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Zirconium Phosphate Chloride Dimethyl Sulfoxide, a Reactive Precursor of a Large Family of Layered Compounds

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After the synthesis of the first derivatives of α-zirconium phosphate,[1] in which organic functional groups of various kinds are covalently attached to the inorganic α-layers, a large variety of derivatives of layered phosphates were prepared. Some of these exhibit particular characteristics such as ion-exchange and catalytic properties,[2a] interlayer microporosity,[2b,3] and high protonic conduction.[2c,4] Furthermore, the growth of multilayers, in which an ordered orientation of polar asymmetrical diphosphonate groups may give rise to considerable nonlinear optical effects, is an area that has important prospects for the near future,[2d,5] while photoactive and photoelectroactive derivatives show exciting promise even for the storage of solar energy.[6]

While the derivatives of α-zirconium phosphate have been obtained by direct synthesis,[2b,7] the derivatives of *γ*-zirconium phosphate are generally prepared by topotactic reactions[2b,8] in which the original bidentate anionic ligands $O_2P(OH)_2^-$, attached to the external part of the *γ*-layers, are directly substituted by other bidentate anionic ligands $O_2PR'R^-$ (R and R′ = H, OH, organic residuals).

It seemed of interest to find out whether the $O_2P(OH)_2^-$ ligands could be replaced by a couple of monodentate anionic−monodentate neutral ligands. Preliminary experiments were performed using the couple Cl^-−dimethyl sulfoxide under the following experimental conditions: A 1 g sample of $Zr(PO_4)$-$O_2P(OH)_2 \cdot 2H_2O$ was dispersed in 50 mL of 5 M HCl in dimethyl sulfoxide (dmso), and the dispersion was kept in a closed vessel at 75 °C. After 2 days, the solid was removed and contacted again with a new solution for an additional 2 days. Ion-chromatography analysis of phosphate groups and chlorides, as well as C, H, and Zr elemental analysis, showed that, within the experimental errors, the product obtained had the expected composition $Zr(PO_4)Cl(dmso)$ (**1**). The compound was stable until about 180 °C while the greater part of the dmso and Cl was lost in the range 200−400 °C. Taking into account that a total weight loss of 33.6% was found at 1100 °C and assuming that at this temperature an equimolar mixture of ZrP_2O_7 and ZrO_2 was formed, a formula weight of 293 was deduced for **1**. This is in good agreement with the value 299.5 found by chemical analyses. However, preliminary X-ray analysis showed that the structure of the original *γ*-layers was lost. The structure of **1** was thus solved "ab initio" by using X-ray powder diffraction data.[9] These structural data clearly showed that **1** was homologous to $Zr(PO_4)F(dmso)$, recently prepared by Clearfield by direct precipitation.[10] A scheme of the reaction, also showing the structural changes, is shown in Figure 1.

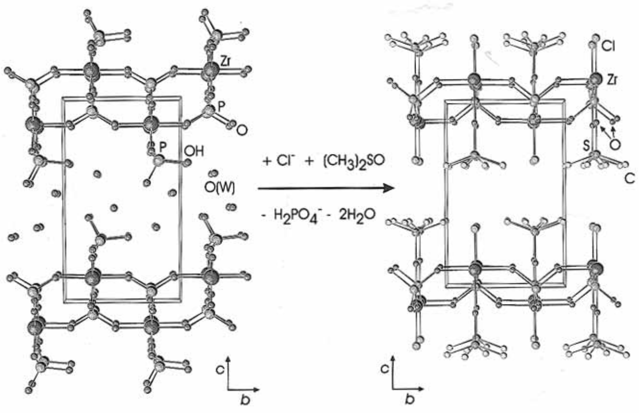

Figure 1. Comparison of the structures of *γ*-zirconium phosphate (left) and $Zr(PO_4)Cl(dmso)$ (right) showing the structural changes occurring in the substrate during the reaction with HCl in dmso. Carbon atoms of dmso groups have occupancy 0.5. The structure of *γ*-zirconium phosphate was taken from ref 11.

This reaction cannot be considered a pure topotactic reaction since the replacement of the external $O_2P(OH)_2$ groups also induces a small structural rearrangement of the layers. However, the preparation of the chloro derivative using the above reaction is important, since all our attempts to prepare it by direct synthesis under conditions similar to those used by Clearfield for the fluoro derivative were unsuccessful. We will examine here the new compound mainly from the point of view of its high reactivity toward some monodentate inorganic L^- ligands. To understand the reasons for the high reactivity of **1**, in contrast to the low reactivity of the F derivative, let us examine the

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(9) The structure was solved from X-ray powder diffraction data (conventional diffractometer, Cu Kα radiation, with a graphite monochromator on the diffracted beam) by Patterson and difference Fourier maps followed by Rietveld refinement, using the GSAS software (Larson, A.; von Dreele, R. B. *GSAS, Generalized Structure Analysis System*; Los Alamos National Laboratory: Los Alamos, NM, 1988). The unit cell was found to be tetragonal; $a = 6.5988(7)$ Å, $c = 10.2478(4)$ Å, space group $P4/n$, $Z = 2$. The final agreement factors were $R_{wp} = 0.086$, $R_p = 0.066$, and $R_F = 0.065$.

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generic topotactic reaction

$$\mathrm{Zr(PO_4)L_a(dmso)} + \mathrm{L_b}^- \rightleftharpoons \mathrm{Zr(PO_4)L_b(dmso)} + \mathrm{L_a}^- \quad (1)$$

in which a ligand L_a, initially only in the solid phase, must be substituted by a ligand L_b, initially only in solution. It is reasonable to assume that considerations similar to those used for normal ligand exchange processes in solids[12] can be applied to this process. Thus, the higher the molar fraction of the ligand L_b in solution is and the higher its relative affinity for the solid phase, the more equilibrium 1 will be shifted toward the right. The relative affinity coefficient, or selectivity coefficient, is usually expressed as $S_{\mathrm{Lb/La}} = (\bar{X}_{\mathrm{Lb}}X_{\mathrm{La}})/(\bar{X}_{\mathrm{La}}X_{\mathrm{Lb}})$, where $\bar{X}$ and X represent the molar fractions of the species in the solid phase and in solution, respectively. Since the two ligands are covalently attached to zirconium, it is also reasonable to suppose that the relative affinity for the solid phase will be influenced by the relative tendency of the ligands to be coordinated by zirconium(IV). Thus, the formation constants of complexes could be used to make a qualitative series of relative tendency of monodentate anionic ligands to be coordinated by zirconium. This series may in turn be used to make simple predictions about equilibrium 1. By using the cumulative constant values for Cl^-, F^-, and OH^- ligands,[13] the sequence $OH^- \gg F^- \gg Cl^-$ can be derived. Experiments performed with diluted solutions of HF in dmso showed that **1** was almost completely converted into $Zr(PO_4)F$(dmso), exhibiting an X-ray diffraction pattern very close to that of the compound obtained by direct precipitation even when a stoichiometric amount of HF was used. In order to have a better estimation of the relative affinity of the couple F^-/Cl^- for the solid phase, the relative affinity coefficient $S_{\mathrm{F/Cl}}$ was determined. The high value of this coefficient ($S_{\mathrm{F/Cl}} = 7.8$) confirmed that the tendency of chlorides to be bonded to the solid phase is much lower than that of fluorides. The relatively low tendency of Cl^- ligands to be coordinated by zirconium makes **1** an ideal precursor for the preparation of other derivatives by topotactic reactions.

Another interesting example is the topotactic reaction with OH^- ligands. Due to the very high tendency of this ligand to be coordinated by Zr(IV) (e.g., its K_1 value is 2×10^{14} L/mol, while that of Cl^- is about 8 L/mol), the formation of the hydroxy derivative was expected even when **1** was simply contacted with pure water. The following reaction, almost completely shifted toward the right, was found:

$$\mathrm{Zr(PO_4)Cl(dmso)} + 5\mathrm{H_2O} \rightleftarrows \mathrm{Zr(PO_4)OH(H_2O)\cdot 3H_2O} + \mathrm{HCl} + \mathrm{dmso} \quad (2)$$

Note that, since the reaction was carried out in water, the neutral dmso ligand of **1** was also substituted. We conclude that **1** is indeed a very good precursor for the preparation of a large family of new layered derivatives of general formula $Zr(PO_4)L(L')$ in which L and L′ are monoanionic and neutral monodentate ligands, respectively. Since the layered structure is essentially determined by the two planes of zirconium atoms bridged by internal PO_4^{3-} groups, the inorganic polymeric matrix $[ZrPO_4]_n$ of a single layer of **1** can be considered as a planar peg to which a large variety of monodentate anionic and neutral ligands can be attached on both of the faces.

Owing to the wide choice of L and L′ ligands, this new class of layered materials is expected to be very rich in compounds with particular properties. Preliminary experiments performed with acid sulfate ligands and even with anions, such as chromate and molybdate, which cannot be supplied as free acidic species, seem to be very encouraging for the preparation of layered compounds containing functional groups of catalytic and electrochemical interest.

Finally, we note that **1** can also be considered as an inorganic exchanger of monovalent anions. Only a few inorganic anion exchangers are presently known, of which hydrotalcite is one of the most important, especially for the preparation of catalytic inorganic derivatives.[14] However, in comparison to hydrotalcite, catalysts with greater stability in acid solutions could be obtained from **1**.

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Supporting Information Available: Text detailing the X-ray data collection and structure determination of **1**, tables of atomic coordinates and bond distances and angles for **1**, text giving the experimental details for the preparations and characterizations of **1** and its fluoro and hydroxy derivatives and the procedure for the determination of $S_{\mathrm{F/Cl}}$, and figures showing XRD patterns for **1** and a projection of **1** down the *a* axis (6 pages). Ordering information is given on any current masthead page.

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