ligand into the inner sphere in the interchange mechanism, both enthalpy and entropy of activation are lowered.

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Halometal Derivatives of $W_{12}PO_{40}^{3-}$ and Related ^{183}W NMR Studies

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$(Bu_4N)_4ClTiW_{11}PO_{39}$, $(Bu_4N)_3(H)ClTiW_{11}PO_{39}$, $(Bu_4N)_4ClSnW_{11}PO_{39}$, and $(Bu_4N)_4(H)ClAlW_{11}PO_{39}$ have been prepared. The first was converted to $(Bu_4N)_4CH_3OTiW_{11}PO_{39}$ and to salts of $TiW_{11}PO_{40}^{5-}$. ^{183}W NMR spectra were obtained for $ClTiW_{11}PO_{39}^{4-}$, $CpFe(CO)_2SnW_{11}PO_{39}^{5-}$, and $TiW_{11}PO_{40}^{5-}$, and a detailed assignment of the resonances was made for $TiW_{11}PO_{40}^{5-}$ on the basis of spin–spin couplings.

Introduction

Derivatives of Keggin-structure heteropolytungstates that have aquo, oxo, hydroxo, organic, or organometallic ligands on a peripheral heteroatom have been reported.[1-4] This paper adds halogen and alkoxyl to the list by describing derivatives of $W_{12}PO_{40}^{3-}$ that have chlorine bonded to a peripheral titanium, tin, or aluminum heteroatom and conversion of the chlorotitanium derivative to a methoxytitanium analogue. Related tungsten NMR studies are also presented, including unambiguous assignments of the tungsten resonances in the spectrum of $TiW_{11}PO_{40}^{5-}$, a hydrolysis product of $ClTiW_{11}PO_{39}^{4-}$. These assignments differ from those that would have been made on the basis of an existing scheme[6a] for assigning tungsten resonances in derivatives of $W_{12}PO_{40}^{3-}$.

Preparation and Properties

Treatment of $(Bu_4N)_4H_3W_{11}PO_{39}$[2] with titanium tetrachloride, aluminum chloride, or stannic chloride gives $(Bu_4N)_4ClTiW_{11}PO_{39}$, $(Bu_4N)_4(H)ClAlW_{11}PO_{39}$, and $(Bu_4N)_4ClSnW_{11}PO_{39}$. While the first two preparations proceed satisfactorily in dichloroethane, the use of anhydrous media in the preparation of $(Bu_4N)_4ClSnW_{11}PO_{39}$ gives erratic results. Unidentified mixtures containing excess tin and chlorine are frequently obtained. These problems are avoided by the use of slightly moist acetonitrile as the solvent for this reaction; good yields of $(Bu_4N)_4ClSnW_{11}PO_{39}$ are then obtained reproducibly.

Charge considerations suggest that basicity should increase in the order $W_{12}PO_{40}^{3-} < ClTiW_{11}PO_{39}^{4-} < ClAlW_{11}PO_{39}^{5-}$. Accordingly, we observed no reaction of hydrogen chloride with $W_{12}PO_{40}^{3-}$ in dichloroethane, reversible protonation of $ClTiW_{11}PO_{39}^{4-}$ under the same conditions, and have isolated $ClAlW_{11}PO_{39}^{5-}$ *only* as the protonated salt $(Bu_4N)_4(H)ClAlW_{11}PO_{39}$.

$(Bu_4N)_4ClTiW_{11}PO_{39}$ reacts smoothly with sodium methoxide in methanol/acetonitrile to form $(Bu_4N)_4CH_3OTiW_{11}PO_{39}$ and with tetrabutylammonium hydroxide in acetonitrile to give the previously reported[2] $TiW_{11}PO_{40}^{5-}$ anion. The latter anion was also prepared from $TiCl_4$ and $W_{11}PO_{39}^{7-}$ in buffered aqueous solution.

The infrared spectra of the new salts described above all closely resemble the spectrum of $(Bu_4N)_3W_{12}PO_{40}$ in the 700–1000-cm^{-1} region, except for slight changes in band positions. The asymmetric phosphate stretching region is of more interest. It has been noted[3a,5] that the triply degenerate phosphate stretch in the spectrum of $W_{12}PO_{40}^{3-}$ is frequently split into two bands because of loss of tetrahedral symmetry when a WO^{4+} group is replaced by a hetero group. The degree of splitting varies with the nature of the hetero group and the strength of the bond between it and its associated phosphate oxygen. Thus, $CpTiW_{11}PO_{39}^{4-}$ displays two bands in this region (1088, 1060 cm^{-1}), while $C_6H_5SnW_{11}PO_{39}^{4-}$ has only one.[3a,b] For the unprotonated halogenated derivatives and $CH_3OTiW_{11}PO_{39}^{4-}$, the situation is reversed. The titanium species exhibit only one phosphate stretch (1075 cm^{-1}) while $ClSnW_{11}PO_{39}^{4-}$ displays two (1055, 1080 cm^{-1}). The protonated anions $(H)ClTiW_{11}PO_{39}^{3-}$ and $(H)ClAlW_{11}PO_{39}^{4-}$ have a relatively broad band in this region with unresolved shoulders.

^{183}W NMR Spectra

The ^{183}W NMR spectrum of $(Bu_4N)_5TiW_{11}PO_{40}$ in CH_3CN/CD_3CN at 30 °C (Figure 1) provides support for the monosubstituted C_s structure because of the observed six resonances, five of relative intensity 2 and one of relative intensity 1. Peaks are labeled alphabetically in sequence from low to high field for use in later discussion, and it is seen they are in a 2:2:1:2:2:2 order. In contrast, the ^{183}W NMR spectrum of $CpTiW_{11}PO_{40}^{4-}$ has been shown by Gansow, Ho, and Klemperer[6a] to have the multiplets in a 2:1:2:2:2:2 order. Assignments were made for these resonances by using a charge distribution scheme which would require that the spectra of *all* $RMW_{11}PO_{39}^{n-}$ species, wherein RM has a charge less than 4, should have at least four resonances of intensity 2 upfield of the resonance of intensity 1. Since we observe only three

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(1) (a) Weakley, T. J. R.; Malik, S. A. *J. Inorg. Nucl. Chem.* **1967**, *29*, 2935–2944. (b) Komura, A.; Hayashi, M.; Imanaga, H. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 87–91.

(2) (a) Tourné, C. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1968**, *266*, 702. (b) Tourné, C.; Tourné, G. *Bull. Soc. Chim. Fr.* **1969**, 1124. (c) Ho, R. K. C. Ph.D. Thesis, Columbia University, 1979.

(3) (a) Ho, R. K. C.; Klemperer, W. G. *J. Am. Chem. Soc.* **1978**, *100*, 6772–6774. (b) Knoth, W. H. *Ibid.* **1979**, *101*, 759–760. (c) Zonnevijlle, F.; Pope, M. T. *Ibid.* **1979**, *101*, 2731–2732.

(4) Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 2211–2213.

(5) Rocchiccioli-Deltcheff, C.; Thouvenot, R. *J. Chem. Res., Synop.* **1977**, 46–47.

(6) (a) Gansow, O. A.; Ho, R. K. C.; Klemperer, W. G. *J. Organomet. Chem.* **1980**, *187*, C27–C31. (b) Prior to the work reported in ref 6a, a 2:2:1:2:2:2 pattern was reported for the ^{183}W spectrum of $W_{11}SiO_{39}^{8-}$ (Acerete, R.; Hammer, C. F.; Baker, L. C. W. *J. Am. Chem. Soc.* **1979**, *101*, 267–269).

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Table I. Chemical Shift-Spin Coupling Matrix[a] of 0.23 M $(Bu_4N)_5TiW_{11}PO_{40}$ in CH_3CN/CD_3CN

intens		A	B	C	D	E	F	J_{W-P}
2	A	−57.20			24.4		16.8	1.6
2	B		−92.60	19.4	9.7	7.5		1.1
1	C		19.0	−101.94			8.8	1.4
2	D	24.3	9.8		−106.73	11.5	20.5	1.2
2	E		(7.5)		(11.5)	−109.16		1.2
2	F	17.0		8.6	20.4		−117.95	1.0

[a] Diagonal elements are the chemical shifts (ppm) at 30 °C relative to external aqueous Na_2WO_4; negative values represent lower frequency than the reference. Spin-spin couplings (Hz) are read horizontally for the component measured; the worst agreement between J_{ij} and J_{ji} is 0.4 Hz. The two values in parentheses are not easily measured because of overlap, so the values are based on measurement of the other component.

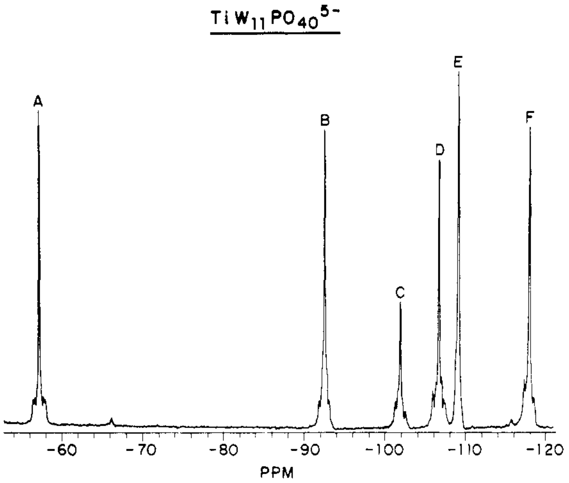

Figure 1. ^{183}W spectrum of 0.23 M $(Bu_4N)_5TiW_{11}PO_{40}$ in 12.5 mL of CH_3CN/CD_3CN at 30 °C. The spectrum is the sum of 195 000 shots recorded with an H_1 pulse length of 400 μs ($\pi/2$) with a recycle delay of 2.1 s. The fid was apodized by exponential multiplication with 0.5-Hz line broadening. The chemical shift scale is with respect to external aqueous Na_2WO_4 with negative values to lower frequency.

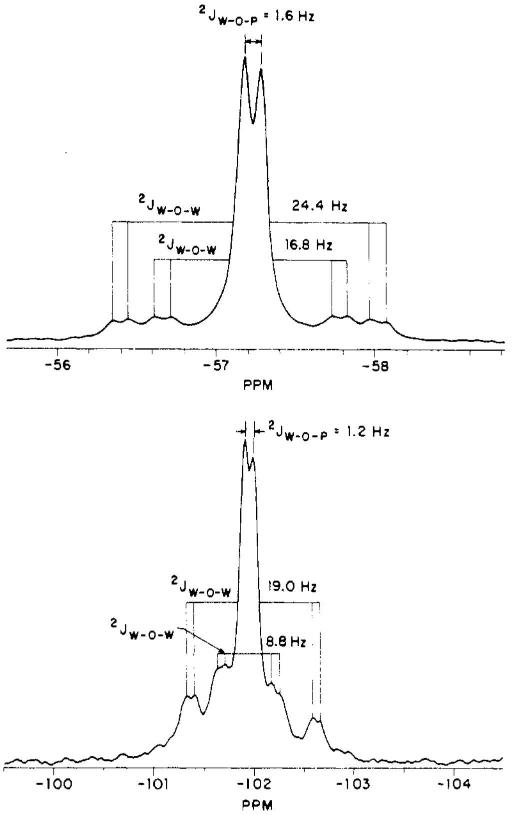

Figure 2. (a) Top: Expanded region around W_A showing two-bond W–O–W coupling of two different isotopomers. (b) Bottom: Expanded region around the unique W_C showing one large and one small coupling due to isotopomers.

resonances of intensity 2 upfield of the resonance of intensity 1 in the spectra of both $TiW_{11}PO_{40}{}^{5-}$ and $CpFe(CO)_2SnW_{11}PO_{39}{}^{4-}$ (Figures 1, 4b; Table II), this *approach* to assigning resonances cannot be correct. Additional inconsistency in the ordering of these multiplets is seen in the spectrum of $ClTiW_{11}PO_{39}{}^{4-}$ (Figure 4a), in which the resonance of intensity 1 is at lowest field.

We believe a more satisfactory approach to assigning tungsten resonances in these anions is to analyze the structure that can be seen at the base of the major peaks in a well-resolved spectrum. This structure is attributed to all the possible pairwise isotopomers between the 14.4% abundant ^{183}W species. Threefold and higher species are not observed. Enlarged portions of the spectrum around W_A and W_C are shown in Figure 2. Two-bond W–O–P coupling is apparent and splits all lines into equal-intensity doublets. The ^{183}W satellite lines are not always symmetrically disposed about the strong central line, indicating that second-order AB coupling patterns prevail. When couplings tend toward the AX limit, the lines are symmetrical about the central resonance, demonstrating negligible isotope shift. Clearly, this spectral content allows the connectivity between tungsten atoms to be deduced, and assignment of resonances to specific sites is unambiguous. The only peak without clearly resolved satellites is W_E, because two small couplings produce spectral overlap.

The chemical shift–spin coupling matrix is shown in Table I. Measured shifts are with respect to external aqueous Na_2WO_4 and are subject to susceptibility differences and residual lock frequency differences. However, since chemical shift differences are well-defined, reported shifts are quoted to 0.01 ppm. Assignments were made on the basis of measured equivalence between both outer components in an AB quartet; generally, agreement was better than 0.2 Hz. The only peak with ill-defined couplings was W_E, but by difference, this must contain two small couplings. Pronounced second-order effects proved useful in indicating the direction of the coupling partner. Spectral simulations successfully reproduced all second-order effects by using the central line as the zero-order shift along with measured couplings.

The couplings group into two distinct sets, one with $J \sim 9 \pm 2$ Hz and the other with $J \sim 20 \pm 4$ Hz. Lefebvre et al.[7] have observed similar phenomena in the ^{183}W NMR spectra of $H_2W_{12}FO_{39}{}^{5-}$ and β-$W_{12}SiO_{40}{}^{4-}$. They have demonstrated that the smaller coupling in the former represents an edge sharing of oxygen by two tungsten-centered octahedra while the larger J corresponds to a corner connection.

With the assumption that $^2J_{W-O-W} \sim 9$ Hz and $^2J_{W-O-W} \sim 20$ Hz in our compounds also reflect edge coupling and corner coupling, respectively, an unambiguous assignment in $(Bu_4N)_5TiW_{11}PO_{40}$ is possible. With use of the atom labeling scheme of Figure 3, $W_6 = W_C$ by integration of intensities.

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[7] Lefebvre, J.; Chauveau, F.; Doppelt, P.; Brevard, C. *J. Am. Chem. Soc.* **1981**, *103*, 4589–4591.

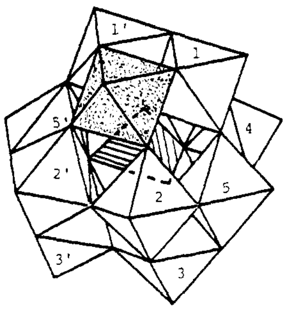

Figure 3. Atom-numbering scheme for $TiW_{11}PO_{40}^{5-}$. The shaded octahedron represents the Ti-centered site. The unique tungsten W_6 is obscured in the figure.

Table II. ^{183}W NMR Chemical Shifts (ppm) and Intensities of Monosubstituted Keggin Anions

$TiW_{11}PO_{40}^{5-}$	−57.2 (2), −92.6 (2), −101.9 (1), −106.7 (2), −109.2 (2), −118.0 (2)
$ClTiW_{11}PO_{39}^{4-}$	−88.3 (1), −92.3 (2), −96.5 (2), −108.3 (2), −108.5 (2), −108.8 (2)
$CpFe(CO)_2SnW_{11}PO_{39}^{4-}$	−106.5 (2), −108.8 (2), −123.4 (1), −127.4 (2), −127.9 (2), −192.7 (2)

Since J_{BC} = 19.2 Hz, W_B is corner coupled to W_6 and from the labeling must be W_3. Similarly, W_F is edge coupled (J_{CF} = 8.7 Hz) and $W_F = W_4$. Because W_F (W_4) is additionally coupled via corners to W_A and W_D (J_{AF} = 16.9 Hz, J_{DF} = 24.4 Hz), W_A is *either* W_1 *or* W_5 and W_D is *either* W_5 *or* W_1. Since W_B (W_3) is also edge coupled to W_D and W_E, then $W_D = W_2$ *or* W_5 and $W_E = W_5$ *or* W_2. The only consistent way to combine both of these either/or choices is $W_D = W_5$, $W_A = W_1$, and $W_E = W_2$, thus completing the assignment. Note that simply the *number* of large and small couplings is often sufficient to assign a resonance. For example, W_1 has *only* corner connections to inequivalent tungstens so *only* two large couplings are anticipated. Similarly, W_2 has *only* edge couplings to inequivalent tungstens. Couplings to $^{47,49}Ti$ are not observed. In the above assignment, the tungsten atoms that are bonded to titanium atoms via two oxygen atoms (octahedral edge sharing) are shifted downfield substantially (−57.2 ppm) while those bonded to titanium via one oxygen (octahedral corner sharing) are shifted upfield (−109.2 ppm). Detailed analysis of the spectrum of an isomer of $Ti_2W_{10}PO_{40}^{7-}$ [8] shows the same phenomena. While two examples do not establish a rule, these assignments, which we believe to be unambiguous, are in sharp contrast to those that would have been made on the basis of the earlier mentioned charge distribution scheme which requires both sets of tungsten atoms closest to titanium to be at high field.

The ^{183}W spectrum of $ClTiW_{11}PO_{39}^{4-}$ (Figure 4a) cannot be assigned on the basis of coupling arguments because of the near overlap of three lines at −108.3, −108.5, and −108.8 ppm. Integrated intensities confirm the C_s structure.

Chemical shifts for all compounds studied are collected in Table II.

Experimental Section

Materials and Instrumentation. $(Bu_4N)_4H_3W_{11}PO_{39}$ was prepared by the method of Ho.[2] The other materials are referenced in the text or are commercially available. The ^{31}P NMR spectra were determined on a Varian Associates FT-80A spectrometer.

^{183}W NMR spectra were obtained at 15 MHz on a Nicolet NT 360WB spectrometer using 20-mm sample tubes. $\pi/2$ pulse lengths in nonpolar organic solvents were 100 μs; however, in the strongly ionic heteropolyanion solutions reported here, this value increased substantially to 400–500 μs. This effect is not yet understood since the quality factor of the receiver coil decreases by a factor of 2, which should produce only a 40% increase in pulse length. Spectra were recorded with tip angles of $\pi/6$–$\pi/2$ with 2–5-s recycle delays; T_1 measurements on $H_3W_{12}PO_{40}$ yield values of 3–6 s under a variety of conditions. Typically, 10000–50000 shots were collected; however, the spectrum of $TiW_{11}PO_{40}^{5-}$ is 200000 acquisitions.

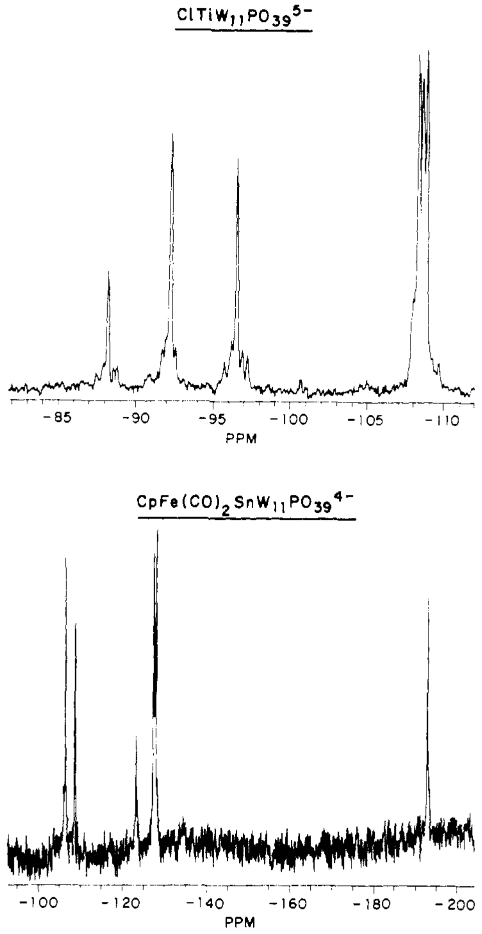

Figure 4. (a) Top: ^{183}W NMR spectrum of approximately 7 g of $(Bu_4N)ClTiW_{11}PO_{39}$ in 12.5 mL of 80% DMF/20% CD_3CN at 50 °C. The spectrum is the sum of 20000 shots recorded with an H_1 pulse length of 200 μs ($\pi/4$) with a recycle delay of 1.0 s. The fid was apodized with 0.5-Hz line broadening by exponential multiplication. (b) Bottom: ^{183}W NMR spectrum of approximately 7 g of $K_4CpFe(CO)_2SnW_{11}PO_{39}$ in 12.5 mL of D_2O at 30 °C. The spectrum is the sum of 15000 shots recorded with a H_1 pulse length of 100 μs ($\pi/8$) with a recycle delay of 4.1 s. The fid was apodized by exponential multiplication with 1.0-Hz line broadening.

$(Bu_4N)_4ClTiW_{11}PO_{39}$. $(Bu_4N)_4H_3W_{11}PO_{39}$ (16 g, 5.3 mmol) and titanium tetrachloride (0.7 mL) were stirred in dichloroethane (300 mL) for 30 min under nitrogen. The mixture was filtered. The filtrate was concentrated to about 20 mL and refiltered. The two solid fractions were combined. Two such reactions were made; the crude products from each (11.1 g from one experiment, 9.6 g from the other) were combined at this point and recrystallized from boiling acetonitrile (105 mL) to obtain 5.7 g of highly crystalline $(Bu_4N)_4ClTiW_{11}PO_{39}$. The mother liquor was concentrated to half its original volume, reheated to boiling, and then allowed to stand for 16 h to obtain an additional 6.2 g (total 11.9 g, 30%) of the same product.

Anal. Calcd for $[(C_4H_9)_4N]_4ClTiW_{11}PO_{39}$: C, 20.60; H, 3.89; N, 1.50; Cl, 0.95; Ti, 1.28; W, 54.21. Found: C, 20.66; H, 3.99; N, 1.40; Cl, 1.02; Ti, 1.22; W, 53.62.

The ^{31}P NMR spectrum in acetonitrile consists of a singlet at −14.3 ppm.

$(Bu_4N)_3(H)ClTiW_{11}PO_{39}$. Hydrogen chloride was bubbled through a suspension of $(Bu_4N)_4ClTiW_{11}PO_{39}$ (0.63 g, 0.17 mmol) in 1,2-dichloroethane (50 mL) in a dinitrogen atmosphere. The solid dissolved rapidly. Purging the solution with dinitrogen caused reprecipitation of $(Bu_4N)_4ClTiW_{11}PO_{39}$. The solution was again saturated with hydrogen chloride to obtain a clear solution. The slow addition of cyclohexane caused the crystallization of $(Bu_4N)_3(H)ClTiW_{11}PO_{39}$ (0.41 g, 84%).

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(8) Domaille, P. J.; Knoth, W. H., submitted for publication in *Inorg. Chem.*

Anal. Calcd for $[(C_4H_9)_4N]_3(H)ClTiW_{11}PO_{39}$: C, 16.52; H, 3.15; N, 1.20; Ti, 1.37; Cl, 1.02; O, 17.9. Found: C, 16.75; H, 3.15; N, 1.05; Ti, 1.27; Cl, 0.85; O, 17.0.

The ^{31}P NMR spectrum of the protonated salt in dichloroethane consisted of a singlet at −13.30 ppm.

$(Bu_4N)_4ClSnW_{11}PO_{39}$. Water (6 drops) was added to a solution of $(Bu_4N)_4H_3W_{11}PO_{39}$ (30 g, 9.9 mmol) and stannic chloride (9 mL, 77 mmol) in acetonitrile (300 mL). The clear solution was stirred 1 h. Water was added slowly with stirring until the solution was cloudy. Crystalline $(Bu_4N)_3ClSnW_{11}PO_{39}$ (2.5 g) separated on standing. Additional crops of 11.4 and 9.0 g (total yield 22.9 g (61%)) were obtained by adding additional water to the filtrate until a new cloud point was reached, letting crystallization occur, and then repeating the procedure.

Anal. Calcd for $[(C_4H_9)_4N]_4ClSnW_{11}PO_{39}$: C, 20.22; H, 3.82; N, 1.47; Cl, 0.93; Sn, 3.12; W, 53.20. Found: C, 19.79; H, 3.69; N, 1.41; Cl, 0.88; Sn, 2.68; W, 53.98.

The ^{31}P NMR spectrum in acetonitrile consisted of a major resonance at −12.78 ppm and a minor resonance at −15.35 ppm, which is assigned to $W_{12}PO_{40}{}^{3-}$ present in trace amounts.

$(Bu_4N)_4(H)ClAlW_{11}PO_{39}$. Aluminum chloride (1.5 g, 11.3 mmol) was added in a nitrogen atmosphere to a mixture of $(Bu_4N)_4H_3W_{11}PO_{39}$ (20 g, 6.7 mmol) and dichloroethane (300 mL), which was then stirred for 30 min. The mixture was filtered; the filtrate was concentrated to about 30 mL and refiltered. The filter cake from the first filtration was extracted with acetonitrile (100 mL) at ambient temperature, and the extract was evaporated to dryness. The residue was combined with the filter cake from the second filtration above and recrystallized from boiling acetonitrile (16 mL) to obtain 1.5 g (6%) of $(Bu_4N)_4HClAlW_{11}PO_{39}$.

Anal. Calcd for $[(C_4H_9)_4N]_4(H)ClAlW_{11}PO_{39}$: C, 20.72; H, 3.91; N, 1.51; Cl, 0.96; Al, 0.73; W, 54.52. Found: C, 19.72; H, 3.72; N, 1.47; Cl, 0.84; Al, 0.67; W, 54.31. Carbon analysis on this compound has consistently been about 1% low; the reason for this is not known. Other analyses are consistently good.

The ^{31}P NMR spectrum in acetonitrile consists of a singlet at −12.8 ppm.

$(Bu_4N)_4CH_3OTiW_{11}PO_{39}$. In a dinitrogen atmosphere, methanol (2.5 mL) containing 1.1 mmol of sodium methoxide was added to a solution of $(Bu_4N)_4ClTiW_{11}PO_{39}$ (3.79 g, 1 mmol) in acetonitrile (75 mL). The mixture was initially clear but became cloudy within 5 min. Stirring was continued for 1 h. The mixture was filtered; evaporation of the filtrate left 3.4 g of a white residue, which was extracted with boiling dichloroethane. The insoluble portion was recrystallized from acetonitrile to obtain 0.45 g (12%) of $(Bu_4N)_4CH_3OTiW_{11}PO_{39}$.

Anal. Calcd for $[(C_4H_9)_4N]_4CH_3OTiW_{11}PO_{39}$: C, 20.95; H, 3.98; N, 1.50; Cl, 0.0. Found: C, 20.93; H, 3.98; N, 1.48; Cl, 0.18.

The proton NMR spectrum exhibited a sharp singlet at 4.3 ppm for the methoxyl protons as well as resonances for $(C_4H_9)_4N^+$. The ratio of methoxyl protons to CH_2N protons observed was 1:13 (calculated 1:11). The ^{31}P NMR spectrum in acetonitrile consisted of one resonance, at −13.92 ppm. A mixture of this product and $(Bu_4N)_4ClTiW_{11}PO_{39}$ in acetonitrile had a ^{31}P NMR spectrum that displayed two distinct resonances, at −13.90 and −14.2 ppm.

$TiW_{11}PO_{40}{}^{5-}$. (a) From $ClTiW_{11}PO_{39}{}^{4-}$. A 2-mL quantity of 1 M methanolic solution of tetrabutylammonium hydroxide was added to $(Bu_4N)_4ClTiW_{11}PO_{39}$ (0.8 g, 0.21 mmol) in acetonitrile (60 mL). The clear colorless solution was stirred for 15 min and then diluted with ether (400 mL). Filtration after brief stirring gave $(Bu_4N)_5TiW_{11}PO_{40}\cdot H_2O$ (0.57 g, 68%).

Anal. Calcd for $[(C_4H_9)_4N]_5TiW_{11}PO_{40}\cdot H_2O$: C, 24.19; H, 4.62; N, 1.76; Cl, 0.0. Found: C, 24.07; H, 4.45; N, 1.72; Cl, 0.16.

The infrared spectrum agreed with that reported[2] for $(Bu_4N)_5TiW_{11}PO_{40}\cdot H_2O$. The ^{31}P NMR spectrum in acetonitrile at 60 °C consisted of one resonance, at −14.00 ppm. The addition of an acetonitrile solution of $Cs_2B_{12}Br_{12}$[9] to one of $(Bu_4N)_5TiW_{11}PO_{40}$ precipitated $Cs_5TiW_{11}PO_{40}$, identical by infrared analysis with that prepared below.

(b) From $TiCl_4$ and $W_{11}PO_{39}{}^{7-}$. A solution of lithium acetate (20 g) in water (30 mL) was brought to pH 6 with acetic acid. A solution of phosphotungstic acid (20 g, 6.5 mmol) in water (70 mL) was added to form $W_{11}PO_{39}{}^{7-}$ in situ. A 2-ml quantity of titanium tetrachloride was added dropwise with stirring. After the addition, the mixture was refluxed for 20 min, cooled to ambient temperature, and filtered through analytical filter aid. Cesium chloride (20 g) was added to the filtrate. The precipitated solid was recrystallized from water (200 mL). The recrystallized solid was reheated in boiling water (200 mL); it did not dissolve. Aqueous cesium hydroxide was added to raise the pH from 4.5 to 5.8 while the mixture was cooling. It was then reheated to boiling. Most of the solid dissolved; the pH fell back to 4.7. It was again brought to pH 5.8 with aqueous cesium hydroxide, and the solution was reheated to boiling. All the solid dissolved; crystalline $Cs_5TiW_{11}PO_{40}\cdot 3H_2O$ (5.8 g, 26%) separated when the solution cooled.

Anal. Calcd for $Cs_5TiW_{11}PO_{40}\cdot 4H_2O$: Cs, 19.10; Ti, 1.38; W, 58.15; H_2O, 2.07. Found: Cs, 18.8; Ti, 1.33; W, 57.97; H_2O, 2.46.

Acknowledgment. Fine technical assistance was given by G. Watunya, M. P. Stepro, and G. A. Andrejack.

Registry No. $(Bu_4N)_4ClTiW_{11}PO_{39}$, 83720-98-3; $(Bu_4N)_3(H)ClTiW_{11}PO_{39}$, 83721-00-0; $(Bu_4N)_4ClSnW_{11}PO_{39}$, 83731-17-3; $(Bu_4N)_4(H)ClAlW_{11}PO_{39}$, 83731-19-5; $(Bu_4N)_4CH_3OTiW_{11}PO_{39}$, 83781-15-1; $[(C_4H_9)_4N]_5TiW_{11}PO_{40}$, 83721-02-2; $Cs_5TiW_{11}PO_{40}$, 83721-03-3; $K_4CpFe(CO)_2SnW_{11}PO_{39}$, 74870-14-7; $(Bu_4N)_4H_3W_{11}PO_{39}$, 83721-04-4; $W_{11}PO_{39}{}^{7-}$, 12412-84-9; $TiCl_4$, 7550-45-0; $AlCl_3$, 7446-70-0; $SnCl_4$, 7646-78-8; sodium methoxide, 124-41-4; tetrabutylammonium hydroxide, 2052-49-5; ^{183}W, 14265-81-7.

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