Syntheses and X-ray Powder Structures of Two Zinc Propylenebis(phosphonates)

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The crystal structures of two new zinc compounds of propylenebis(phosphonic acid) were determined ab initio from their powder diffraction data. These compounds were prepared by the reaction of zinc chloride with the phosphonic acid at different pH conditions. The compound, $Zn(HO_3PC_3H_6PO_3H)$ (**1**), crystallizes in the monoclinic space group $P2_1/n$ with $a = 18.167(3)$ Å, $b = 5.083(1)$ Å, $c = 8.658(1)$ Å, $\beta = 93.630(2)°$ and $Z = 4$. The other compound, $Zn_3[(HO_3PC_3H_6PO_3)_2]{\cdot}2H_2O$ (**2**), also crystallizes in the monoclinic symmetry but with space group $C2/c$. Crystal data: $a = 20.5853(4)$ Å, $b = 5.0472(1)$ Å, $c = 18.0140(4)$ Å, $b = 97.226(1)°$, $Z = 4$. The intensities of the structure factors were extracted from the powder patterns using the Le Bail method and were used for structure solution by direct methods. The structures were then completed by Fourier methods and refined by Rietveld methods. In structure **1**, the metal atoms are tetrahedrally coordinated by four oxygen atoms, two each from two independent phosphonates. The remaining oxygen atom of both phosphonate groups is protonated and is involved only in hydrogen bonding. The metal phosphonate interactions lead to double chains that are linked to each other through the organic linkages, leading to two-dimensional slabs or sheets. These slabs are connected through hydrogen bonds, thus forming a loosely held three-dimensional metal phosphonate network. In the case of compound **2**, only one of the phosphonate groups is protonated, while the other is completely deprotonated. In this structure, there are two independent metal atoms that are tetrahedrally coordinated. One is coordinated completely by phosphonate oxygen atoms, while the coordination of the other zinc atom is by two phosphonate oxygens and two water oxygen atoms. The structure is interesting in that it consists of large one-dimensional pores whose dimensions are determined by the length of the organic moiety. Thus, this structure provides a starting point for a broad exploration of a new class of metal phosphonate porous materials with varied pore sizes.

Introduction

It is now 20 years since the first zirconium phosphonates were synthesized.[1] Since then, this field of research has grown very large, necessitating publication of periodic summaries and reviews.[2] Many of the phosphonates have robust layered structures. The late Martin Dines conceived of the idea that α,ω-diphosphonic acids might form similar layered compounds but with the layers cross-linked into three-dimensional compounds. By spacing the bis(phosphonic acids) using phosphate or phosphite ion spacers, it was expected that porous products would result.[3] Although materials with high surface area were produced,[3,4] the situation is more complex than originally supposed.[5] Only a few compounds with a regular microporous structure have been prepared.[6,7] A major difficulty in working with four-valent metals is the very low solubility of their phosphonates, especially the bis(phosphonates). As a result, the compounds are usually amorphous or semicrystalline and unsuitable for crystal structure determination.

About 10 years ago we and others began a systematic examination of phosphonate compounds of divalent metals.[8] These compounds are soluble in acid solution

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and many of them were crystallized and their structures determined. These successes led us to examine the synthesis and structures of bis(phosphonates), and these investigations were also fruitful. A number of aryl cross-linked derivatives of Zn[9] and Cu[10] have been prepared and more recently alkyl chain compounds have been synthesized and their structures determined.[11] The copper propylenebis(phosphonate) yielded a structure containing unidimensional tunnels parallel to the *a*-axis that were filled with water molecules. Several additional porous compounds have been synthesized by using templates.[12] In this paper we describe two additional zinc propylenebis(phosphonates), one with unidimensional tunnels and the other a layered compound with the layers connected by hydrogen bonds.

Experimental Section

Materials and Methods. All reagents were of analytical grade (Aldrich) and used without further purification. Thermogravimetric analysis was carried out with a TA 4000 unit, at a heating rate of 10 °C/min under a nitrogen atmosphere. The IR spectrum was recorded on a Perkin-Elmer 1720-X FTIR unit by the KBr disk method.

Synthesis of $Zn[(HO_3PC_3H_6PO_3H]$ (1). This compound was prepared by the reaction of 0.51 g (2.5 mmol) of 1,3-propylenebis(phosphonic acid) with 0.68 g (5 mmol) of $ZnCl_2$ in 30 mL of deionized distilled water. The solution was transferred into a Teflon-lined bomb that was heated in an oven at 190° C for 1 week. Since no precipitate was formed, the solution was removed from the bomb and was allowed to evaporate at room temperature. When the solution became almost dry, it was mixed with 5 mL of water and allowed to stand at room temperature. A white crystalline powder formed after about 1 day which was collected by filtration, washed, and dried in air (yield, 0.1 g, 15%). Anal. Calcd for $Zn[HO_3PC_3H_6PO_3H]$: C, 13.46; H, 2.81. Found: C, 13.04; H, 2.81.

Synthesis of $Zn_3[(HO_3PC_3H_6PO_3)_2]\cdot 2H_2O$ (2). A 0.68 g portion of $ZnCl_2$ (5 mmol) was mixed with 0.51 g (2.5 mmol) of 1,3-propylenebis(phosphonic acid) in 20 mL of deionized distilled water. The pH of the solution was raised slowly to 2.5 with 1 N NaOH. On stirring for 2 min, the compound $Zn_2[(O_3PC_3H_6PO_3)]$ precipitated (yield = 0.02 g). The structural characterization of this compound was reported earlier.[11] This compound was filtered off and the filtrate was transferred to a plastic bottle and kept in an oven at 60 °C. The contents in the bottle turned into a gel in about 1 h and on continuing the reaction overnight a crystalline powder sample of a new material precipitated. The precipitate formed was filtered, washed, and dried in air (yield, 0.25 g, 46.4% based on the phosphonic acid). Anal. Calcd for $Zn_3[(HO_3PC_3H_6PO_3)_2]\cdot 2H_2O$: C, 11.35; H, 2.84; H_2O, 5.68. Found: C, 11.06; H, 2.88, H_2O (TGA), 5.18.

X-ray Data Collection. The X-ray source was a rotating anode operating at 50 kV and 180 mA with a copper target and graphite-monochromated radiation. X-ray powder data for the samples were collected using a Rigaku computer automated diffractometer. The samples for the data collection were prepared by using an aerosol suspension chamber[13] to reduce the influence of preferred orientation effects. In this method the finely ground sample particles were dispersed into an aerosol through the action of a fluidized bed of spherical beads. The aerosol is then carried up through a column and is collected by a filter paper mounted on a casette by the action of a vacuum pump. The procedure yields random orientation of the particles within the pores of the filter paper. Room-temperature data for both compounds were collected between 7° and 107° in 2θ using a step size of 0.01° and a count time of 6 s per step. The powder patterns were indexed by Ito methods.[14] The following initial unit cell dimensions were obtained: $Zn[HO_3PC_3H_6PO_3H]$, $a = 18.2$ Å, $b = 5.09$ Å, $c = 8.67$ Å, and $\beta = 93.6°$ (FOM = 23); $Zn_3[(HO_3PC_3H_6PO_3)_2(H_2O)_2]$, $a = 20.56$ Å, $b = 5.04$ Å, $c = 18.0$ Å, and $\beta = 97.36°$ (FOM = 26). Systematic absences were consistent with the space group $P2_1/n$ for the compound $Zn[HO_3PC_3H_6PO_3H]$ and $C2/c$ for $Zn_3[(HO_3PC_3H_6PO_3)_2(H_2O)_2]$.

Structure Solution and Refinement. The X-ray powder patterns for both the compounds were decomposed by the Le Bail method[15] using the program EXTRA.[16] The extracted intensities were input into SIRPOW,[17] a direct methods program applied to powder data for the solution of crystal structures. For $Zn[HO_3PC_3H_6PO_3H]$, the extraction procedure produced 210 independent observations (final $R_p = 0.12$). An E-map computed for a solution with the best figure of merit revealed the approximate positions of all the atoms in the structure except the central carbon atom of the propylene chain. In the case of $Zn_3[(HO_3PC_3H_6PO_3)_2(H_2O)_2]$, 235 independent reflections, extracted using EXTRA (final $R_p = 0.099$), were input to SIRPOW. The E-map in this case contained the positions of two Zn atoms, two P atoms, and four oxygen atoms. The remaining atoms (three oxygen and three carbon atoms) in this structure were located from difference Fourier maps calculated after initial Rietveld refinement. For the final Rietveld refinement, data in the range 10−107° and 10.5−100.0° were used for compounds **1** and **2**, respectively.

The structural models as obtained above were used for Rietveld refinement of the full pattern in GSAS.[18] After the initial refinement of scale, background function, unit cell parameters, and profile parameters, the atomic positions were refined with soft constraints for the phosphonate groups. The P−O, P−C, and C−C bond distances were constrained to distances of 1.53(2), 1.80(2), and 1.50(2) Å, respectively. The tetrahedral angles about the P atoms were constrained by applying a value of 2.53(2) Å and 2.73(2) Å for O···O and O···C nonbonded distances. The C−C bond distances in the alkyl chain were held to a value of 1.50(2) Å, and the distance between the two end C atoms of the propylene group were constrained to a value of 2.46(2) Å to obtain the tetrahedral angle about the central C atom. Difference Fourier maps were then calculated which allowed the positioning of the remaining atoms in the structures. The full structures were then refined with the above-mentioned soft constraints with a weight of 50. The preferred orientation factors were refined to a value very close to 1.0. All the atoms were refined isotropically. Neutral atomic scattering factors, as stored in GSAS, were used for all atoms. No corrections were made for absorption.

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Table 1. Crystallographic Data

	$Zn[(HO_3PC_3H_6PO_3H)$ (**1**)	$Zn_3[HO_3PC_3H_6PO_3)_2]\cdot 2H_2O$ (**2**)
formula	$C_3H_8O_6P_2Zn$	$C_6H_{18}O_{14}P_4Zn_3$
fw	267.3	634.02
space group	$P2_1/n$ (No. 14)	$C2/c$ (No. 15)
a (Å)	18.167(3)	20.5853(4)
b (Å)	5.083(1)	5.0472(1)
c (Å)	8.658(1)	18.0140(4)
β (deg)	93.630(2)	97.226(1)
V(Å^3)	797.9(4)	1856.8(1)
Z	4	4
d_{calcd} (g/cm^3)	2.22	2.27
pattern range (2θ)	$10-107^{o}$	$10-100^{o}$
no. of unique reflcns	942	947
no. structural params	48	51
R_{wp}	0.094	0.075
R_p	0.070	0.057
R_F	0.046	0.054

Table 2. Positional and Thermal Parameters for $Zn[HO_3PC_3H_6PO_3H]$

	x	y	z	U_{iso},[a] Å^2
Zn1	0.1910(1)	0.0645(4)	0.0574(3)	0.012(1)
P1	0.1545(2)	0.2816(8)	0.4029(5)	0.027(2)
P2	0.1304(2)	−0.4046(8)	−0.1303(4)	0.015(2)
O1[b]	0.1229(4)	0.0909(13)	0.5265(8)	0.015(2)
O2	0.2137(4)	0.4435(13)	0.4866(8)	0.015
O3	0.1871(4)	0.1152(14)	0.2784(8)	0.015
O4	0.1207(4)	−0.1703(13)	−0.0207(8)	0.015
O5[b]	0.1636(4)	−0.2995(17)	−0.2789(8)	0.015
O6	0.1777(4)	−0.6109(13)	−0.0545(8)	0.015
C1	0.0809(4)	0.4811(15)	0.3257(11)	0.033(2)
C2	−0.0136(4)	−0.3340(17)	−0.2599(12)	0.033
C3	0.0404(3)	−0.5312(15)	−0.1912(11)	0.033

[a] $U_{iso} = B_{iso}/8\Pi^2$. [b] O1 and O5 are protonated.

Table 3. Positional and Thermal Parameters for $Zn_3[(HO_3PC_3H_6PO_3)_2(H_2O)_2]$

	x	y	z	U_{iso}, Å^2
Zn1	0.8217(1)	0.4163(4)	0.1970(1)	0.014(1)
Zn2	0	0.0252(7)	0.25	0.023(1)
P1	0.8195(2)	0.6372(9)	0.3614(2)	0.012(2)
P2	0.8925(2)	−0.0937(9)	0.1379(2)	0.013(2)
O1[a]	0.7860(3)	0.4360(14)	0.4101(4)	0.021(3)
O2	0.7687(3)	0.8194(12)	0.3224(4)	0.021
O3	0.8542(3)	0.4824(15)	0.3040(3)	0.021
O4	0.8893(4)	0.1736(12)	0.1762(4)	0.021
O5	0.9508(3)	−0.2502(13)	0.1789(4)	0.021
O6	0.8292(3)	−0.2570(14)	0.1381(4)	0.021
O7[b]	0.0239(4)	0.2929(12)	0.1774(4)	0.021
C1	0.8821(4)	0.8120(15)	0.4225(4)	0.019(5)
C2	0.8588(4)	0.8759(21)	0.4969(4)	0.019
C3	0.9105(4)	1.0460(18)	0.5424(3)	0.019

[a] O1 is protonated. [b] O7 represents water oxygen atom.

Table 4. Bond Lengths (Å) and Bond Angles (deg) for $Zn[HO_3PC_3H_6PO_3H]$

Zn1−O2	1.898(6)	Zn1−O3	1.936(6)
Zn1−O4	1.845(6)	Zn1−O6	1.921(6)
P1−O1	1.578(6)	P1−O2	1.505(5)
P1−O3	1.520(6)	P1−C1	1.775(6)
P2−O4	1.540(6)	P2−O5	1.550(6)
P2−O6	1.482(5)	P2−C3	1.805(5)
C1−C2	1.499(7)	C2−C3	1.513(7)
O2−Zn1−O3	109.4(3)	O2−Zn1−O4	109.6(3)
O2−Zn1−O6	105.3(3)	O3−Zn1−O4	112.4(4)
O3−Zn1−O6	111.9(4)	O4−Zn1−O6	108.0(3)
O1−P1−O2	106.8(5)	O1−P1−O3	108.3(4)
O1−P1−C1	108.0(4)	O2−P1−O3	110.2(5)
O2−P1−C1	111.6(4)	O3−P1−C1	111.7(5)
O4−P2−O5	108.1(5)	O4−P2−O6	111.1(5)
O4−P2−C3	108.5(4)	O5−P2−O6	111.5(5)
O5−P2−C3	105.9(4)	O6−P2−C3	111.5(5)
P1−C1−C2	115.5(5)	C1−C2−C3	108.2(6)
C2−C3−P2	115.8(5)		

Table 5. Bond Lengths (Å) and Bond Angles (deg) for $Zn_3[(HO_3PC_3H_6PO_3)_2(H_2O)_2]$

Zn1−O2	1.913(6)	Zn1−O3	1.988(6)
Zn1−O4	1.927(6)	Zn1−O6	1.977(6)
Zn2−O5	2.073(7) × 2	Zn2−O7	1.985(7) × 2
P1−O1	1.558(5)	P1−O2	1.500(5)
P1−O3	1.544(5)	P1−C1	1.814(6)
P2−O4	1.521(6)	P2−O5	1.550(5)
P2−O6	1.543(5)	P2−C3	1.820(5)
C1−C2	1.514(7)	C2−C3	1.523(7)
O2−Zn1−O3	115.0(3)	O2−Zn1−O4	120.8(3)
O2−Zn1−O6	104.8(3)	O3−Zn1−O4	97.5(3)
O3−Zn1−O6	109.9(4)	O4−Zn1−O6	108.6(3)
O5−Zn2−O5	95.1(4)	O5−Zn2−O7	101.2(3) × 2
O5−Zn2−O7	136.4(3) × 2	O7−Zn2−O7	94.2(4)
O1−P1−O2	109.4(4)	O1−P1−O3	108.9(4)
O1−P1−C1	107.9(4)	O2−P1−O3	110.5(4)
O2−P1−C1	112.7(4)	O3−P1−C1	107.4(4)
O4−P2−O5	108.4(5)	O4−P2−O6	112.8(5)
O4−P2−C3	109.7(4)	O5−P2−O6	109.1(4)
O5−P2−C3	106.4(4)	O6−P2−C3	110.2(4)
P1−C1−C2	111.2(5)	C1−C2−C3	108.6(6)
C2−C3−P2	111.8(5)		

Crystallographic and experimental parameters are given in Table 1, positional parameters in Tables 2 and 3, and bond parameters in Tables 4 and 5. The final Rietveld refinement difference plots are shown in Figure 1.

Results

Thermogravimetric Study. Compound **1** shows a weight loss of 4.97% between 290 and 380 °C, corresponding to the loss of one water molecule due to the condensation of phosphonate hydroxyl groups. The second weight loss occurs at around 523 °C, due to the burning of the organic group, and the weight loss continues even beyond 1000 °C as the carbon is slowly oxidized. The total weight loss of 16.26% observed up to 1000 °C agrees well with the calculated value of 16.45%, assuming that the final decomposition product is $Zn(PO_3)_2$. The lattice water molecules in compound **2** are released between 153 and 199 °C. The observed weight loss (4.89%) for this process is in agreement with the loss of 5.67% of the weight calculated for two water molecules in the formula. The condensation of the hydroxyl groups occurs between 199 and 376 °C. This process releases 2.2% of the weight, slightly less than the expected value of 2.84%. The TGA curve shows the loss of organic groups in the region 515−555 °C. A total weight loss of 15.68% observed up to 1000 °C is in good agreement with the calculated weight loss of 16.71%.

Structure of $Zn[HO_3PC_3H_6PO_3H)]$ (1). The structure consists of one Zn atom and one propylenebis(phosphonate) group in the asymmetric portion of the unit cell, both occupying general positions. The protonation of the bisphosphonate ligand at both the functional ends results in a 1:1 composition between the metal and phosphonate in this compound. The singly protonated phosphonate groups at either end thus have only two oxygen atoms for coordination to zinc atoms. A section of the structure depicting the bridging mode of phosphonate groups along with the metal coordination is shown in Figure 2. The zinc atoms are tetrahedrally coordinated by phosphonate oxygen atoms. The P1 phosphonate group provides two oxygen atoms (O2

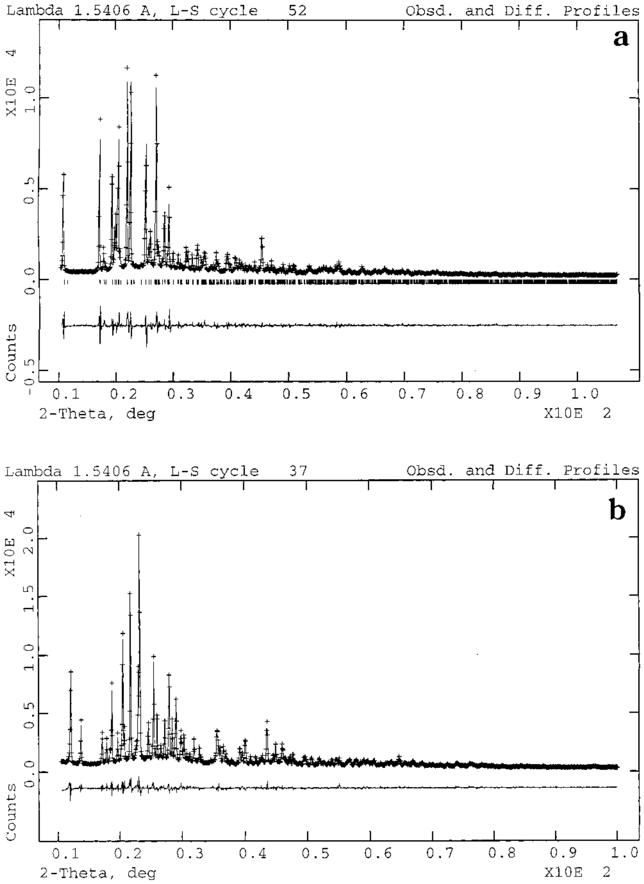

Figure 1. Observed (+) and calculated (−) profiles for the Rietveld refinement of compound **1** (a) and compound **2** (b). The difference plot shown below is on the same intensity scale.

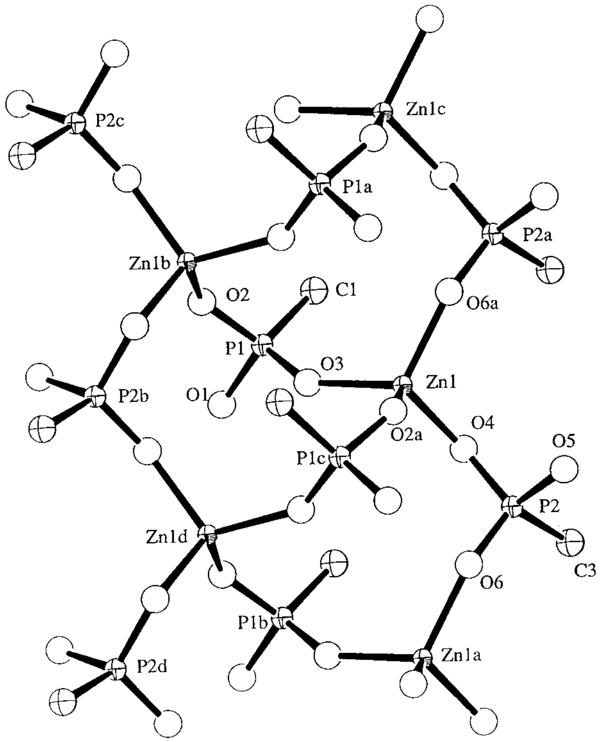

Figure 2. A section of the structure of compound **1** together with the atom numbering scheme showing the phosphonate−Zn connectivity.

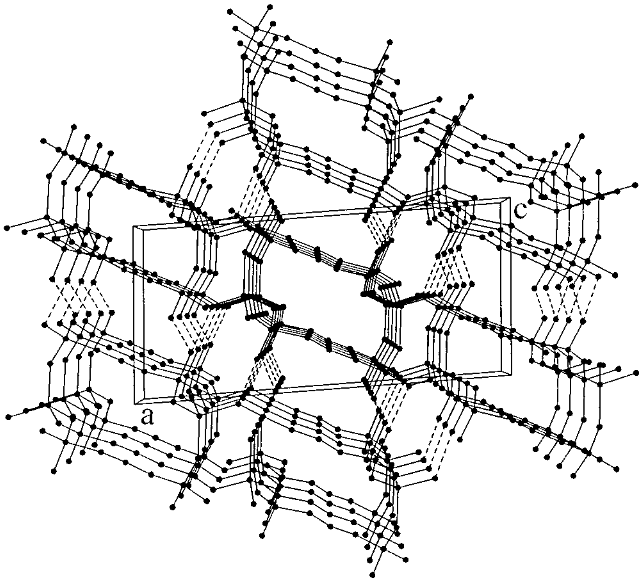

Figure 3. Schematic view down the *b*-axis of the unit cell contents of compound **1** showing the formation of unidimensional channels parallel to *b*.

and O3) for metal coordination, bridging across two Zn atoms, while the remaining two binding sites (O4 and O6) are provided by two P2 phosphonate groups. Oxygen atoms O1 of P1 and O5 of P2 are protonated and accordingly they are not involved in metal binding. The metal atoms display regular tetrahedral geometry. The Zn−O bond lengths are in the range 1.85(1)−1.94(1) Å and the associated bond angles vary between 105.3(3)° and 112.4(4)°. Similarly, the phosphonate groups including the propylene group show regular bond lengths and angles. As expected, the P−OH bond lengths in both the phosphonate groups are slightly longer than the P−O bond lengths involving deprotonated oxygen atoms.

The metal−phosphate bridging interactions lead to double chains with alternating Zn and P tetrahedra. These double chains run along the *b*-axis direction of the crystal in such a way that the phosphonate hydroxyl groups are projected away from the axis of the chains. The double chains are connected to each other along the [101] direction through the propylene groups to form infinite double sheets, as shown in Figure 3. The interactions, at the same time, produce unidimensional tunnels parallel to the *b*-axis consisting of two propylenebis(phosphonate) groups and two zinc atoms (16 atoms in all) that can be seen at the center of the *ac*-plane (Figure 3). These pores are not wide, as the neighboring alkylene chains are spaced at an interval of about *c*/2 (4.33 Å). These larger tunnels alternate with smaller tunnels circumscribed by 10 atoms. The sheets described above are connected to each other along the [101] diagonal direction through the hydrogen bonds (broken lines in Figure 3). There are two hydrogen-bonding interactions involved in holding the sheets together (O5···O1 = 2.667(9), O5···O2 = 2.625 Å) and both involve the protonated oxygen O5 of the P2 phosphate group.

Structure of $[Zn_3(HO_3PC_3H_6PO_3)_2\cdot 2H_2O]$ (2). Unlike compound **1**, the metal to bis(phosphonate) ratio in this case is 3:2. The doubly protonated bis(phosphonate) ligand as found for compound **1** exchanges one of its protons for Zn^{2+} ions, leading to compound **2**. The structure, therefore, contains two independent Zn at-

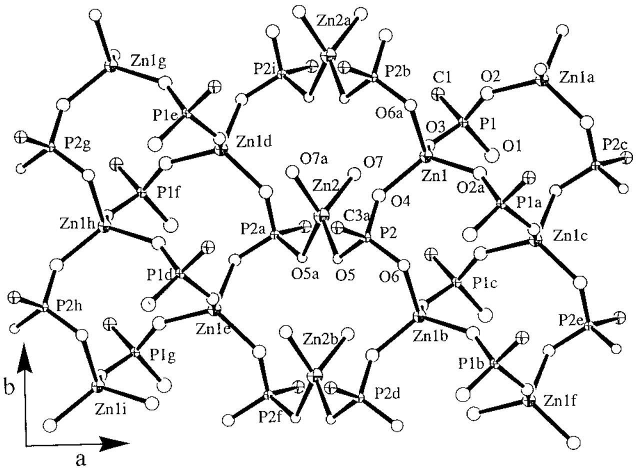

Figure 4. A section of the structure of compound **2** together with the atom numbering scheme showing the phosphonate−zinc connectivity.

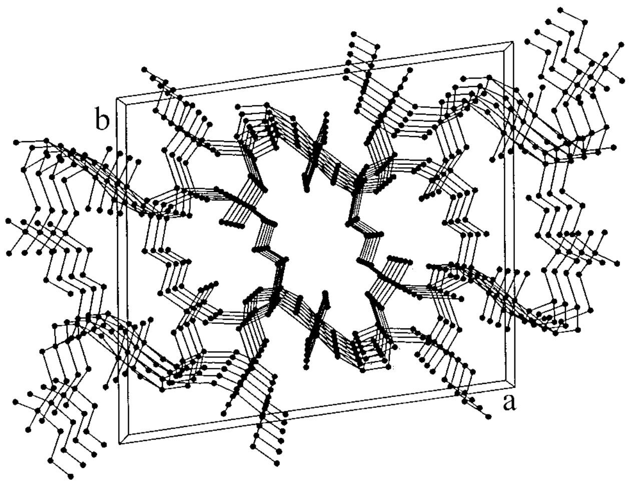

Figure 5. Schematic view down the *b*-axis of the unit cell contents of compound **2** showing the formation of elliptical and circular tunnels parallel to the *b*-axis direction.

oms, both displaying regular tetrahedral geometries. The metal atom Zn1 occupies a general position and is coordinated by phosphonate oxygens O2 and O3 of two separate P1 groups and O4 and O6, also from two P2 groups. The other metal atom, Zn2, is located on a 2-fold axis and its coordination sites are occupied by symmetry-related positions of O5 and O7. Oxygen atom O5 comes from the P2 phosphonate group while O7 represents the oxygen atom of the water molecule. This leaves one oxygen atom, O1 of a P1 group, not coordinated to metal atoms, indicating that it is bonded to the proton. The binding modes of the phosphonate groups and the metal coordination environment are shown in Figure 4. The coordination about the metal atom Zn1 is slightly distorted. The Zn−O bond lengths are in the range of 1.91(1)−1.99(1) Å and the tetrahedral bond angles vary between 97.5(3)° and 120.8(3)°. The geometry of Zn2 shows even more distortion in its tetrahedral geometry. The bond lengths Zn2−O5 (2.07(1) Å) and Zn2−O7 (1.99(1) Å) are slightly longer that those observed for Zn1, while the angles show very large deviation from the expected value. Angles involving symmetry related atoms, O5−Zn2−O5′ (95.1(4)°) and O7′−Zn2−O7 (94.2(4)°), are noticeably acute, while one set of angles involving O7 and O5 have significantly expanded (about 27°) versus the expected value. The other set of O7−Zn2−O5 (101.2(3)°) bond angles is very close to that expected for tetrahedral geometry.

The crystal structure of **2** is similar to that of **1** in many respects. The interaction of Zn1 with the phosphonate groups P1 and P2 is similar, as can be seen in Figures 2 and 4. These connections lead to double chains with alternating Zn and P atoms that run along the shortest axis of the crystal. The alkylene chains connect these double chains along the *c*-axis direction, thereby forming the metal phosphonate sheets, as found in compound **1**. The difference in the structures of **1** and **2** is basically in the way the sheets are connected to each other. In the structure of **2**, the sheets are linked to each other through direct bonding of Zn2 to O5 atoms in the neighboring sheets. On the other hand, such sheets in **1** are connected by hydrogen bonds involving protonated O5 atoms. The bridging of sheets by Zn2 produces large pores within the structure that can be seen at the center of the unit cell in Figure 5. These pores are elliptical in shape, formed by bridging of two neighboring bis(phosponates) by zinc atoms. The pore opening in the *ac*-plane may be represented by linkages of the following type:

$$\text{Zn2−O5−P2−C}_3\text{H}_6\text{−P1−O3−Zn1−O6−P1−O5−}$$
$$\text{Zn2−O5−P2−C}_3\text{H}_6\text{−P2−O5}$$

The coordinated water molecules (O7) are projected into the center of these pores, creating a hydrophilic environment between the two alkyl chains. These elliptically shaped tunnels alternate in the *c*-axis direction with more circular unidimensional tunnels outlined by a 16-atom framework. The lone hydroxyl group present in the structure projects into these circular tunnels and is involved in only one hydrogen-bonding interaction with (O1···O6 = 2.61(1) Å). Apart from binding to Zn2, the water oxygen atom is involved in three possible hydrogen-bonding interactions: O7···O3 (2.66(1) Å), O7···O4 (2.83(1) Å), and O7···O5 (2.75(1) Å).

Discussion

The compound $Zn(HO_3PC_3H_6PO_3H)$ (1) was prepared under highly acidic conditions (pH ~1.5), and as described in the results section, the Zn atom replaces only one proton from each of the phosphonate groups, leaving the other proton intact on one of the oxygen atoms of each phosphonate group. These hydroxyl groups do not take part in metal coordination and therefore the four coordination sites of the Zn atom are filled by four remaining oxygen atoms from four separate bis(phosphonate) ligands. The structure of this compound is very similar to that of $Zn[HO_3P(C_6H_4)_2PO_3H]$,[9a] particularly in terms of the metal−phosphonate backbone that exists as double chains in these compounds. The double chains are covalently linked by either propylene or the biphenylene groups to form sheets which in turn are held together in the lattice through hydrogen bonds involving the hydroxyl groups. We earlier showed[9b] that, on increasing the pH to 9, the biphenylenebis(phosphonate) exchanges its protons to form $Zn_2[O_3PC_{12}H_8PO_3)(H_2O)_2]$, with loss of half of the phosphonic acid as the soluble sodium salt. In the process, Zn transforms from tetrahedral to octahedral coordination. In contrast, the protonated propylene compound **1** does not deprotonate in mild alkali media but is stable to pH 9. This stability may be due to the greater density of hydrogen bonds. Instead, the compound $Zn_2(O_3PC_3H_6PO_3)$ must be directly prepared under less acidic conditions.[11] Compared to other fully deprotonated Zn phosphonate compounds, the Zn propylene compound, $[Zn_2(O_3PC_3H_6PO_3)]$, is different, because it does not contain any water molecules and the Zn atoms are found in tetrahedral environment. In the hydrated compounds, the Zn atoms are octahedrally coordinated by the oxygen atoms of the phosphonate groups and water molecules. Compounds **1** and **2** are insoluble in water and all common organic solvents.

The compound $Zn_3[(HO_3PC_3H_6PO_3)(H_2O)]_2$ (**2**) was prepared at pH ~2.5 and it is the intermediate between $Zn(HO_3PC_3H_6PO_3H)$ (**1**) and $[Zn_2(O_3PC_3H_6PO_3)]$. The structures of **1** and **2** are strikingly similar in terms of the double-chain structure. A comparison of Figures 3 and 5 shows the mechanism involved in converting compound **1** to **2**. One of the protons that is bonded to O5 in **1** is replaced by the zinc atoms, and as a consequence, the hydrogen-bonding scheme, involving that particular oxygen, is replaced by O5′−Zn2−O5 covalent bonds between two neighboring phosphonate groups. These newly exchanged Zn atoms occupy a special position (2-fold axis) and therefore only half a Zn atom takes the position of the one replaced proton, which essentially satisfies the charge neutrality in the compound. The interesting aspect of the structure of $Zn_3[(HO_3PC_3H_6PO_3)(H_2O)]_2$ is that it consists of a three-dimensional structure with large elliptical pores. The coordinated water molecules are projected into the openings of these pores, which makes it easier to remove them on controlled heating. On the basis of the structure of **2**, it is possible that, on dehydration, the Zn atoms (Zn2) will be able to bind to the neighboring phosphate oxygen atoms with some minor readjustments in their positions. The new open space thus created should be able to absorb small- and medium-sized molecules that are potentially exposed to coordinatively unsatisfied Zn atoms on the walls of the channel. This novel property, along with the fact that the size of the pores can be controlled by changing the length of the alkyl chains of the phosphonates and that the alkyl chains can be properly functionalized, makes this class of materials highly interesting.

Recently, a number of other metal compounds containing alkylene and arylene bis(phosphonates) were prepared and structurally characterized.[9−11] The compounds of ethylenebis(phosphonates), as well as phenylenebis(phosphonates), have the general formula $[M_2(O_3PRPO_3)(H_2O)_2]$ ($M = Cu, Zn$; $R = C_2H_2, C_6H_5$), and their layer structures were found to be similar to that observed for a series of monophosphonate compounds of the type $M(O_3PR)(H_2O)$ ($M = Cu, Zn, Mn, Cd$; $R =$ methyl, ethyl, phenyl), reported earlier.[8] All these compounds contain central two-dimensional layers formed by metal−O_3P−C interactions. The major difference in the structures of mono- and bis(phosphonates) is in the metal to phosphonate composition and in interlayer separation. In the case of the monophosphonates, the metal-to-phosphonate ratio is 1:1 and the organic moieties on either side of the layers project away, toward the interlamellar region, creating an organic bilayer between the hydrophilic metal−phosphate groups. The only interaction between the successive layers in their structures is van der Waals forces operating between the organic groups. The bis(phosphonate) structures also contain alternating hydrophilic and hydrophobic regions, as in the case of monophosphonates, but their layers are inseparable, as the organic groups are covalently connected to the metal−phosphonate layers on either sides. The metal to P ratio in all these compounds remains the same (1:1), but that between metal and organic group is 1:1 or 1:0.5, for mono- and bis(phosphonates), respectively.

The reaction of 4,4′-biphenylylenebis(phosphonic acid) carried out under similar conditions as that mentioned for other bis(phosphonates) yielded the compounds $Cu[HO_3P(C_6H_4)_2PO_3H]$ and $Zn[HO_3P(C_6H_4)_2PO_3H]$ for Cu and Zn, respectively. In both compounds, the phosphonate groups are singly protonated and that makes it difficult for them to bridge the metal ions to form the regular two-dimensional M−O_3P−C type layers. Consequently, the metal phosphonate linkages in the Cu compound leads to linear chains that are bridged into layers by the aryl phosphonate groups and held together in the lattice through hydrogen bonds. Similar types of hydrogen-bonded networks exist, even in the case of the Zn compound, but the metal−phosphate groups form double chains with alternating Zn and P atoms. When the phosphonates are deprotonated by increasing the pH of the reaction, the compounds precipitated in different crystalline form. In the case of Zn, structure analysis using powder data showed that the compound formed under this reaction condition corresponds to the formula $Zn_2[(O_3PC_{12}H_8PO_3)(H_2O)_2]$. This compound is isostructural to that of Zn−phenylenebis(phosphonate) compound $Zn_2[(O_3PC_6H_4PO_3)(H_2O)_2]$ and is formed by the involvement of all the phosphonate oxygen atoms in metal binding. In the case of the propylene bis(phosphonic acid), all three compounds, diprotonated, monoprotonated, and unprotonated, were found to form under slightly different conditions of pH. Temperature variation and hydrothermal or templated procedures may lead to even greater complexity of structure. These options are under investigation.

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