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Synthesis, Structure, and Reactivity of Some Functionalized Zinc and Copper(II) Phosphonates

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Functional analogues (R = $(CH_2)_2CO_2H$, $(CH_2)_2Br$, $(CH_2)_2NH_3{}^+NO_3{}^-$) of the two structural models, $Zn^{II}(O_3PR){\cdot}H_2O$ and $Cu^{II}(O_3PR){\cdot}H_2O$ (R = *n*-alkyl, phenyl), were prepared in a mixture of acetone and water. Attempts to graft an aromatic amine on the carboxyl function of $Zn(O_3P(CH_2)_2CO_2H){\cdot}H_2O$ led to the formation of $Zn(O_3P(CH_2)_2CO_2H){\cdot}0.5C_6H_5NH_2$, $Zn[Zn(O_3P(CH_2)_2CO_2)]_2{\cdot}3H_2O$ and $Zn_3(O_3P(CH_2)_2CO_2)_2$ (monoclinic $P2_1/c$ (No. 14), $a = 8.126(1)$ Å, $b = 9.237(1)$ Å, $c = 8.587(2)$ Å, $\beta = 106.26(3)°$, $Z = 2$, $R = 0.036$, $R_w = 0.037$). No amide formation was detected. However, the desired $Zn(O_3P(CH_2)_2CONHC_6H_5)$ product was directly synthesized, according to an original one-step procedure involving the three molecular precursors: zinc nitrate, (2-carboxyethyl)-phosphonic acid and aniline. If aniline was replaced by sodium hydroxyde, a pillared layered phosphonate was obtained: $Zn(O_3P(CH_2)_2CO_2H){\cdot}1.5H_2O$ (orthorhombic *Pccn* (No. 56), $a = 9.885(1)$ Å, $b = 10.020(1)$ Å, $c = 16.438(3)$ Å, $Z = 8$, $R = 0.062$, $R_w = 0.074$).

Introduction

Recent studies in our laboratory have been focused on the synthesis and crystal structure determination of di- and trivalent layered metal phosphonates.[1−4] After their structures were known, it was possible to have an accurate understanding of the original magnetic properties observed for some of these materials: $Fe^{II}(O_3PC_2H_5){\cdot}H_2O$,[2] α-$Cu^{II}(O_3PR)$ and β-$Cu^{II}(O_3PCH_3)$.[3] At the same time, divalent metal phosphonates have excited many, and a lot of work has been carried out by Mallouk et al. and Clearfield et al., reporting the synthesis and structures of various members of the $M^{II}(O_3PR){\cdot}H_2O$ series (M^{II} = Mg, Mn, Co, Ni, Zn, Cd, Cu ; R = *n*-alkyl or phenyl)[5,6] along with the possibility of replacing the water molecule coordinated to the metal center with different amines.[5d,7]

Parallel to our magnetic studies, it seemed interesting to us to explore the possibility of using these materials as supports for catalytic species fixed on these matrixes by covalent bonds. This task could be achieved by reaction on the $M^{II}(O_3PR){\cdot}H_2O$ layer surface through reactive groups present on the R organic moities (R = $(CH_2)_nCO_2H$, $(CH_2)_nNH_2$, $(CH_2)_nBr$, ...). Functionalized tetravalent metal phosphonates $M^{IV}(O_3PR)_2$ (R = functional group) have been known since the early 1980s[8] but very little organic chemistry describing the reactivity of the organic functions was reported until a recent work of Burwell et al.[9] that described the synthesis and the reactivity of the layered $Zr(O_3PCH_2CH_2COCl)_2$ toward organic molecules such as amines, alcohols and Bu_3SnH. Even if some examples of functionalized divalent metal phosphonates have been reported in the literature,[10] to our knowledge, only four structural determinations have been described. Glowiak et al. reported the linear $Cu(HO_3PCH_2NH_2)_2$ complex,[11] and Fenot et al., the layered $Zn(O_3PCH_2NH_3)_2{\cdot}4H_2O$.[12] We already reported a study on the structure of $Fe(HO_3PC_2H_4CO_2H)_2$ in which the carboxyl group was connected to the metal center, thus excluding any possibility of using the carboxylic acid function.[1d] Finally, a recent publication of Clearfield et al.[13] described the structure of $Zn^{II}(O_3PCH_2Cl){\cdot}H_2O$, as a potential intermediate for the preparation of divalent metal aminophosphonates, by nucleophilic substitution of the chlorine atom by one of the two ends of an alkyldiamine. In this paper, we report that the direct preparation of divalent metal aminophosphonates as well as other functionalized compounds is possible. The reaction of

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Table 1. TGA, XRD and ^{31}P MAS NMR Data for **2a–c** and **3a–c**

compound	dehyd temp (°C) % wt loss[a]	cell param (Å and deg)	^{31}P MAS NMR δ (ppm)
$Zn(O_3PCH_2CH_3){\cdot}H_2O$	90 9.4 (9.4)	$a = 5.67(1)$ $b^b = 10.14(2)$ $c = 4.79(1)$	37.4
2a $Zn(O_3P(CH_2)_2CO_2H){\cdot}H_2O$	85 7.9 (7.7)	$a = 5.66(1)$ $b^b = 24.68(3)\ (2 \times 12.34)$ $c = 9.43(1)\ (2 \times 4.71)$ $\beta = 91.3(1)$	37.6
2b $Zn(O_3P(CH_2)_2Br){\cdot}H_2O$	95 6.8 (6.7)	$a = 5.73(1)$ $b^b = 11.37(2)$ $c = 4.85(1)$ $\beta = 93.7(1)$	32.8
2c $Zn(O_3)P(CH_2)_2NH_3^+NO_3^-){\cdot}H_2O$	90 6.85 (6.7)	$d^b = 14.5(1)$	33.9
$Cu(O_3PCH_2CH_3){\cdot}H_2O$	160 9.5 (9.5)	$a = 7.47(1)$ $b^b = 9.94(1)$ $c = 7.51(1)$ $\beta = 93.1(1)$	
3a $Cu(O_3P(CH_2)_2CO_2H){\cdot}H_2O$	155 7.8 (7.7)	$a = 7.39(1)$ $b^b = 12.54(2)$ $c = 7.55(1)$ $\beta = 93.3(1)$	
3b $Cu(O_3P(CH_2)_2Br){\cdot}H_2O$	160 6.9 (6.7)	$a = 7.65(1)$ $b^b = 11.26(1)$ $c = 7.67(1)$ $\beta = 89.5(1)$	
3c $Cu(O_3P(CH_2)_2NH_3^+NO_3^-){\cdot}H_2O$	170 dehydration concomitant with P–C bond scission	$d^b = 14.1(1)$	

[a] Theoretical values in parentheses. [b] Interlayer spacing.

functionalized phosphonic acids with zinc or copper nitrate in water/organic solvent mixtures leads to $M^{II}(O_3PR){\cdot}H_2O$ layered phosphonates ($R = (CH_2)_2CO_2H$, $(CH_2)_2Br$, $(CH_2)_2NH_3^+NO_3^-$) in which the arrangement within the layer is respectively related to the two corresponding structural models of $Zn(O_3PR){\cdot}H_2O$[5] and $Cu(O_3PR){\cdot}H_2O$[6] *n*-alkyl phosphonates. Then we investigate the reactivity of the carboxylic acid function of $Zn(O_3P(CH_2)_2CO_2H){\cdot}H_2O$ toward aromatic amines, and describe an original "one pot" synthesis of zinc phosphonates containing amide linkages, starting from zinc nitrate, 2-(carboxyethyl)phosphonic acid and aromatic amines.

Experimental Section

Materials. Except for $H_2O_3P(CH_2)_2Br$, all starting materials were purchased from Aldrich Chemical Co. and were used as received. $H_2O_3P(CH_2)_2Br$ was prepared in 95% yield by treating $(C_2H_5O)_2OP(CH_2)_2Br$ (0.06 mol) with trimethylchlorosilane (0.48 mol) and dry potassium bromide (0.36 mol) in 50 mL of refluxing acetonitrile for 2 days. The solution was then filtered on celite, evaporated and distilled under vacuum (bp 78–80 °C –0.1 mmHg). The resulting colorless liquid was stirred with 10 mL of water for 2 h. The aqueous phase was washed with dichloromethane and evaporated to dryness to obtain the expected (2-bromoethyl)phosphonic acid; ^1H NMR (CD_3COCD_3) δ 8.9 (s, 2H, OH), 3.6 (m, 2H, $BrCH_2$), 2.45 (m, 2H, PCH_2) ppm.

Synthesis of $Zn(O_3P(CH_2)_2CO_2H){\cdot}1.5H_2O$, 1. A 2 mmol sample of (2-carboxyethyl)phosphonic acid and 2 mmol of zinc nitrate were placed in a Pyrex tube (10 mm diameter; 180 mm length; 70% fill volume) with 6 mL of a 1 N sodium hydroxyde solution and water. The tube was then sealed and warmed at 110 °C for 2 weeks (internal pressure: *ca.* 1.5 bars). The solid product **1** was collected by filtration, washed with water and acetone, and dried at room temperature to a constant weight (yield: 85%). Anal. Calcd: P, 12.67; C, 14.74; H, 3.30. Found: P, 12.91; C, 14.93; H, 3.35. IR (KBr) 3600–3200 (s, v br), 1635 (s), 1583 (s), 1432 (s), 1407 (s), 1151(s), 1070 (vs), 981(s), 954 (s) cm^{-1}; TGA room temperature to 180 °C, 11.1% (– 1.5 H_2O).

General Procedure for the Synthesis of the Functionalized Zinc and Copper $M^{II}(O_3PR){\cdot}H_2O$ Phosphonates ($R = (CH_2)_2CO_2H$, $(CH_2)_2Br$, $(CH_2)_2NH_3^+NO_3^-$)), 2a–c, 3a–c. The appropriate phosphonic acid (1 mmol) and zinc (respectively copper) nitrate (1 mmol) were stirred and warmed to 60 °C in 50 mL of a mixture of 5% water in acetone for 3 days. The solid was isolated as described above to give respectively **2a**, **2b**, **2c**, **3a**, **3b**, **3c** in 80% yield. **2a** Anal. Calcd: P, 13.17; C, 15.29; H, 2.97. Found: P, 13.25; C, 15.29; H, 2.91. ^{13}C CP MAS NMR δ(COOH) 182.0 ppm, δ(CH_2) 26.7 and 22.7 ppm. **2b** Anal. Calcd: P, 11.46; C, 8.87; H, 2.22. Found: P, 11.73; C, 9.07; H, 2.14. **2c** Anal. Calcd: P, 11.50; C, 8.90; N, 10.39; H, 3.34. Found: P, 11.80; C, 9.12; N, 10.32; H, 3.30. **3a** Anal. Calcd: P, 13.27; C, 15.41; H, 3.00. Found: P, 13.10; C, 15.47; H, 2.95. **3b** Anal. Calcd: P, 11.54; C, 8.94; H, 2.23. Found: P, 11.64; C, 9.35; H, 2.22. **3c** Anal. Calcd: P, 11.58; C, 8.97; N, 10.46; H, 3.36. Found: P, 11.71; C, 9.19; N, 10.30; H, 3.50. Their TGA, XRD and ^{31}P MAS NMR (for **2a–c**) data are summarized in Table 1. The main infrared absorption bands are given in Table 2.

The different ways of preparation for compounds **4**, **5**, **6**, **7a,b** are illustrated in Schemes 1 and 2

Synthesis of $Zn(O_3P(CH_2)_2CO_2H){\cdot}0.5C_6H_5NH_2$, 4. To a suspension of **2a** (0.5 mmol) in acetonitrile (30 mL) was added aniline (2.5 mmol), and the mixture was stirred at 60 °C for 1 week. **4** was isolated as described above in 95% yield. Anal. Calcd: P, 11.73; C, 27.29; N, 2.65; H, 3.24. Found: P, 11.86; C, 27.21; N, 2.65; H, 3.04. IR (KBr) 3280 (m), 3200–2600 (m, v br), 1703 (vs), 1094 (s), 1052 (vs), 1012 (s) cm^{-1}; TGA room temperature to 220 °C, 0%; ^{31}P MAS NMR δ 28.5 and 34.1 ppm.

Synthesis of $Zn[Zn(O_3P(CH_2)_2CO_2)]_2{\cdot}3H_2O$, 5. To a suspension of **2a** (0.5 mmol) in water (30 mL) was added aniline (2.5 mmol), and the mixture was stirred at 60 °C for 4 days. **5** was isolated as described above, as a white powder in 75% yield. Anal. Calcd: P, 11.22; C, 13.05; H, 2.55. Found: P, 11.46; C, 13.45; H, 2.46. IR (KBr) 3425 (m, br), 3285 (m, br), 1582 (s), 1069 (vs), 980 (s), 954 (s) cm^{-1}; TGA room temperature to 100 °C, 9.7% (–3 H_2O) and 100 to 300 °C, 0%; ^{31}P MAS NMR δ 32.5 ppm. XRD: $a = 5.13(1)$, $b = 10.81(1)$, $c = 28.68(3)$ Å.

Synthesis of $Zn_3(O_3P(CH_2)_2CO_2)_2$, 6. The crystals used for the structural determination were prepared by mixing zinc nitrate (1mmol), (2-carboxyethyl)phosphonic acid (1mmol) and aniline (3mmol) with water, in the teflon cell (20 mL capacity) of an autoclave. After sealing and reaction at 140 °C in a drying oven for 4 days (internal pressure: *ca.* 4 bars), **6** was obtained in 83% yield. Anal. Calcd: P, 12.43; C, 14.46; H, 1.62. Found: P, 12.81; C, 14.64; H, 1.64. IR (KBr) 1600

Table 2. Selected Representative Infrared Bands in Compounds **2a**−**c** and **3a**−**c** (cm^{-1})

$M^{II}(O_3PR)\cdot H_2O$	M = Zn	M = Cu
R = C_2H_5	$\nu(OH(H_2O))$ 3440 (s), 3400 (s)	3240 (s), 3004 (s)
	$\delta(OH(H_2O))$ 1630 (m)	1575 (m)
	$\nu(PO_2)$ 1080 (vs), 975 (vs)	1074 (s), 1040 (s), 1021 (s)
R = $(CH_2)_2CO_2H$	$\nu(OH(H_2O))$ 3468 (s), 3435 (s)	3235 (s), 3030 (s)
	$\delta(OH(H_2O))$ 1615 (m)	1573 (m)
	$\nu(PO_2)$ 1078 (vs), 987 (vs)	1086 (s), 1038 (s), 1016 (s)
	$\nu(C{=}O)$ (CO_2H) 1701 (vs)	1697 (vs)
R = $(CH_2)_2Br$	$\nu(OH(H_2O))$ 3417 (s)	3255 (s), 3042 (s)
	$\delta(OH(H_2O))$ 1615 (m)	1573 (m)
	$\nu(PO_2)$ 1072 (vs), 979 (vs)	1079 (s), 1028 (s), 1012 (s)
R = $(CH_2)_2NH_3^+NO_3^-$	$\nu(OH(H_2O))$ 3450 (s), 3420 (s)	3235 (s), 3030 (s)
	$\delta(OH(H_2O))$ 1616 (m)	1595 (m)
	$\nu(PO_2)$ 1082 (vs), 981 (vs)	1079 (s), 1028 (s)
	$\nu(NH(NH_3^+))$ 2900−3200 (s, vb)	masked by $\nu(OH(H_2O))$
	$\nu(NO_2(NO_3^-))$ 1384 (vs)	1384 (vs)

(vs), 1125 (m), 1005 (s, sh), 985 (vs) cm^{-1}; TGA room temperature to 300 °C, 0%; ^{31}P MAS NMR δ 35.3 ppm.

Synthesis of $Zn(O_3P(CH_2)_2CONHR)$, (R = C_6H_5) 7a and (R = 4-Br-C_6H_4) 7b. 1 mmol of (2-carboxyethyl)phosphonic acid and 1 mmol of zinc nitrate were placed in a Pyrex tube with 6 mmol of aniline (respectively 4-bromoaniline) in 10 mL of water. The tube was then sealed and warmed at 140°C for 1 week. **7a** and **7b** were washed several times with hot ethanol, filtered, and isolated as colorless crystalline compounds in 75% yield. **7a.** Anal. Calcd: P, 10.59; C, 36.95; N, 4.78; H, 3.44. Found: P, 10.85; C, 36.45; N, 4.64; H, 3.41. IR (KBr) 3296 (s), 1656 (vs), 1551(m), 1175 (m), 1112 (s), 1055 (vs), 987 (s), 964 (m) cm^{-1}; TGA room temperature to 300 °C, 0%; ^{31}P MAS NMR δ 35.2 ppm; ^{13}C CP MAS NMR δ(CONH) 172.0 ppm, δ(phenyl) 137.8, 129.0, 126.0 and 122.5 ppm, $\delta(CH_2)$ 30.5 and 24.0 ppm. **7b.** IR (KBr) 3291 (s), 1656 (vs), 1541(m), 1175 (m), 1110 (s), 1055 (s), 986 (s), 964 (m) cm^{-1}; TGA room temperature to 300 °C, 0%; ^{31}P MAS NMR δ 35.2 ppm.

General Methods. For all the compounds described in this paper, the chemical analyses were performed by the CNRS Analysis Laboratory (Vernaison). ^{31}P solid state MAS NMR spectra were recorded at room temperature on a MSL-400 NMR Bruker spectrometer at the frequency of 161.98 MHz. Samples were spun in an Andrew type rotor at a speed of *ca.* 8 kHz. ^{13}C CP-MAS NMR spectra were run at the frequency of 100.62 MHz, with a spinning rate of 5 kHz. The ^1H90°−pulse width was 7.3 μs with a contact time of 3 ms and a pulse repetition of 6 s. Chemical shifts were externally referenced to 85 wt % H_3PO_4 for ^{31}P and to TMS for ^{13}C. 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, that were run in an air atmosphere from room temperature to 300 °C at a scan rate of 5 °C/min. The X-ray powder diffraction patterns were collected at room temperature in Debye−Scherrer geometry using an INEL CPS 120 detector. Monochromated Cu Kα_1 radiation was used. To obtain a better signal/background ratio, a homogeneous thin layer of powder was put on the external side of a 0.1 mm diameter capillary with modeling clay as a sticking agent. The 20 first reflection positions were determined with the program PROLIX, specially designed to analyze INEL data,[14] and subsequently processed by the auto-indexing program TREOR.[15] The cell constants were finally refined using the U-FIT program.[16] For some of the samples, the diffraction patterns only showed several orders of 0*k*0 reflections, restricting us to calculation of the interlayer spacings only (*b*-axis repeat distance).

X-ray Structure Analysis. $Zn(O_3P(CH_2)_2CO_2H)\cdot 1.5H_2O$, 1. A colorless platelet having approximate dimensions 0.075 × 0.225 × 0.375 mm^3 was mounted on a glass fiber. All measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Cell constants and an orientation matrix for data collection were obtained from least-squares refinement of the setting angles of 25 randomly oriented reflections in the range $10° \le 2\theta \le 35°$, corresponding to an orthorhombic 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 ψ-scan measurements was applied and the data were corrected for Lorentz and polarization effects. The data were collected out to 60° in 2θ using the $\omega-2\theta$ scan technique ($h = -15, 15$; $k = 0, 16$; $l = 0, 26$). On the basis of the systematic absences and the successful refinement of the structure, the space group was found to be *Pccn*. The atomic scattering factors were taken from Cromer and Waber,[17] and anomalous dispersion corrections were taken from Cromer and Ibers.[18] For the data reduction, structure solution and refinement, the MOLEN program (1990 version) was used on a microVAX 3900 computer. A total of 4162 reflections were measured, of which 907 were unique with the condition $I \ge 3\sigma(I)$.

The position of the zinc and phosphorus atoms were determined from a three-dimensional Patterson map, with the oxygen and the carbon atoms being found from successive difference Fourier maps. The non-hydrogen atoms were refined anisotropically, except for the water oxygen atoms O(6) and O(7) that were refined isotropically due to the limited number of reflections. The final cycle of full-matrix least-squares refinement for 98 variables converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of R = 0.062 and R_w = 0.074. Crystallographic data and refinement conditions are listed in Table 3. Positional and thermal parameters are given in Table 4, and selected bond distances and angles are listed in Table 5.

$Zn_3(O_3P(CH_2)_2CO_2)_2$, 6. A colorless parallelepipedic crystal of approximate dimensions 0.25 × 0.355 × 0.40 mm^3 was mounted on a glass fiber. All measurements were made on a Siemens P-4 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The data were collected out to 60° using the $\omega-2\theta$ scan technique, as described for the previous structure ($h = 0, 14$; $k = 0, 16$; $l = -15, 15$). For the data reduction, structure solution and refinement, programs in the SHELXTL PLUS package,[19] were used on a microVAX 3900 computer. On the basis of the systematic absences and the successful refinement of the structure, the space group was found to be $P2_1/c$. Of the 5061 reflections which were collected, 1495 were unique and observed with $I \ge 4\sigma(I)$. The structure was solved by a combination of direct methods and Fourier syntheses. The positions of the H atoms were located from a last difference Fourier map and refined with fixed thermal parameters. The final cycle of full-matrix least-squares refinement for 110 variables converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of R = 0.036 and R_w = 0.037. Positional and thermal parameters are given in Table 6, and selected bond distances and angles are listed in Table 7.

Results

According to the experimental conditions, various compounds (**1**, **2a**, **4**, **5**, **6**, **7a,b**) were selectively obtained from the reaction of 2-carboxyethylphosphonic acid and zinc nitrate in the presence of a base. Two of them were isolated as crystals

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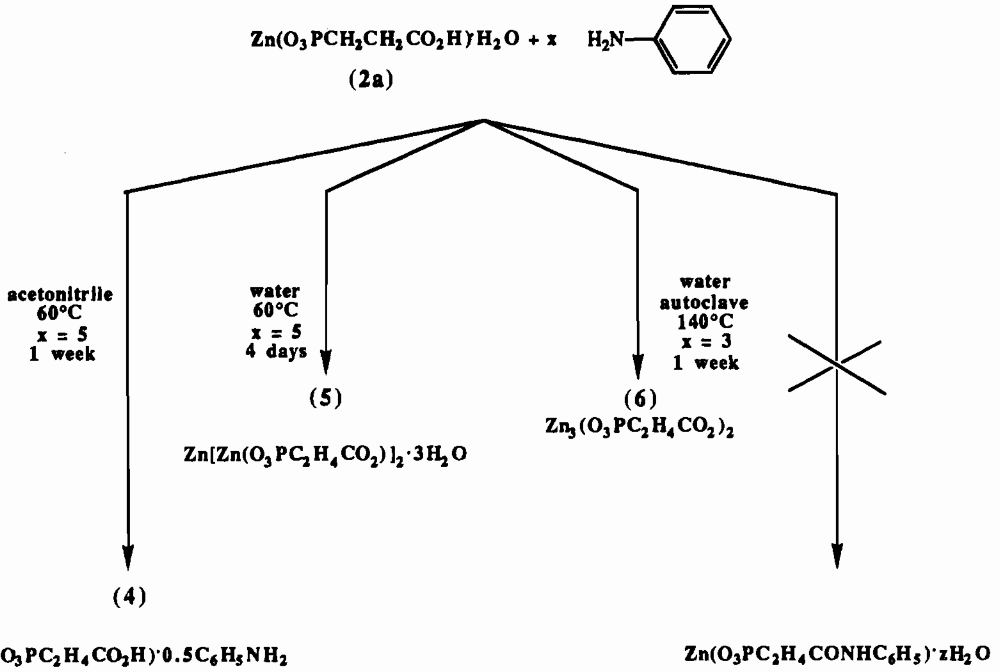
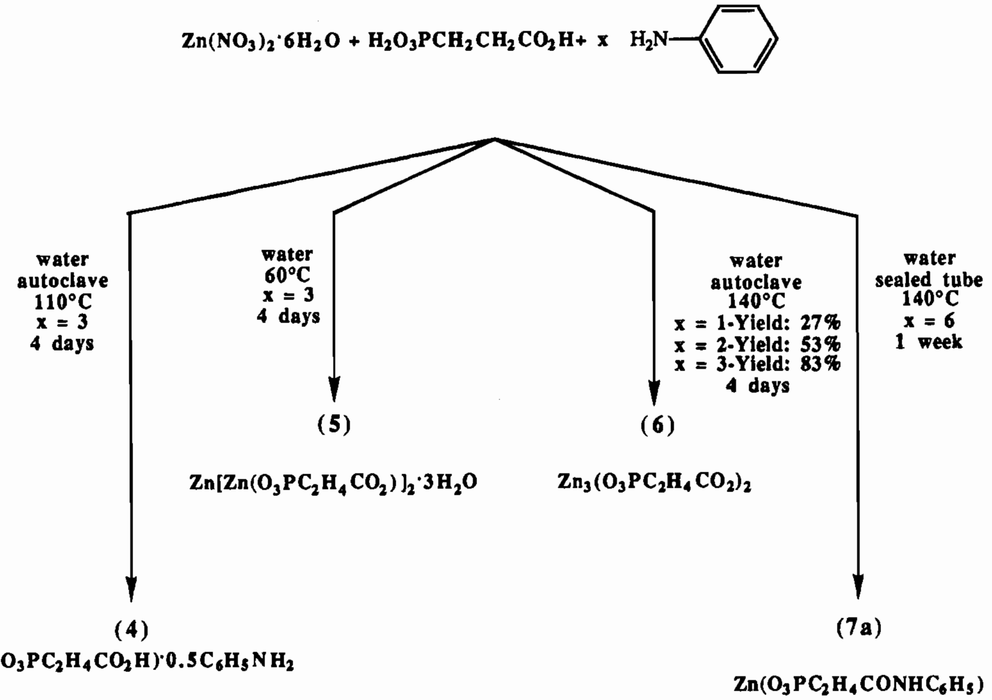
Scheme 1



Scheme 2



suitable for a X-ray structure determination: $Zn(O_3P(CH_2)_2CO_2H)\cdot 1.5H_2O$ (1), and $Zn_3(O_3P(CH_2)_2CO_2)_2$ (6).

$Zn(O_3P(CH_2)_2CO_2H)\cdot 1.5H_2O$ (1). The structure consists of a three-dimensional framework that may be pictured as being built up from ZnO_4 and RPO_3 tetrahedra forming layers (*a,b* plane—Figure 1). Each layer is connected to the next upper and lower layers through the carboxyl end of the $(CH_2)_2CO_2H$ radicals that are oriented perpendicular to the (*a,b*) plane (Figure 2). Each Zn atom is bound to three different phosphorus atoms via Zn—O—P links and to the carbonyl oxygen (Figure 3), with Zn—O distances close to 1.95 Å. Each phosphorus atom is connected to three different Zn atoms via oxygen bridges. In the layer, the linkage of the Zn and P tetrahedra displays a strict alternation of zinc and phosphorus, forming eight-membered rings, in which the water molecules O(6) and O(7) are located. A weak hydrogen bonding network is probably present between these two water molecules and the two O(1) and O(5) oxygens of the framework [*d*O(6)—O(1) = 2.42(1); *d*O(6)—O(5) = 2.36(1); *d*O(6)—O(7) = 2.51(1) Å]. A very similar layer arrangement of ZnO_4 and PO_4 (instead of RPO_3) tetrahedra was reported by Harrison et al.[20] in ZnPO/dab-A, a zincophosphate containing cationic 1,4-diazabicyclo[2.2.2]octane guests.

$Zn_3(O_3P(CH_2)_2CO_2)_2$ (6). Figure 4 shows the coordination environment of the two types of Zn atoms and the numbering scheme used in the tables. One of them, Zn(1), is four-coordinated by three oxygens of the phosphonate groups and one oxygen (O(4)) of a carboxyl group. The $Zn(1)O_4$ tetrahedra

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(20) Harrison, W. T. A.; Martin, T. E.; Gier, T. E.; Stucky, G. D. *J. Mater. Chem.* **1992**, *2*, 175.

Table 3. Crystallographic Data for the Zinc(Carboxyethyl)phosphonates

	1	**6**
chem formula	$ZnPO_{6.5}C_3H_8$	$Zn_3P_2O_{10}C_6H_8$
fw	244.46	498.24
a, Å	9.885(1)	8.126(1)
b, Å	10.020(1)	9.237(1)
c, Å	16.438(3)	8.587(2)
α, deg	90	90
β, deg	90	106.26(3)
γ, deg	90	90
V, Å^3	1628.3(6)	618.7(4)
Z	8	2
space group	4Pccn (No. 56)	$P2_1/c$ (No. 14)
ϱ_{calcd}, g cm^{-3}	1.99	2.67
T, °C	25 ± 1	25 ± 1
λ (Mo Kα), Å	0.7107	0.7107
μ, cm^{-1}	32.73	60.80
R	0.062	0.036
R_w	0.074	0.037

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

Table 4. Positional Parameters and Thermal Parameters for the Atoms of $Zn(O_3PC_2H_4CO_2H)\cdot 1.5H_2O$

atom	x	y	z	U_{eq}, Å^2
Zn	0.3562(1)	0.4034(1)	0.20335(8)	0.0184(3)
P	0.0729(3)	0.3627(3)	0.2872(2)	0.0170(5)
O(1)	0.1620(8)	0.4186(9)	0.2202(5)	0.024(1)
O(2)	0.0711(8)	0.9174(8)	0.2191(5)	0.022(1)
O(3)	0.0664(9)	0.2107(8)	0.2876(6)	0.024(1)
O(4)	0.084(1)	0.166(1)	0.0987(5)	0.033(3)
O(5)	0.227(1)	0.026(1)	0.0414(6)	0.044(3)
O(6)	0.0846(8)	0.5619(8)	0.1109(5)	0.019(1)
O(7)	0.25	0.75	0.131(1)	0.049(4)
C(1)	0.141(1)	0.412(1)	0.3822(7)	0.027(3)
C(2)	0.084(1)	0.341(2)	0.4548(8)	0.030(3)
C(3)	0.139(1)	0.111(1)	0.0384(7)	0.023(3)

[a] The zinc, phosphorus, oxygen (except the water molecules O(6) and O(7) that were refined isotropically), and carbon atoms were refined anisotropically and are given in the form of the equivalent displacement parameter defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*A_{ij}$.

Table 5. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Zn(O_3PC_2H_4CO_2H)\cdot 1.5H_2O$

Zn−O(1)	1.946(8)	P−O(3)	1.524(8)
Zn−O(2)^{a}	1.952(8)	P−C(1)	1.77(1)
Zn−O(3)^{b}	1.953(9)	C(1)−C(2)	1.50(2)
Zn−O(4)^{b}	1.948(9)	C(2)−C(3)^{d}	1.55(2)
P−O(1)	1.517(8)	C(3)−O(4)	1.26(1)
P−O(2)^{c}	1.529(8)	C(3)−O(5)	1.22(2)
O(1)−Zn−O(2)^{a}	105.8(3)	O(1)−P−C(1)	108.4(5)
O(1)−Zn−O(3)^{b}	109.3(4)	O(2)^{c}−P−O(3)	108.6(5)
O(1)−Zn−O(4)^{b}	117.0(4)	O(2)^{c}−P−C(1)	108.2(5)
O(2)^{a}−Zn−O(3)^{b}	107.5(3)	O(3)−P−C(1)	107.0(5)
O(2)^{a}−Zn−O(4)^{b}	109.5(4)	P−C(1)−C(2)	115(1)
O(3)^{b}−Zn−O(4)^{b}	107.3(4)	C(1)−C(2)^{e}−C(3)	115(1)
O(1)−P−O(2)^{c}	111.0(5)	C(2)−C(3)−O(4)^{d}	114(1)
O(1)−P−O(3)	113.4(5)	O(4)−C(3)−O(5)	126(1)

[a] Atom related by $^1/_2 - x$, $^3/_2 - y$, z. [b] $^1/_2 - x$, $^1/_2 - y$, z. [c] $-x$, $-^1/_2 + y$, $^1/_2 - z$. [d] x, $-^1/_2 - y$, $-^3/_2 + z$. [e] x, $-^1/_2 - y$, $-^1/_2 + z$.

Table 6. Positional Parameters and Thermal Parameters for the Atoms of $Zn_3(O_3PC_2H_4CO_2)_2$

atom	x	y	z	U_{eq},[a] Å^2
Zn(1)	0.57480(8)	0.87818(7)	0.11942(8)	0.0145(2)
Zn(2)	0.5	0	0.5	0.0126(3)
P	0.6343(2)	0.2104(1)	0.2404(2)	0.0111(4)
O(1)	0.5855(5)	0.0993(4)	0.1026(4)	0.015(1)
O(2)	0.4792(5)	0.8474(4)	0.3022(4)	0.014(1)
O(3)	0.3822(5)	0.6492(4)	0.1025(4)	0.022(1)
O(4)	0.1975(5)	0.3131(4)	0.3528(6)	0.030(2)
O(5)	0.7373(5)	0.5818(5)	0.1190(6)	0.039(2)
C(1)	0.8491(6)	0.2648(6)	0.2662(6)	0.017(2)
C(2)	−0.0250(7)	0.1403(7)	0.3169(8)	0.029(2)
C(3)	0.1611(7)	0.1799(6)	0.3537(7)	0.021(2)
H(11)	0.847(9)	0.351(8)	0.339(9)	0.05
H(12)	0.845(9)	0.298(8)	0.161(9)	0.05
H(21)	0.953(9)	0.088(8)	0.405(9)	0.05
H(22)	−0.036(9)	0.077(8)	0.24(1)	0.05

[a] See Table 4.

Table 7. Bond Lengths (Å) and Angles (deg) for the Non-Hydrogen Atoms of $Zn_3(O_3PC_2H_4CO_2)_2$

Zn(1)−O(1)^{a}	2.051(3)	Zn(2)−O(5)^{g}	2.057(4)
Zn(1)−O(1)^{b}	1.996(3)	P−O(1)	1.532(4)
Zn(1)−O(2)	1.957(4)	P−O(2)^{f}	1.548(4)
Zn(1)−O(4)^{c}	1.896(4)	P−O(3)^{f}	1.503(4)
Zn(2)−O(2)^{d}	2.177(4)	P−C(1)	1.770(5)
Zn(2)−O(2)^{e}	2.177(4)	C(1)−C(2)^{h}	1.519(8)
Zn(2)−O(3)^{f}	2.016(4)	C(2)−C(3)	1.501(8)
Zn(2)−O(3)^{g}	2.016(4)	C(3)−O(4)	1.266(7)
Zn(2)−O(5)^{f}	2.057(4)	C(3)−O(5)^{f}	1.204(7)
O(1)^{a}−Zn(1)−O(1)^{b}	81.8(1)	O(3)^{f}−Zn(2)−O(5)^{f}	91.5(2)
O(1)^{a}−Zn(1)−O(2)	103.6(2)	O(3)^{f}−Zn(2)−O(5)^{g}	88.5(2)
O91)^{a}−Zn(1)−O(4)^{c}	105.4(2)	O(3)^{g}−Zn(2)−O(5)^{f}	88.5(2)
O(1)^{b}−Zn(1)−O(2)	118.8(2)	O(3)^{g}−Zn(2)−O(5)^{g}	91.5(2)
O(1)^{b}−Zn(1)−O(4)^{c}	120.4(2)	O(5)^{f}−Zn(2)−O(5)^{g}	180
O(2)−Cn(1)−O(4)^{c}	116.5(2)	O(1)−P−O(2)^{f}	110.9(2)
O(2)^{d}−Zn(2)−O(2)^{e}	180	O(1)−P−O(3)^{f}	111.8(2)
O(2)^{d}−Zn(2)−O(3)^{f}	92.5(2)	O(1)−P−C(1)	108.6(3)
O(2)^{d}−Zn(2)−O(3)^{g}	87.5(2)	O(2)^{f}−P−O(3)^{f}	108.8(2)
O(2)^{d}−Zn(2)−O(5)^{f}	89.6(2)	O(2)^{f}−P−C(1)	107.4(2)
O(2)^{d}−Zn(2)−O(5)^{g}	90.4(2)	O(3)^{f}−P−C(1)	109.1(2)
O(2)^{e}−Zn(2)−O(3)^{f}	87.5(2)	P−C(1)−C(2)^{h}	112.5(4)
O(2)^{e}−Zn(2)−O(3)^{g}	92.5(2)	C(1)−C(2)^{i}−C(3)	115.7(5)
O(2)^{e}−Zn(2)−O(5)^{f}	90.4(2)	C(2)−C(3)−O(4)	117.3(5)
O(2)^{e}−Zn(2)−O(5)^{g}	89.6(2)	C(2)−C(3)−O(5)^{f}	117.0(5)
O(3)^{f}−Zn(2)−O(3)^{g}	180	O(4)−C(3)−O(5)^{f}	125.7(6)

[a] Atom related by x, $1 + y$, z. [b] $1 - x$, $1 - y$, $-z$. [c] $1 - x$, $^1/_2 + y$, $^1/_2 - z$. [d] x, $-1 + y$, z. [e] $1 - x$, $1 - y$, $1 - z$. [f] $1 - x$, $-^1/_2 + y$, $^1/_2 - z$. [g] x, $^1/_2 - y$, $^1/_2 + z$. [h] $1 + x$, y, z. [i] $-1 + x$, y, z.

are arranged in edge-sharing pairs, resulting in Zn−O−Zn−O parallelograms (intermetallic distances: 3.058(1) Å). The other, Zn(2), is six-coordinated by two oxygens (O(5)) of two carboxyl groups and four phosphonate oxygens. Each oxygen of the PO_3 groups is bonded to metal atoms, ensuring the connection of the $Zn(1)O_4$ and $Zn(2)O_6$ polyhedra within layers, in the (b,c) plane (Figure 5). The organic groups extend roughly perpendicular to these layers, that are linked together via the carboxyl moieties, thus leading to a three-dimensional network (Figure 6), as previously observed for compound **1**. However, in this case the two oxygens (O(4) and O(5)) of the CO_2 units are bonded, forming bridges between Zn(1) and Zn(2) atoms.

Discussion

The purpose of our studies was to use functionalized divalent metal phosphonates as supports for catalytic species such as simple Mn(porphyrin)Cl complexes that were found to be active homogeneous catalysts for many oxidation reactions, with H_2O_2 as oxidizing agent in the presence of nitrogen base cocatalysts.[21] The immobilization of these metallic complexes on a solid insoluble support might lead to supported catalysts, easy to separate from the reaction medium also with possible reactivity enhancement due to support effects. In this field, many experiments have reported the adsorption of porphyrins in

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(21) Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8462 and references therein.

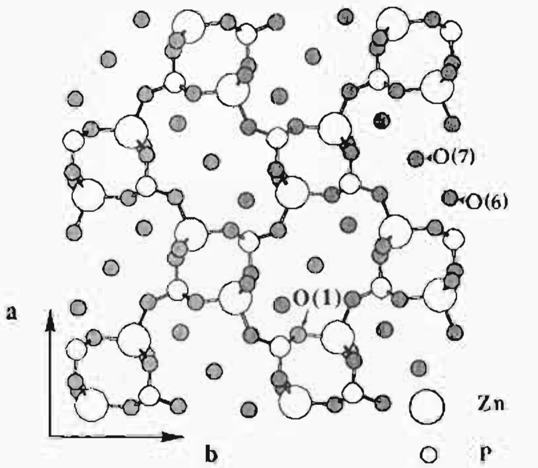

Figure 1. Schematic representation of a $Zn(O_3P(CH_2)_2CO_2H)\cdot1.5H_2O$ layer as seen perpendicular to the *c*-axis. The organic chain bound to phosphorus, except the carbonyl oxygen, have been omitted for clarity.

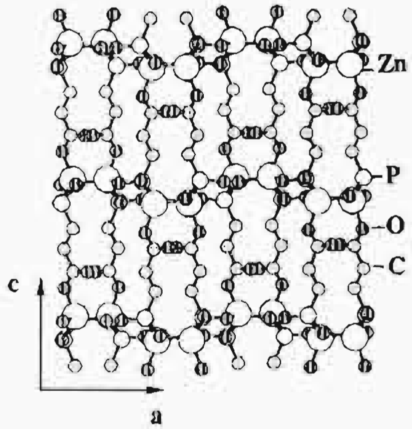

Figure 2. Schematic representation of $Zn(O_3P(CH_2)_2CO_2H)\cdot1.5H_2O$ as seen perpendicular to the *b*-axis. The water molecules O(6) and O(7) have been omitted for clarity.

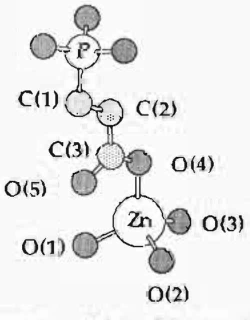

Figure 3. Schematic representation of the coordination about the zinc atom in $Zn(O_3P(CH_2)_2CO_2H)\cdot1.5H_2O$, and the numbering scheme used in the tables.

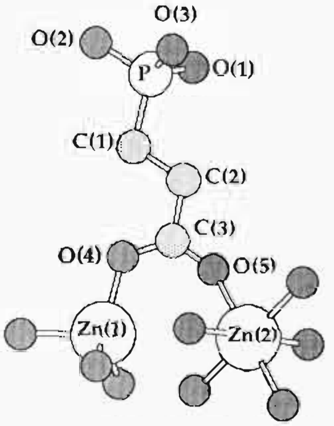

Figure 4. Schematic representation of the coordination about the two types of zinc atoms in $Zn_3(O_3P(CH_2)_2CO_2)_2$.

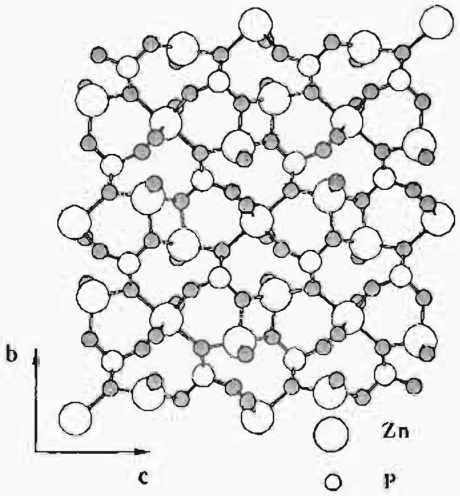

Figure 5. Schematic representation of a $Zn_3(O_3P(CH_2)_2CO_2)_2$ layer as seen perpendicular to the *a*-axis. The organic chain bound to phosphorus, except the two carboxyl oxygens, have been omitted for clarity.

aluminosilicates[22] and more recently in the α phase of zirconium hydrogen phosphate $Zr(O_3POH)_2\cdot H_2O$ (α-ZrP).[23] However the covalent binding of porphyrins on solid supports has not received much attention until now.[24] The anchoring of a porphyrin complex on a phosphonate matrix $M^{II}(O_3PR)\cdot xH_2O$ could be achieved through organic binding groups present on the R radical and able to provide stable links with the catalytic center. It was then of interest to prepare functionalized divalent metal phosphonates with well known structures such as analogs of the well characterized $M^{II}(O_3PR)\cdot H_2O$ structures (R = *n*-alkyl, phenyl).

It has been shown in the literature that two types of structural arrangements are obtained for these compounds: the first one is observed in the case of zinc, nickel, cobalt, iron, manganese, magnesium and cadmium with an octahedral environment for the metal ion,[2-5] the second for copper, present in a tetragonal pyramidal configuration.[6] In both cases, one coordination site of the metal atom is occupied by the water molecule. Consequently, zinc and copper were selected for this work, in order to show that functionalized analogues of the two structural types were accessible. The first experiments were carried out using (2-carboxyethyl)phosphonic acid and zinc nitrate according to an usual procedure (i.e. aqueous medium, with neutralization of the diprotic phosphonic acid groups by addition of NaOH, necessary for the precipitation of the phosphonate compounds in quantitative yield). On the basis of its infrared spectrum, it was obvious that the carboxyl function of the resulting material, $Zn(O_3P(CH_2)_2CO_2H)\cdot1.5H_2O$ (**1**), was coordinated to the metal center (ν(C=O) 1583 cm^{-1}), as confirmed by XRD. In this compound, the carboxylic acid functions are connected to the zinc atoms and consequently are not available to undergo grafting reactions with organic molecules. Therefore, experi-

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(22) (a) Cady, S. S.; Pinnavaia, T. J. *Inorg. Chem.* **1978**, *17*, 1505. (b) Kameyama, H.; Suzuki, H.; Amano, A. *Chem. Lett.* **1988**, 1117. (c) Carrado, K. A.; Winans, R. E. *Chem. Mater.* **1990**, 2, 328. (d) Giannelis, E. P. *Chem. Mater.* **1990**, 2, 627. (e) Barloy, L.; Lallier, J. P.; Battioni, P.; Mansuy, D.; Piffard, Y.; Tournoux, M.; Valim, J. B.; Jones, W. *New J. Chem.* **1992**, *16*, 71.

(23) Kim, R. M.; Pillion, J. E.; Burwell, D. A., Groves J. T., Thompson, M. E. *Inorg. Chem.* **1993**, *32*, 4509.

(24) Battioni, P.; Bartoli, J. F.; Mansuy, D.; Bryun, Y. S.; Traylor, T. G. *J. Chem. Soc. Chem. commun.* **1992**, *32*, 2893.

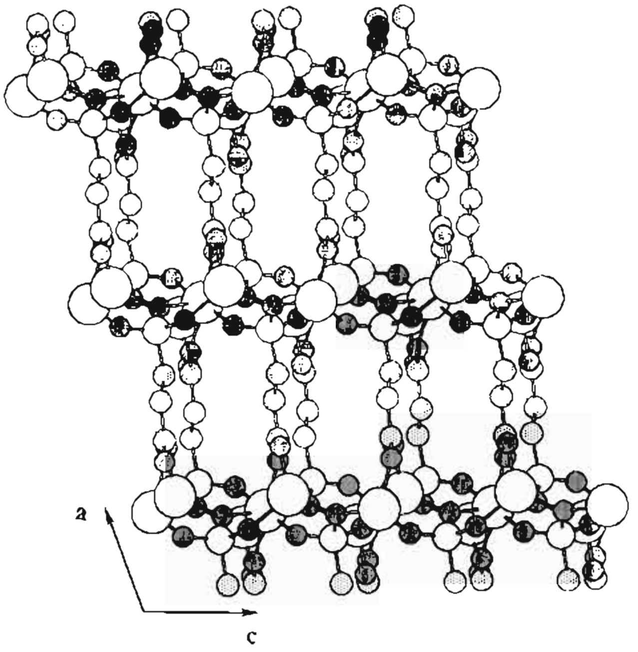

Figure 6. Schematic representation of $Zn_3(O_3P(CH_2)_2CO_2)_2$ as seen perpendicular to the *b*-axis.

ments were undertaken in a non-aqueous medium (acetone) in an attempt to avoid the complexation of the carboxyl function by the metal center, leading to a mixture of a $Zn^{II}(O_3P(CH_2)_2CO_2H)\cdot H_2O$ phase and its $Zn^{II}(O_3P(CH_2)_2CO_2H)$ anhydrous form, in which the carboxylic acid groups were not bound to the zinc atoms (ν(C=O) 1701 cm^{-1}). The presence of hydrated zinc phosphonate was due to the use of hydrated zinc nitrate as metal precursor. When a mixture of 5% water in acetone was used as solvent, pure $Zn^{II}(O_3P(CH_2)_2CO_2H)\cdot H_2O$ was obtained. Thus, this experimental protocol was repeated with zinc and copper nitrate on the one hand, and three functionalized phosphonic acids $H_2O_3P(CH_2)_2X$ (X = CO_2H, Br, NH_2) on the other hand, yielding the corresponding $M^{II}(O_3P(CH_2)_2Y)\cdot H_2O$ compounds: M = Zn [**2a** (Y = CO_2H), **2b** (Y = Br), **2c** (Y = $NH_3^+NO_3^-$)]; M = Cu [**3a** (Y = CO_2H), **3b** (Y = Br), **3c** (Y = $NH_3^+NO_3^-$)]. In compounds **2c** and **3c**, the interlayer amine was protonated in a comparable manner to $Zr^{IV}(O_3P(CH_2)_2NH_3^+Cl^-)_2$.[25]

Infrared, TGA, and XRD data demonstrate that the arrangement within the layers of **2a**–**c** (respectively **3a**–**c**) was the same as in the well known *n*-alkyl and phenyl $Zn(O_3PR)\cdot H_2O$ (respectively $Cu(O_3PR)\cdot H_2O$) compounds. By comparison of the infrared spectra of **2a**–**c** and $Zn(O_3PC_2H_5)\cdot H_2O$, strong similitudes are observed for the frequencies of the absorption bands related to the coordinated water molecule and the PO_3 group, characteristic of the metal linkage within the slabs (Table 2 and Figure 7). In addition, the IR bands at 1700 cm^{-1} for **2a**, and at 1384 and 2900–3200 cm^{-1} for **2c**, give evidence of the presence of CO_2H, and $NH_3^+NO_3^-$ ends respectively, in these two compounds. TGA curves of **2a**–**c** indicate that the first weight transition corresponds to the loss of the water molecule that occurs at the same temperature as for the zinc ethylphosphonate analogue (Table 1). Moreover, the cell parameters (*a* and *c* within the layer) of **2a** and **2b** (Table 1) are very similar to those observed for $Zn(O_3PC_2H_5)\cdot H_2O$ (a = 5.67, c = 4.79 Å)[4a] and $Zn(O_3PCH_2Cl)\cdot H_2O$ (a = 5.70, c = 4.78 Å).[13] The *b* and *c* parameters of **2a** are doubled (2 × 12.34 and 2 × 4.71 Å, respectively), probably because of a slight distortion of the structure induced by hydrogen bonding interactions between the CO_2H groups. From these observations, we can reasonably assume that the layer arrangement in compounds **2a**–**c** is similar to that described for the *n*-alkyl, and phenyl zinc analogues. The same discussion and conclusions can be developed in the case of the **3a**–**c** copper compounds.

Our first experiments to study the reactivity of the functional ends present in the interlayer space of the phosphonates described above, were started using **2a**, $Zn(O_3P(CH_2)_2CO_2H)\cdot H_2O$. The first reactions involved treatment of **2a** with aniline, having in mind that the product of a grafting reaction should be a layered phosphonate with an aromatic secondary amide end on the radical bound to phosphorus. The choice of aniline for this goal was guided by the fact that the porphyrins we wish to immobilize on these materials are functionalized by aminophenyl groups. Depending on the experimental conditions, three new compounds were selectively prepared from **2a**: $Zn(O_3P(CH_2)_2CO_2H)\cdot 0.5C_6H_5NH_2$ (**4**), $Zn[Zn(O_3P(CH_2)_2CO_2)]_2\cdot 3H_2O$ (**5**), and $Zn_3(O_3P(CH_2)_2CO_2)_2$ (**6**) (see Scheme 1).

Compound **4** was prepared from $Zn(O_3P(CH_2)_2CO_2H)\cdot H_2O$ in acetonitrile and probably results from the displacement of the water coordinated to zinc, by aniline in non-aqueous medium. This phenomenon is very similar to that previously reported for divalent metal alkyl- and phenylphosphonates $M^{II}(O_3PR)$ (obtained by thermal treatment of the corresponding hydrates), that intercalate *n*-alkylamines if exposed to amine vapor or suspended in a non-aqueous solution of an amine, leading to $M^{II}(O_3PR)\cdot(RNH_2)$, in which the amine occupies the empty coordination site created upon dehydration.[5d,7a,7c] In our case, due to the size of aniline, only half of the sites are occupied by the amine, the other half remaining vacant. This hypothesis is supported by the following experimental observations: (*i*) the frequency of the IR carbonyl stretch absorption (1703 cm^{-1}) shows that the CO_2H units are not complexed by the amine or the zinc atoms. (*ii*) In $Zn(O_3P(CH_2)_2CO_2H)\cdot H_2O$ one of the coordination sites is occupied by the water molecule. If half of these sites were empty and the other half occupied by the nitrogen atom of aniline, there would be two types of environment for the phosphorus atoms, consistent with the two signals (28.5 and 34.1 ppm) of equal intensity observed on the ^{31}P MAS NMR spectrum of **4**. (*iii*) From the XRD powder spectrum of **4**, the interlayer distance is found to be 14.9 Å and does not contradict the hypothesis of aniline bonded to the zinc atoms, with the axis of the phenyl ring roughly perpendicular to the layers. On the basis of its infrared, TGA and XRD data (see Experimental Section), compound **5** appears to be identical to the $Zn[Zn(O_3P(CH_2)_2CO_2)]_2\cdot 3H_2O$ phase previously described by Cao et al.[26] This structure is built up from $Zn(O_3P(CH_2)_2CO_2)$ layers, with a hydrated zinc atom $[Zn(H_2O)_3]$ present in the interlayer space and coordinated by two oxygen atoms of two carboxyl groups. Compound **6** is three-dimensional, made of layers connected by the organic chain in the same way as in compound **1**, with in this case the carboxyl groups that are bridging ZnO_4 and ZnO_6 units. In conclusion, none of these three materials corresponds to the expected amidation reaction, indicating that, as in the case of $Zr(O_3P(CH_2)_2CO_2H)_2$,[9] an activation of the carboxylic acid function might be necessary, according to the following route:

$$-CO_2H \xrightarrow{NH_3} -CO_2NH_4 \xrightarrow{SOCl_2} -COCl \xrightarrow{RNH_2} -CONHR$$

Before using this relatively heavy strategy, attempts to prepare $Zn(O_3P(CH_2)_2CONHC_6H_5)\cdot xH_2O$ were performed in aqueous

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(25) Rosenthal, G. L.; Caruso, J. *Inorg. Chem.* **1992**, *31*, 3104.

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

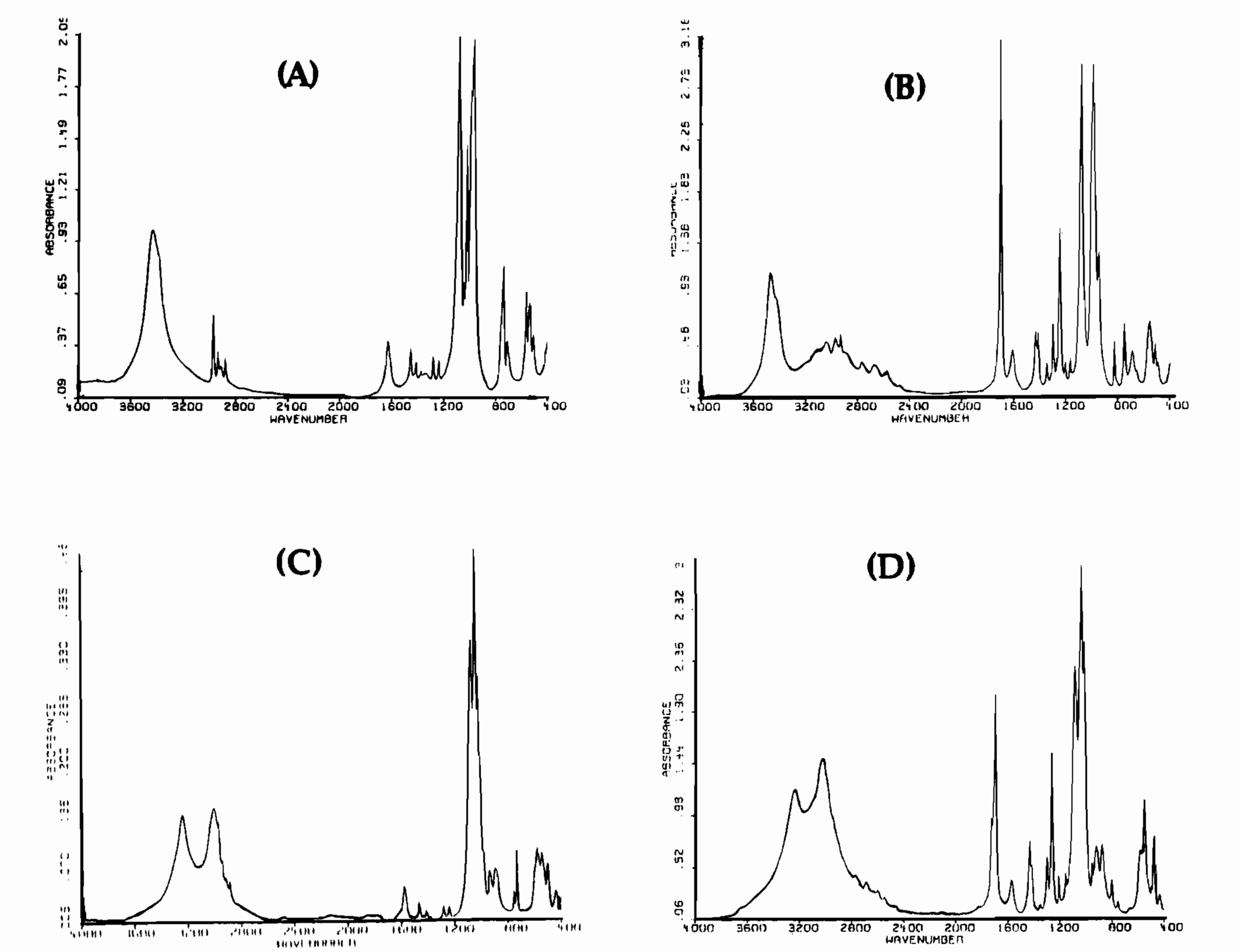

Figure 7. Comparative infrared absorption spectra of ethyl [(A) M = Zn; (C) M = Cu] and 2-carboxyethyl [(B) M = Zn; (D) M = Cu] $M^{II}(O_3PR)\cdot H_2O$ compounds.

media from zinc nitrate and (2-carboxyethyl)phosphonic acid, with addition of aniline that could play the role of the neutralizing agent as well as that of the grafting agent. In fact, according to the experimental conditions, compounds **4**, **5**, and **6** were isolated again (Scheme 2), showing that the use of $Zn(O_3P(CH_2)_2CO_2H)\cdot H_2O$ as starting material, was not necessary for the synthesis of these three compounds. The role of the amine as neutralizing agent is clearly illustrated in the case of the preparation of **6**. When only 1 equiv of amine per mole of (2-carboxyethyl)phosphonic acid was added, the reaction yield was 23%, and increased to 53 and 83% when two and respectively three equivalents of amines were used. Thus, as in the *n*-alkyl series,[4a] the reaction yield is influenced by the neutralization of the diprotic phosphonic acid function and the use of 3 equiv of amines in this case is consistent with the fact that the acidity of the carboxylic acid group is stronger than the second acidity of the PO_3H_2 group. The most interesting result was observed when an aniline/phosphonic acid ratio greater than 3 was used. The "excess" of aniline that is not used in the neutralization step, can then participate in the formation of the desired amide linkage and $Zn(O_3P(CH_2)_2CONHC_6H_5)$ (**7a**) was selectively obtained, according to an efficient and original one-step protocol. In the same way, when 4-bromoaniline was used instead of aniline, $Zn(O_3P(CH_2)_2CONHC_6H_4Br)$ (**7b**) was directly prepared. The IR spectra of **7a** and **7b** are similar (Figure 8), with characteristic absorptions for amide I at 1650, amide II at 1550 and NH stretches at 3300 cm^{-1}, consistent with the values reported in the literature.[9,27] The amide II band is due to the interaction between N−H bending and C−N stretching frequencies in a trans geometry. Moreover, the bands in the PO_3 region are rigorously superimposable, implying that similar arrangement within the layer are present for the two compounds. Additional evidence for the formation of the amide linkage is given by (*i*) the ^{13}C CP-MAS NMR spectrum of **7a** with a carbonyl resonance at ca. 172 ppm (182 ppm for the carboxylic acid derivative **2a**), and the phenyl ring signals present at 137.8, 129.0, 126.0, and 122.5 ppm. (*ii*) the basal spacing obtained from the powder XRD spectra of **7a**. The interlayer spacing, from the acid form **2a** (12.3 Å) to the amide form **7a** (23.9 Å), with chains perpendicular to the inorganic layers, would be expected to increase at least by two times the dimension of aniline (*ca.* 4.5 Å). The higher value observed probably accounts for a deformation of the structure, induced by the bulky phenyl ring. No structural information concerning the layers of compounds **7a,b** could be obtained from their X-ray data, as the cristallinity of the samples was poor. However, we can suppose that these two products correspond to the anhydrous form of the structural model described for $Zn(O_3PR)\cdot H_2O$, in which the coordination number for the Zn atom is thought to be 5.[7a,b] This is consistent with the result obtained when manganese was used instead of zinc, in the same experimental conditions as that decribed for

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[27] Zabicky, J. *The chemistry of amides*; John Wiley and Sons: London, U.K., 1970.

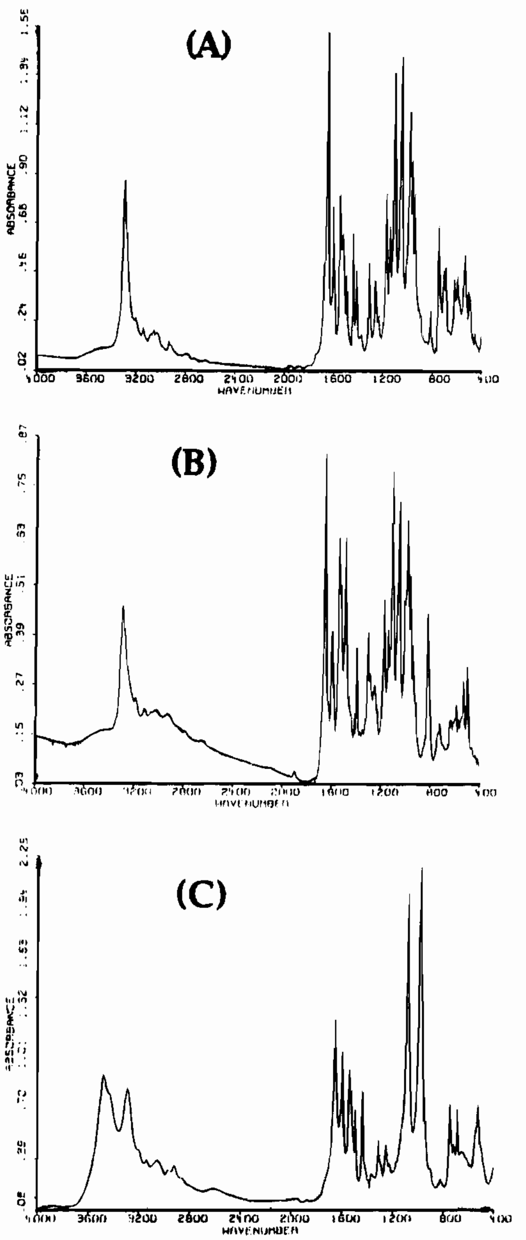

Figure 8. Comparative infrared absorption spectra of (A) Zn($O_3P(CH_2)_2CONHC_6H_5$), (B) $Zn(O_3P(CH_2)_2CONHC_6H_4Br)$, and (C) $Mn(O_3P(CH_2)_2CONHC_6H_5)\cdot H_2O$.

the synthesis of **7a**. A hydrated material was produced: $Mn(O_3P(CH_2)_2CONHC_6H_5)\cdot H_2O$ with an interlayer spacing of 23.8 Å and an infrared spectrum exhibiting the NH, amide I and amide II bands (3295, 1660, 1546 cm^{-1}), while the frequency of the main bands related to the H_2O and PO_3 vibration (3485, 3431 (ν(OH)); 1603 (δ(OH)); 1087, 989 ($\nu(PO_2)$) cm^{-1}) (Figure 8) are nearly identical to that of $Mn(O_3PC_2H_5)\cdot H_2O$ (3488, 3433 (ν(OH)); 1605 (δ(OH)); 1088, 987 ($\nu(PO_2)$) cm^{-1}). Moreover, TGA data for the two manganese compounds show that the first weight loss occurs at the same temperature (170 °C), corresponding to the release of the water molecule. The conclusion is that $Mn(O_3P(CH_2)_2CONHC_6H_5)\cdot H_2O$ adopts a structural arrangement within the layers, identical to that observed for the $M^{II}(O_3PR)\cdot H_2O$ model (M^{II} = Zn, Co, Ni, Mn ; R = alkyl). Compounds **7a,b** probably correspond to the anhydrous form of this $M^{II}(O_3PR)\cdot H_2O$ structure, in which the dehydration is thought to be topotactic in the case of the zinc compounds, with a five-coordination that is fairly common for the zinc ions.[7a,b] For manganese, the five-coordination is rare and this trend would explain why a hydrated material is produced in this case, in which the metal atom is octahedrally coordinated. Some attempts to prepare single crystals of **7a** for a structural determination, are in progress in order to confirm this hypothesis.

Conclusion

As illustrated in the case of $Zn(O_3P(CH_2)_2CO_2H)\cdot H_2O$, grafting reactions on the functionalized $M^{II}(O_3P(CH_2)_2Y)\cdot H_2O$ compounds (M = Zn , Cu; Y = CO_2H, Br, $NH_3^+NO_3^-$) are expected to be difficult, requiring a preliminary activation of the reactive groups. However, an easy and original one-step reaction leading to lamellar zinc phosphonates with amide linkage, $Zn(O_3P(CH_2)_2CONHAr)$, has been reported. This method appears to be a potential and attractive route for the immobilization of organic molecules (with for example catalytic, electrical or photoconducting properties) on lamellar phosphonate frameworks. Many experiments are in progress to generalize this procedure to amines insoluble in water (in organic media), alkylamines, diamines (for the formation of pillared materials), chiral amines and catalytic centers functionalized by amino ends (for supported catalysis). Results will be described in a subsequent paper. Additionally, some research using liquid and solid state NMR, has been started to discern the mechanism involved in these reactions.

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Supplementary Material Available: Tables giving a full presentation of the crystal data and anisotropic thermal parameters for non-hydrogen atoms (3 pages). Ordering information is given on any current masthead page. A tabulation of observed and calculated structure factors for the two structures is available upon request from B.B. for up to 1 year from the date of publication.