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Preparation, Characterization, and Structure of Zirconium Fluoride Alkylamino-*N*,*N*-bis Methylphosphonates: A New Design for Layered Zirconium Diphosphonates with a Poorly Hindered Interlayer Region

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Abstract: This paper reports the preparation and characterization of the homologous series of layered zirconium fluoride *n*-alkylamino-*N*,*N*-bis methylphosphonates, of general formula $ZrF(O_3PCH_2)_2NHC_nH_{2n+1}$ ($n = 1, 2, 3, 4, 5, 6, 8, 9, 10$), in which the two phosphonic groups of each diphosphonate building block participate in the assembly of a single lamella, because they are joined to zirconium atoms belonging to the same layer. The crystal structure of one of the series of these zirconium diphosphonates, $ZrF(O_3PCH_2)_2NHC_5H_{11}$, has been solved "ab initio" by X-ray powder diffraction data. The structure is monoclinic, space group $P2_1/c$. The zwitterionic character of the diphosphonate moiety is a distinctive feature which acts as a structure-orienting factor, generating a layer framework which is different from the other structures known for zirconium phosphates and phosphonates. This compound undergoes a phase transition at 117 °C which involves a rearrangement of the interlayer alkyl chains. The structure of the high-temperature phase has been refined by the Rietveld method. Because only one organic residue is associated with two phosphonate tetrahedra, a poorly hindered interlayer region is formed, and alkyl chains bonded to adjacent layers are interdigitated. Preliminary experiments have shown that these compounds are able to intercalate organic molecules, such as *n*-alkanols, from very dilute water solutions.

Introduction

In recent years, zirconium phosphates and phosphonates have been extensively researched. Their characteristics make them very interesting both from a fundamental point of view and in many application fields.[1,2] They are easily obtained as low-dimensional, especially layered, solids having different structures, corresponding to different chemical features. A variety of functional groups, that can range from superacidic to basic, from lyophilic to highly hydrophilic, can be inserted in them by means of various procedures.[1-3] They are generally very insoluble compounds. This feature, although attractive for many potential applications, makes it difficult to deduce their structural characteristics. Large crystals prepared from zirconium phosphates or phosphonates are very rare, and structural characterizations are mostly from powder diffraction data.[4] Nevertheless, a number of different layered structures have already been solved using powder diffraction methods.[5] In many cases, these studies were crucial for the development of the chemistry of a given compound. For example, γ-zirconium phosphates and phosphonates were first prepared in the 1960s[6] and have been the object of growing interest since 1990,[1] just after the publication of the structure of γ-zirconium phosphate.[7] Zirconium diphosphonates, in which diphosphonate groups covalently join adjacent inorganic layers, are of special interest. A series of these compounds, named pillared layered zirconium diphosphonates, has been reported. An accurate control of the dimensions and reactivity of the interlayer space has been achieved by selecting the appropriate organic R group.[8]

This paper reports the investigation of a new series of layered zirconium diphosphonates, in which the two phosphonic groups of each diphosphonate building block participate in the assembly

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of a single lamella, being joined to zirconium atoms belonging to the same layer. The aim was to associate only one organic residue to each two phosphonate tetrahedra, with the consequent formation of layered compounds with an available space in a poorly hindered interlayer region. To obtain this, a series of alkylamino-*N*,*N*-bis methylphosphonates, in which the alkyl chain length varied from 1 to 10 carbon atoms, was used as building blocks. The crystal structure of one of these zirconium diphosphonates was solved by X-ray powder diffraction data. A new framework of the layers was found, which adds to the other main layered structures known for zirconium phosphates and phosphonates (α-, γ-, λ-, and ZrPMIDA types).[1,5] In this new structure, the zwitterionic character of the diphosphonic building blocks acted as a structure-orienting factor.

Experimental Section

Synthesis Procedures. Reagents. $ZrOCl_2 \cdot 8H_2O$ was a Merck Pro Analysi product. All of the other chemicals were Carlo Erba RPE grade.

Preparation of Diphosphonic Acids. The alkylamino-*N*,*N*-bis methylphosphonic acids, of formula $(H_2O_3PCH_2)_2NC_nH_{2n+1}$ (hereafter PCn) with $n = 1, 2, 3, 4, 5, 6, 8, 9$, and 10, were synthesized according to the Moedritzer−Irani method.[9]

After synthesis, the diphosphonic acids, which were obtained as white microcrystalline solids, were purified by recrystallization using ethanol as solvent. The solids were then characterized by the determination of their fusion temperatures, C, H, and N elemental analysis, acid−base titration, and X-ray powder diffraction qualitative phase analysis.

Preparation of Zirconium Diphosphonates. Zirconium fluoride aminoalkyl-*N*,*N*-bis methylphosphonates (hereafter ZrPCn) were prepared as follows: a clear solution containing 0.05 mol L^{-1} of Zr(IV), 0.1 mol L^{-1} of the diphosphonic acid, and 0.75 mol L^{-1} of hydrofluoric acid (1.25 mol L^{-1} for PC6−PC10) was prepared using a 1/2 (v/v) water−methanol mixture as solvent. The solution (typically 0.160 L) was maintained in a closed Teflon vessel at 80 °C until a white precipitate was formed. The reaction times ranged from 20 days (ZrPC1) to 1 h (ZrPC10). When a precipitate was formed in a time shorter than 24 h, the solid was left to stand in the mother liquor at 80 °C for at least 24 h. The precipitates were separated by centrifugation and washed four times with the water−methanol mixture. Finally, they were dried in an oven at 70 °C.

Analytical Procedures. The composition of all of the compounds prepared was determined by combining several analytical techniques.

Zirconium, phosphorus, and fluorine contents were determined as ZrO_2, phosphates, and fluorides, respectively, after mineralization of the zirconium salt. A 200 mg portion of the sample was mixed with an excess of equimolar Na_2CO_3 and K_2CO_3 mixture, put in a ceramic vessel, and gradually heated to 800 °C in an oven. The calcined solid was then recovered with water, filtered on paper, and washed to quantitatively transfer the soluble sodium and potassium phosphates formed into the washing water. Phosphate and fluoride amounts in this washing solution were determined by ion chromatography. The residual filtered solid was washed with 0.1 M hydrochloric acid to dissolve the excess alkaline carbonates, then washed with water, and finally calcined to ZrO_2, which was determined gravimetrically.

Fluorine was also determined using an alternative method. About 0.100 g of sample was refluxed for 3 h with 10 mL of 1 M NaOH up to complete hydrolysis. After being filtered and appropriately diluted, the solution was injected into the ion chromatographer.

Instrumental Procedures. C, H, and N elemental analysis was performed with a Carlo Erba 1106 Analyzer.

Ion chromatography was performed with a Dionex series 2000 i/sp instrument, using an IonPack AS4A column and a buffer solution, of the following composition: 1.7×10^{-3} M in $NaHCO_3$, 1.8×10^{-3} M in Na_2CO_3 (3.5×10^{-3} M for fluoride ions) as eluent.

Table 1. Crystal Data and Refinement Details for ZrPC5, Phase I and Phase II

	phase I	phase II
empirical formula	$ZrP_2FO_6NC_7H_{16}$	$ZrP_2FO_6NC_7H_{16}$
formula weight	382.4	382.4
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a/Å	13.1874(3)	14.341(2)
b/Å	8.8723(3)	8.869(2)
c/Å	10.9793(3)	10.932(1)
β/°	96.594(3)	94.51(1)
volume/Å^3	1276.10(6)	1386.1(3)
Z	4	4
T/°C	25	150
calculated density/g cm^{-3}	1.99	1.83
pattern range, 2θ/°	11−140	10−70
step scan increment, 2θ/°	0.02	0.02
step scan time/s	30	10
no. of data	6450	3052
no. of reflections	2427	600
no. of variables	85	76
R_p [a]	0.077	0.061
R_{wp} [b]	0.107	0.081
R_{F^2} [c]	0.054	0.102
χ[d]	2.84	2.15

[a] $R_p = \sum|I_o - I_c|/\sum I_o$. [b] $R_{wp} = [\sum w(I_o - I_c)^2/\sum w I_o^2]^{1/2}$. [c] $R_{F^2} = \sum|F_o^2 - F_c^2|/\sum|F_o^2|$. [d] $\chi = [\sum w(I_o - I_c)^2/(N_o - N_{var})]^{1/2}$.

Coupled thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were performed with a Netzsch STA490C thermoanalyzer under a 20 mL min^{-1} air flux with a heating rate of 5 °C min^{-1}.

^{31}P MAS NMR spectra were obtained with a Varian 400 MHz spectrometer by collecting undecoupled single pulse spectra (frequency 161.9 MHz, spinning rate 5600 Hz, reference 85% phosphoric acid).

X-ray powder diffraction (XRD) patterns for structure determination and Rietveld refinement of ZrPC5 at room temperature (Phase I) were collected according to the step scanning procedure with Cu Kα radiation on a Philips APD X'PERT diffractometer, PW3020 goniometer equipped with a bent graphite monochromator on the diffracted beam. 0.5° divergence and scatter slits and a 0.1 mm receiving slit were used. The LFF ceramic tube operated at 40 KV, 40 mA. To minimize preferred orientations, the sample was carefully sideloaded onto an aluminum sample holder with an oriented quartz monocrystal underneath.

XRD patterns for Rietveld refinement of ZrPC5 at 150 °C (Phase II) were collected with a Philips PW1710 diffractometer, equipped with an A. Paar HTK camera, under the same conditions used for Phase I. Further acquisition details are reported in Table 1.

Other XRD patterns were recorded using larger slits, a 0.03° 2θ step size, and a 1 s counting time in the 2−60° 2θ range.

Structure Determination and Refinement. ZrPC5, Phase I. A first determination of cell parameters was made using the TREOR90 program.[10] For this, a preliminary peak-profile fitting, using pseudo-Voigt functions for the determination of the position of Kα_1 maxima, was carried out.

Indexation gave the following monoclinic cell: $a = 13.194(2)$ Å, $b = 8.878(1)$ Å, $c = 10.984(1)$ Å, $\beta = 96.61(2)$° as the best solution (M(20) = 27). The refined unit cell parameters are reported in Table 1. The analysis of the indexed pattern clearly revealed the presence of the following limiting reflection conditions: $0k0$, $k = 2n$ and $h0l$, $l = 2n$, which suggested $P2_1/c$ as the probable space group. In addition, a systematic comparison of the number of peaks found and the number

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of possible peaks, in all monoclinic space groups using the Checkcell program,[11] estimated $P2_1/c$ as the best choice.

The structure was solved by direct methods with the EXPO program,[12] by which 10 of the 18 atoms of the asymmetric unit were detected. A series of Rietveld refinements alternated with Fourier difference maps, performed with the GSAS program,[13] revealed the positions of the remaining three oxygen atoms and all carbon atoms of the alkyl chain.

The whole structure was then refined with GSAS. Scale factor, background (12 terms cosine Fourier series), zero shift, cell parameters, and peak profile were first refined. Atomic parameters were then refined. All of the atoms were refined isotropically, and neutral atomic scattering factors were used. Thermal parameters of heavy atoms (Zr and P) were refined independently, while those of light atoms (F, O, N, and C) were initially set at reasonable values. They were then refined by constraining the program to apply the same shifts. The shape of the profile was modeled by a pseudo-Voigt function (eight parameters) in which a parameter for asymmetry at low angle was included.[14] A March−Dollase correction[15] along the *h*00 direction was applied for preferred orientation. However, a very small correction was necessary, as shown by the value of coefficient R_o, close to 1 (0.96). No correction was made for absorption. No geometric restraints on bond distances and angles were used. The first peak of the pattern, at about 6.7° 2θ, was excluded from the refinement because of its strong asymmetry. At the end of the refinement, the shifts in all parameters were less than their standard deviations.

ZrPC5 at 150 °C, Phase II. The structure of Phase II was refined with the Rietveld method, using the structural parameters previously determined for Phase I as the starting model. Thermal parameters were set at reasonable values and were not refined. Stereochemical restraints were introduced for bond distances (2.03(5) Å for Zr−O, 1.55(5) Å for P−O, 1.80(5) Å for P−C, 1.54(5) Å for C−C, and 1.55(5) Å for C−N bonds) to avoid divergence in the first stages of refinement. The statistical weight of these restraints was decreased to a small value as the refinement proceeded, but it was not possible to set it at zero, because of unrealistic light atom bond distances. The first peak of the pattern, at about 6.3° 2θ, was excluded from the refinement because of its strong asymmetry.

Results and Discussion

The diphosphonic acids used for the synthesis of the series of zirconium diphosphonates have the general formula $(H_2O_3PCH_2)_2NC_nH_{2n+1}$ and are amphiphilic species. Their hydrophilic character, and hence their solubility in water, decreases as *n* increases. After preliminary tests, we decided to use a water/methanol 1:2 v/v mixture as the solvent for all of the zirconium diphosphonate syntheses.

The reaction between zirconium and the selected phosphonic acids was expected to produce the layered compounds schematically shown in Figure 1.

Note that both of the phosphonate groups were expected to be bonded to the same layer, because of the geometrical features of the diphosphonate moieties. This model was substantially confirmed, with some important differences, which will be discussed later.

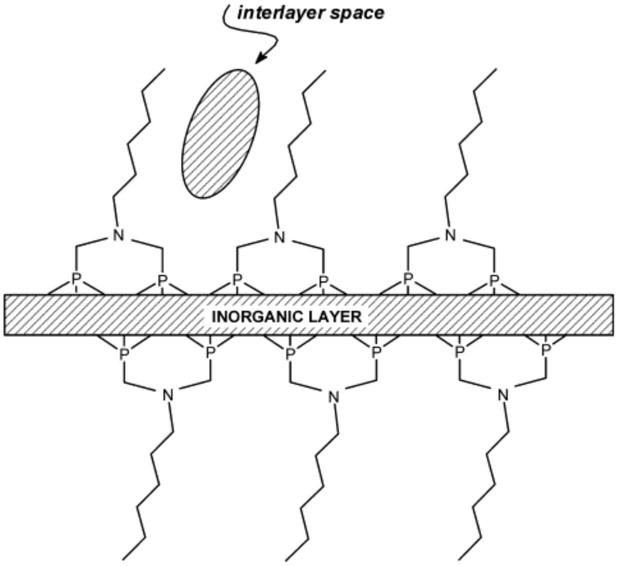

Figure 1. Schematic arrangement of a layered diphosphonate in which both phosphonic groups are bonded to the same face of the layer. The formation of a poorly hindered interlayer region is shown.

The ZrPCn samples obtained had a similar composition, consisting of a mole of diphosphonate and a mole of fluoride per mole of zirconium. The following general formula was derived for all of the compounds obtained: $ZrF(O_3PCH_2)_2NHC_nH_{2n+1}$. For all of the samples investigated, thermogravimetry experiments showed the absence of weakly held species, such as included or intercalated solvents. Titrations with sodium hydroxide of the solids obtained indicated the total absence of acidic protons. These data suggested the hypothesis that fluorine was coordinated to zirconium and the nitrogen of the amino group was protonated by a phosphonate group, as reported in the above general formula. The determination of the structure of ZrPC5 confirmed this hypothesis.

Most of the samples prepared were obtained as poorly crystalline powders, as assessed by XRD patterns. The patterns were typical of layered compounds being characterized by a strong peak at low 2θ values (which can be associated with the scattering of dense layer planes) and other much less intense peaks at higher 2θ values. Accordingly, the *d* values of the first intense diffraction peak represent the interlayer distances of the compounds. These *d* values, when plotted as a function of the number of carbon atoms, n_C, in the alkyl chain of the diphosphonic moiety, show a good linear correlation, that follows the equation d (Å) $= 9.28 + 1.04n_C$ (Figure 2). This means that each carbon atom added to the alkyl chain causes a constant increment (Δ) of the interlayer distance equal to 1.04 Å.

As already discussed elsewhere,[16] these observations clearly indicate a structural homology between the samples. They can be interpreted on the basis of the simple model depicted in Figure 1, in which the aminoalkyl tails are bonded to the inorganic zirconium phosphonate layers and directed toward the interlayer region. Alkyl chains bonded to adjacent layers are probably interdigitated and tilted, because of the small value of Δ, which is less than the expected value for one alkyl chain

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[11] Laugier, J.; Bochu, B. *LMGP-Suite*; ENSP/Laboratoire des Matériaux et du Génie Physique, BP 46. 38042 Saint Martin d'Hères, France.

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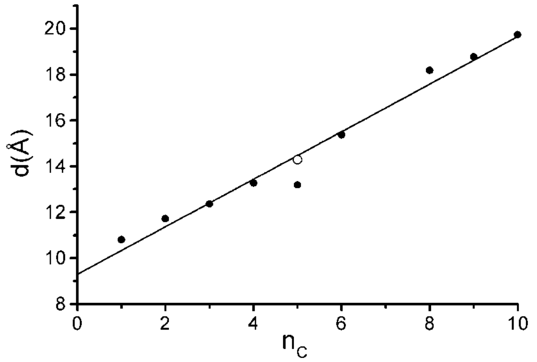

Figure 2. Dependence of the interlayer distance, *d*, of ZrPCn compounds vs the number of carbon atoms, n_C, in the alkyl chain of the diphosphonate group. ● refers to room-temperature data, while ○ refers to 150 °C.

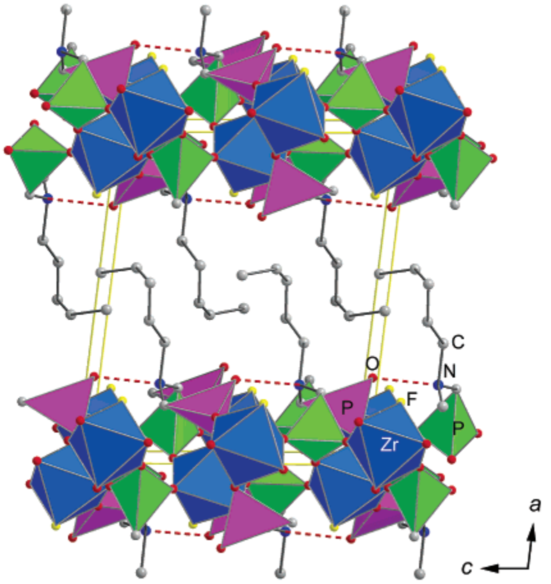

Figure 3. Polyhedral structure of ZrPC5, Phase I, viewed along the *b* axis. Zirconium octahedra are blue, tridentate phosphonates are green, and bidentate phosphonates are pink.

in extended conformation (1.27 Å/n_C). However, the solution of the structure of ZrPC5, the most crystalline sample of the series, showed important differences from this model.

Structure Description of ZrPC5, Phase I. Figure 3 shows a polyhedral representation of the structure of Phase I, while Figure 4 shows a connectivity detail.

Table 1 lists the crystal data and refinement details, and Figure 5 shows the final Rietveld and difference plot.

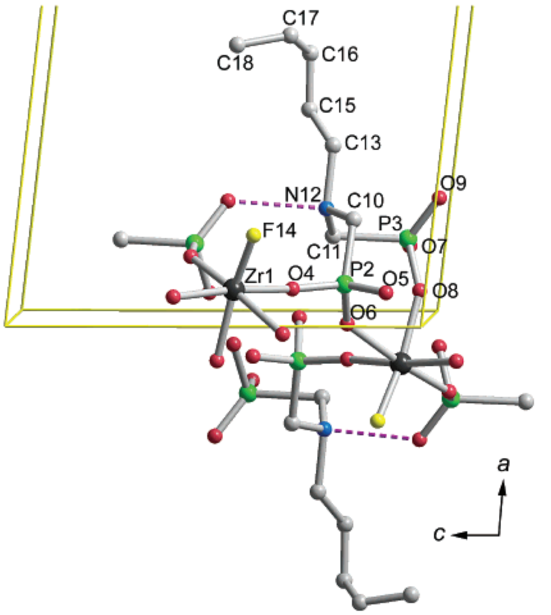

Figure 4. A detail of the structure of ZrPC5, Phase I, showing the connectivity of atoms.

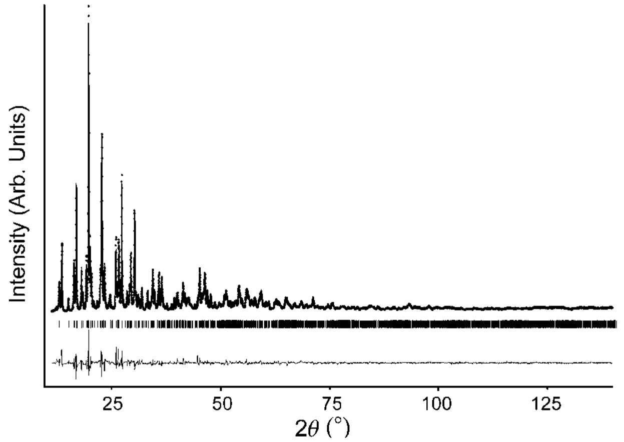

Figure 5. Rietveld and difference plot for ZrPC5, Phase I.

The structure is composed of two zirconium atoms placed in two parallel planes that are about 2.2 Å apart. They are octahedrally coordinated to five oxygen atoms bonded to five different phosphonate groups and one fluorine atom, which occupies the most external coordination position in relation to the layer surface. The five coordinating oxygens belong to five different tetrahedral phosphonate groups, so that each octahedron shares five corners with the five tetrahedra. Two phosphonate groups, cis-coordinated to zirconium, come from the same moiety, so that each zirconium atom is coordinated only to four diphosphonates. The two phosphonate heads of each diphosphonate group are nonequivalent. One of them acts as a tridentate bivalent group and is bonded to three different zirconium atoms, two of which belong to the nearest zirconium plane, and the third to the farthest plane. The phosphorus atom of this phosphonate group lies just inside the layer, approximately in the same plane containing the zirconium atoms faced to the diphosphonate group. The second phosphonate is more external and acts as a monovalent bidentate group, because it is bonded to two different zirconium atoms, which belong to two different planes. A third oxygen atom of this phosphonate head is not involved in the octahedral environment of zirconium, and it points toward the nitrogen atom of an adjacent diphosphonate group of the same layer. The O9···N12 distance is 2.68 Å, indicating that a hydrogen bond is present between the two atoms or that (more likely) the amino group is protonated by the phosphonate. We were not able to locate the hydrogen between N and O atoms by our diffraction data. However, some experimental data support the protonation hypothesis: no acidic groups were found in the solids by titration with sodium hydroxide, and single-crystal structural data of similar aminophosphonic systems show the same zwitterionic behavior.[17]

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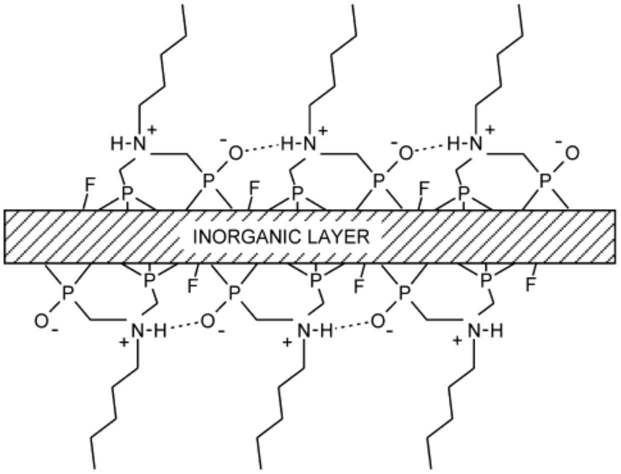

Figure 6. A schematic picture of the layer framework found for ZrPCn compounds, in which the zwitterionic character of the diphosphonate moiety is shown.

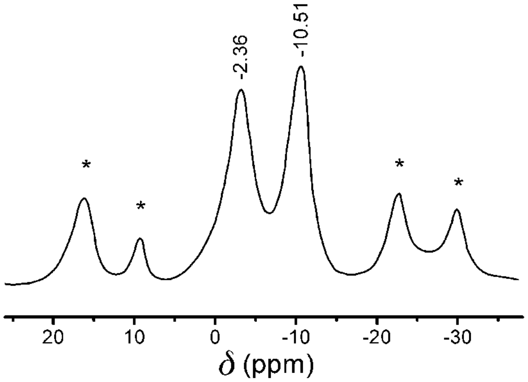

Figure 7. ^{31}P MAS NMR spectrum for ZrPC5. The signals marked with an asterisk are sidebands of the main signals.

Figure 6 is a scheme of the structure found, which shows the layer network more clearly.

We believe that this zwitterionic structural motif acts as a structure-orienting factor, inducing the formation of the atypical layer framework observed.

The O9···N12 interaction forces the phosphonate group to be external to the inorganic layer. Moreover, the protonation of the amino group induces the introduction of the fluoride anion, to complete the valence and coordination of zirconium.

The aminoalkyl tails point toward the interlayer regions from both sides of the inorganic layers. Alkyl chains bonded to adjacent layers are interdigitated. This is because the free area associated to each alkyl chain (48.6 Å^2, $a \times b/2$) is more than twice its estimated van der Waals cross section (18.6 Å^2).[18] To the best of our knowledge, this unusual feature has not been observed in any other zirconium phosphonate. In these alkyl chains, the nitrogen and the first three carbon atoms are close to a trans−trans conformation (N12−C13−C15−C16 torsion angle = 167.1°), while the last two carbon atoms are bent back probably to fill the whole space available (C13−C15−C16−C17 and C15−C16−C17−C18 torsion angles = 58.5° and 64.4°, respectively). Figure 7 shows the ^{31}P MAS NMR spectrum for Phase I. The presence of only two resonances (−2.4 and −10.5 ppm) with approximately the same area is in agreement with the structure found. The lower field resonance belongs to P2, which is connected with three metal atoms, while the higher field resonance derives from P3, which is connected with only two metal atoms and is more shielded. Similar spectra were obtained for the other zirconium diphosphonates prepared.

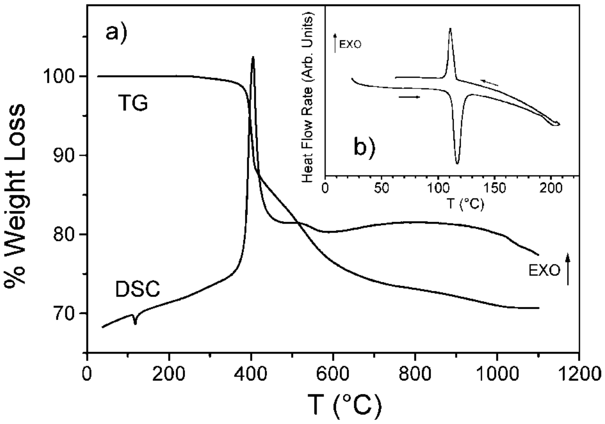

Figure 8. (a) TG and DSC analysis for ZrPC5. (b) DSC curve of a heating−cooling cycle in the temperature range 20−200 °C.

Thermal Behavior of ZrPC5. Figure 8a shows the TG and DSC curves for ZrPC5.

Weight starts to be lost at about 350 °C, when the organics begin to decompose. At the end of the analysis, at 1100 °C, only cubic ZrP_2O_7 was found. The DSC curve shows a sharp endothermic peak with a maximum at 117 °C, T_{onset} = 112 °C, and an associated enthalpic effect of 8.67 kJ/mol, with no weight loss and therefore because of a solid-state phase transition. The transition is reversible, even after many heating−cooling cycles. Figure 8b shows the DSC curve for a heating−cooling cycle in the range 20−200 °C. During the cooling process, the maximum of the exothermic peak is slightly shifted at a lower temperature (111 °C, T_{onset} = 108 °C), and the enthalpic effect is −8.44 kJ/mol. XRD patterns taken at 150 °C showed that the interlayer distance of the compound increased by more than 1 Å, from 13.2 to 14.3 Å. A structural model of the phase formed (Phase II) was obtained by the refinement of the room-temperature structure. The XRD data of this phase are not as good as those at room temperature, because of the high-temperature camera used, and especially the system for loading the sample, which has to be spread on a fixed platinum lamina. Figure 9 shows a picture of the refined structure.

Table 1 lists the crystal data and refinement details, while Figure 10 shows the final Rietveld plot.

In the high-temperature phase, the *a* axis (the direction of layer packing) is longer, and the *b* and *c* axes (parallel to the layers) are shorter than they are in the low-temperature phase. The O9···N12 distance is slightly increased (2.92 Å), and the alkyl chains are close to their extended conformation (torsion angles are now N12−C13−C15−C16 = 150.3°, C13−C15−C16−C17 = 162.8°, C15−C16−C17−C18 = 175.7°). These observations suggest that the thermal effect observed by DSC is associated with the loss of O9···N12 interaction, which produces a relaxation of the whole alkylamino residue and can explain its conformational change.

Finally, note that the interlayer distance of Phase II is close to the regression straight line of Figure 2 (○), thus justifying the anomalous low interlayer distance of Phase I. This also

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(18) Kitaigorodsky, A. I. In *Molecular Crystals and Molecules*; Loebl, E. M., Ed.; Academic Press: New York, 1973; p 61.

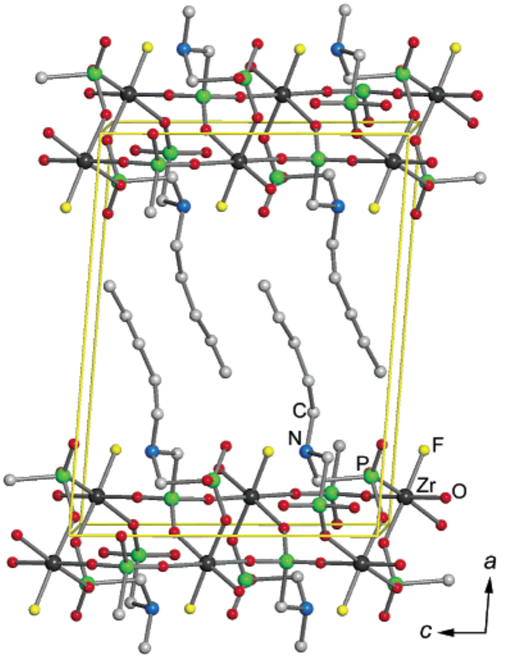

Figure 9. Ball-and-stick representation of the structure of ZrPC5, Phase II.

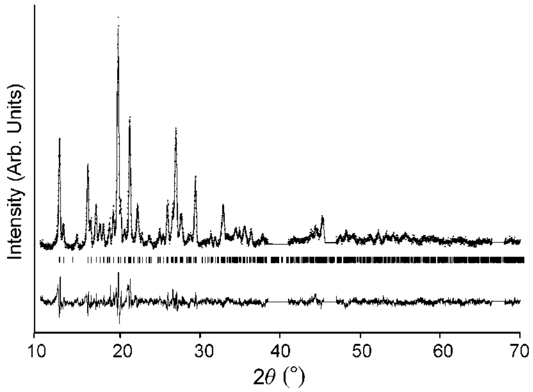

Figure 10. Rietveld and difference plot for ZrPC5, Phase II. The three pattern regions at about 39.8, 46.2, and 52.1° 2θ were excluded from the refinement because of the strong reflections of the platinum sample holder.

indicates that alkyl chains in all of the other ZrPCn compounds are close to their extended conformation, as observed in the high-temperature phase of ZrPC5.

No other ZrPCn compounds showed similar phase transitions, presumably because their low degree of crystallinity does not allow a sufficiently ordered interlayer region.

Other ZrPCn Compounds. Because of the strict homogeneity of composition and chemicophysical characteristics, all of the zirconium diphosphonates investigated may have the same kind of structure. Experiments are in progress to obtain more crystalline samples to confirm this hypothesis by means of a complete structural characterization.

Intercalation Reactions on ZrPCn Compounds. Even though potentially each organic pendant group has a very large free area around it (48.6 Å^2), the packing of the layers tends to fill this space, unless strong and directional interactions are created between adjacent layers. Because alkyl chains are neither sterically hindered nor rigid moieties, they are interdigitated and bent to find the best reciprocal contacts, and no permanently free space is available. However, this space could be recovered when these materials act as hosts for suitable species. Preliminary experiments using ZrPC5 and ZrPC8 have shown that these compounds can easily intercalate *n*-alkanols from very dilute water solutions (up to 1% v/v alkanol), with the formation of intercalation compounds with expanded basal spacings. Figure 11 shows the dependence of the interlayer distance of the intercalation compounds obtained for ZrPC8 as a function of the alkanol chain length, while Figure 12 shows a comparison between XRD patterns of ZrPC8 before and after intercalation of octanol from 1% v/v octanol in water.

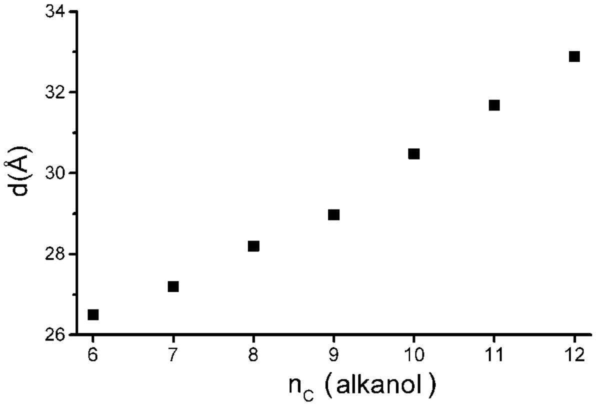

Figure 11. Interlayer distances of *n*-alkanol intercalation compounds of ZrPC8 as a function of the number of carbon atoms in the alkanol chain, n_C.

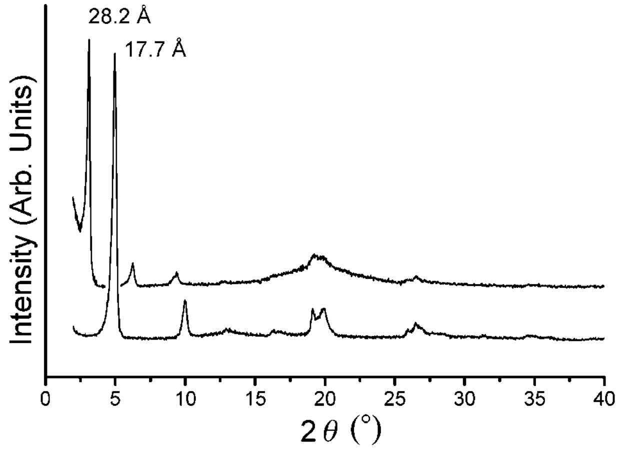

Figure 12. XRD patterns of (a) ZrPC8, (b) ZrPC8 after contact with a 1% v/v octanol in water solution.

Conclusion

A new class of zirconium diphosphonates has been prepared and characterized, in which the two phosphonic heads of each diphosphonate group are bonded to the same inorganic layer. They have a new layer framework which adds to the other main layered structures known for zirconium phosphates and phosphonates, that is, of α-, γ-, λ-, and ZrPMIDA types. The presence of only one organic residue per zirconium, as well as the large free area potentially available to each of these groups, make these compounds very interesting for incorporating functional species with selected properties by means of intercalation reactions and/or by varying the dimensions and reactivity of the organic groups bonded to the layers.

For these reasons, this class of compounds is expected to be as flexible and versatile as other well-developed zirconium phosphate structures for application in several fields, such as ionic or molecular recognition, protonic conductivity, and magnetooptical devices.

Acknowledgment. This work was supported by CNR. The authors wish to dedicate this paper to Prof. Giulio Alberti on the occasion of his 72nd birthday.

Supporting Information Available: Tables of fractional atomic coordinates, isotropic thermal parameters, selected bond lengths and angles for ZrPC5, Phase I and II (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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