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Anionic Ligand Exchange on $ZrPO_4Cl(dmso)$: Alkoxide and Carboxylate Derivatives

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This paper reports the preparation and characterization of a series of organic derivatives of $ZrPO_4Cl(CH_3)_2SO$ obtained by topotactic anion exchange of chloride ligands with several *n*-alkoxide (RO) and carboxylate groups (RCOO). Exchange with alkoxides, with an alkyl chain length from 2 to 8 carbon atoms, gave products of general formula $ZrPO_4RO(CH_3)_2SO$. In these derivatives alkoxide groups, covalently bonded to zirconium atoms via Zr–O bonds, point toward the interlayer region. Carboxylate derivatives, of general formula $ZrPO_4[(RCOO)(CH_3)_2SO]_{1-x}(OH\ H_2O)_x$, were obtained using benzoate ($x = 0$), nitrobenzoate ($x = 0.3$), and phenylacetate ($x = 0.2$) groups. The thermal behavior of these organic derivatives is discussed. Due to this reactivity, $ZrPO_4Cl(CH_3)_2SO$ is an attractive precursor for materials chemistry.

Introduction

Many layered solids are able to host several neutral or ionic species in the interlayer region, by means of intercalation or ion exchange reactions. In the resulting compounds, host−guest interactions are generally weak, being of van der Waals or polar type.

Layered zirconium phosphates (hereafter ZrP) are known to be good ion exchangers and intercalating hosts for cationic or polar species, since they usually bear acidic P−OH groups directed toward the interlayer region.[1] A special behavior is shown by $ZrPO_4[O_2P(OH)_2]\cdot 2H_2O$ (γ-ZrP). In this compound, the $O_2P(OH)_2$ groups, covalently bonded to zirconium on the external part of layers, can be replaced by other O_2PRR' groups by means of ligand exchange reactions. A large variety of zirconium phosphate phosphonates, of general formula $ZrPO_4O_2PRR'$, in which the organic groups are covalently bonded to the inorganic layers, has been prepared using soft conditions.[1,2] We demonstrated that the structure of inorganic layers does not change appreciably during these reactions occurring on the surface of γ-layers.[3] Therefore, these ligand exchange reactions are of topotactic type, and the approximate disposition of organic moieties that occupy the interlayer region can be easily predicted on the basis of general stereochemistry rules.

Following the work of Clearfield and co-workers,[4] we recently prepared a new layered zirconium phosphate, of formula $ZrPO_4Cl(CH_3)_2SO$ (hereafter λ-ZrP), in which zirconium atoms are coordinated by four phosphate groups in four equatorial positions lying on the layer plane and by a couple of anionic and neutral monodentate ligands, Cl^- and dimethyl sulfoxide (hereafter dmso), in trans-axial positions.[5] Due to the relative weakness of Zr−Cl bonds, we found that it is possible to replace chloride ligands with other inorganic anionic ligands, such as OH^-, sulfate, chromate, or molybdate, by simple topotactic exchange reactions of type

$$ZrPO_4Cl(dmso) + L^- \rightarrow ZrPO_4L(dmso) + Cl^-$$

in which the parent compound is dispersed in a solution of the corresponding anions to be exchanged.[6]

We found of interest to investigate the possibility to introduce organic groups covalently bonded to λ-ZrP layers,

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[1] (a) Clearfield, A.; Costantino, U. In *Comprehensive Supramolecular Chemistry*; Alberti, G., Bein, T., Eds.; Pergamon Elsevier Science Ltd.: Oxford, U.K., 1996; Vol. 7, p 107. (b) Alberti, G. In *Comprehensive Supramolecular Chemistry*; Alberti, G., Bein, T., Eds.; Pergamon Elsevier Science Ltd.: Oxford, U.K., 1996; Vol. 7, p 151. (c) Clearfield A. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley & Sons: New York, 1998; Vol 47, p 374.

[2] (a) Alberti, G.; Casciola, M.; Costantino U.; Vivani, R. *Adv. Mater*. **1996**, *8*, 291. (b) Alberti, G.; Murcia-Mascarós, S.; Vivani, R. *J. Am. Chem. Soc*. **1998**, *120*, 9291.

[3] Alberti, G.; Vivani, R.; Murcia Mascarós, S. *J. Mol. Struct.* **1998**, *469*, 81.

[4] Poojary, D. M.; Zhang, B.; Clearfield, A. *J. Chem. Soc., Dalton Trans.* **1994**, 2453.

[5] Alberti, G.; Bartocci, M.; Santarelli, M.; Vivani, R. *Inorg. Chem*. **1997**, *36*, 3574.

[6] Alberti, G.; Masci, S.; Vivani, R. *Inorg. Chem*. **2002**, *41*, 1913.

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and this work describes the preparation and characterization of alkoxide and carboxylate derivatives of λ-ZrP.

Experimental Section

Reagents. All reagents were C. Erba RPE grade. They were used without further purification.

Preparation of $ZrPO_4Cl(dmso)$. It was prepared as previously described.[6]

Preparation of Short-Chain Alkoxide Derivatives (Number of Carbon Atoms in the Alkyl Chain = 2−4). A 1 g amount of $ZrPO_4Cl(dmso)$ was contacted, under nitrogen, with 68 mL of 0.1 M *n*-tributylamine solution using the corresponding anhydrous *n*-alkanol as solvent. The reaction mixture was maintained in a closed glass container at a temperature of 20 °C lower than the alkanol boiling point, for 4 days. The solid was then separated by centrifugation, washed twice with 100 mL of alkanol, dried at 70 °C for 2 h, and finally stored under nitrogen atmosphere.

Preparation of Long-Chain Alkoxide Derivatives (Number of Carbon Atoms in the Alkyl Chain = 5−8). For these derivatives, the λ-butoxide derivative, $ZrPO_4C_4H_9O(dmso)$, prepared as described above, was used as precursor. A 1 g amount of $ZrPO_4C_4H_9O(dmso)$ was contacted, under nitrogen, with 68 mL of 0.1 M *n*-tributylamine solution using the corresponding anhydrous *n*-alkanol as solvent. The reaction mixture was maintained in a closed vessel at 80 °C, for 4 days. The solid was then treated as described above.

Anal. Calcd (found) for $ZrPO_4C_4H_9O(CH_3)_2SO$: Zr, 26.97 (27.2); P, 9.17 (9.20); C, 21.29 (20.95); H, 4.73 (4.52). Similar results were obtained for all other alkoxide derivatives.

Preparation of Carboxylate Derivatives. A 1 g amount of $ZrPO_4Cl(dmso)$ was contacted with 68 mL of a 0.05 M RCOOH ($R = C_6H_5$, $C_6H_4NO_2$, $CH_2C_6H_5$) and 0.05 M RCOONa solution using a 1:1 v/v dmso−water mixture as solvent. The solid was maintained in this solution for 3 days at 75 °C, and then it was separated by centrifugation and washed twice with 100 mL of a 1:1 v/v dmso−water mixture. Finally it was dried at 80 °C.

Anal. Calcd (found) for $ZrPO_4C_6H_5CO_2(CH_3)_2SO$: Zr, 23.68 (23.54); P, 8.05 (7.95); C, 28.04 (27.84); H, 2.86 (3.22).

Characterization of the Products. The zirconium content of samples was determined gravimetrically by dissolving a weighed amount (0.150 g) in a few drops of concentrated HF, followed by precipitation with Cupferron and subsequent calcination to ZrO_2.

Phosphates and chlorides were determined by ion chromatography. About 0.100 g of sample was refluxed for 3 h with 10 mL of 1 M NaOH; after filtration and suitable dilution, the solution was injected into a Dionex series 2000 i/sp instrument, using an IonPack AS4A column and a buffer solution, with composition 1.7×10^{-3} M $NaHCO_3$ and 1.8×10^{-3} M Na_2CO_3, as eluent.

Thermogravimetric analysis (TG) was carried out in air on a Stanton Redcroft STA 780 apparatus from room temperature to 1100 °C at 5 °C/min heating rate.

Carbon and hydrogen elemental analysis was performed by a Carlo Erba 1106 analyzer.

FT-IR spectra were recorded using a Bruker JFS V FT-IR spectrometer, in the 400−4000 cm^{-1} spectral range. The samples were prepared as pressed pellets in anhydrous KBr.

J-modulated ^{13}C liquid NMR spectra of the samples were obtained by a Bruker DPX 200 spectrometer. About 50 mg of sample was dissolved in a few drops of concentrated HF and 0.5 mL of D_2O.

X-ray powder diffraction (XRD) patterns were measured using a Philips APD X′PERT diffractometer using the Cu Kα radiation, with a 0.03° 2θ step size and 1 s counting time in the 2−40° 2θ range at room temperature. Unit cell parameters have been first determined on the basis of 200 and 00*l* reflections, and then they were refined using the CELREF program.[7] Finally a whole profile fit, using the Le Bail method, has been performed with the GSAS program.[8]

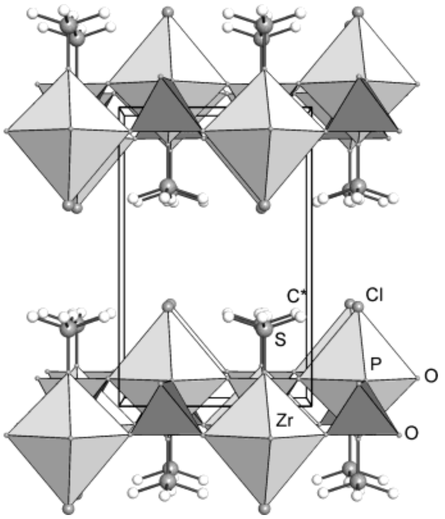

Figure 1. Structure of $ZrPO_4Cldmso$. Asterisk indicates methyl groups of dmso having occupancy 0.5.

Results and Discussion

Alkoxide Derivatives of λ-ZrP. Figure 1 shows the structure of a λ-ZrP layer. The unit cell is tetragonal, space group *P*4/*n*, with parameters $a = 6.5955(1)$ Å and $c = 10.2422(4)$ Å.[6]

Chlorine atoms occupy an external position with respect to the layer surface and are more exposed than the contiguous dmso sites. Different from other zirconium phosphates, the layers of λ-ZrP do not bear acidic or strongly polar groups. Therefore, it is expected that this compound cannot intercalate guest species very easily. In agreement to this, any intercalation compound of λ-ZrP is today known, and when the solid was suspended in pure alkanols, no intercalation reaction occurred, even under heating. On the other hand, we showed that this compound is able to exchange chlorine atoms with other anionic species, and alkoxide ions could be exchanged with reactions of type

$$ZrPO_4Cl(dmso) + RO^- \rightarrow ZrPO_4RO(dmso) + Cl^-$$

However, alkoxide ions are very strong Brönsted bases, and the concentration of the free anion in pure alkanol is, generally, extremely low. We found that this reaction can be promoted provided that the RO^- concentration in the contact solution is increased. Preliminary experiments have been performed using the *n*-butoxide/*n*-butanol system. The preparation of a butoxide derivative has been achieved by three independent routes, which consisted in dispersing $ZrPO_4Cl(dmso)$ in an anhydrous butanol solution of (a) KOH,

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

(8) Larson, A. C.; von Dreele, R. B. *Generalized Crystal Structure Analysis System*; Los Alamos National Laboratory: Los Alamos, NM, 2001.

(b) sodium butoxide, or (c) an alkylamine. However, among them, the use of a *n*-tributylamine solution was preferred. In fact, the use of KOH hydroxyl ions, other than to favor the deprotonation of the alkanol, was found to activate the direct OH/Cl exchange on λ-ZrP, with the partial conversion into the undesired $ZrPO_4OH$dmso product; furthermore, tributylammonium chloride, which is formed during the RO/Cl exchange reaction using tributylamine, is more soluble in the alcoholic medium than sodium or potassium chloride formed when using RONa or KOH solutions, respectively. These inorganic salts were collected as solid phases, mixed with the λ-alkoxide derivative. Finally, among other alkylamines, tributylamine was selected because of its high basicity and large dimensions that prevented a direct reaction with the host compound. During this investigation we have found that small amines are able to replace dmso, bonded to zirconium atoms in λ-ZrP, by a topotactic neutral ligand exchange reaction. This process is faster in λ-alkoxide derivatives, where the interlayer region is expanded due to the presence of RO residues. Therefore, when these amines are used as bases to favor alkanol deprotonation for RO/Cl anion exchange reactions, an appreciable amount of amine/dmso exchange was also observed. A deeper investigation on this interesting behavior will be reported elsewhere. However we found that this reaction can be avoided when using a large amine, such as tributylamine, very likely because it does not meet the steric requirements of λ-ZrP sites.

J-modulated ^{13}C liquid NMR of a sample dissolved in HF confirmed the absence of amines after the reaction and, in the same time, the presence of both alkoxide and dmso in the exchanged solid, while ion chromatography revealed the total absence of chlorides.

The RO/Cl exchange reaction in the presence of 0.1 M tributylamine occurred in one step, as assessed by XRD patterns, which showed that the $ZrPO_4Cl$(dmso) phase gradually disappeared while the amount of $ZrPO_4RO$(dmso) phase gradually increased. This reaction needed about 4 days for the full conversion in ethoxide, propoxide, and butoxide derivatives, while for the higher alkoxides (from pentoxide to octanoxide) times increased considerably. Therefore, we decided to prepare the long-chain alkoxide derivatives starting from the preenlarged butoxide derivative, $ZrPO_4C_4H_9O$(dmso), as precursor. Reaction times were thus limited to 4 days in all the syntheses. All the alkoxide derivatives from 2 to 8 carbon atoms in the alkyl chain were obtained as pure phases, with composition $ZrPO_4RO$(dmso). Their XRD patterns are typical of layered materials (Figure 2).

The *d* values of the strong peak at low 2θ values can be therefore associated with the interlayer distance. These *d* values, when plotted as a function of the number of carbon atoms, n_C, in the alkyl chain of alkoxide groups, show a good linear correlation that follows the equation

$$d\ (\text{Å}) = 2.0n_C + 7.7 \qquad (1)$$

This plot is reported in Figure 3.

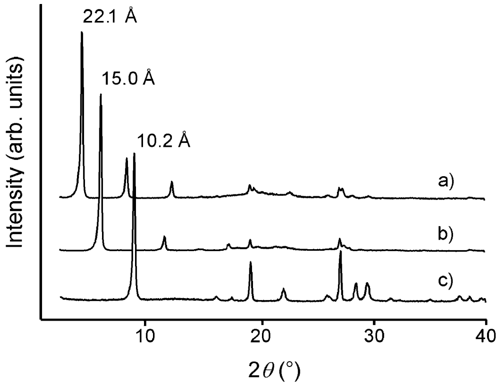

Figure 2. XRD patterns of eptanoxide (a) and butoxide (b) derivatives of λ-ZrP compared to that of the parent compound $ZrPO_4Cl$(dmso) (c).

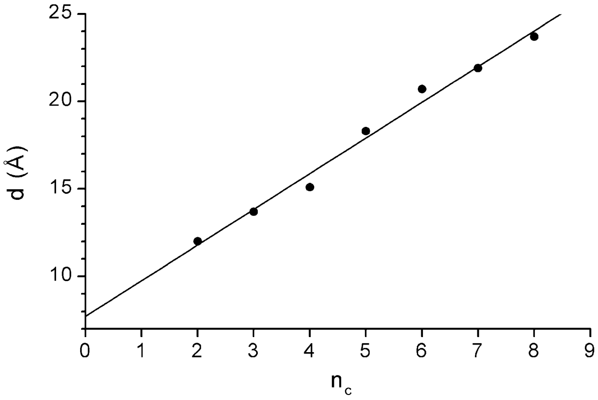

Figure 3. Interlayer distance of alkoxide derivatives of λ-ZrP as a function of the number of carbon atoms in the alkyl chain.

If we reasonably assume that the process cannot appreciably change the structure of the inorganic backbone of layers, some useful information on the arrangement of alkyl groups can be derived. Each carbon atom added to the alkyl chains causes a constant increment (Δ) of the interlayer distance equal to 2.0 Å. Therefore, the alkyl chains in the different samples should be all in the same conformation that can be reasonably assumed to be their all-trans conformation. Under this model, the interlayer distances of different samples should follow the equation

$$d\ (\text{Å}) = mn_C 1.27 \sin \alpha + B \qquad (2)$$

where *m* is the number of monomolecular films in which the chains are arranged between the layers and 1.27 Å is the increment in length for an all-trans alkyl chain per each additional carbon atom.[9] By the combination of eqs 1 and 2, $\Delta = 2.0 = m1.27 \sin \alpha$. From composition data *m* must be equal to 2, and α can be estimated to be about 52°. This value is close to that calculated (55°) for an alkyl chain in trans conformation with the first Zr−O bond perpendicular to the plane of layers and a tetrahedral Zr−O−C angle. From these data it is possible to build a structural model in which alkoxide groups are coordinated to zirconium atoms belonging to a λ-type layer and are directed toward the interlayer region from both sides of layers. Figure 4 shows a schematic model of the hexanoxide derivative of λ-ZrP.

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(9) (a) Lagaly, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 575. (b) Costantino, U.; Vivani, R.; Zima, V.; Benes, L.; Melánová, K. *Langmuir* **2002**, *18*, 1211.

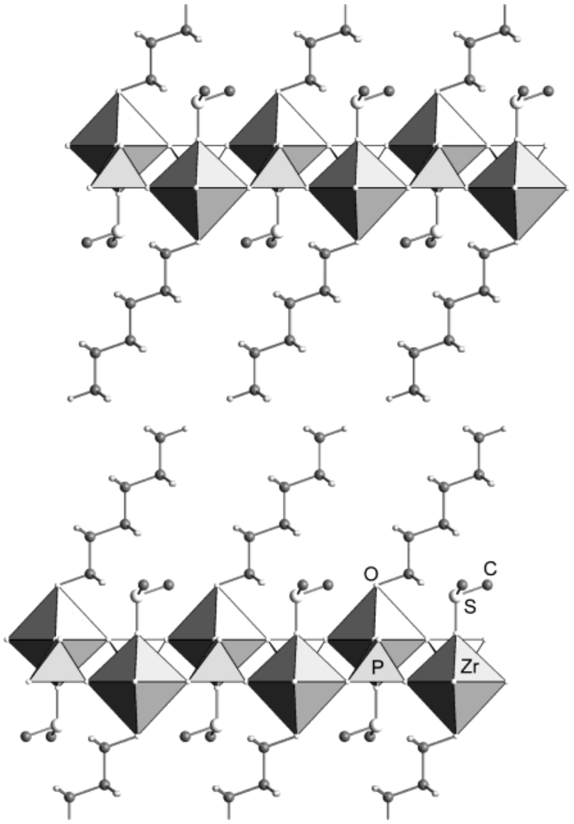

Figure 4. Schematic model of the structure of the hexanoxide derivative of λ-ZrP.

The *B* parameter of eq 2 is a constant and represents the interlayer distance of the structural residue when $n_C = 0$, which roughly corresponds to the presence of one hydroxyl group in the alkoxide site.

Alkoxide derivatives are obtained as poorly crystalline compounds, as assessed by their XRD patterns (Figure 2). Although these patterns are broadened and not suitable for structural analysis, we found that they are consistent with tetragonal unit cells of λ-type, that is with the *a* value of about 6.6 Å and the *c* parameter corresponding to the interlayer distance. For example, XRD pattern of the butoxide derivative can be indexed with the tetragonal unit cell $a = 6.601(1)$ Å and $c = 15.016(3)$ Å, and for the eptanoxide derivative $a = 6.607(1)$ Å and $c = 22.115(3)$ Å. Figure 5a shows the whole profile fit for the butoxide derivative pattern.

Therefore, in agreement with the hypothesis of a topotactic process, the replacement of chlorides with alkoxide ions, and even the successive replacement of short-chain with long-chain alkoxides, did not change appreciably the inorganic framework of layers.

Due to the high reactivity of the basic alkoxide groups, these derivatives are not stable in air. A slow conversion into the hydroxyl derivative, $ZrPO_4OH(dmso)$, was observed, due to the reaction with water coming from air humidity. On the other hand, alkoxide derivatives can be used as preenlarged substrates in which large anionic species can be introduced more easily than in the parent compound. In a recent paper we successfully used the butoxide derivative of λ-ZrP as a precursor for the introduction of a large magnetic moiety (a nitronyl nitroxide radical) inside this structure.[10]

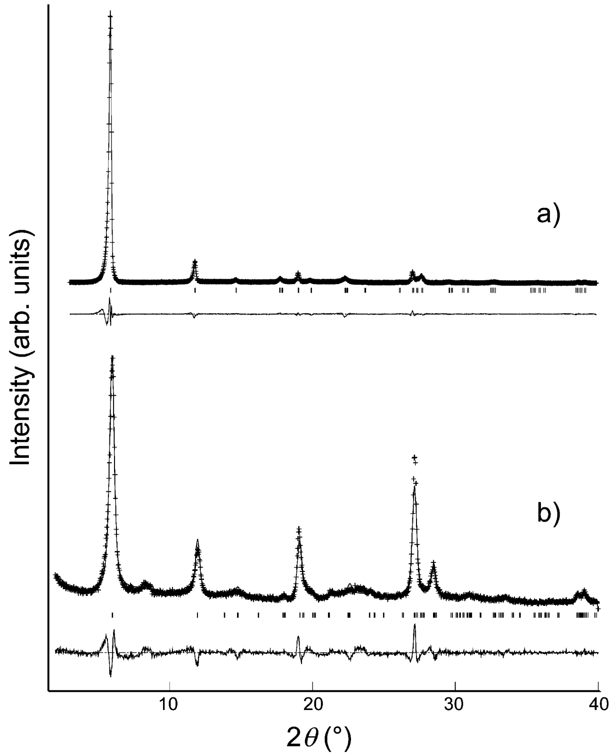

Figure 5. Whole profile fit, with the Le Bail method, for the butoxide derivative (under the $P4/n$ space group, $R_p = 0.104$) (a) and for the benzoate derivative of λ-ZrP (under the $P4_2/n$ space group, $R_p = 0.108$) (b).

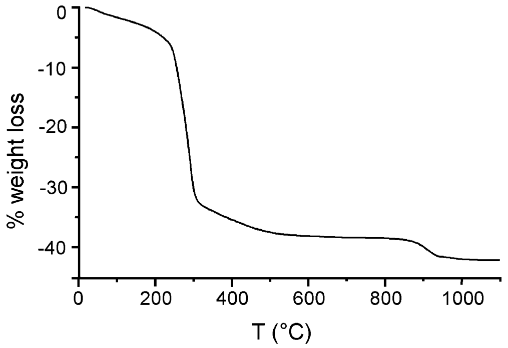

Figure 6. TG curve for the butoxide derivative of λ-ZrP.

Thermal Behavior. Figure 6 shows the TG curve of the butoxide derivative of λ-ZrP. Weight loss starts at about 200 °C, with the unresolved loss of both butoxide and dmso moieties. At the end of the analysis, at 1100 °C, the formation of an equimolar mixture of zirconium oxide and zirconium pyrophosphate was assumed, according to the following reaction of decomposition:

$$ZrPO_4C_4H_9O(dmso) + nO_2 \rightarrow 1/2ZrO_2 + 1/2ZrP_2O_7 + \text{gaseous products}$$

The calculated % weight loss is 43.8%, in good agreement with that experimentally found (42.3%). TG curves for all other alkoxide derivatives are in agreement with this model.

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(10) Caneschi, A.; Gatteschi, D.; Vaz, M. G. F.; Costantino, U.; Nocchetti, M.; Vivani, R. *Inorg. Chim. Acta* **2002**, *338*, 127.

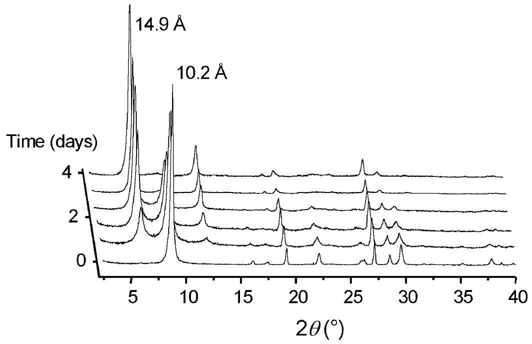

Figure 7. Evolution, as a function of reaction time, of XRD patterns for the product of benzoate/chloride exchange reaction on λ-ZrP.

Carboxylate Derivatives of λ-ZrP. (a) Benzoate Derivative. Carboxylate/Cl exchange reaction on λ-ZrP was first tested with benzoate groups, by contacting the parent compound with the free acid or one of its salt solutions, using several solvents. While the reaction was extremely slow in pure organic solvents, we found that the use of aqueous solvents and the increase of the free benzoate fraction (obtained by the addition of its salt forms) improved the exchange rate. On the other hand, a certain degree of hydrolysis on the sample was often found, because of the concomitant OH/Cl exchange reaction. Best conditions were the use of an equimolar mixture of benzoic acid and sodium benzoate in 1:1 v/v water−dmso mixture as solvent, at 75 °C, in which the reaction

$$\mathrm{ZrPO_4Cl(dmso)} + \mathrm{C_6H_5COO^-} \rightarrow \mathrm{ZrPO_4C_6H_5COO(dmso)} + \mathrm{Cl^-}$$

was completed in about 3 days. The reaction occurred in one step, with the gradual conversion of the parent compound ($d = 10.2$ Å) into the benzoate phase ($d = 14.9$ Å), as shown by XRD pattern of the product, taken at different times, reported in Figure 7.

The final product was pure, with the composition $\mathrm{ZrPO_4C_6H_5COO(dmso)}$ (compound **I**). Figure 8 shows a hypothetical model of the benzoate derivative, built up under the hypothesis that the structure of λ-layers does not appreciably change due to the exchange reaction. As for alkoxide derivatives, the crystallinity degree of this product is not sufficient for a complete structural analysis. However, we found that the XRD pattern of this compound is compatible with the tetragonal cell of λ-type with $a = 6.585(1)$ Å and $c = 29.702(7)$ Å (see Figure 5b), that is with the a parameter similar to that of $\mathrm{ZrPO_4Cldmso}$, while the c parameter is the double of the interlayer distance. The interlayer distance of this derivative, 14.9 Å, is now changed according to the increased dimensions of the anionic ligands bonded to zirconium.

Different from alkoxide derivatives, carboxylate derivatives are stable in air at room temperature, very probably because of the low basic strength of carboxylate groups.

Thermal Behavior. Figure 9 shows the TG curve for **I**. Weight loss is composed of two well-defined steps. The first step occurs between 200 and 250 °C, temperature at which the sample reaches a constant weight. This first step corresponds to a weight loss of 20.50% and is ascribed to the loss of 1 mol of dmso/mol of zirconium. The compound obtained after heating for 2 h at 220 °C had the composition $\mathrm{ZrPO_4C_6H_5COO}$ (hereafter **II**) and, once formed, is stable from room temperature up to about 300 °C. The loss of dmso causes a change of the interlayer distance from 14.9 to 13.2 Å, at room temperature, as shown by the XRD pattern (Figure 10). The second step of weight loss starts at about 400 °C and can be ascribed to the decomposition of organics. At the end of the analysis, at 1100 °C, an equimolar mixture of $\mathrm{ZrO_2}$ and $\mathrm{ZrP_2O_7}$ was formed according to the following process:

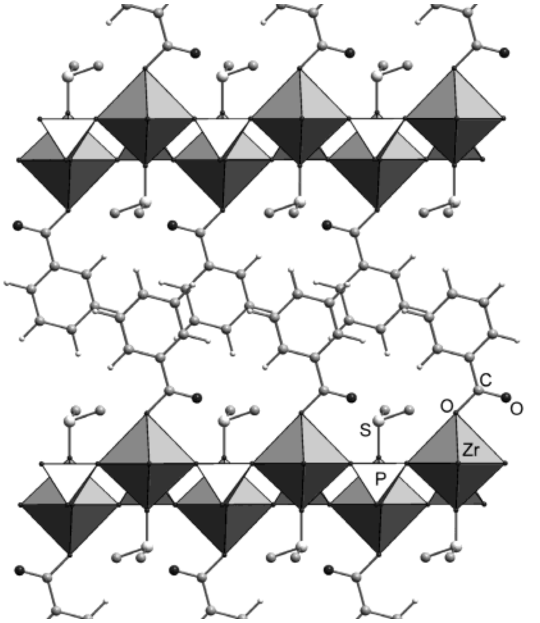

Figure 8. Schematic model of the structure of the benzoate derivative of λ-ZrP.

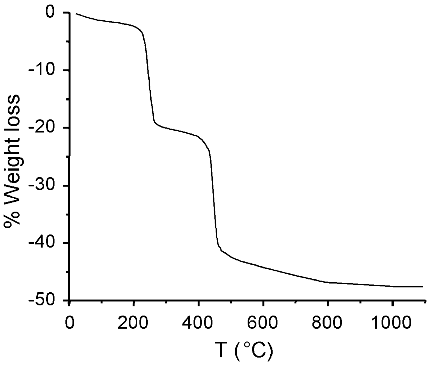

Figure 9. TG curve for the benzoate derivative of λ-ZrP.

$$\mathrm{ZrPO_4C_6H_5COO(dmso)} \rightarrow \mathrm{ZrPO_4C_6H_5COO} + \text{gaseous products} \rightarrow 1/2\mathrm{ZrO_2} + 1/2\mathrm{ZrP_2O_7} + \text{gaseous products}$$

The calculated weight loss is 49.58%, in good agreement with that found experimentally (47.50%).

FT-IR Study. FT-IR analysis confirms composition data. Figure 11a,b shows IR spectra of **I** and **II**, respectively. The spectrum of the parent compound is also reported for comparison. Spectra of parent compound and **I** show the

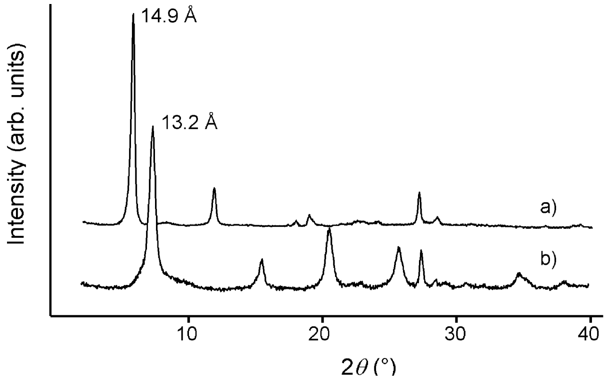

Figure 10. XRD patterns of the benzoate derivative of λ-ZrP before (a) and after heating at 220 °C for 2 h (b).

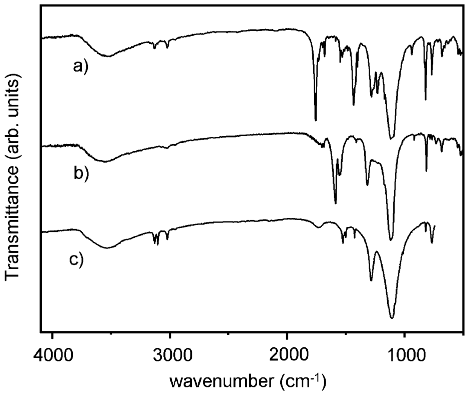

Figure 11. FT-IR spectra of the benzoate derivative of λ-ZrP before (a) and after heating at 200 °C for 2 h (b). The spectrum of $ZrPO_4Cl(dmso)$ is also reported for comparison (c).

typical bands around 3000 cm^{-1}, ascribed to C−H stretching vibration of dmso. These bands are absent in **II**, confirming the loss of dmso.

The sharp band at 1657 cm^{-1} in I is due to C=O stretching vibration of carboxylate group. This band is shifted at lower frequency in **II** (1488 cm^{-1}). In this sample, a further band is present, at 1454 cm^{-1}. These data might be interpreted on the basis of the changes in the coordination of carboxylate groups by metal atoms, due to thermal loss of dmso. Before dmso loss, zirconium atoms are trans coordinated by dmso and benzoate groups, these latter acting as monodentate (η^1) ligands, as shown in the model of Figure 8. The presence of a sharp band at 1334 cm^{-1}, which is probably due to the C−OZr stretching vibration, may support this model. After the loss of dmso, zirconium atoms remain unsaturated, and there is sufficient room to coordinate benzoate groups as bidentate (η^2) ligands, as schematically shown in Figure 12. This bonding condition implies that the two carboxylate C−O bonds are almost equivalent, with a bond order less than two. Therefore, the two bands at 1488 and 1454 cm^{-1} may be ascribed to antisymmetric and symmetric stretching vibrations, respectively, of bidentate carboxylate groups.[11] This change in coordination of carboxylate groups, from η^1 to η^2, tends to saturate zirconium coordination sphere and may justify the stability of **II**. However, in the absence of accurate structural data, we cannot exclude any other hypothesis.

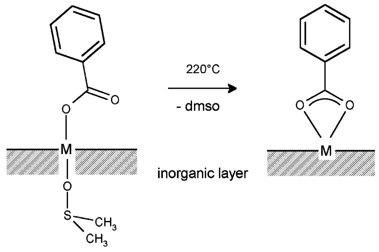

Figure 12. Hypothetical change in the benzoate−metal atom bonding before and after dmso loss, at 220 °C, for the benzoate derivative of λ-ZrP.

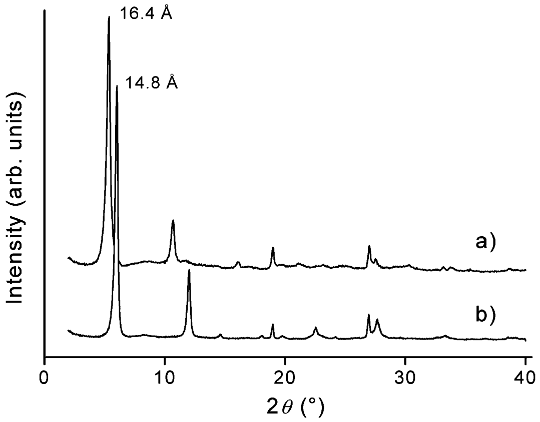

Figure 13. XRD patterns of phenylacetate (a) and 2-nitrobenzoate (b) derivatives of λ-ZrP.

The low-frequency regions of IR spectra of benzoate derivatives are dominated by phosphate vibration bands, while the sharp bands around 700 cm^{-1} may be assigned to aromatic C−H out-of-plane bending vibrations.

(b) Other Carboxylate Derivatives. On the basis of benzoate exchange, two other carboxylate groups were successfully exchanged of λ-ZrP, namely 2-nitrobenzoate and phenylacetate groups, giving rise to the following derivatives: $ZrPO_4[C_6H_4(NO_2)COO(dmso)]_{0.7}[OH\ H_2O]_{0.3}$ and $ZrPO_4[C_6H_5CH_2COO(dmso)]_{0.8}[OH\ H_2O]_{0.2}$. In both derivatives a small amount of hydrolysis, that is the exchange of chlorine atoms and dmso groups by hydroxyl and water, respectively, was found by chemical analysis. However, XRD patterns of these two derivatives clearly show the presence of only one phase (Figure 13). Very likely, these hydrolyzed groups are desordered in the structure and/or they form a small amount of amorphous phase not detected by XRD analysis.

The amount of hydrolysis is higher for nitrobenzoate derivative, probably due to the lateral steric hindrance of nitrobenzoate groups that prevents a full exchange. The interlayer distance of this derivative was 14.8 Å. As expected, this value is close to that of the benzoate derivative, because the nitro group, in the *ortho* position, does not evidently contribute to the steric hindrance along the *c* axis. On the contrary, the interlayer distance of phenylacetate derivative is higher, 16.4 Å, due to the increased dimensions of this group along the *c* axis.

Thermal behaviors of these two derivatives are close to that already described for the benzoate derivative: dmso is lost in a well-defined step, in the 200−250 °C temperature range, with the formation of a stable compound. FT-IR

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(11) Nakamoto, K. *Infrared spectra of inorganic and coordination compounds*; John Wiley & Sons: New York, 1963.

spectra, before and after dmso loss, show similar features that can be analogously discussed.

Conclusion

This work shows that alkoxide and carboxylate groups can be successfully introduced in λ-ZrP by topotactic ligand exchange, with the formation of two distinct classes of organic derivatives. It is likely that other classes of organic derivatives can be also formed using different anionic ligands. This reactivity can be useful for the preparation of solids containing in the interlayer region a vast variety of functionalized organic groups.

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