

## New Architectures for Zirconium Polyphosphonates with a Tailor-Made Open-Framework Structure

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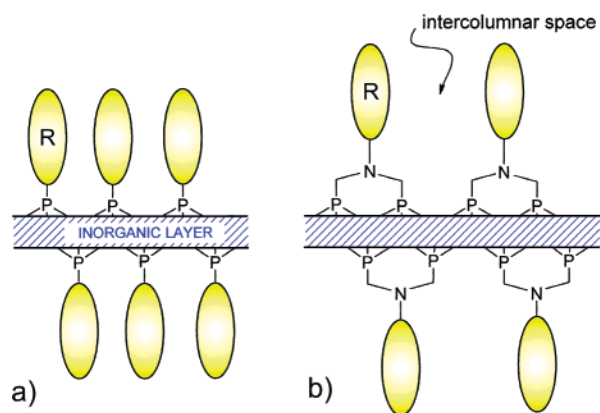
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Received December 16, 2005

The use of tetraphosphonic building blocks for the preparation of inorganic–organic zirconium derivatives has led to the formation of novel compounds with a modular structure. This is based on the different connection of polymeric 1D inorganic units covalently connected by organic groups. The different kinds of connections generate two different open-framework structures. These structures have been solved “*ab initio*” by powder X-ray diffraction data. Very likely, the dimensions of the channels inside these structures may be tuned by the right choice of the interlinking organic group.

The assembly of hybrid inorganic–organic building blocks for the preparation of tailor-made open-framework structures is a topic of growing interest in the field of materials chemistry, owing to their potential application in catalysis, molecular separation, proton conduction, and so on.<sup>1</sup> Metal phosphonate based compounds are widely studied for this purpose.<sup>2</sup> During a recent research on this topic, we found that the use of multidentate building blocks, such as tetraphosphonate groups, can induce the formation of open-framework compounds with a modular structure, made of inorganic polymeric units linked by organic groups. It resulted in two prototypes of open-framework structures with cavities inside, the dimensions of which could be tailored by the right choice of interlinking organic groups. These compounds belong to the vast family of zirconium phosphonates. Among other metal phosphonates, the zirconium derivatives are of special interest. They are very insoluble compounds, and their structure and reactivity, especially those of layered zirconium phosphonates of  $\alpha$  and  $\gamma$  types, can be easily modified and tailored for specific purposes. A large number of layered zirconium inorganic–organic derivatives in which organic groups are covalently bonded to the inorganic layers are known today.<sup>3</sup>

More recently, we prepared a new family of zirconium diphosphonates, by using diphosphonic building blocks with



**Figure 1.** Schematic structure of the layers of an  $\alpha$ -zirconium phosphonate (a) and a zirconium (*R*)-amino-*N,N*-bis(methylphosphonate) (b). In this last class of compounds, the layers have a lower density of organic groups (represented by ellipses).

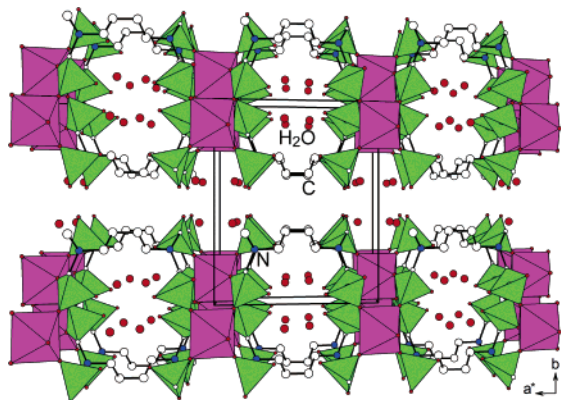
the two phosphonate groups placed at the same part of the organic group.<sup>4</sup> These zirconium derivatives showed a new architecture of layers, with the number of organic groups per mole of compound reduced by half with respect to traditional zirconium diphosphonates, as depicted in Figure 1. Because of the large cross section available per each interlayer organic group, these compounds featured interesting intercalation properties, even toward nonpolar guest molecules.<sup>5</sup>

As the logical advancement of this research, we have recently used the tetraphosphonic building blocks **1** and **2** (see Chart 1), with the aim of further reducing the organic group density in an inorganic framework structure.<sup>6</sup> The surprising results of this investigation are reported in the present paper.

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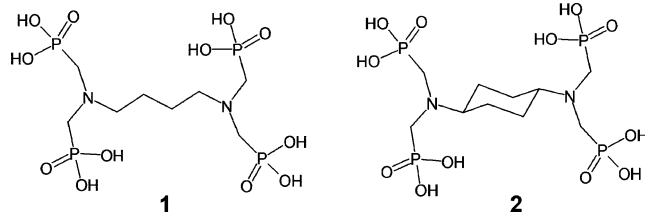
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**Figure 2.** Polyhedral representation of the structure of **3** viewed along the  $c$  axis. Octahedra are  $\text{ZrO}_6$ ; tetrahedra are  $\text{PO}_3\text{C}$  (white).

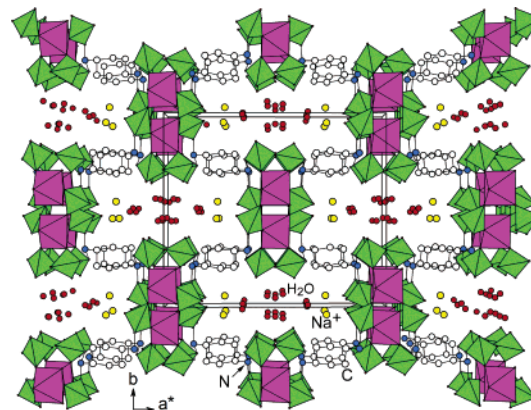
**Chart 1.** Molecular Structure of the Tetraphosphonic Building Blocks



The zirconium derivatives of **1** and **2** obtained had formulas  $\text{Zr}(\text{HPO}_3\text{CH}_2)_2\text{N}-\text{C}_4\text{H}_8-\text{N}(\text{CH}_2\text{PO}_3\text{H})_2\cdot 4\text{H}_2\text{O}$  (**3**) and  $\text{Zr}(\text{PO}_3\text{CH}_2)_2\text{N}-\text{C}_6\text{H}_{10}-\text{N}(\text{CH}_2\text{PO}_3)_2\text{Na}_2\text{H}_2\cdot 5\text{H}_2\text{O}$  (**4**), respectively. Because of their low solubility, these compounds were obtained as fine powders, and all of our attempts to obtain single crystals of them were unsuccessful. Therefore, their structure was solved “*ab initio*” by powder X-ray diffraction methods.<sup>6</sup>

**3** has a layered 2D structure in which the tetraphosphonic group contributes to the formation of one layer, connecting the  $\text{ZrO}_6$  octahedra along the sheet direction, as depicted in Figure 2.

These layers are about 13 Å thick and are stacked with an A–A sequence. The interlayer region is occupied by two water molecules. Each layer is formed by the connection, through the butyldiamino groups, of inorganic 1D polymeric units running along the  $c$  axis. These units are constituted by a double row of  $\text{ZrO}_6$  octahedra connected to the phosphonate tetrahedra. Butyl chains covalently link these units from opposite parts, along the  $a$  axis, generating original intralayer channels running along the  $c$  axis. The vertical size of these channels (about 10 Å, between atomic centers) is determined by the height of the inorganic building unit, whereas the horizontal size (about 3.5 Å) depends on the length of the alkyl chain. These channels are partially occupied by two water molecules per formula unit. The tetraphosphonic groups contain two pairs of nonequivalent phosphonate tetrahedra. One of them is doubly connected to two different Zr atoms; its P–OH group points toward the channel and forms H bonds with the intrachannel water molecules. The other pair of phosphonate groups is mono-



**Figure 3.** Polyhedral representation of the structure of **4** viewed along the  $c$  axis. Octahedra are  $\text{ZrO}_6$ ; tetrahedra are  $\text{PO}_3\text{C}$ .

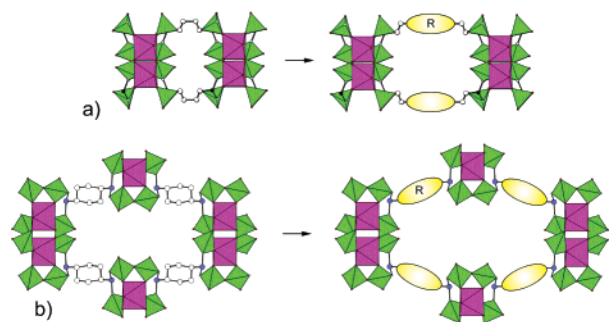
dentate and is placed on the external part of the layers. Two vertexes of these tetrahedra, occupied by an OH and a terminal O atom, point toward the interlayer region. The alkyl chains are in a gauche conformation, with a torsion angle between the four C atoms of 84.1°. In this compound, there are four acidic P–OH groups per formula unit. However, ion-exchange experiments of **3** with  $\text{Na}^+$  or  $\text{Li}^+$  showed that only two of the four acidic P–OH groups per formula unit were exchanged. The resulting products showed an increase of the basal spacing that is consistent with the ionic radii of the two guest species. These results can indicate that only the P–OH groups pointing toward the interlayer region are involved in the ion-exchange process, while those placed inside the channel region probably are too hindered.

Compound **4** has a 3D open-framework structure made of inorganic polymeric units bridged by cyclohexyl groups in a “brickwall-like” building texture, as shown in Figure 3.

Despite the increased dimensionality, this structure closely resembles that of **3**. The inorganic polymeric units show the same connectivity between zirconium octahedra and phosphonate tetrahedra. In **4**, these blocks are shifted from each other by  $1/2a$  and  $1/2b$ , and their connection, operated by the organic groups, generates rectangular channels, running along the  $c$  axis, with dimensions of about  $12 \times 5$  Å (calculated perpendicularly to the  $c$  axis and between atomic centers). These channels are occupied by five water molecules and two Na atoms per formula unit. These guest species form a number of strong interactions and H bonds with each other and with the framework P–O groups. Also, in this compound, the phosphonate groups of the tetraphosphonate moiety are paired in two nonequivalent phosphonate tetrahedra. One of them is doubly connected with Zr atoms and bears only one anionic P–O group, while the other is monodentate and bears one anionic and one neutral P–O group. Two of these four anionic groups are probably protonated, while the other two are balanced by Na ions, coming from the sodium hydroxide used to dissolve compound **2** in the synthesis solution. Extraframework hydration water molecules can be easily removed by conditioning the sample over  $\text{P}_4\text{O}_{10}$  with the formation of an anhydrous phase. After equilibration at 75% relative humidity for several hours,

(6) Compound **1** was recently used to prepare a manganese(II) derivative with a compact pillared-layered structure: Stock, N.; Rauscher, M.; Bein, T. *J. Solid State Chem.* **2004**, *177*, 642–647.

## COMMUNICATION



**Figure 4.** Possible tailoring of the dimensions of the channels in the structures of **3** (a) and **4** (b) by using different tetraphosphonate building blocks. The elliptic shapes represent generic organic groups.

rehydration is fully reversible, assessing that the framework structure is maintained during the dehydration–rehydration process.

The strong analogies between the structures of **3** and **4** can be presumed as two different ways to covalently connect the same polymeric building unit by organic groups. In both of these two arrangements, the dimensions of the channels formed inside the structure depend on the size and geometry of the interlinking organic groups. This feature offers intriguing possibilities to obtain new open-framework compounds with a similar structure, in which cavities can be

tuned for specific purposes by selecting a proper organic group, as depicted in Figure 4.

Despite their open-framework structure, these first two examples showed a negligible surface area and porosity (by nitrogen adsorption and desorption experiments). Very likely, this is due to the nonrigid character of the interlinking groups, which cannot avoid the relaxation of the structure after the removal of hydration water molecules.

In conclusion, taking also into account the relative easiness with which the organic building blocks and their zirconium derivatives can be prepared, these compounds offer a new chance for the synthesis of open-framework materials with a tailor-made structure.

**Acknowledgment.** This research was supported by the Centro di Eccellenza on “Materiali innovativi nanostrutturati per applicazioni chimiche, fisiche e biomediche” (Project CLABO1P7BR).

**Supporting Information Available:** Synthetic procedures and characterization data (elemental and thermal analysis, ion exchange experiments, etc.), Rietveld plots, ORTEP drawings, and crystallographic information files for **3** and **4** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC052146A