a platinum working electrode. Typical cyclic voltammograms for $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{2+}$ are shown in Figure 2.

There are two well-defined oxidative responses in the potential region 0.0–2.4 V. The former potentials (E_f) were calculated as the average of the cathodic (E_{pc}) and anodic (E_{pa}) peak potentials, and the values are 0.86 and 2.03 V vs SCE. The peak-to-peak separations ($\Delta E_p = E_{pa} - E_{pc}$) at a scan rate of 50 mV/s are 90 and 100 mV, respectively. Under our experimental conditions, the reversible couple Fc^+/Fc (E_f = 0.40 V vs SCE) has a ΔE_p of 80 mV, which was used as the criterion for electrochemical reversibility. Also, the ratio of anodic to cathodic peak currents (i_{pa}/i_{pc}) is ~1 for each of the processes. Coulometric oxidation at 1.06 V gave[14] n = 1.01 for the net electrochemical oxidation of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{2+}$. The above facts suggest that the $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{2+}$ ion undergoes a chemically and electrochemically reversible one-electron oxidation process, generating the mixed-valence species $[Ru^{III}Ru^{IV}(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{3+}$. The cyclic voltammogram of the one-electron-oxidized solution is identical with the voltammogram shown in Figure 2, but as expected, this time the response at 0.86 V becomes reductive. The oxidized solution can be quantitatively reduced (applied potential 0.66 V, n = 0.88), giving back $[Ru^{III}_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{2+}$. Attempted electrolysis at 2.10 V to generate the two-electron-oxidized dimer causes decomposition of the tribridged core. Thus, the species $[Ru^{IV}_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{4+}$ is stable only on the time scale of cyclic voltammetry.

The tribridged complex also exhibits two reductive responses (Figure 2). The less negative wave with an E_f of −0.65 V is quasireversible (ΔE_p = 100 mV at a scan rate of 50 mV/s). This is assigned to the reduction of the $Ru^{II}Ru^{III}$ state. At this level of reduction, a μ-hydroxo bridge formation is definitely[2,15] a possibility, given the fact that the diruthenium(III) complex as isolated contained sufficient water of crystallization. An additional irreversible reductive response is seen with E_f = −0.92 V and ΔE_p = 240 mV. No attempt was made to examine the chemical and electrochemical properties of the coulometrically reduced solutions, since it is expected that this would lead to decomposition of the tribridged structure, yielding mononuclear ruthenium(II) compounds.[16]

Stability and Optical Spectrum of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{3+}$. Though stable under dry anaerobic conditions, electrochemically and/or chemically (see below) generated acetonitrile solutions of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{3+}$ are very sensitive to air. Under aerobic conditions, such red solutions slowly turn purplish blue, the color of the diruthenium(III) precursor. Figure 1 exhibits the visible spectrum of the coulometrically oxidized 3+ ion in deoxygenated acetonitrile solution. The molar extinction coefficient (ϵ_{Ru}) for the intense peak at 494 nm is estimated to be 3890 M^{-1} cm^{-1}. The spectral feature is very similar to[11] that observed with a related species, $[Ru^{IV}Ru^{III}(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(Me_3tacn)_2]^{3+}$. The strong band at 564 nm of LMCT origin for $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{2+}$ is considerably blue shifted (λ_{max} = 494 nm) for $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{3+}$. The oxidation of $[Ru_2(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{2+}$ in deoxygenated acetonitrile could also be achieved chemically by 1.06 equiv of ammonium cerium(IV) nitrate.

We have done the following controlled experiments to identify the actual component of air responsible for the quantitative reduction of the 3+ ion to the 2+ ion. Incremental amounts of deoxygenated water (0.05–0.30 mL) were added to the deoxygenated MeCN solutions (0.29 mM in 2+ species) of chemically generated 3+ ion. We observe that the greater the amount of added water, the faster the progress of reduction. These experiments confirm that under aerobic conditions the moisture of air acts as the reducing agent. Clean isosbestic points at 417 and 525 nm are observed when the reaction is followed spectrophotometrically. Thermodynamically, the 3+ ion is capable of oxidizing water. The E_f value of the $Ru^{IV}Ru^{III}/Ru^{III}Ru^{III}$ couple is ~200 mV more positive than that of the O_2/H_2O couple (pH ~7). The high moisture sensitivity of the oxidized species has made its isolation as a pure salt in the solid state thus far unachievable. This novel reactivity property is currently under investigation. Efforts are underway to synthesize this tribridged core with other transition-metal ions using MeL as the capping ligand.

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Registry No. $(MeL)RuCl_3$, 137467-27-7; $[Ru_2O(O_2CCH_3)_2(MeL)_2](ClO_4)_2$, 137467-29-9; $[Ru^{III}Ru^{IV}(\mu\text{-}O)(\mu\text{-}O_2CCH_3)_2(MeL)_2]^{3+}$, 137467-30-2; MeL, 137495-65-9; 2-(2-(methylamino)ethyl)pyridine, 5638-76-6; 2-(chloromethyl)pyridine, 4377-33-7.

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(2,4-Pentanedionato)vanadium(III) and -vanadium(II) Complexes: Synthesis from the Oxovanadium Reductive Chlorination and Their Structural Characterization

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In spite of the recent active investigations on vanadium(III) and vanadium(II) chemistry,[2] there are still rather few starting materials easily accessible for (i) organometallic functionalization, (ii) reduction at the metal center, or (iii) solubility in organic solvents for carrying out reactions on oxygen-rich substrates,[3] except for the well-known $VCl_3(THF)_3$[4] and $[V_2(\mu\text{-}Cl_3)(THF)_6]^+$,[4] which, however, do not contain any ancillary ligands to be usable for the purposes outlined above. In this context we report the synthesis of some vanadium(III) and vanadium(II) acetylacetonate complexes.

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The syntheses of $VCl_3(THF)_3$[5] and $[VO(acac)_2]$[6] have been performed as reported in the literature. Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer. The magnetic measurements have been carried out with a Faraday balance.

Solid-State Structures of 2 and 4. Crystallographic data, atomic coordinates, and selected bond distances and angles are reported in Tables I–V.

Preparation of $[V(acac)Cl_2(THF)_2]$ (2). Method A. To a blue suspension of $TiCl_3(THF)_3$ (13.21 g, 35.6 mmol) in THF (100 mL) was added $[VO(acac)_2]$ (9.40 g, 35.6 mmol) under stirring. The reaction mixture was heated for a few minutes until all the solid dissolved. Very little impurities are filtered out sometimes. A green-red solution was obtained, which was kept on standing at room temperature for 24 h. $[V(acac)Cl_2(THF)_2]$ precipitated as a green crystalline solid (53%). Anal. Calcd for $C_{13}H_{23}Cl_2O_4V$: C, 42.75; H, 6.35; Cl, 19.43. Found: C, 43.02; H, 6.56; Cl, 19.33. The solid was found to be free of titanium by atomic absorption.

Method B. To a solution of acacH (2.85 mL, 27.6 mmol) in THF (75 mL) was added NaH (0.66 g, 27.6 mmol). Gas evolution took place, and

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Table I. Crystal Data for Complexes **2** and **4**

complex	**2**	**4**
formula	$C_{13}H_{23}Cl_2O_4V$	$C_{17}H_{31}Cl_3O_5VZn$
cryst system	monoclinic	monoclinic
space group	$C2/c$	$P2_1/n$
cell params at 295 K		
a/Å	15.200 (3)	12.878 (2)
b/Å	8.799 (1)	16.452 (2)
c/Å	13.699 (2)	11.764 (2)
β/deg	114.54 (1)	99.68 (1)
Z	4	
no. of unique obsd data	1171	2399
intens measmt	*a*	*a*
struct refinement	*b*	*b*
$R = \sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$	0.055	0.046

[a] For intensities and background the "three-point" technique was used. [b] Refinement was by blocked full-matrix least squares first isotropically and then anisotropically for all non-hydrogen atoms. All the hydrogen atoms either located in difference maps or put in idealized calculated positions were introduced in the refinement as fixed contributors (U_{iso} = 0.08 Å^2). The final difference maps showed no unusual features, with no significant peak with chemical meaning above the general background.

Table II. Fractional Atomic Coordinates (×10^4) for Complex **2**

atom	x/a	y/b	z/c
V	0	446 (1)	2500
Cl	640 (1)	2263 (2)	3867 (1)
O1	1283 (2)	307 (4)	2331 (3)
C1	2222 (4)	201 (9)	3214 (5)
C2	2922 (4)	−137 (9)	2760 (6)
C3	2399 (5)	96 (8)	1579 (6)
C4	1362 (4)	−84 (8)	1341 (4)
O2	−488 (3)	−1192 (4)	1404 (3)
C5	−822 (5)	−3513 (7)	499 (4)
C6	−441 (3)	−2582 (5)	1480 (4)
C7	0	−3358 (8)	2500

Table III. Fractional Atomic Coordinates (×10^4) for Complex **4**

atom	x/z	y/b	z/c
Zn	2719 (1)	1275 (0)	7480 (1)
V	542 (1)	2257 (1)	7424 (1)
Cl1	2449 (1)	2590 (1)	8107 (2)
Cl2	3439 (2)	492 (1)	8907 (2)
Cl3	3205 (2)	1203 (1)	5776 (2)
O1	1111 (3)	1107 (2)	7172 (3)
O2	−925 (3)	1830 (3)	6803 (4)
O3	−116 (3)	3414 (3)	7663 (4)
O4	712 (3)	2628 (2)	5740 (4)
O5	345 (4)	1910 (3)	9131 (4)
C1	1201 (6)	−306 (4)	6776 (6)
C2	563 (5)	457 (4)	6833 (5)
C3	−509 (5)	449 (4)	6513 (6)
C4	−1205 (5)	1115 (4)	6468 (5)
C5	−2342 (6)	1001 (5)	6013 (7)
C6	−1092 (7)	3676 (5)	6993 (8)
C7	−1290 (9)	4472 (6)	7336 (10)
C8	−470 (6)	4724 (5)	8297 (8)
C9	329 (5)	4070 (4)	8403 (7)
C10	348 (7)	2193 (5)	4714 (6)
C11	762 (10)	2596 (8)	3775 (8)
C12	1261 (9)	3323 (8)	4216 (9)
C13	1297 (9)	3307 (6)	5444 (8)
C14	1063 (8)	1461 (8)	9951 (8)
C15	568 (10)	1220 (8)	10859 (9)
C16	−495 (9)	1535 (9)	10618 (9)
C17	−605 (8)	1967 (7)	9564 (8)

Table IV. Selected Bond Distances (Å) and Angles (deg) for Complex **2**[a]

V–Cl	2.344 (2)	O2–C6	1.227 (6)
V–O1	2.061 (4)	C6–C7	1.446 (6)
V–O2	1.989 (4)		

O2–V–O2′	87.1 (2)	Cl′–V–O1	92.8 (1)
O1–V–O2′	88.2 (2)	Cl–V–O2	176.4 (1)
O1–V–O2	86.9 (2)	Cl–V–O1	91.8 (1)
O1–V–O1′	173.2 (2)	Cl–V–Cl′	94.0 (1)
Cl′–V–O2	89.4 (1)		

[a] Primed atoms have coordinates −x, y, $^1/_2 - z$.

Table V. Selected Bond Distances (Å) and Angles (deg) for Complex **4**

Zn–Cl1	2.331 (2)	V–O4	2.119 (5)
Zn–Cl2	2.194 (2)	V–O5	2.143 (5)
Zn–Cl3	2.201 (3)	O1–C2	1.306 (7)
Zn–O1	2.060 (4)	O2–C4	1.273 (8)
V–Cl1	2.513 (2)	C1–C2	1.508 (10)
V–O1	2.068 (4)	C2–C3	1.369 (9)
V–O2	2.033 (4)	C3–C4	1.411 (9)
V–O3	2.121 (5)	C4–C5	1.484 (10)

Cl3–Zn–O1	105.3 (1)	O1–V–O5	89.5 (2)
Cl2–Zn–O1	109.8 (1)	O1–V–O4	92.0 (2)
Cl2–Zn–Cl3	121.1 (1)	O1–V–O3	177.3 (2)
Cl1–Zn–O1	88.9 (1)	O1–V–O2	87.9 (2)
Cl3–Zn–Cl1	114.7 (1)	Cl1–V–O5	91.3 (2)
Cl1–Zn–Cl2	111.7 (1)	Cl1–V–O4	89.3 (1)
O4–V–O5	178.5 (2)	Cl1–V–O3	98.8 (1)
O3–V–O5	90.1 (2)	Cl1–V–O2	171.7 (2)
O3–V–O4	88.4 (2)	Cl1–V–O1	83.9 (1)
O2–V–O5	89.7 (2)	Zn–Cl1–V	83.5 (1)
O2–V–O4	90.0 (2)	Zn–O1–V	102.8 (2)
O2–V–O3	89.4 (2)		

suspension was kept on stirring for some hours until NaH was completely dissolved, and then the mixture was refluxed for 1 h. $VCl_3(THF)_3$ (10.31 g, 27.6 mmol) was added under stirring to the white suspension of acacNa. The reaction mixture was heated for a few minutes until all the solid reacted. A green suspension was obtained, from which **2** was extracted using the mother liquor. The solution was then cooled at 0 °C (yield 73.5%). Anal. Calcd for $C_{13}H_{23}Cl_2O_4V$: C, 42.75; H, 6.35; Cl, 19.43. Found: C, 42.67; H, 6.26; Cl, 19.36. μ_{eff} = 2.85 μ_B at 291 K.

Preparation of [V(acac)ClZnCl$_2$(THF)$_3$] (4). To a green solution of the complex [V(acac)Cl$_2$(THF)$_2$] (7.16 g, 19.6 mmol) in THF (100 mL) was added zinc dust (4.6 g, 70.36 mmol) under stirring. The suspension was kept on stirring for several hours and then filtered in order to eliminate the zinc excess. A violet solution was obtained, from which, after standing a few hours at room temperature, a violet crystalline solid

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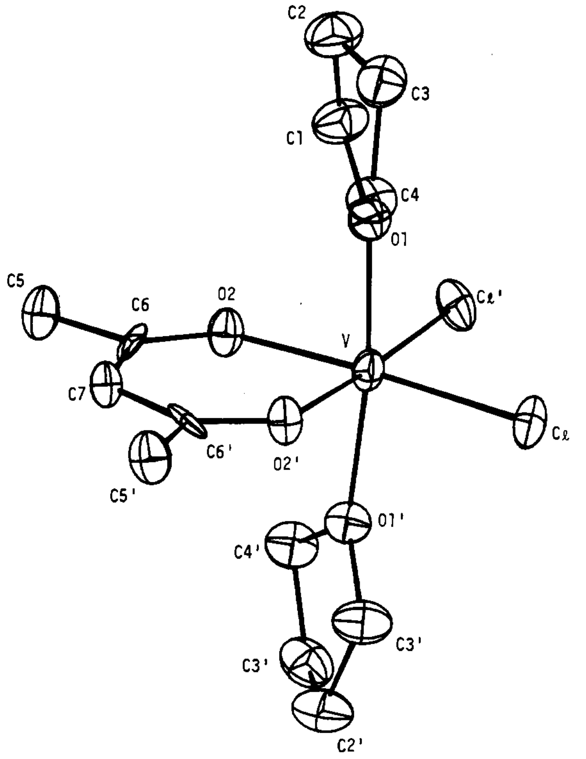
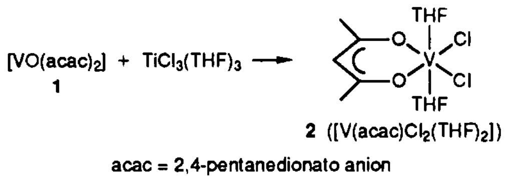


Figure 1. ORTEP drawing of complex **2** (30% probability ellipsoids).

precipitated (yield 35%). Anal. Calcd for $C_{17}H_{31}Cl_3O_5VZn$: C, 37.95; H, 5.81; Cl, 19.77. Found: C, 37.90; H, 6.12; Cl, 19.84. The yield of **4** can be increased up to 70% by adding anhydrous $ZnCl_2$ to the mother liquor. μ_{eff} = 3.89 μ_B at 293 K.

Results and Discussion

Oxovanadium complexes are among the most easily accessible compounds of vanadium.[6] They have been shown to be easily convertible into the corresponding vanadium(III) chloride derivatives by a reductive deoxochlorination using $TiCl_3(THF)_3$. Such a transformation has been achieved in case of the oxovanadium cation bonded to a tetradentate ligand.[7] When we applied the same reaction to the oxovanadium(IV) complexes containing bidentate ligands, like acetylacetonato, the reaction gave the results exemplified in eq 1.



(1)

In reaction 1 the reductive deoxygenation of the oxovanadium requires an oxygen and acac transfer to titanium, though we did not identify such a sacrificial species. Following the experimental procedure reported, the separation of the vanadium from the titanium species does not cause any difficulty, because of the significant differences in solubility. As for other deoxygenation reactions using $TiCl_3$, the titanium oxo species resulted to be quite soluble.[7] Reaction 1 is an interesting alternative synthesis, mainly when the vanadyl compounds[8] are available from air-aqueous solution procedures, to the normal one employing $VCl_3(THF)_3$ as starting material (eq 2).

$$VCl_3(THF)_3 + acacNa \xrightarrow[-NaCl]{THF} \mathbf{2} \qquad (2)$$

Complex **2** has been equally well obtained by using the latter procedure (see Experimental Section). In many cases, however,

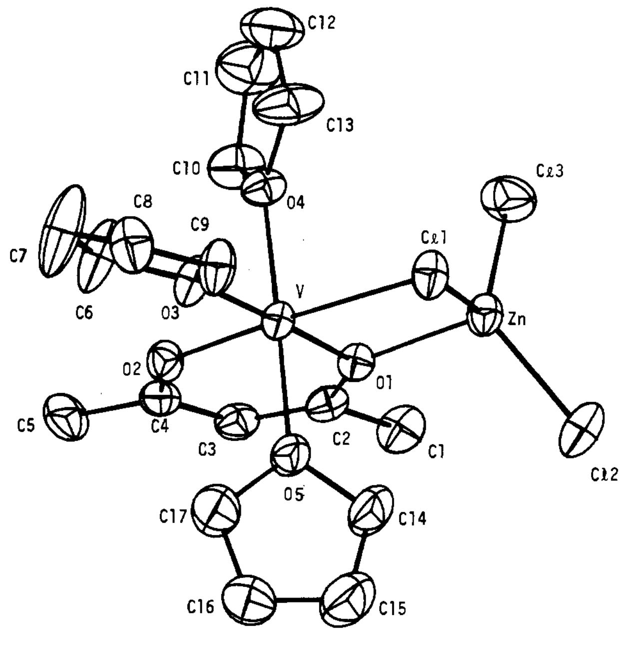
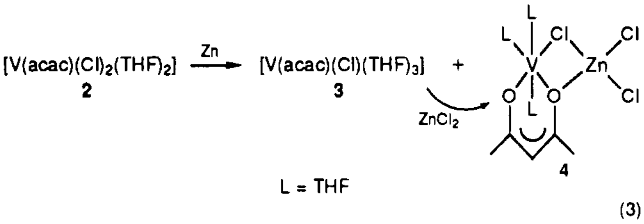


Figure 2. ORTEP drawing of complex **4** (30% probability ellipsoids).

we found that by using $VCl_3(THF)_3$ polysubstitution of the chloride by bidentate ligands occurs, so preventing formation of compounds like **2** but rather forming compounds like VL_2Cl and VL_3 (L being a monoanionic bidentate ligand) despite the V:L molar ratio used.[2a] The structure of **2** has been determined by an X-ray analysis and is shown in Figure 1.

Reduction of **2** was achieved using metallic zinc.



(3)

We never isolated **3** from the THF solution, but its presence was inferred from the solid-state isolation of its adduct with $ZnCl_2$, **4**. The stoichiometry of the adduct justifies why the yield is lower than 50% based on the starting vanadium complex. The addition of $ZnCl_2$ to the solution induced the precipitation of a further amount of **3** in the form of **4**.

The structure of **2** consists of discrete molecules having an imposed crystallographic C_2 symmetry (Figure 1), the 2-fold axis running through vanadium and the C7 carbon atom of the acac ligand. Coordination around the metal is pseudooctahedral involving the oxygen atoms from acac, two *cis*-chlorines, and two oxygens from THF. The V–Cl and V–O bond lengths compare well with those observed in other vanadium complexes.[7,9] Vanadium lies in the plane of the acac ligand that shows a remarkable localization of the double bond between oxygen and carbon [O2–C6 = 1.277 (6), C6–C7 = 1.446 (8) Å].

The structure of **4** (Figure 2) consists of bimetallic molecules [*mer*-$(THF)_3V(\mu$-acac$)(\mu$-$Cl)ZnCl_2$], where a $ZnCl_2$ unit is bonded to the [V(acac)Cl$(THF)_3$] moiety through a bridging chlorine atom and a bridging oxygen atom from the acac that acts, as usual, as a chelating ligand for vanadium(II). As a consequence of the bridging mode, the two V–O_{acac} distances are significantly different each other and longer than the corresponding one in **2**. All the distances in the coordination sphere of vanadium are

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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.

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Metathetical and Reductive Deintercalation of α-Zirconium Phosphate Derivatives

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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 $[Int]_xH_yZr(PO_4)_2$ (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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