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Layered Zirconium Phosphate Chloride Dimethyl Sulfoxide as a Two-Dimensional Exchanger of Anionic Ligands. Part I. Substitution of Chloride with Inorganic Monodentate Ligands

Giulio Alberti,* Silvia Masci, and Riccardo Vivani

Department of Chemistry, University of Perugia, via Elce di Sotto, 8, 06123 Perugia, Italy

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Crystalline $ZrPO_4Cl(CH_3)_2SO$ was prepared by direct precipitation in the presence of oxalic acid as a zirconium complexing agent. The structure of $ZrPO_4Cl(CH_3)_2SO$, refined with the Rietveld method using X-ray powder diffraction data, was confirmed to be close to that of the compound prepared using γ-zirconium phosphate as a precursor. Chloride anions directly bonded to zirconium were found to act as weak ligands; this made possible their replacement with other monodentate anionic ligands. The preparation and a preliminary characterization of a series of inorganic derivatives obtained by topotactic replacement of Cl with OH, Br, MSO_4 (M = H, NH_4, Na), $NaMoO_4$, and $HCrO_4$ anions is reported. The possibility of replacement of chloride also with organic anions, such as alkoxides and carboxylates, and the possibility of substituting also dimethyl sulfoxide with other neutral ligands, as shown by preliminary study, makes $ZrPO_4Cl(CH_3)_2SO$ a useful and very flexible precursor for materials chemistry.

Introduction

The layered structures of many metal phosphates can be seen as formed by octahedra–tetrahedra building block combinations in which the metal, usually octahedrally coordinated, shares its corners or edges with tetracoordinated oxyanions of phosphorus. By limiting our attention to zirconium, which is the most investigated tetravalent metal, two main layered structures are known, usually indicated as α- and γ-zirconium phosphates (hereafter α- and γ-ZP).[1–3] Their organic derivatives, also known as α- and γ-zirconium phosphonates, have been prepared for long time,[4,5] and their cation exchange, intercalation, and proton conduction properties are now documented by an extensive literature.[6,7]

More recently, two new layered compounds, $ZrPO_4F(CH_3)_2SO$ and $ZrPO_4Cl(CH_3)_2SO$, were reported. The former compound was obtained by Clearfield et al.[8] by a direct hydrothermal synthesis using dimethyl sulfoxide (dmso) as solvent; the latter was prepared in our laboratory by replacement of the bidentate anionic $H_2PO_4^-$ ligands of γ-ZP, $ZrPO_4H_2PO_4$, with couples of a monodentate anionic (Cl^-) and a neutral ligand (dmso).[9] Both compounds crystallize in the tetragonal system, space group *P*4/*n*. Their layer is composed of two planes of zirconium atoms octahedrally coordinated. Four equatorial positions, lying in the layer plane, are occupied by four oxygen atoms of four different tetrahedral PO_4 groups. The remaining axial positions, perpendicular to the layer, are occupied by fluoride or chloride anions and dmso as a neutral ligand.

Preliminary research performed in our laboratory clearly showed that both anionic and neutral ligands of $ZrPO_4$-Cldmso can be topotactically replaced by a variety of other ligands, generating thus a large family of derivative compounds with the same type of layered structure. On the other hand, we found that the fluoride derivative was unreactive for similar topotactic replacements. The layered derivatives obtained from the precursor $ZrPO_4$Cldmso have been for-

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* To whom correspondence should be addressed. E-mail: ric@unipg.it. Fax: +39 075 585 5566.

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mulated as $ZrPO_4(L\ L')$, where L L′ is a generic couple of monodentate anionic and neutral ligands.[9] To better distinguish them from α- and γ-ZP derivatives, these compounds will be named here λ-ZP derivatives, in which λ simply means that they are derived by topotactic ligand substitution, and hence, they are structure-related with the parent compound $ZrPO_4$Cldmso.

In this paper, a new method for the preparation of the precursor $ZrPO_4$Cldmso by direct precipitation will be reported. The preparation of a sample of high crystallinity allowed us to refine and confirm its structure.

The preparation and characterization of a series of inorganic λ-ZP derivatives, obtained for the replacement of Cl anions of $ZrPO_4$Cldmso with OH, Br, MSO_4 (M = H, NH_4, Na), $NaMoO_4$, and $HCrO_4$ anions will then be presented.

The difference between the reactivity of $ZrPO_4$Cldmso and $ZrPO_4$Fdmso toward topotactic replacements is discussed on the basis of structural and chemical considerations.

Experimental Section

Reagents. All reagents were C. Erba RPE reagents, except zirconium oxychloride octahydrate, which was a Merck reagent. They were used without further purification.

Preparation of the Precursor $ZrPO_4$Cldmso. Two solutions, named A and B, were separately prepared. Solution A was obtained by mixing, at 80 °C, $ZrOCl_2\cdot8H_2O$ (0.5 g, 1.55×10^{-3} mol) previously dissolved in 37% HCl (13 cm^3, Zr/Cl molar ratio = 1/100) and oxalic acid (3.5 g, 6.7×10^{-2} mol, $Zr/H_2C_2O_4$ molar ratio = 1/43) previously dissolved in dmso (25 cm^3). Solution B was prepared by mixing 85% w/w H_3PO_4 (0.1 cm^3, 1.48×10^{-3} mol, Zr/P molar ratio = 1/0.95) and dmso (31 cm^3). Solutions A and B were then mixed at room temperature, and a clear solution, having the following composition, was obtained: $[Zr(IV)] = 0.022$ M, $[HCl] = 2.2$ M, $[H_3PO_4] = 0.022$ M, $[H_2C_2O_4] = 0.93$ M, dmso = 81% v/v.

The final solution was heated at 70 °C in a Teflon hydrothermal bomb for 6 days. The product was filtered off, washed twice with anhydrous ethanol, dried, and stored under P_4O_{10}.

Anal. Found (calcd): % C 8.2 (8.0); % H 2.1 (2.0); Zr 3.2×10^{-3} mol/g (3.3×10^{-3}); PO_4 3.2×10^{-3} mol/g (3.3×10^{-3}); Cl 3.2×10^{-3} mol/g (3.3×10^{-3}). Weight loss at 1100 °C: 33.8%.

Preparation of the Inorganic Derivatives of $ZrPO_4$Cldmso. $ZrPO_4$Fdmso. A 1 g portion of $ZrPO_4$Cldmso was contacted twice with 110 cm^3 of 0.03 M HF using dmso as solvent at 75 °C for 3 days for each contact. The solid was then washed with water and dried at 80 °C.

Anal. Found (calcd): % C 8.2 (8.5); % H 2.1 (2.1); Zr 3.6×10^{-3} mol/g (3.5×10^{-3}); PO_4 3.4×10^{-3} mol/g (3.5×10^{-3}); F 3.5×10^{-3} mol/g (3.5×10^{-3}). Weight loss at 1100 °C: 31.0%.

$ZrPO_4$OHdmso·$1.5H_2O$. A 1 g portion of $ZrPO_4$Cldmso was suspended in 350 cm^3 of a 5% (v/v) dmso/water mixture and maintained at room temperature under stirring for 24 h. The solid was then separated by centrifugation and stored under 75% relative humidity.

Anal. Found (calcd): % C 7.4 (7.8); % H 2.4 (3.2); Zr 3.2×10^{-3} mol/g (3.2×10^{-3}); PO_4 3.3×10^{-3} mol/g (3.2×10^{-3}). Weight loss at 1100 °C: 35.4%.

$ZrPO_4$Brdmso·0.5dmso. A 1 g portion of $ZrPO_4$OH dmso·$1.5H_2O$ prepared as described was contacted twice with 357 cm^3 of a 3 M HBr and 3 M LiBr solution using a 50% v/v ethanol/dmso as solvent and maintained at 70 °C for 10 h under stirring. After the second contact, the solid was washed with anhydrous ethanol and dried at 60 °C.

Anal. Found (calcd): % C 8.9 (9.4); % H 2.1 (2.3); Zr 2.5×10^{-3} mol/g (2.6×10^{-3}); PO_4 2.6×10^{-3} mol/g (2.6×10^{-3}); Br 2.6×10^{-3} mol/g (2.6×10^{-3}). Weight loss at 1100 °C: 49.4%.

$ZrPO_4NH_4SO_4$dmso. A 1 g portion of $ZrPO_4$Cldmso was suspended in 64 cm^3 of a 0.473 M $(NH_4)_2SO_4$ solution using a 33% (v/v) dmso/water mixture as solvent. The solid was maintained in this solution for 24 h at 75 °C under stirring, and then it was separated by centrifugation and washed three times with 100 cm^3 of water. It was dried at 80° and then stored over P_4O_{10}.

Anal. Found (calcd): % C 6.7 (6.3); % H 2.5 (2.6); % N 3.4 (3.7); Zr 2.5×10^{-3} mol/g (2.6×10^{-3}); PO_4 2.6×10^{-3} mol/g (2.6×10^{-3}); SO_4 2.4×10^{-3} mol/g (2.6×10^{-3}). Weight loss at 1100 °C: 42.0%.

$ZrPO_4NaSO_4$dmso. A 1 g portion of $ZrPO_4$Cldmso was suspended in 100 cm^3 of a 0.4 M Na_2SO_4 solution using a 25% (v/v) dmso/water mixture as solvent. The synthesis was carried out as described for $ZrPO_4NH_4SO_4$dmso.

Anal. Found (calcd): % C 6.5 (6.3); % H 2.2 (1.6); Zr 2.5×10^{-3} mol/g (2.6×10^{-3}); PO_4 2.6×10^{-3} mol/g (2.6×10^{-3}); SO_4 2.4×10^{-3} mol/g (2.6×10^{-3}); Na 2.4×10^{-3} mol/g (2.6×10^{-3}).

$ZrPO_4(HSO_4)_{0.6}(OH)_{0.4}$dmso. A 1 g portion of $ZrPO_4$Cldmso was suspended in 667 cm^3 of a 0.252 M H_2SO_4 solution using a 90% (v/v) propanol/water mixture as solvent. The solid was maintained in this solution for 14 h at 70 °C under stirring, and then it was separated by centrifugation and washed twice with 100 cm^3 of anhydrous ethanol. It was dried at 80° and then stored over P_4O_{10}.

Anal. Found (calcd): % C 6.9 (7.3); % H 2.4 (2.1); Zr 2.9×10^{-3} mol/g (3.0×10^{-3}); PO_4 3.1×10^{-3} mol/g (3.0×10^{-3}); SO_4 1.8×10^{-3} mol/g.

$ZrPO_4HSO_4$dmso. A 1 g portion of $ZrPO_4$OHdmso was suspended in 570 cm^3 of a solution obtained by adding 6.6 cm^3 HSO_3Cl to dmso. The solid was maintained in this solution for 14 h at room temperature under stirring, and then it was separated by centrifugation and washed twice with 100 cm^3 of anhydrous ethanol. It was dried at 80° and then stored over P_4O_{10}.

Anal. Found (calcd): % C 6.3 (6.6); % H 2.1 (1.9); Zr 2.9×10^{-3} mol/g (2.8×10^{-3}); PO_4 2.8×10^{-3} mol/g (2.8×10^{-3}); SO_4 2.8×10^{-3} mol/g; (2.8×10^{-3}). Weight loss at 1100 °C: 37.3%.

$ZrPO_4NaMoO_4$dmso·$1.5H_2O$. A 1 g portion of $ZrPO_4$Cldmso was suspended in 56 cm^3 of a 0.295 M $Na_2MoO_4\cdot2H_2O$ solution using a 36% (v/v) dmso/water mixture as solvent. The initial pH of this solution (8.1) was set at 7.1 by adding a few drops of concentrated HNO_3.

The solid was maintained in this solution for 8 h at 90 °C under stirring; afterward, it was separated by centrifugation and washed twice with 100 cm^3 of formamide and finally with anhydrous ethanol. It was then dried at 80°.

Anal. Found (calcd): % C 5.4 (5.1); % H 1.6 (1.9); Zr 2.1×10^{-3} mol/g (2.1×10^{-3}); PO_4 2.0×10^{-3} mol/g (2.1×10^{-3}); MoO_4 1.9×10^{-3} mol/g (2.1×10^{-3}); Na 1.9×10^{-3} mol/g (2.1×10^{-3}).

$ZrPO_4HCrO_4$dmso·$1.5H_2O$. A 1 g portion of $ZrPO_4$Cldmso was suspended in 100 cm^3 of a 0.103 M K_2CrO_4 solution using 28% (v/v) dmso/water mixture as solvent. The initial pH of this solution, close to 10, was set at 3.2 by adding a few drops of concentrated HNO_3. The solid was maintained in this solution for 19 h at 70 °C under stirring; afterward, it was separated by centrifugation and washed twice with 100 cm^3 of formamide and finally with anhydrous ethanol. It was then dried at 80°.

Anal. Found (calcd): % C 5.7 (5.9); % H 2.7 (2.5); Zr 2.4 × 10^{-3} mol/g (2.4 × 10^{-3}); PO_4 2.4 × 10^{-3} mol/g (2.4 × 10^{-3}); CrO_4 2.2 × 10^{-3} mol/g (2.4 × 10^{-3}).

Analytical and Instrumental Procedures. 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.

Anions (phosphate, fluoride, chloride, bromide, sulfate, chromate, and molybdate) were determined by ion chromatography. About 0.100 g of sample was refluxed for 3 h with 10 cm^3 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 having 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.

Chromates were also determined as chromium by atomic absorption spectroscopy using a Perkin-Elmer 3100 spectrometer.

Sodium was determined by atomic emission spectroscopy using a Perkin-Elmer 3100 spectrometer.

Coupled TGA and DTA curves were obtained by a Stanton Redcroft STA 780 thermoanalyzer, at heating rates between 1 and 5 °C/min.

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

Hydration water was determined by TG analysis, heating the sample at 110 °C until a constant weight was reached.

FT-IR spectra were recorded using a Bruker JFS V FT-IR spectrometer, in the 400−7000 cm^{-1} spectral range. The samples were prepared as pressed pellets in anhydrous KBr.

SEM micrographs were recorded by a Philips XL30 scanning electron microscope, fitted with an LaB_6 electron gun.

X-ray powder diffraction (XRD) patterns for structure determination and Rietveld refinement of $ZrPO_4Cldmso$ were collected according to the step scanning procedure in the range 6°−130° 2θ (0.01° step size and 30 s counting time) 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, 0.1 mm receiving slit were used. The LFF 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.

Other XRD patterns were recorded using a 0.03° 2θ step size and 1 s counting time in the 2°−40° 2θ range.

Structure Refinement of $ZrPO_4Cldmso$. XRD pattern and unit cell parameters (determined with the TREOR90 program[10]) are close to those first reported: the cell is tetragonal, $a = 5.696$ Å, and $c = 10.242$ Å. A Rietveld refinement was therefore performed (with the GSAS program[11]) using, as starting model, the structural parameters previously determined.[9] The refinement substantially confirmed the structure previously reported. Figure 1 shows the refined structure.

Results and Discussion

Direct Synthesis of $ZrPO_4Cldmso$. To improve the degree of crystallinity of $ZrPO_4Cldmso$, previously obtained by γ-ZP,[9] attempts to prepare the precursor by direct synthesis were carried out.

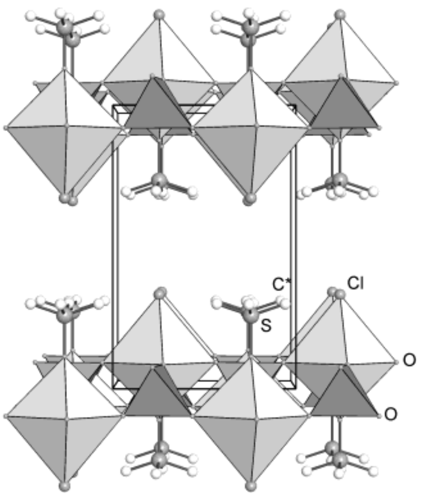

Figure 1. Structure of $ZrPO_4Cldmso$. Methyl groups of dmso indicated with an asterisk have occupancy 0.5.

The strategy adopted is a modification of the thermal zirconium fluoro complex decomposition[12,13] that essentially consists of leaving these complexes to thermally decompose in a solution containing the suitable reagents. However, under the synthesis conditions used here, the presence of fluoride ions in the reaction solution caused the formation of the inert compound $ZrPO_4Fdmso$; we therefore used oxalic acid as a weaker complexing agent.

A series of experiments allowed us to optimize the synthesis. As expected, the oxalate/zirconium molar ratio in the solution was found to affect the degree of crystallinity of the product obtained. This ratio ranged from 20 to 100, giving products with increasing crystallinity. Unfortunately, the higher crystallinity was accompanied by a dramatic decrease in the yield of the reaction and a consistent increase of the reaction time. The $C_2O_4^{2-}$/Zr molar ratio was finally set to 43 as the best compromise.

The compound, obtained as described in the Experimental Section, consists of a white powder of platelike microcrystals, with homogeneous dimensions around 10 μm diameter and about 1 μm thick, as assessed by SEM images (see Figure 2). Figure 3a shows a thermogravimetric curve of the compound. The weight loss starts at about 200 °C, with the simultaneous loss of chloride and dmso. 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:

$$2\mathrm{ZrPO_4Cldmso} + n\mathrm{O_2} \rightarrow \mathrm{ZrO_2} + \mathrm{ZrP_2O_7} + \text{gaseous products}$$

The calculated % weight loss is 35.2, in agreement with that experimentally found (33.8).

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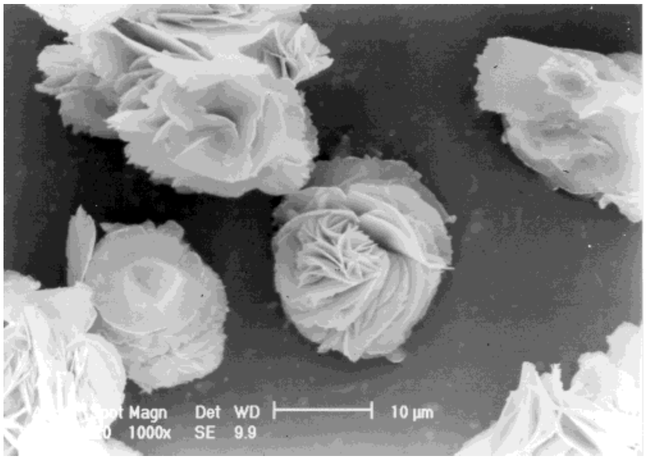

Figure 2. SEM micrographs of $ZrPO_4Cldmso$.

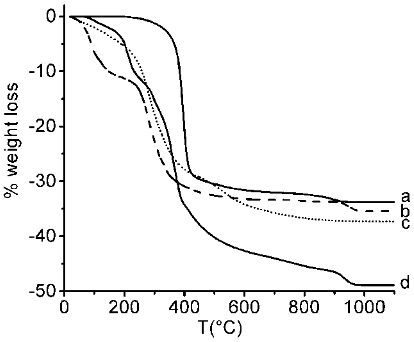

Figure 3. TGA of (a) $ZrPO_4Cldmso$, (b) $ZrPO_4OHdmso{\cdot}1.5H_2O$, (c) $ZrPO_4HSO_4dmso$, and (d) $ZrPO_4Brdmso{\cdot}0.5dmso$. Static atmosphere, heating rate 5 °C/min.

General Considerations on the Topotactic Reactions of $ZrPO_4Cldmso$. The topotactic replacement of ligands in a generic $ZrPO_4LL'$ compound can be written as

$$ZrPO_4LL' + L'' \rightleftharpoons ZrPO_4LL'' + L'$$

where L′ and L″ are a couple of anionic or neutral ligands.

The relative affinity (or selectivity) coefficient can be defined as $S_{L''/L'} = (\bar{X}_{L''}X_{L'})/(\bar{X}_{L'}X_{L''})$, where $\bar{X}$ and X are the molar fractions of the two ligands in the solid phase and in solution, respectively.

In a given solvent, the value of $S_{L''/L'}$ coefficient will depend on the relative tendency of these ligands to be coordinated to the tetravalent metal ion as well as on the environment of the sites of exchange that can sterically hinder the replacement.

Before discussing the reactivity of this precursor, let us examine some structural peculiarities. In its layers, zirconium atoms are arranged in two parallel planes (Figure 1). Both chloride and dmso ligands face the layer surface, but they occupy two nonequivalent positions, as shown by the van der Waals surface of a λ-layer, in which the ligands have been omitted (Figure 4). This picture clearly shows that the layer is not flat but undulated. The anionic site is placed on a relief, and it will be called the "mountain" site, while the neutral site is placed in a hollow, and it will be called the "valley" site. The free area available for a couple of neutral−anionic ligands is 43.5 Å^2 (i.e., larger than in α- and γ-type structures, 24.0 Å^2 and 35.3 Å^2, respectively).

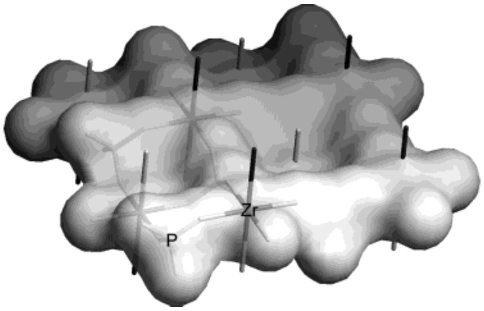

Figure 4. van der Waals surface of a λ-layer. The anionic and neutral ligands have been removed to better evidence "mountain" and "valley" positions.

In the case of $ZrPO_4Cldmso$, the anionic ligands are expected to be more reactive than the neutral ones, because they occupy the more accessible "mountain" site. Accordingly, the precursor was found to be very reactive to anionic replacement, and a series of inorganic derivatives with different anions in the "mountain" position were easily prepared by topotactic reactions, as described later.

In agreement with a very low reactivity of its "valley" sites, attempts to replace dmso with other neutral ligands were unsuccessful. However, recent experiments have shown that dmso can be replaced by neutral ligands with a high affinity for zirconium, such as amines. It seems, however, that the total reaction also involves the "mountain" sites, because the Cl^- ions are also eluted; after the reaction, the "mountain" sites were occupied by the amine, while electroneutrality was preserved by hydroxyl groups found in the "valley" positions. The complex mechanism of this reaction will be discussed elsewhere.[14]

Fluoride Derivative. It is known that the tendency of F^- anions to be coordinated to zirconium is very high; accordingly, a high value of $S_{F/Cl}$ (7.8) was found.[9]

To avoid a dissolution−recrystallization mechanism caused by the fluoride solution, the conversion of $ZrPO_4Cldmso$ into the fluoride derivative was achieved by carefully maintaining a very low F^- concentration during the reaction. Sequential contacts of the parent compound with dilute F^- solutions were therefore performed. The high affinity of zirconium for fluoride was confirmed with a full conversion into $ZrPO_4Fdmso$. The derivative obtained had the same XRD pattern and composition of that prepared by Clearfield et al. by direct synthesis.[8]

Hydroxyl Derivative. It is known that zirconium exhibits a high affinity for OH^-. Thus, Cl^- of the precursor is expected to be completely exchanged even with a very low concentration of OH^-. Experiments have shown that $ZrPO_4Cldmso$ is not stable in pure water.[9] However, we found that a small amount of dmso in water (at least 5% v/v) is sufficient to stabilize the neutral ligand in the solid phase, at room temperature. In this solvent, only the Cl/OH anionic exchange was observed, with the formation of a compound of composition $ZrPO_4OHdmso{\cdot}1.5H_2O$. The reaction proceeds very quickly and is almost complete in about 2 h,

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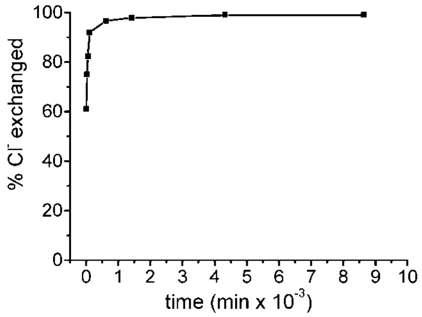

Figure 5. % of chloride replacement as a function of the time when $ZrPO_4$-Cldmso is suspended in 5% dmso/water mixture.

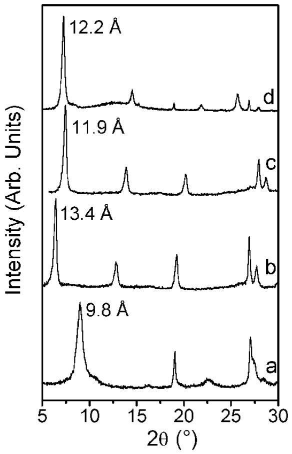

Figure 6. XRD patterns for (a) $ZrPO_4OHdmso{\cdot}1.5H_2O$, (b) $ZrPO_4Brdmso{\cdot}0.5dmso$, (c) the same as in (b) after the loss of intercalated dmso when heated at 140 °C, and (d) $ZrPO_4HSO_4dmso$.

as shown in the kinetic curve of Figure 5. At low pH values, the reaction is strongly inhibited, because of the lowered OH^- concentration. We found that the presence of 0.1 M HCl completely inhibits such exchange.

The TG curve of the hydroxyl derivative is reported in Figure 3b. Thermal decomposition proceeds first by the loss of the intercalation water, then the loss of dmso; finally, the condensation of phosphates to pyrophosphates is observed. If we assume the formation of an equimolar mixture of zirconium oxide and zirconium pyrophosphate at 1100 °C, the calculated % weight loss at that temperature is in good agreement with that experimentally found (37.0 vs 35.5).

According to the hypothesis of a topotactic process, the replacement of chlorides with hydroxyl groups should not change appreciably the structure of the parent compound. Although the XRD pattern, reported in Figure 6a, is very broadened and not suitable for structural analysis, we found that it is consistent with the following tetragonal unit cell: $a = 6.56$ Å; $c = 9.90$ Å. Furthermore, the peaks relative to the layer framework are still well evident (the 110 and 200 reflections at $d = 4.65$ and 3.28 Å, respectively), indicating that the layers maintained the λ-structure. When the compound is heated at 150 °C and intercalation water is lost, the interlayer distance decreases from 9.8 to 9.2 Å, a value close to that of $ZrPO_4Fdmso$. Structural models can show that in both compounds the interlayer distance depends on the dmso dimensions because of the small size of both hydroxyl and fluoride anions.

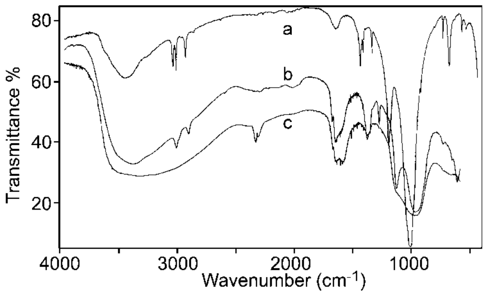

Figure 7. FT-IR spectra of (a) $ZrPO_4Cldmso$, (b) $ZrPO_4OHdmso{\cdot}1.5H_2O$, and (c) $ZrPO_4OHH_2O{\cdot}(H_2O)_3$.

The Cl/OH exchange reaction is reversible: by contacting the solid with a 1.5 M HCl solution in dmso at 75 °C for 24 h, the original chloride phase is restored.

Figure 7 compares FT-IR spectra of $ZrPO_4Cldmso$, $ZrPO_4$-OHdmso, and $ZrPO_4OHH_2O{\cdot}(H_2O)_3$. Note that the bands at 2920, 3000, and 3020 cm^{-1} related to symmetric and asymmetric stretching of dmso methyl groups and those at 1420 and 1320 cm^{-1} related to symmetric and asymmetric bending of the same groups are present in Cl−dmso and OH−dmso spectra and no longer visible in OH−H_2O, where dmso was replaced by water.

Bromide Derivatives. The replacement of Cl^- with Br^- ions was attempted in order to obtain a compound with a higher interlayer distance and weaker interactions between the anions and the inorganic backbone and which is, therefore, more reactive than $ZrPO_4Cldmso$. Unfortunately, our attempts to obtain such material by contacting the chloride form with solutions of bromidric acid in various conditions were unsuccessful. Therefore, we decided to use the hydroxyl form, $ZrPO_4OHdmso{\cdot}1.5H_2O$ prepared as described in the Experimental Section, as precursor, in the hope that a possible neutralization reaction between the OH^- from the solid and the strong acid from the solution could force the Br^- exchange according to the following reaction:

$$ZrPO_4OHdmso + HBr \rightleftharpoons ZrPO_4Brdmso + H_2O$$

This strategy was successful, and a compound of formula $ZrPO_4Br_{0.8}(OH)_{0.2}dmso{\cdot}0.5dmso$ was first prepared by contacting $ZrPO_4OHdmso{\cdot}1.5H_2O$ with a 2 M HBr solution in dmso.

The full exchange was finally achieved by forcing the reaction with the use of 3 M HBr and 3 M LiBr in ethanol/dmso solvent (see Experimental Section). A compound of formula $ZrPO_4Brdmso{\cdot}0.5dmso$ was obtained.

Figure 3d shows the TG curve for the bromide derivative. The dmso is lost in two steps: 0.5 mol of dmso per formula weight, corresponding to the intercalated solvent in the interlayer space, is lost at lower temperatures (about 100 °C). A further 1.0 mol per formula weight, corresponding to the dmso bonded to zirconium, is lost at about 200 °C. The compound has an interlayer distance of 13.4 Å, which decreases to 11.9 Å when heated at 140 °C, because of the loss of interlayer dmso (Figure 6b,c). Experiments are in progress to compare the reactivity of such material with that of the parent compound.

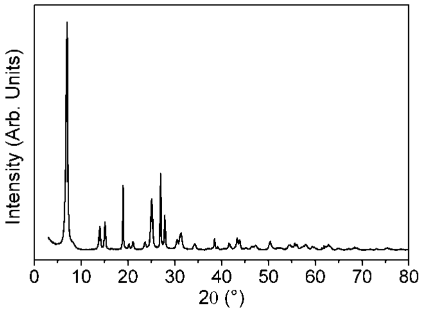

Figure 8. XRD pattern for $ZrPO_4NH_4SO_4$dmso.

The experimental % weight loss at 1100 °C (49.4) perfectly agrees with that calculated if we assume the formation of an equimolar mixture of zirconium oxide and zirconium pyrophosphate.

Sulfate Derivatives. Materials containing acid sulfate groups on their surface are of interest for potential applications as catalysts or as protonic conductors. The Cl/HSO_4 exchange was therefore investigated. Because of the low affinity of acid sulfate groups for zirconium, it was difficult to complete the reaction by contacting the parent compound directly with sulfuric acid. In most of our attempts, we found that the hydroxyl group was in strong competition with HSO_4^-. The best results achieved led to a 60% replacement of HSO_4^-, the remaining chlorides being replaced by hydroxyl groups, $ZrPO_4(HSO_4)_{0.6}(OH)_{0.4}$dmso, and attempts to use more drastic conditions resulted in an increase of OH^- content in the sample.

Another approach was therefore used. A 0.1 M chlorosulfonic solution in dmso was left to react with $ZrPO_4$OHdmso. The complete conversion into $ZrPO_4HSO_4$dmso was achieved by the following reaction:

$$\mathrm{ZrPO_4OHdmso + ClSO_3H \rightleftharpoons ZrPO_4HSO_4dmso + HCl}$$

Figure 3c shows the TG curve for the obtained compound, while Figure 6d shows its XRD pattern.

At the end of TG analysis, at 1100 °C, the formation of β-$Zr_2(PO_4)_2SO_4$ was observed, as assessed by the comparison of the XRD pattern with that from ref 15.

Sulfate derivatives are very sensitive toward hydrolysis: the presence of 5% v/v of water in dmso is sufficient to reconvert the solid into the OH−dmso form.

The use of ammonium or sodium sulfate for the ion exchange allowed us to prepare other sulfate derivatives, in which the acidic proton of the sulfate group was replaced by the respective cation. In this case, the topotactic reactions were performed directly on λ-$ZrPO_4$Cldmso. Probably because of the presence of the cationic moiety in the interlayer region, these derivatives were obtained with a relatively high degree of crystallinity. The XRD pattern of $ZrPO_4NH_4SO_4$dmso (shown in Figure 8) was indexed with the TREOR90 program,[10] and cell parameters were determined: the cell is tetragonal, $a = 6.609(1)$ Å, $c = 12.660(5)$ Å (M(20) = 18, F20 = 24), and it is undoubtedly λ-type, confirming the topotactic nature of the anion ligand exchange reaction involved.

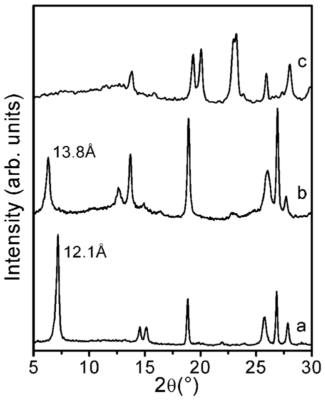

Figure 9. XRD pattern for (a) $ZrPO_4(HCrO_4)$dmso, (b) $ZrPO_4NaMoO_4$-dmso, and (c) $ZrPO_4NaMoO_4$dmso after heating at 500 °C in oxygen atmosphere.

Chromate and Molybdate Derivatives. For potential applications as catalysts, the preparation of derivatives containing chromate and molybdate were also investigated. The reactions

$$\mathrm{ZrPO_4Cldmso + HCrO_4^- \rightleftharpoons ZrPO_4HCrO_4dmso + Cl^-}$$

and

$$\mathrm{ZrPO_4Cldmso + NaMoO_4^- \rightleftharpoons ZrPO_4NaMoO_4dmso + Cl^-}$$

were carried out successfully.

Figure 9a,b shows XRD patterns of the prepared compounds, respectively. These two patterns can be easily indexed with the following tetragonal unit cells: $a = 6.616$ Å, $c = 12.098$ Å for the chromate derivative, and $a = 6.610$ Å, $c = 27.83$ Å for the molybdate derivative. Note that these unit cells are λ-type; only, the c parameter for molybdate derivative is doubled with respect to its interlayer distance. To confirm the topotactic nature of the anion exchange, the reactions were followed by XRD analysis. We found that they proceeded by a progressive increase of the final products and a simultaneous decrease of the peaks of the parent compound, without the appearance of any other phases.

The presence of dmso in the structure is also assessed by FT-IR spectra that show the characteristic absorption bands of such species.

Both samples showed a peculiar thermal behavior: because of the redox properties of chromate and molybdate groups, TG curves were different whether the analyses were carried out in reducing or oxidizing atmosphere (Figure 10). Especially for the molybdate derivative, thermal analysis in oxygen shows an initial weight loss and a characteristic weight increase, because of an oxidation process leading to a compound that is thermally stable from 400 to 600 °C. The XRD pattern of this compound is shown in Figure 9c.

Conclusion

The present study clearly shows that the chlorides present on the reactive “mountain” sites of $ZrPO_4$Cldmso can be

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(15) Piffard, Y.; Verbaere, A.; Kinoshita, M. *J. Solid State Chem.* **1987**, *71*, 121.

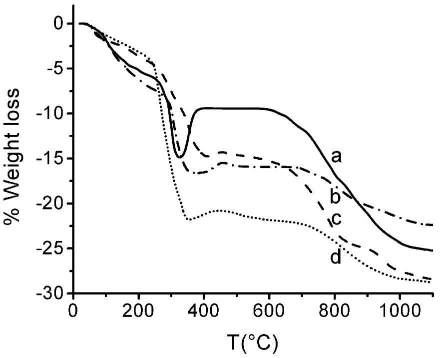

Figure 10. TG curve for (a) $ZrPO_4NaMoO_4$dmso in oxygen, (b) $ZrPO_4$-$NaMoO_4$dmso in nitrogen, (c) $ZrPO_4(HCrO_4)$dmso in oxygen, and (d) $ZrPO_4(HCrO_4)$dmso in nitrogen. Gas flux 40 cm^3/min; heating rate 5 °C/min.

topotactically replaced by a variety of inorganic ligands, thus originating a large family of λ-inorganic derivatives. Because the layered structure does not change appreciably during anionic ligand exchange, it is possible to predict the environment around functional groups introduced in these compounds. This feature could be of interest for the preparation of tailor-made materials for application in catalysis, ionic or molecular recognition, and ionic or protonic conductivity. Finally, preliminary experiments showed that dmso can be also replaced with other neutral ligands. This opportunity, along with the possibility to introduce a large number of anionic organic ligands with specific properties, makes λ-ZP a very flexible and intriguing compound for materials chemistry.

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Supporting Information Available: Rietveld refinement details, Rietveld plot, tables of crystallographic data, structural parameters, and selected bond lengths and angles for $ZrPO_4Cl$dmso. This material is available free of charge via the Internet at http://pubs.acs.org.

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