL PLUS package<sup>14</sup> were used on a microVAX 3900 computer. A total of 4064 unique reflections were measured, of which 1863 with  $I \geq 2\sigma(I)$  were considered observed.

The structure was solved by a combination of direct methods and Fourier syntheses. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed on the methylene and phenyl groups in calculated positions and were refined by riding on the carbon atoms, with fixed thermal parameters. The final cycle of full-matrix least-squares refinement for 181 variables converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of  $R = 0.053$  and  $R_w = 0.060$ . Crystallographic data and refinement conditions are listed in Table 1. Positional and thermal parameters are given in Table 2, and selected bond distances and angles are listed in Table 3.

**$\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5))\cdot 0.67\text{H}_2\text{O}$ , **B**.** The structure determination was undertaken using a colorless parallelepipedic crystal of approximate dimensions  $0.10 \times 0.17 \times 0.25$   $\text{mm}^3$ . The unit cell parameters were refined from 25 automatically centered reflections on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The data were collected out to  $60^\circ$  (in  $2\theta$ ) using the  $\omega$ - $2\theta$  scan technique, as described for the previous structure ( $h = -22, 22$ ;  $k = -1, 10$ ;  $l = -1, 14$ ). For the data reduction and structure solution and refinement, programs in the SHELXTL PLUS package<sup>14</sup> were used on a microVAX 3900 computer. On the basis of the systematic absences, the space group was found to be  $P2_1/c$ . Of the 3442 unique reflections which were collected, 1581 were observed with  $I \geq 2\sigma(I)$ . The structure was solved by a combination of direct methods and Fourier syntheses. The non-

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**Table 2.** Positional and Thermal Parameters for the Atoms of  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2)$ 

atom	x	y	z	$U_{\text{eq}}, \text{\AA}^2$
Zn	0.42023(7)	0.4337(1)	0.79320(3)	0.0221(2)
P(1)	0.4190(1)	0.9308(3)	0.81222(6)	0.0206(3)
P(2)	0.6398(2)	0.6752(3)	0.88897(6)	0.0256(3)
O(1)	0.5284(4)	0.9377(8)	0.7772(2)	0.0297(9)
O(2)	0.3365(4)	1.1518(7)	0.8094(2)	0.0256(9)
O(3)	0.3264(4)	0.7205(7)	0.8021(2)	0.0253(9)
O(4)	0.5808(4)	0.4617(7)	0.8586(2)	0.033(1)
C(10)	0.5186(6)	0.904(1)	0.8828(2)	0.026(1)
C(20)	0.6946(7)	0.615(1)	0.9613(3)	0.027(2)
C(21)	0.643(1)	0.702(2)	1.0023(4)	0.033(2)
C(22)	0.685(1)	0.636(2)	1.0577(4)	0.044(3)
C(23)	0.777(1)	0.492(2)	1.0730(4)	0.048(3)
C(24)	0.816(2)	0.376(4)	1.0338(6)	0.044(3)
C(25)	0.777(2)	0.444(4)	0.9776(4)	0.033(2)
C(30)	0.7879(7)	0.769(1)	0.8647(4)	0.027(2)
C(31)	0.8424(8)	0.652(2)	0.8282(3)	0.030(3)
C(32)	0.960(1)	0.722(3)	0.8108(4)	0.039(3)
C(33)	1.020(1)	0.915(3)	0.8281(8)	0.047(3)
C(34)	0.964(1)	1.037(3)	0.863(1)	0.039(2)
C(35)	0.850(1)	0.970(2)	0.884(1)	0.031(3)

<sup>a</sup> The zinc, phosphorus, oxygen, and carbon atoms were refined anisotropically and are given in the form of the equivalent displacement parameter defined as  $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* A_{ij}$ .

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2)$ 

Zn—O(1) <sup>a</sup>	1.902(4)	P(1)—C(10)	1.828(6)
Zn—O(2) <sup>b</sup>	1.923(4)	P(2)—O(4)	1.511(5)
Zn—O(3)	1.951(4)	P(2)—C(10)	1.789(6)
Zn—O(4)	2.038(4)	P(2)—C(20)	1.791(7)
P(1)—O(1)	1.518(4)	P(2)—C(30)	1.784(7)
P(1)—O(2)	1.526(4)	C—C <sup>c</sup>	1.34(1)
P(1)—O(3)	1.524(4)		
O(1) <sup>a</sup> —Zn—O(2) <sup>b</sup>	114.0(2)	O(2)—P(1)—C(10)	107.5(3)
O(1) <sup>a</sup> —Zn—O(3)	108.3(2)	O(3)—P(1)—C(10)	106.5(3)
O(1) <sup>a</sup> —Zn—O(4)	114.1(2)	O(4)—P(2)—C(10)	112.7(3)
O(2) <sup>b</sup> —Zn—O(3)	118.3(2)	O(4)—P(2)—C(20)	109.9(3)
O(2) <sup>b</sup> —Zn—O(4)	102.1(2)	O(4)—P(2)—C(30)	110.7(3)
O(3)—Zn—O(4)	99.2(2)	C(10)—P(2)—C(20)	107.4(3)
O(1)—P(1)—O(2)	113.2(2)	C(10)—P(2)—C(30)	109.4(3)
O(1)—P(1)—O(3)	114.1(2)	C(20)—P(2)—C(30)	106.5(4)
O(1)—P(1)—C(10)	103.0(2)	P(1)—C(10)—P(2)	111.9(3)
O(2)—P(1)—O(3)	111.8(2)	C—C—C <sup>c</sup>	119(1)

<sup>a</sup> Atom related by  $1 - x, -1/2 + y, 3/2 - z$ . <sup>b</sup> Atom related by  $x, -1 + y, z$ . <sup>c</sup> Phenyl ring average value.

hydrogen atoms were refined anisotropically. The hydrogen atoms were placed on the methylene, methyl, and phenyl groups in calculated positions and were refined by riding on the carbon atoms, with fixed temperature factors. The final cycle of full-matrix least-squares refinement for 147 variables converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of  $R = 0.048$  and  $R_w = 0.054$ . Positional and thermal parameters are given in Table 4, and selected bond distances and angles are listed in Table 5.

## Results

**Structure of  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2)$ , A.** The structure consists of infinite chains running parallel to the  $b$  axis (Figure 1). The zinc atoms are tetrahedrally coordinated (Figure 2) with three oxygen atoms from the phosphonate groups (Zn—O: 1.90–1.95 Å) and one oxygen atom from the phosphine oxide moiety (Zn—O: 2.04 Å). The structure is built up from eight-membered rings (Zn—O—P(1)—O—Zn—O—P(1)—O, classically observed in zinc phosphonates<sup>3,15,16</sup>), forming a “ladderlike”

**Table 4.** Positional and Thermal Parameters for the Atoms of  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)) \cdot 0.67\text{H}_2\text{O}$ 

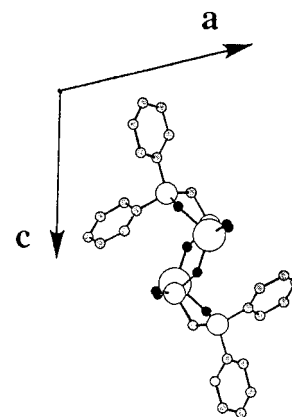
atom	x	y	z	$U_{\text{eq}}, \text{\AA}^2$
Zn	0.41802(4)	0.40730(8)	0.61634(5)	0.0217(2)
P(1)	0.60161(8)	0.5926(2)	0.6928(1)	0.0200(3)
P(2)	0.6868(1)	0.2921(2)	0.5642(1)	0.0251(3)
O(1)	0.6381(2)	0.7320(5)	0.7991(3)	0.0250(9)
O(2)	0.5776(2)	0.6758(5)	0.5570(3)	0.0248(9)
O(3)	0.5293(2)	0.4823(6)	0.7228(3)	0.0293(9)
O(4)	0.6677(2)	0.3914(5)	0.4344(3)	0.0249(9)
O(5) <sup>b</sup>	0.8224(7)	0.756(2)	0.929(1)	0.047(4)
C(10)	0.6930(4)	0.4416(7)	0.7004(5)	0.024(1)
C(20)	0.6099(4)	0.1186(8)	0.5652(6)	0.026(2)
C(30)	0.7925(4)	0.1907(9)	0.5956(6)	0.026(2)
C(31)	0.8148(6)	0.048(1)	0.6824(9)	0.030(3)
C(32)	0.8964(9)	-0.025(2)	0.713(1)	0.038(3)
C(33)	0.9575(8)	0.047(2)	0.659(1)	0.044(3)
C(34)	0.9374(6)	0.184(2)	0.569(1)	0.037(3)
C(35)	0.8547(5)	0.261(1)	0.5142(8)	0.030(2)

<sup>a</sup> See Table 2. <sup>b</sup> Refined occupancy: 0.64(2).

**Table 5.** Selected Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)) \cdot 0.67\text{H}_2\text{O}$ 

Zn—O(1) <sup>a</sup>	1.914(3)	P(1)—C(10)	1.816(5)
Zn—O(2) <sup>b</sup>	1.935(3)	P(2)—O(4)	1.504(3)
Zn—O(3)	1.912(4)	P(2)—C(10)	1.786(5)
Zn—O(4) <sup>b</sup>	1.992(4)	P(2)—C(20)	1.771(6)
P(1)—O(1)	1.516(4)	P(2)—C(30)	1.789(6)
P(1)—O(2)	1.505(3)	C—C <sup>c</sup>	1.36(1)
P(1)—O(3)	1.505(4)		
O(1) <sup>a</sup> —Zn—O(2) <sup>b</sup>	110.7(2)	O(2)—P(1)—C(10)	107.2(2)
O(1) <sup>a</sup> —Zn—O(3)	113.4(2)	O(3)—P(1)—C(10)	107.6(3)
O(1) <sup>a</sup> —Zn—O(4) <sup>b</sup>	105.1(2)	O(4)—P(2)—C(10)	112.1(2)
O(2) <sup>b</sup> —Zn—O(3)	112.7(2)	O(4)—P(2)—C(20)	112.3(3)
O(2) <sup>b</sup> —Zn—O(4) <sup>b</sup>	100.0(1)	O(4)—P(2)—C(30)	109.3(3)
O(3)—Zn—O(4) <sup>b</sup>	113.8(2)	C(10)—P(2)—C(20)	109.7(3)
O(1)—P(1)—O(2)	111.9(2)	C(10)—P(2)—C(30)	104.9(3)
O(1)—P(1)—O(3)	112.4(2)	C(20)—P(2)—C(30)	108.2(3)
O(1)—P(1)—C(10)	103.6(2)	P(1)—C(10)—P(2)	117.8(3)
O(2)—P(1)—O(3)	113.4(2)	C—C—C <sup>c</sup>	119.9(8)

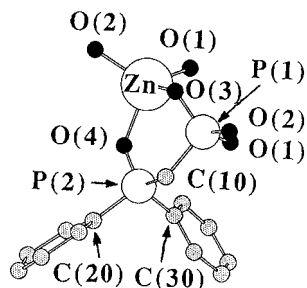
<sup>a</sup> Atom related by  $1 - x, -1/2 + y, 3/2 - z$ . <sup>b</sup> Atom related by  $1 - x, 1 - y, 1 - z$ . <sup>c</sup> Phenyl ring average value.

**Figure 1.** Schematic representation of  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2)$  viewed down the  $b$  axis.

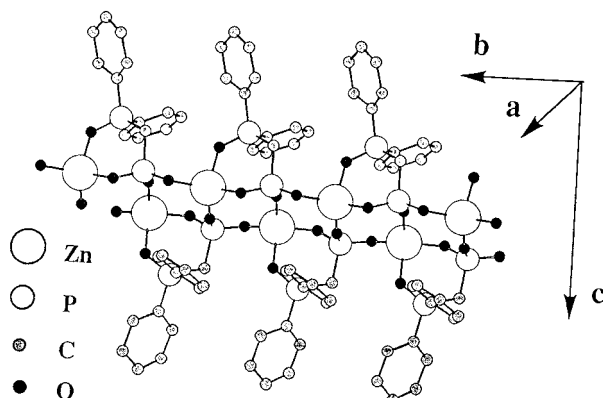
arrangement (Figure 3). Smaller six-membered rings (Zn—O—P(1)—C(10)—P(2)—O) are also present on each side of the chain, and the phenyl groups are arranged on the outside of the chains, whose arrangement is dictated by packing forces (in the  $a$  and  $c$  directions), as already observed in 1-D uranium phenylphosphonate structures.<sup>17</sup>

(15) Cao, G.; Rabenberg, L. K.; Nunn, C. M.; Mallouk, T. E. *Chem. Mater.* **1991**, *3*, 149.

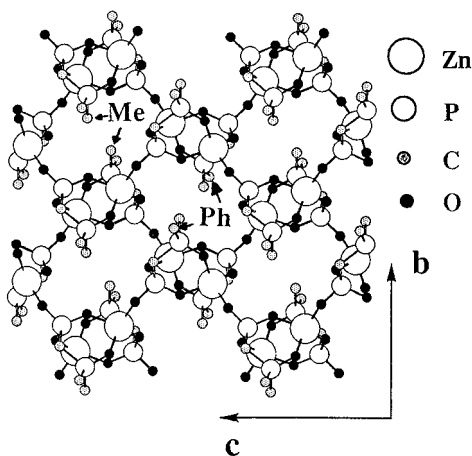
(16) Drumel, S.; Janvier, P.; Bujoli-Doeuff, M.; Bujoli, B. *J. Mater. Chem.* **1996**, *6*, 1843.



**Figure 2.** Schematic representation of the coordination about the zinc atoms in  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2)$  and the numbering scheme used in the tables.

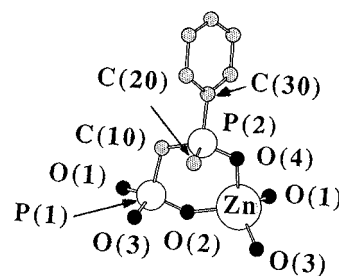


**Figure 3.** View of  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)_2)$ , showing the connection within the chains.

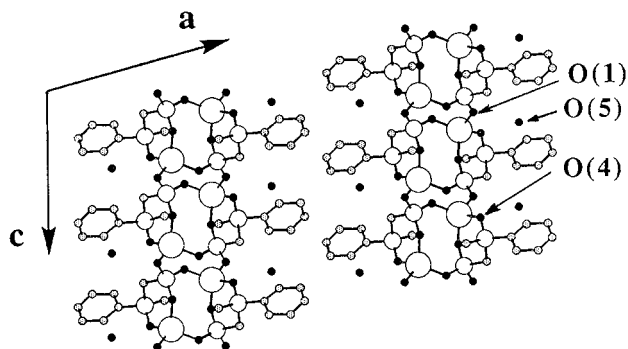


**Figure 4.** Schematic representation of a  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)) \cdot 0.67\text{H}_2\text{O}$  layer as seen perpendicular to the  $a$  axis. The water molecule O(5) and the carbon atoms that are not directly bonded to the phosphorus atoms have been omitted for clarity (Me = methyl, Ph = phenyl)

**Structure of  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)) \cdot 0.67\text{H}_2\text{O}$ , B.** The structure consists of layers ( $bc$  plane; Figure 4) in which the zinc atoms are tetrahedrally coordinated in a manner similar to that observed for compound A (Figure 5; three oxygen atoms from phosphonate groups [ $\text{Zn}-\text{O}$ : 1.91–1.94 Å] and one oxygen atom from the phosphine oxide [ $\text{Zn}-\text{O}$ : 1.99 Å]). In each layer, the zinc atoms are arranged in 16-membered rings, constructed by corner-sharing of four  $\text{ZnO}_4$  tetrahedra and four  $\text{PO}_3\text{C}$  tetrahedra, and the methyl groups of the phosphine oxide point toward these cavities. The sheet linkage of these rings results in eight-membered rings ( $\text{Zn}-\text{O}-\text{P}(1)-\text{O}-\text{Zn}-\text{O}-$



**Figure 5.** Schematic representation of the coordination about the zinc atoms in  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)) \cdot 0.67\text{H}_2\text{O}$  and the numbering scheme used in the tables.



**Figure 6.** Schematic representation of  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)) \cdot 0.67\text{H}_2\text{O}$  as seen perpendicular to the  $b$  axis.

$\text{P}(1)-\text{O}$ ), flanked on each side ( $ac$  plane; Figure 6) by two smaller rings ( $\text{Zn}-\text{O}-\text{P}(1)-\text{C}(10)-\text{P}(2)-\text{O}$ ). The phenyl groups are oriented toward the interlayer space, with the usual  $d$  spacing (ca. 15.9 Å) observed for layered phenyl metal phosphonates. For the lattice water molecules (O(5)) between the layers, the occupancy refined to 0.64(2), totally accounting for 0.67 mol of water, which was the amount determined by chemical analyses as well as thermogravimetric measurements (water loss: found, 3.85%; expected, 3.90%). We presume that the water molecules are weakly hydrogen-bonded to the phosphonate oxygen atom O(1) ( $\text{O}(5)-\text{O}(1) = 2.89(2)$  Å), thus explaining the low temperature (30–40 °C) at which the dehydration takes place.

## Discussion

The new preparation of phosphonic acid precursors **1** and **2** was achieved in good yields by reaction of the lithium salt of diethyl methylphosphonate with diphenylphosphinyl chloride and methylphenylphosphinyl chloride, respectively, followed by the hydrolysis of the diethyl phosphonate ester groups using concentrated hydrochloric acid.

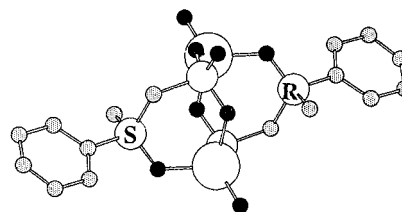
If we compare the structures of the previously described  $\text{Zn}(\text{O}_3\text{PC}_2\text{H}_4\text{NH}_2)$  and  $\text{Zn}(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2\text{H}) \cdot 1.5\text{H}_2\text{O}^3$  with that of compound **B**,  $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)) \cdot 0.67\text{H}_2\text{O}$ , we can see in the three cases a similar arrangement of 16- and 8-membered rings within the layers. For the three compounds, the zinc atoms are tetrahedrally coordinated by three phosphonate oxygen atoms, the fourth vertex being occupied by one atom present on the functional end of the phosphonic acid precursor: a nitrogen atom (from  $\text{NH}_2$ ) or an oxygen atom (from  $\text{CO}_2\text{H}$  or  $\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)$ ). For the two first products, the phosphonic acid groups act as “pillars”, leading to three-dimensional pillared structures. For phase **B**, however, the two ends ( $\text{PO}_3$  and  $\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)$ ) are present in the same layer, participating in the cohesion of the bidimensional network. In this case no PLP is observed, probably because the phosphine oxide moiety is too bulky to allow such an arrangement, and

(17) Poojary, D. M.; Grohol, D.; Clearfield, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1508. Grohol, D.; Subramanian, M. A.; Poojary, D. M.; Clearfield, A. *Inorg. Chem.* **1996**, *35*, 5264.

the dimensionality is only 2. Moreover, we can notice that the methyl groups are present in the plane of the sheets (*bc*—Figure 4), being accommodated within the 16-membered rings. For steric reasons, it is thus obvious that a similar situation cannot be expected when the methyl group is replaced by a phenyl ring, when precursor **1** is used. Due to the size of the two phenyl groups of the phosphine oxide, there is insufficient space to allow the usual distance observed between adjacent PO<sub>3</sub> attachments in the layers of phosphonates, and the structure is forced to arrange as chains, leading to compound **A**, in which the dimensionality is now 1.

This observation clearly demonstrates that the geometry and steric bulk of the organic precursor have a significant influence on the dimensionality of the final product, and the inorganic framework has to adapt itself to the constraints induced by the shape of the organic radical bound to phosphorus.

A final point worth discussing concerns the configuration of the phosphorus atoms (P(2)) of the phosphine oxide in compound **B**. As precursor **2** was prepared in the form of the racemic mixture (*R* + *S*), it is interesting to note that, in the 8-membered rings (Zn—O—P(1)—O—Zn—O—P(1)—O) present in the structure (Figure 7), the O<sub>3</sub>PCH<sub>2</sub>P(O)(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>) units are arranged in pairs of opposite configurations. This observation leaves a question about the structure that would be obtained if a pure enantiomeric form (*R* or *S*) of precursor **2** was used, and work is in progress to attempt the preparation of the suitable organic precursor to obtain an answer to this question. Experiments are also underway to covalently immobilize compounds **1** and **2** as organic–inorganic hybrid materials, without coor-



**Figure 7.** Detail of the structure of Zn(O<sub>3</sub>PCH<sub>2</sub>P(O)(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>))·0.67H<sub>2</sub>O showing the pairs of O<sub>3</sub>PCH<sub>2</sub>P(O)(CH<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>) blocks of opposite configurations (*R* and *S*).

dination of the phosphine oxide moiety, which could subsequently be complexed (e.g., by WO<sub>5</sub>) for application as supported oxidation catalysts.<sup>18</sup>

**Acknowledgment.** We thank Dr. Yves Piffard (UMR CNRS 6502) for help with the X-ray structure refinements and Dr. Dominique Massiot (UPR CNRS 4212) for the solid state MAS NMR measurements.

**Supporting Information Available:** Tables giving a full presentation of the crystal data, anisotropic thermal parameters for non-hydrogen atoms, atomic coordinates of calculated hydrogen atoms, and nonessential bond lengths and angles (7 pages). Ordering information is given on any current masthead page.

IC970392J

(18) Fredoueil, F.; Gelbard, G.; Bujoli, B. Work in progress. For examples of catalytic applications of R<sub>3</sub>P=O—WO<sub>5</sub> complexes, see: Gelbard, G.; Sherrington, D. C.; Breton, F.; Benelmoudeni, M.; Charreyre, M.; Dong, D. In *Metal-containing Polymeric Materials*; Pittman, J., Ed.; Plenum Press: New York, 1996; p 265.