significantly longer than those observed in **2** as a consequence of the decreased oxidation state of the metal and of the bridging modes, the most significant lengthening involving the V–Cl distance [2.513 (2) vs 2.344 (2) Å]. Vanadium is displaced by 0.081 (1) Å from the equatorial plane. Coordination around vanadium is octahedral, and that around zinc is nearly tetrahedral, the distortions being mainly due to the bridging mode of the ligands [Cl1–Zn–O1 = 88.9 (1)°].

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Supplementary Material Available: Complete listings of crystallographic data, fractional atomic coordinates for the hydrogen atoms, anisotropic thermal parameters, and bond distances and angles for complexes **2** and **4** (9 pages); listings of observed and calculated structure factors for complexes **2** and **4** (19 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Vermont, Burlington, Vermont 05405

Metathetical and Reductive Deintercalation of α-Zirconium Phosphate Derivatives

Guy L. Rosenthal* and James Caruso

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Introduction

In recent years, layered solids have attracted scientific attention due to their potential as high-performance electronic materials,[1] chemical sensors,[2] catalysts[3] and synthetic reagents.[4] The two-dimensional nature of such materials allows them to include a variety of chemical species within a solid network, precipitating changes in both "host" lattice and "guest" species.

α-Zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP), has proven to be a versatile layered host solid for a variety of inclusion (intercalation) reactions,[5] due to its relative ease of synthesis, the chemical robustness of the lattice, and the variety of ions which can be placed in the interlayer galleries by exchange with the acidic protons.[6]

The reaction chemistry of these ion-exchanged derivatives is only beginning to be explored. In particular, the reversibility of the intercalation reaction itself has a direct bearing on the utility of such materials. The sterically restricted microenvironment created by the interlamellar region is ideal for selective synthetic and catalytic reactions involving intercalated species. However, if the incorporation of species from the solution or gas phases within the interlamellar region is chemically irreversible, the potential utility of the parent solid and its derivatives as catalysts and synthetic reagents is severely limited.

In this study, we have prepared a representative variety of cation-exchanged derivatives of α-ZrP and investigated several chemical paths to deintercalation, the removal of guest ions from the lattice and replacement with protons or sodium ions.

Experimental Section

α-Zirconium phosphate was prepared in powder form by the method of Clearfield, et al.[7] and refluxed in 85% H_3PO_4 for 13 days. Butylammonium zirconium phosphate (BAZrP) was prepared by suspending 2.0 g (6.6 mmol) of α-ZrP in 200 mL of an aqueous solution that was 0.25 M in n-$C_4H_9NH_2$ and 0.25 M in n-$C_4H_9NH_3Cl$ for 24 h.

Ultraviolet–visible spectra were obtained on a Perkin-Elmer Lambda 4 system using quartz cuvets for solutions and silicone grease mulls[8] for solid samples. Infrared spectra were obtained on a Nicolet Series 6000 FTIR instrument. X-ray powder diffraction was performed on an Enraf-Nonius FR590 Guinier system, using an internal silicon standard with all samples.

Table I. Stoichiometries and Interlayer Spacings (Å) for α-Zirconium Phosphate Derivatives $[\mathrm{Int}]_xH_yZr(PO_4)_2$ (α-ZrP and BAZrP Included for Reference)

[Int]	x	interlayer spacing[a]
α-ZrP		7.6
BAZrP		18.6
Cu^{2+}	0.96	9.7
Ni^{2+}	1.01	9.5
Zn^{2+}	1.02	8.9
$Fe(C_5H_5)_2^+$	0.22	11.8
$Co(C_5H_5)_2^+$	0.48	13.2

[a] Interlayer spacings determined from 001 reflections (1 = 1, 3, 4) in powder diffraction patterns.

Elemental analyses (intercalating metal, Zr, P, N) of the zirconium phosphate derivatives were performed by Schwartzkopf Microanalytical Laboratory. They indicated that a small amount (less than 0.05 mol/mol of Zr) of $C_4H_9NH_3^+$ remained in the lattice after the exchange reactions.

Intercalation Reactions. Copper(II) nitrate, nickel(II) chloride, and zinc(II) nitrate were used as hydrates obtained from Aldrich. Intercalations of the aqueous metal ions[9] were performed by suspending 500 mg (1.1 mmol) of BAZrP in 30 mL of 0.3 M aqueous solutions of the ions. Solid products were gravity filtered and washed with water. Stoichiometries (elemental analysis) and interlayer spacings (powder X-ray diffraction) of intercalation derivatives are summarized in Table I. Analyses indicated a nearly complete replacement of alkylammonium ions with M(II) ions.

$Fe(C_5H_5)_2^+$[$Fe(Cp)_2^+$] was intercalated by oxidizing ferrocene to ferrocenium with sulfuric acid[10] and then following the procedure for the other ionic complexes. Although the interlayer spacing of the derivative was anomalously small (Table I), the resulting solid was blue in color (λ_{max} = 618 nm) when washings were colorless. Neutral ferrocene in benzene solution was not observed to intercalate after 72 h at room temperature.

Cobaltocene derivatives were prepared by two methods. A surface-exchanged derivative resulted when 150 mg (0.5 mmol) of α-ZrP was suspended in a solution of 50 mg of $Co(C_5H_5)_2$[$Co(Cp)_2$] in 30 mL of freshly distilled toluene under reflux (115 °C) in a steady stream of dry nitrogen for 6 h. The product had a light green color after washing with THF and toluene until washings were colorless, but the powder X-ray diffraction pattern matched that of α-ZrP. The fully intercalated derivative (λ_{max} = 263 nm) was prepared by reacting 170 mg (0.9 mmol) of $Co(Cp)_2$ with 170 mg (0.6 mmol) of α-ZrP in the same manner for 50 h.[11]

Deintercalation Reactions. Strong acid reactions were performed by suspending 200 mg (0.6 mmol) of phosphate in 25 mL of HCl solution, varying in concentration between 0.5 and 0.01 M, for 1–6 days. Acetic acid reactions were performed in similar fashion with 1.0 M solutions kept at room temperature for 48 h and then under reflux for 4 days. Solid products were gravity filtered and washed with water.

For deintercalation with acetylacetone (Hacac), 2.0 mL of Hacac was added to a suspension of 300 mg (0.8 mmol) of phosphate in 50 mL of water and stirred for 24 h. For complete reaction, this suspension was refluxed for 24 h. For deintercalation with sodium *N,N*-diethyldithiocarbamate [Na(ddtc)], 500 mg (1.3 mmol) of phosphate was added to 30 mL of a 0.30 M aqueous solution of Na(ddtc) and stirred for 24 h.

Reductive deintercalations were performed by suspending 25 mg (0.05–0.07 mmol) of phosphate and 2.7 g of a 1% Na/Hg amalgam in 50 mL of freshly distilled THF for 24 h under nitrogen. Similar results were obtained by reaction of 20 mg (0.04–0.06 mmol) of phosphate with

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* To whom correspondence should be addressed.

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50 mL of 0.005 M sodium naphthalenide solution in THF.

Results and Discussion

A variety of strategies were employed to exchange intercalated Cu(II), Ni(II), and Zn(II) with protons from solution and regenerate α-ZrP. Using a 0.5 M HCl solution, the deintercalation reaction was complete within 24 h in all cases and the product solid was found to be poorly crystalline α-ZrP.[12] With less concentrated solutions of HCl, the reaction simply proceeded more slowly, until at 0.01 M the solid remained colored (Cu, Ni) and did not display an X-ray pattern characteristic of α-ZrP after 6 days.

Using acetic acid, no deintercalation reaction was observed, nor was any reaction noted between CH_3COOH and intercalated ions, even after 4 days of reflux in a 1.0 M acid solution.

The most intriguing results were obtained by adding 2.0 mL of acetylacetone to a slurry of 300 mg of CuZrP in 50 mL of water. Within seconds, formation of the deep blue, insoluble $Cu(acac)_2$ complex, characterized by UV–visible and IR spectra, was apparent. At room temperature after 48 h, the deintercalation did not proceed to completion, as evidenced by the blue color of the zirconium phosphate product and persistence of a diffuse diffraction peak at 9.7 Å. However, under reflux for 24 h the blue color disappears and a surprisingly crystalline α-ZrP product is formed. This result was not obtained in the Ni or Zn derivatives, suggesting that the favorable formation of the particularly stable $Cu(acac)_2$ complex drives the deintercalation reaction in that case.

Similarly, when ZnZrP is suspended in a Na(ddtc) solution, crystalline $Zn(ddtc)_2$ is produced, characterized by X-ray powder diffraction, while the diffraction pattern of ZnZrP disappears. No zirconium phosphate phase is apparent in the diffraction pattern due to loss of crystallinity. When CuZrP is suspended in Na(ddtc) solution, a small amount of $Cu(ddtc)_2$ is produced and characterized by UV–visible absorption,[13] presumably by deintercalation at the surfaces of microcrystals, but the powder diffraction pattern of CuZrP remains intact, with no sign of the distinctive strong line pattern of $Cu(ddtc)_2$.[14] These results further indicate the importance of complex formation in the deintercalation reaction.

The reversibility of aqueous transition metal ion intercalation in the presence of a strong acid indicates no strong kinetic barrier to the forward reaction in equation 1, and the position of the equilibrium at varying pH suggests that the equilibrium constant is on the order of 10^1.

$$MZr(PO_4)_2(s) + 2H^+(aq) \leftrightarrow Zr(HPO_4)_2(s) + M^{2+}(aq) \qquad (1)$$

However, the introduction of acetylacetone introduces the alternate equilibrium in eq 2, whose equilibrium constant is

$$MZr(PO_4)_2(s) + 2Hacac(aq) \leftrightarrow Zr(HPO_4)_2(s) + M(acac)_2(s) \qquad (2)$$

particularly large compared to that of eq 1 for M = Cu. When viewed in the light of the inability of acetic acid to affect the deintercalation, it is clear that the high formation constant of the $Cu(acac)_2$ complex compensates for its lower acidity ($pK_a = 9$) relative to acetic acid ($pK_a = 5$).

To our knowledge, this is the first clear demonstration that the deintercalation reaction can be performed by a relatively weak acid, provided that its conjugate base complexes strongly with the deintercalated guest cation. This evidence also confirms the lack of a significant kinetic barrier to the reaction involving the removal of guest species from the intercalated host and replacement with aqueous H^+.

When ferrocenium-intercalated zirconium phosphate was suspended in a 0.5 M HCl solution for 48 h, no change in appearance or X-ray powder pattern of the solid product was observed. Ferrocenium was observed in the filtrate, presumably due to proton exchange with surface-adsorbed ions, and the absorption at 262 nm ($\epsilon = 7079$)[15] showed that nearly 25% of the total $Fe(Cp)_2^+$ was removed by the acid exchange.

Upon reaction with a 1% Na/Hg amalgam in THF, however, nearly quantitative removal of $Fe(Cp)_2$ was affected. The amount of deintercalated ferrocene was measured at 96–100% by UV absorption at 262 nm and the solid product was noncrystalline. When the reduction was performed with sodium naphthalenide, the degree of deintercalation was monitored by absorption at 440 nm ($\epsilon = 9.1$)[16] and determined to be 100 ± 10%. The solid product was very light brown in color and poorly crystalline, with one weak reflection at 8.64 Å, indicative of a Na^+-intercalated product.[17]

When the surface-exchanged cobaltocenium compound was suspended in THF with a 1% Na/Hg amalgam or sodium naphthalenide, within 2 h the solution turned the distinctive pink color of cobaltocene, indicating reduction of the surface-bound ions. Similar treatment of the fully intercalated product for 24 h also yielded a small amount of desorbed $Co(Cp)_2$, presumably from reduction of surface adsorbed $Co(Cp)_2^+$, but the solid product maintained its appearance and its interlayer spacing of 13.2 Å, indicating no reaction with intercalated cobaltocenium ions. UV absorption at 324 nm ($\epsilon = 17\,378$)[15] indicated that only 15–25% of the cobaltocenium ions were reduced to cobaltocene.

While the strong and weak acid reactions indicate that metathetical strategies are often sufficient to remove intercalated species, they also indicate that stronger conditions may be necessary. The sodium reactions suggest that controlled reductive (even electrochemical) deintercalations can be useful in removing species which have formed or reacted in the interlayer gallery. Inclusion of reactive species in the inert and protective α-ZrP layers may also prove useful in storage and in limiting reactivity. Solid α-ZrP is truly showing its potential as a "solid solvent" for a variety of chemical purposes.

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Supplementary Material Available: A table of elemental analyses for zirconium phosphate derivatives (1 page). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

Homonuclear ^{31}P *J*-Resolved 2D Spectra of Rhodium(I) Phosphine Complexes in the Solid State

Gang Wu and Roderick E. Wasylishen*

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Introduction

Homonuclear *J*-resolved 2D NMR spectroscopy is one of the basic techniques widely used in solution-state NMR studies;[1] however, the application of this 2D technique has not been extensively used for the study of solid materials.[2-4] In this note we demonstrate the utility of this technique in studying ^{31}P NMR spectra of two square-planar rhodium(I) phosphine complexes of

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* To whom all correspondence should be addressed.

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