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Conclusions

It has been previously established that U(IV) exists as a hexachloro complex in basic $AlCl_3$–EMIC. Rotating disk electrode voltammetry has confirmed $[UCl_6]^{2-}$ reduces reversibly to $[UCl_6]^{3-}$; however, it is difficult to prepare pure solutions of $[UCl_6]^{3-}$ by electrolysis due to the instability of U(III) chloro complexes in the presence of trace amounts of water and oxygen. Although pure solutions of $[UCl_6]^{3-}$ have not been obtained, subtraction of the absorbance due to the small amount of $[UCl_6]^{2-}$ present has yielded a definitive spectrum of $[UCl_6]^{3-}$.

Potentiometric and diffusion coefficient measurements on U(IV)/U(III) in basic $AlCl_3$–EMIC are consistent with data on hexachloro transition-metal redox couples. The data suggest hexachloro anionic metalate complexes are not present in the ionic liquid as simple anions but are associated with one or more EMI^+'s. The Stokes–Einstein coefficients of $[UCl_6]^{2-}$ and $[UCl_6]^{3-}$ are nearly identical with those of transition-metal hexachloro anions in basic $AlCl_3$–EMIC, demonstrating that the sizes of the diffusing ion-pair complexes containing a particular central metal charge state are the same irrespective of the metal center.

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Stabilization of the Defect ("Lacunary") Complex $PMo_{11}O_{39}^{7-}$. Isolation, Purification, Stability Characteristics, and Metalation Chemistry

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All 19 literature citations of the lacunary complex $PMo_{11}O_{39}^{7-}$ deal with aqueous solutions, conditions under which this anion is kinetically labile. Kinetic stabilization of $PMo_{11}O_{39}^{7-}$, a compound of central value in development of the chemistry and applications of defect polymolybdophosphates, is made possible by precipitation of this polyoxoanion from aqueous solutions containing the requisite proportions of the parent Keggin complex α-$H_3PMo_{12}O_{40}$, and OH^-, by addition of n-Bu_4N^+. The yield of the product, $(Bu_4N)_4H_3PMo_{11}O_{39}$ (**1**), versus the byproducts, principally $P_2Mo_{18}O_{62}^{6-}$, varies greatly with the initial concentrations of α-$PMo_{12}O_{40}^{3-}$ and base prior to precipitation. All of the redox couples of **1** in acetonitrile are completely irreversible, unlike those of the parent complex, α-$H_3PMo_{12}O_{40}$, and other polyoxometalates whose structures are comprised of MO_6 octahedra with one terminal oxo group. In contrast to $PMo_{11}O_{39}^{7-}$ in aqueous solution, **1** in acetonitrile solution can be (a) highly purified by recrystallization with no generation of other polymolybdophosphates, (b) reversibly protonated to $H_4PMo_{11}O_{39}^{3-}$, which slowly decomposes to $PMo_{12}O_{40}^{3-}$, $P_2Mo_{18}O_{62}^{6-}$, and $P_2Mo_5O_{23}^{6-}$, and (c) reversibly deprotonated to $H_2PMo_{11}O_{39}^{5-}$ by 1 equiv of OH^- and readily converted to α-A-$PMo_9O_{31}(OH)_3^{6-}$ and $PMo_{12}O_{40}^{3-}$ by >1 equiv of OH^-. **1** can be metalated with several divalent d^n, $n \neq 0$ transition-metal (TM) ions to form the corresponding TM-substituted polymolybophosphates, $PMo_{11}(TM)O_{39}^{5-}$. Unlike Co^{II}, Mn^{II}, or Cu^{II}, metalation with Zn^{II} induces the decomposition of **1**. Effective metalations of **1** can be carried out by a homogeneous one-phase procedure (acetonitrile solvent and TM triflate salt) or by a heterogeneous two-phase procedure (treatment of 3:2 acetonitrile–toluene solution of **1** with an aqueous solution of the TM salt). The rates of exchange of terminal axial ligands, L, in $PM_{11}(TM-L)O_{39}^{n-}$ (M = Mo, W), in the aprotic medium, acetonitrile, which depend on the TM, the axial ligand, and on the polyoxometalate ligand environment, are discussed.

Introduction

One of the most cited of all early-transition-metal polyoxometalates is the heteropoly compound dodecamolybdophosphate, α-$PMo_{12}O_{40}^{3-}$, or in its protonated form, dodecamolybdophosphoric acid, α-$H_3PMo_{12}O_{40}$. This complex and its derivatives have numerous analytical and chemical applications.[1,2] Most significantly, however, they constitute key components in catalysts for relatively new major heterogeneous catalytic processes.[3,4] In the course of trying to prepare pure samples of the defect of "lacunary" form of the Keggin complex, $PMo_{11}O_{39}^{7-}$ (Figure 1), and the d^n, $n \neq 0$, transition-metal- (TM-) substituted complexes derived thereof, $PMo_{11}(TM)O_{39}^{n-}$, and to examine their chemical and catalytic properties, it became apparent that no satisfactorily reliable, reproducible, and selective method for the preparation of these complexes existed under conditions in which they were kinetically stable. This is in sharp contrast to the analogous polyoxotungstates. The preparation of the lacunary form of the poly-

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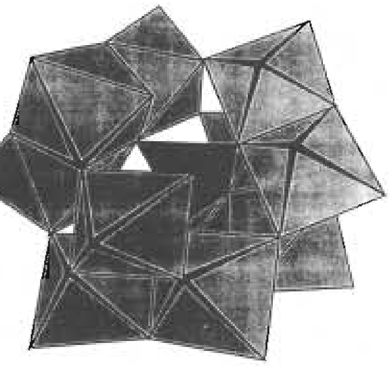

Figure 1. Polyhedral representation of the C_s symmetry "lacunary" structure, $X^{n+}M_{11}O_{39}{}^{(12-n)-}$, where each octahedron represents a MO_6 unit and the tetrahedron represents the centrally located XO_4 unit.

oxotungstate Keggin complex and its TM-substituted derivatives were first reported in 1892 and 1956 respectively,[5] followed by the subsequent development of synthetic routes to these anions in organic media.[6,7]

TM-substituted polyoxotungstate complexes have a number of potential applications in homogeneous catalysis.[7-13] These complexes were first shown to catalyze oxo transfer and hydrocarbon oxidation.[8] Subsequently, reduced forms were reported to deoxygenate organic substrates,[10] and a number of groups are now investigating various homogeneous catalytic properties of these complexes.[7-13] Catalysis by the analogous TM-substituted polymolybdate complexes (TM ≠ V) has yet to be reported.

Of the 19 reports in the literature addressing the defect complex $PMo_{11}O_{39}{}^{7-}$, as such, none report a satisfactory synthetic procedure for isolation of a kinetically stable form of the complex.[14-16] Furthermore, a recent ^{31}P NMR, Raman, and polarographic investigation of the phosphate–molybdate systems in water by Van Veen and co-workers[17] and a quantitative potentiometric and ^{31}P NMR study of the same systems by Pettersson and co-workers[18] have established the complexity of these systems. The number and type of species present in an aqueous solution of sodium molybdate and sodium phosphate depends not only on pH, but also on the Mo/P mole ratio, the overall molybdate concentration, and the age of the solution. At least 18 molybdophosphate species have been identified thus far. The two accounts reporting isolation of $PMo_{11}O_{39}{}^{7-}$ gave in our hands, by ^{31}P NMR, mixtures, with **1** itself present in low yield.[15,16] An inherent limitation of the utility of these literature reports and the chemistry of heteropolymolybdate complexes in general derives from the lability of these species. Unlike the corresponding defect heteropolytungstates, the defect polymolybdophosphates generally equilibrate, rendering attempts to purify them and to rationally investigate their chemistry very difficult.[1] It is clear that the lability of the polymolybdophosphates in water precludes their rigorous purification by chromatographic methods or repeated recrystallizations using this solvent. We report here conditions under which $PMo_{11}O_{39}{}^{7-}$ is kinetically stable permitting (a) rigorous purification by recrystallization, (b) controlled stability and protonation studies, and (c) high-yield preparations of the d^n, $n \neq 0$, transition-metal-substituted complexes, $PMo_{11}(TM)O_{39}{}^{n-}$.

Experimental Section

Materials and Methods. The complexes α-$H_3PMo_{12}O_{40}$, α-$Q_3PMo_{12}O_{40}$ (Q^+ = tetra-*n*-butylammonium cation), and α-$Na_6P_2Mo_{18}O_{62}$ were prepared by literature procedures, and their purity was determined by ^{31}P NMR, infrared and UV–visible spectroscopic analysis.[17-20] The solvents for syntheses, stability studies, spectroscopic investigations, and electrochemical measurements were Burdick and Jackson glass-distilled grade. CD_3CN and D_2O were obtained from Aldrich Chemical Co. and used as received. Deionized water was used

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in the synthesis and stability studies. All other chemicals were commercially available reagent grade quality and were used without any further purification. The electronic absorption spectra of **1**, $Q_4H_3PMo_{11}O_{39}$, and other complexes were recorded as CH_3CN solutions on a Hewlett-Packard (H/P) Model 8451A diode-array UV-visible spectrometer. Infrared spectra (2% sample in KBr) were recorded on a Perkin-Elmer Model 1430 instrument. ^{31}P broad-band proton-decoupled NMR spectra were measured on an IBM WP-200-SY spectrometer, operating at a frequency of 81 MHz. The line widths in ^{31}P NMR spectra of polyoxometalates have varied from laboratory to laboratory; exemplary variance among the polymolybdophosphates is illustrated by some of the values given in Table I (Results and Discussion). In addition, the comparison of ^{31}P NMR chemical shifts from study can be difficult as the diamagnetic susceptibility effects can be substantial.[21] All ^{31}P NMR spectral results in this study were internally consistent and highly reproducible. Approximately 2.5 mL of CD_3CN containing the polymolybdophosphate (~6 mM in nonmetalated species and ~12 mM in TM-substituted species) was placed in a 10-mm-o.d. Pyrex NMR tube equipped with a 5-mm-o.d. coaxial tube, which contained a solution of 0.1% trimethyl phosphate (TMP) in CD_3CN as the external reference. All chemical shifts upfield from TMP are reported as negative values. Aqueous solutions were referenced versus 0.1% TMP in D_2O as described above for CD_3CN solutions or versus 85% H_3PO_4 by the sample replacement method. The probe temperature for all NMR experiments was 25 °C. The pH of the polymolybdophosphate solutions was measured with a Corning 240 pH meter equipped with a Corning semi-micro combination electrode. A standard two-point calibration at pH values of 4.0 and 7.0 was made prior to making the measurements. Cyclic voltammograms were obtained by using a PAR Model 173 potentiostat equipped with a Model 176 current follower, monitored by a Model 175 universal programmer, and plotted on an Omnigraphic Series 100 X-Y recorder (Houston Instruments). A single-compartment cell with a three-electrode configuration was used. The reference electrode was $Ag/AgNO_3$ in CH_3CN containing n-Bu_4NPF_6, the counter electrode was a platinum wire, and the working electrode was a glassy-carbon disk (BAS) with a surface area of 0.07 cm^2. The redox potentials were referenced to the ferrocene/ferrocenium ion (Fc/Fc^+) couple in CH_3CN (~3 mM).[22] Elemental analyses for phosphorus, molybdenum, manganese, cobalt, and copper were carried out by E + R Microanalytical Laboratories, Corona, NY; those for carbon, hydrogen, and nitrogen were obtained by Atlantic Microlab, Inc., Norcross, GA.

Synthesis of the Tetrakis(tetra-*n*-butylammonium) Salt of $PMo_{11}O_{39}^{7-}$, $(n\text{-}Bu_4N)_4H_3PMo_{11}O_{39}$ (1). α-$H_3PMo_{12}O_{40}$ (7.3 g, 4.0 mmol) was dissolved in 40 mL of water, producing an initial concentration of the complex, $[\alpha\text{-}H_3PMo_{12}O_{40}]_0$, of 0.1 M. The pH of the solution was adjusted to 4.3 with Li_2CO_3, and then a precipitate was formed by adding solid n-Bu_4NBr (18 g, 56 mmol, 14 equiv of n-Bu_4N^+ (Q^+)/equiv of α-$PMo_{12}O_{40}^{3-}$) to the solution with vigorous stirring. The crude product was collected on a medium frit, washed with H_2O, aspirated to dryness, and allowed to air dry overnight at room temperature. In contrast to recrystallization from protic media,[15] it was established that the product, $Q_4H_3PMo_{11}O_{39}$, could be recrystallized repeatedly from organic solvents without decomposition. Recrystallization under nonprotic conditions involved dissolving the crude $Q_4H_3PMo_{11}O_{39}$ in ~200 mL of CH_3CN by stirring but with *no* heating to aid dissolution followed by slow evaporation of the solvent at room temperature. ^{31}P NMR analysis of the complex after one, two, and three recrystallizations indicated purities of 92, 97, and 99+%, respectively. In a typical preparation, 6.73 g of a light yellow-green crystalline material was obtained (63% yield based on α-$H_3PMo_{12}O_{40}$) after recrystallization. ^{31}P NMR (CD_3CN): δ -4.4 ppm, $\nu_{1/2}$ 12 Hz. Infrared (cm^{-1}): 1079 (s), 1052 (s) (P-O), 950 (vs) (M-O$_t$), 905 (s), 865 (m) (M-O$_b$-M), 830 (shoulder), 815 (s), 755 (vs, broad) (M-O$_b$-M). UV-visible [CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})]: 215 (8.39×10^4), ~295 shoulder (2.06×10^4).

Anal. Calcd for $C_{64}H_{147}N_4PMo_{11}O_{39}$: C, 28.65; H, 5.52; N, 2.09; Mo, 39.33; P, 1.15. Found: C, 28.67; H, 5.42; N, 2.10; Mo, 39.29; P, 1.15.

Reaction of 1 with *n*-Bu_4NOH. The two methods utilized in the reaction of **1** with n-Bu_4NOH closely followed those of Finke and coworkers[23] for determination of the number of protons on $SiW_9V_3O_{40}^{7-}$. The base, n-Bu_4NOH in methanol, was standardized by titration with aqueous HCl solution (phenolphthalein endpoint).

Method 1: Titration of 1 with *n*-Bu_4NOH. A 15-mL aliquot of a solution of **1** (5.0 mM) in CD_3CN was prepared and divided into five equal portions. To each of these 3-mL aliquots was added varying quantities of the standardized 1.13 N n-Bu_4NOH via syringe as follows (equivalents, microliters of base solution): 0, 0; 1, 13; 2, 26; 3, 39; 4, 52. The samples were analyzed by ^{31}P NMR immediately after the addition of the base. Each sample was then back-titrated with an appropriate amount of 1.10 N HCl to neutralize the added base and analyzed once again by ^{31}P NMR. The NMR resonances were as follows [equivalents of added base, ^{31}P NMR signal in ppm (relative intensity)]: 0, -4.4; 1, -4.3, -4.5 (shoulder); 2, -4.3 (4), -4.5 (shoulder), -4.8 (1), -6.0 (1); 3, -4.3 (3), -4.5 (shoulder), -4.8 (1), -6.0 (1); 4 (much decomposition of **1** as indicated by multiple-line NMR spectrum). The species with δ = -4.3 and -4.5 ppm can be attributed to different protonated forms of **1**, while those with δ = -4.8 and -6.0 ppm can be assigned to α-A-$PMo_9O_{31}(OH)_3^{6-}$ and α-$PMo_{12}O_{40}^{3-}$, respectively.[17,18] Back-titration with acid resulted in the regeneration of **1** (δ = -4.4 ppm) and the formation of α-$PMo_{12}O_{40}^{3-}$ (δ = -6.1) with relative intensities of 3:1, respectively, in all cases except one. The instance in which 1 equiv of each titrant was used resulted in a ^{31}P NMR signal intensity ratio of **1**:α-$PMo_{12}O_{40}^{3-}$ of 5:1.

Method 2: Isolation of the Products Obtained in the Reaction of 1 with Base. Forty milliliters of a CH_3CN solution of **1** (4.7 mM) was divided into five equal portions. To each of these aliquots was added a different amount of 1.13 N n-Bu_4NOH via syringe (equivalents, microliters of base solution): 0, 0; 1, 33; 2, 66; 3, 99; 4, 132. Each sample was stirred for ~5 min and then taken to dryness by removing the solvent at room temperature under high vacuum. The residue from each mixture was redissolved in 3 mL of CD_3CN and analyzed by ^{31}P NMR [equivalents of added base, ^{31}P NMR signal in ppm (relative intensity)]: 0, -4.4; 1, -4.3 (4), -4.5 (shoulder), -4.8 (1); 2, -4.3 (2), -4.5 (shoulder), -4.8 (1), -6.0 (2); 3, +8.0 (1), +1.0 (1), -4.8 (6), -6.1 (10); 4, +8.0 (1), +1.0 (3), -4.8 (1), -6.1 (10). The species with δ = +8.0 and +1.0 ppm are as yet unidentified, the assignments of the remaining chemical shift values are the same as those given above.

Reaction of 1 with 1 equiv of Added Acid. One equivalent of acid (0.5 μL of concentrated H_2SO_4) was added via syringe to a CD_3CN solution of **1** (50 mg, 6.2 mM). The ^{31}P NMR, measured immediately after the addition of the acid, indicated a shift of the signal for **1** from -4.4 to -5.1 ppm. Heating the NMR solution for 1 h at 60 °C (oil bath) resulted in the decomposition of the species at -5.1 ppm and regeneration of **1** (-4.4 ppm) in addition to the formation of α-$PMo_{12}O_{40}^{3-}$ (-6.1 ppm) and $P_2Mo_5O_{23}^{6-}$ (-1.6 ppm)[17,18] in a ratio, based on the relative intensities of ^{31}P NMR signals, of 2:3:2. As an alternative to heating, the acidified NMR solution was allowed to age for 5 days at room temperature before analysis by ^{31}P NMR. In this case, the decomposition of the species with δ = -5.1 ppm led to the production of $P_2Mo_5O_{23}^{6-}$, $P_2Mo_{18}O_{62}^{6-}$ (-5.5 ppm), and α-$PMo_{12}O_{40}^{3-}$ with relative ^{31}P NMR signal intensities of 2:1:4 respectively. Subsequent heating of this solution (60 °C for 1 h) did not alter the product distribution as observed by ^{31}P NMR.

Reaction of 1 with Traces of Added Water. Addition of 1% or 5% (v/v) of water to a 5 mM solution of **1** in CD_3CN (3 mL) does not alter the ^{31}P NMR chemical shift of **1** nor does it cause any decomposition of **1** as observed in the ^{31}P NMR. However, the half-height peak width is narrowed considerably from 12 Hz in "dry" CD_3CN to 6 Hz in "wet" (1% or 5% H_2O) CD_3CN.

Effect of Heating an Acetonitrile Solution of 1. A 6.2 mM solution of **1** in CD_3CN was heated in a 60 °C oil bath for 1.5 h. The ^{31}P NMR indicated a significant amount of decomposition of **1**. There were three species observed in the NMR: -3.3 ppm, -4.4 ppm (**1**), and -6.6 ppm with relative intensities of 1:4:1. The peak at -3.3 ppm can be tentatively assigned to α-B-$PMo_9O_{31}(OH)_3^{6-}$.[18] The species with the signal at -6.6 ppm is as yet unidentified.

Procedures for Metalation of 1: One Phase. In a typical one-phase metalation in aprotic media, 0.055 g (0.15 mmol) of zinc triflate was added to a solution of 0.46 g (0.17 mmol) of **1** in 25 mL of acetonitrile. The product complex $PMo_{11}Zn^{II}O_{39}^{5-}$ was formed immediately as evidenced by the ^{31}P NMR of the crude reaction mixture (δ = -5.1 ppm). However, one other species, $P_2Mo_{18}O_{62}^{6-}$, was also present, which represented roughly 25% of the product mixture.

The metalation of **1** with Co^{II} and Cu^{II} was followed by ^{31}P NMR. For example, the addition of 1 equiv of cobalt triflate (6.4 mg, 0.018 mmol) to a CD_3CN solution of **1** (50.0 mg, 6.2 mM) resulted in an immediate change in the color of the solution to red. ^{31}P NMR analysis of this solution indicated that only one species was produced, $PMo_{11}Co^{II}(L)O_{39}^{5-}$ (δ +345 ppm, $\nu_{1/2}$ 335 Hz). After 20 days the NMR solution was once again analyzed by ^{31}P NMR to find that the signal at +345 ppm had disappeared and three new peaks had formed, with rel-

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(21) Diamagnetic susceptibility effects in ^{31}P NMR spectra: (a) Lagodzinskaya, G. V.; Klimenko, I. Y. *J. Magn. Reson.* **1982**, *49*, 1. (b) Domaille, P. J.; Watunya, G. *Inorg. Chem.* **1986**, *25*, 1239. The latter references also discuss the related affect of the orientation (vertical versus horizontal) of B_0 on the chemical shifts.

(22) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1982**, *54*, 1527.

(23) A particularly thorough experimental examination of the protonation states of complex heteropolyanions in aprotic organic solvents by base titration and related methods: Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947.

ative intensities of 2:2:1 [δ in ppm ($\nu_{1/2}$ in Hz)]: +521 (155); +513 (190); +439 (575). The data indicated that the species present after 20 days are derivatives of $PMo_{11}Co^{II}(L)O_{39}^{5-}$, differing only in the identity of the ligand, L, and/or the degree of protonation. These assignments are discussed later in the text.

An analogous preparation with the copper triflate produced only one ^{31}P NMR signal, that of $PMo_{11}Cu^{II}(L)O_{39}^{5-}$ (δ −35 ppm, $\nu_{1/2}$ 3300 Hz), which persisted as the only species visible in the ^{31}P NMR spectrum after 20 days at 25 °C.

Two Phase. A biphasic extraction technique was devised to metalate **1** more conveniently by using readily available and relatively inexpensive water-soluble transition-metal salts. It should be noted that this method also works well for the analogous tungstates.

$(n\text{-}Bu_4N)_4HPMo_{11}Mn^{II}(CH_3CN)O_{39}$. Exactly 1.0 g (0.37 mmol) of **1** was dissolved in 60 mL of acetonitrile with stirring, and then 40 mL of toluene was added to produce a homogeneous light yellow-green solution. This solution was poured into a separatory funnel to which was added 25 mL of an aqueous solution of $MnSO_4{\cdot}H_2O$ (93 mg, 0.55 mmol, 1.5 equiv). Vigorous shaking of the heterogeneous mixture for ~1 min resulted in an immediate color change of the organic layer to brown suggesting that **1** had rapidly extracted the manganese ion into the organic layer. The water layer was drawn off, and the remaining organic layer was placed in a crystallizing dish and allowed to evaporate slowly at room temperature. The crude brown crystalline product was separated by filtration and recrystallized from acetonitrile; 0.94 g (91% yield based on **1**) of brown crystalline $(n\text{-}Bu_4N)_4HPMo_{11}Mn^{II}(CH_3CN)O_{39}$ was collected. Infrared (cm^{-1}): 1047 (s), 939 (vs), 875 (s), 820 (vs, broad), 760 (shoulder). UV–visible [CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})]: 215 (8.09×10^4), ~280 (2.13×10^4).

Anal. Calcd for $C_{64}H_{145}N_4PMo_{11}Mn(CH_3CN)O_{39}$: C, 28.55; H, 5.37; N, 2.52; Mn, 1.98; Mo, 38.00; P, 1.12. Found: C, 28.61; H, 5.43; N, 2.48; Mn, 1.83; Mo, 38.27; P, 1.13.

$(n\text{-}Bu_4N)_4HPMo_{11}Cu^{II}(CH_3CN)O_{39}$. Following the same biphasic procedure as that outlined above for the manganese-substituted polymolybdophosphate but using instead 1.00 g **1** (0.37 mmol) and 90 mg $CuSO_4$ (0.56 mmol), we obtained 0.63 g (61% yield based on **1**) of bright lime green crystalline material. A small amount, <3% by ^{31}P NMR, of $P_2Mo_{18}O_{62}^{6-}$ persisted after several recrystallizations from acetonitrile. ^{31}P NMR (CD_3CN): δ −35 ppm, $\nu_{1/2}$ 3300 Hz. Infrared (cm^{-1}): 1089 (m), 1062 (s), 945 (vs), 878 (s), 812 (vs), 710 (m). The band at 1089 cm^{-1} is not likely a result of the presence of a small quantity of $P_2Mo_{18}O_{62}^{6-}$ impurity since the other band of the P–O stretch in the Wells–Dawson structure is absent, (1082 and 1008 cm^{-1}).[14j] UV–visible [CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})]: 218 (1.01×10^5), 304 (3.22×10^4); at the wavelength limit of the instrument, 820 nm, an absorbance was observed (820 nm, 35.5 M^{-1} cm^{-1}), the maximum of which was not within the instrument's range of detection.

Anal. Calcd for $C_{64}H_{145}N_4PMo_{11}Cu(CH_3CN)O_{39}$: C, 28.46; H, 5.35; N, 2.51; Cu, 2.28; Mo, 37.88; P, 1.11. Found: C, 27.84; H, 5.20; N, 2.04; Cu, 2.01; Mo, 38.60; P, 1.15.

Addition of 1 equiv of pyridine to a CD_3CN solution of $(n\text{-}Bu_4N)_4HPMo_{11}Cu^{II}(MeCN)O_{39}$ resulted in a shift of the ^{31}P signal to −5 ppm ($\nu_{1/2}$ = 3330 Hz). No noticeable change in color was observed although there was a slight red shift of the lowest energy absorbance in the UV–visible spectrum.

$(n\text{-}Bu_4N)_4HPMo_{11}Co^{II}(L)O_{39}$. Following the same procedure as that outlined above for the manganese substituted polyoxoanion but using instead 1.00 g **1** (0.37 mmol) and 87 mg $CoSO_4$ (0.56 mmol), we obtained 0.78 g (76% yield based on **1**) of red crystalline material. Heating of the red solid (steam bath) under vacuum (0.01 mm Hg) for ~3 h resulted in a change in color of the solid from red to green. Exposure of the green solid to moist air at room temperature resulted in an immediate change in color of the solid from green to brown. Dissolving the dried, green or the "wet", brown material in dry acetonitrile (dried over sieves and stored under nitrogen in a Sure-seal bottle) resulted in a rapid change in color back to red again. This cycle is reversible and can be repeated several times with no apparent destruction of the anion as indicated by ^{31}P NMR (NMR of the green solid was obtained by dissolving it in dry CD_3CN and placing it, under N_2, in an airtight NMR tube fitted with a septum). ^{31}P NMR of the green material, $(n\text{-}Bu_4N)_4HPMo_{11}Co^{II}O_{39}$ (dry CD_3CN) [δ, ppm ($\nu_{1/2}$, Hz)]: 518 (295), 509 (320), 459 (475), 434 (290), with relative intensities of 5:7:1:1.

Analysis of the brown, hydrated material, $(n\text{-}Bu_4N)_4HPMo_{11}Co^{II}(H_2O)O_{39}$ is as follows. ^{31}P NMR (CD_3CN) [δ, ppm ($\nu_{1/2}$ Hz)]: 518 (157), 509 (205), with relative intensities of 1:1. Infrared (cm^{-1}): 1090 (m), 1050 (s), 940 (vs), 872 (s, broad), 820 (vs, broad), 760 (shoulder).

Anal. Calcd for $C_{64}H_{145}N_4PMo_{11}Co(H_2O)O_{39}$: C, 27.87; H, 5.37; N, 2.03; Co, 2.14; Mo, 38.26; P, 1.12. Found: C, 28.16; H, 5.62; N, 2.21; Co, 1.22; Mo, 38.16; P, 1.14.

Analysis of the red material from the initial preparation (before drying), $(n\text{-}Bu_4N)_4HPMo_{11}Co^{II}(L)O_{39}$, is as follows. ^{31}P NMR (CD_3CN) [δ, ppm ($\nu_{1/2}$, Hz)]: 519 (154), 510 (190), 460 (~575), 435 (~500), with relative intensities of 8:10:1:1 respectively, (the signal to noise ratio made accurate determination of the line widths of the two smaller peaks virtually impossible). Infrared (cm^{-1}): 1051 (s), 935 (vs), 870 (s), 812 (vs), 750 (m). UV–visible [CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})]: 214 (4.55×10^4), 514 (144).

Anal. Calcd for $C_{64}H_{145}N_4PMo_{11}Co(CH_3CN)O_{39}$: C, 28.06; H, 5.33; N, 2.05; Co, 2.15; Mo, 38.52; P, 1.13. Found: C, 28.22; H, 5.36; N, 2.15; Co, 1.95; Mo, 38.34; P, 1.17.

Addition of 1 equiv of pyridine to a NMR solution (CD_3CN) of the red or brown material caused the four peaks to coalesce to form one peak; δ = 622, and $\nu_{1/2}$ = 880 Hz. The resulting complex, $(n\text{-}Bu_4N)_4HPMo_{11}Co^{II}(py)O_{39}$, could be crystallized from solution by slow evaporation of the solvent at room temperature. Redissolving the material in CD_3CN and measuring the ^{31}P NMR again gave the same spectrum; δ = 622 ppm. Scaling up the procedure for the synthesis of $(n\text{-}Bu_4N)_4HPMo_{11}Co^{II}(py)O_{39}$ was straightforward and yielded enough dark red crystalline material for a more complete analysis.

Analysis for $(n\text{-}Bu_4N)_4HPMo_{11}Co^{II}(py)O_{39}$ is as follows. ^{31}P NMR (CD_3CN): δ 622 ppm, $\nu_{1/2}$ 880 Hz. Infrared (cm^{-1}): polyoxometalate-based bands at 1048 (s), 933 (vs), 870 (s), 810 (vs), 740 (m); pyridine-based bands at 1605 (w), 1219 (w), 710 (shoulder). UV–visible [CH_3CN; λ, nm (ϵ, M^{-1} cm^{-1})]: 565 (210).

Anal. Calcd for $C_{64}H_{145}N_4PMo_{11}Co(C_5H_5N)O_{39}$: C, 29.40; H, 5.36; N, 2.48. Found: C, 28.72; H, 5.30; N, 2.42.

$(n\text{-}Bu_4N)_4HPMo_{11}Zn^{II}O_{39}$. In a procedure analogous to the preparation of the manganese complex, 1.00 g of **1** (0.37 mmol) and 0.10 g (0.56 mmol) of $ZnSO_4{\cdot}H_2O$ yielded 0.46 g of light green crystalline material. Analysis by ^{31}P NMR revealed a significant contamination of the desired product, $(n\text{-}Bu_4N)_4HPMo_{11}Zn^{II}O_{39}$ (δ = −5.1 ppm), with $P_2Mo_{18}O_{62}^{6-}$ and α-$PMo_{12}O_{40}^{3-}$ with relative intensities of 3:1:1. Repeated recrystallizations did not significantly improve the purity of the desired product. ^{31}P NMR analysis indicated that, at best, a product mixture of 75% $PMo_{11}Zn^{II}O_{39}^{5-}$ was obtainable by this method. No further characterization was performed.

Reaction of 1 with Fe(II). In a preparation analogous to that for the manganese complex above, 0.20 g of **1** (0.075 mmol) and 17 mg (0.11 mmol) of $FeSO_4$ reacted to yield 0.14 g of a pea green powder. Analysis of a CD_3CN solution of the product mixture by ^{31}P NMR indicated the formation of only two products, α-$PMo_{12}O_{40}^{3-}$ and the one-electron-reduced complex $PMo_{12}O_{40}^{4-}$ (δ −2.3 ppm vs TMP);[20b] with relative intensities of 1:2. Infrared (cm^{-1}): 1060 (s), 950 (vs), 875 (s), 809 (vs, broad). These values are very close to those obtained by analyzing authentic α-$PMo_{12}O_{40}^{4-}$ by infrared spectroscopy (1068 (s), 955 (vs), 880 (s), and 810 (vs, broad) cm^{-1}). Authentic α-$PMo_{12}O_{40}^{4-}$ was prepared by treating **1** in CH_3CN with 1 equiv of $[n\text{-}Bu_4N][Re(V)OBr_4]$,[24] evaporating the solvent at room temperature and recrystallizing the green, air-stable product in CH_3CN. Purity was confirmed by ^{31}P NMR[20b] and ^{17}O NMR.[20a]

Results and Discussion

Characterization of Kinetically Stabilized $PMo_{11}O_{39}^{7-}$. Repeated attempts to isolate and purify $PMo_{11}O_{39}^{7-}$ by recrystallization from aqueous solutions failed. A series of experiments indicated that, in aqueous media, the media used in all 19 literature reports citing this compound,[14-16] the compound decomposes or equilibrates at rates too rapid to permit isolation and purification. There are two published procedures for the preparation and isolation of the salts of **1**: that of Fourier and Massart[15] (the NH_4^+ salt) and that of Murata and Ikeda[16] (the Et_4N^+ salt). When the published protocols for preparing the title compound, **1**, given in these two papers were followed, the ^{31}P NMR spectra "A" and "B" in Figure 2 were produced. It should be noted that the final product distribution may have been influenced by a slight modification of the preparations to include a final precipitation of the polymolybdophosphate anions in the reaction mixture with $n\text{-}Bu_4N^+$. The predominant species present in one preparation was the Wells–Dawson heteropolymolybdate, $P_2Mo_{18}O_{62}^{6-}$, with a chemical shift, δ, relative to trimethyl phosphate external standard, of −5.5 ppm. The ^{31}P NMR parameters for this and several other polymolybdophosphates addressed in this study are summarized in Table I.[25] The other literature procedure produced a ~1.5:1

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[24] Cotton, F. A.; Lippard, S. J. *Inorg. Chem.* **1966**, *5*, 9.

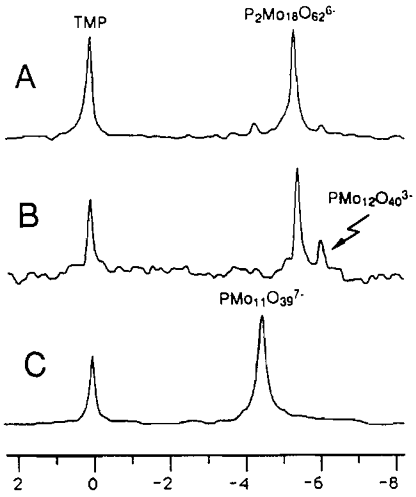

Figure 2. ^{31}P NMR (CD_3CN) spectra generated by following three procedures for the preparation of **1**, where all three procedures involve a final precipitation with n-Bu_4NBr prior to obtaining spectra: (A) acidification of an aqueous mixture of ammonium paramolybdate and H_3PO_4, as per ref 15; (B) acidification of an aqueous mixture of sodium molybdate and sodium phosphate, as per ref 16; (C) alkalinization of an aqueous solution of α-$H_3PMo_{12}O_{40}$, as in this paper.

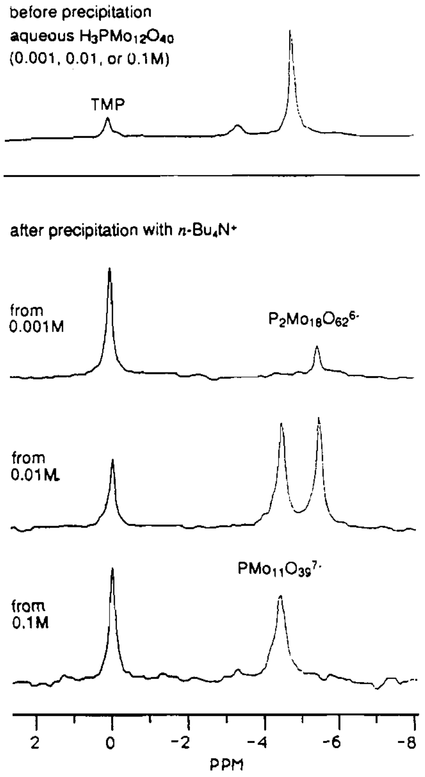

Figure 3. Top: ^{31}P NMR spectrum of an aqueous solution (D_2O in coaxial tube for deuterium lock) of α-$H_3PMo_{12}O_{40}$, pH = 4.3, at three different initial concentrations. Bottom: ^{31}P NMR spectra (CD_3CN solutions) of the polymolybdophosphates precipitated by addition of n-Bu_4NBr to three solutions varying in $[\alpha\text{-}H_3PMo_{12}O_{40}]_0$.

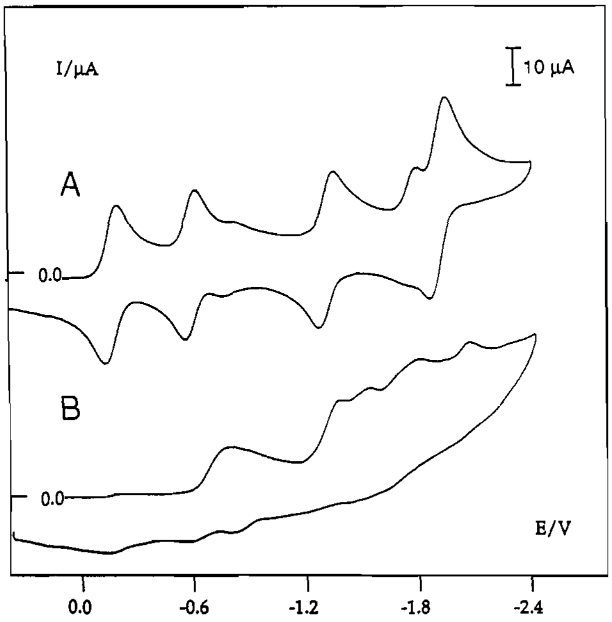

Figure 4. Cyclic voltammograms of α-$Q_3PMo_{12}O_{40}$ (A) and $Q_4H_3PMo_{11}O_{39}$ (B) in CH_3CN under identical conditions: $Ag/AgNO_3$ (0.1M, CH_3CN) reference, ~1.3 × 10^{-3} M polyoxometalate/0.1 M n-Bu_4NPF_6; scan rate of 100 mV/s. The Fc/Fc^+ couple appears at +90 mV.

molar ratio of $P_2Mo_{18}O_{62}^{6-}$ to Keggin ion, α-$PMo_{12}O_{40}^{3-}$. We have found, not surprisingly, given the other reported studies addressing polyoxometalate lability in solution,[1a,14i,26] that by moving from protic to aprotic media, $PMo_{11}O_{39}^{7-}$ becomes substantially more stable. Converting to acetonitrile-soluble salt forms, for example, and working in this solvent, one can rigorously purify (n-$Bu_4N)_4H_3PMo_{11}O_{39}$ (**1**) by repeated recrystallizations in this solvent (see Experimental Section). This kind of kinetic stability, unknown for $PMo_{11}O_{39}^{7-}$ in aqueous media, renders **1** experimentally tractable and facilitates systematic and quantitative investigations of the stability and other physical and chemical properties of this complex.

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(25) The ^{31}P NMR chemical shifts reported in the literature are routinely referenced to 85% H_3PO_4.[21] Therefore, accounting for this difference becomes necessary when the chemical shifts obtained in this study (vs TMP) are compared with those of other researchers (vs 85% H_3PO_4). The choice of deuterium locking solvent alters the chemical shift value as does the solvent in which the polymolybdophosphate anion is dissolved, so these effects must also be considered when comparisons are made with the literature. When the ^{31}P NMR chemical shifts of species dissolved in like deuterated locking solvents are compared (i.e. CD_3CN *or* D_2O), a simple correction is necessary. However, if the locking solvent differs from the solvent in which the polymolybdophosphate species is dissolved, an additional correction must be made to account for the change in chemical shift as a result of the change in field strength. Both of these adjustments to the observed ^{31}P NMR chemical shift can be made by utilizing the following information:

ref	locking solvent	δ, ppm
TMP	CD_3CN	0.00
TMP	D_2O	−2.00
85% H_3PO_4	CD_3CN	−3.76
85% H_3PO_4	D_2O	−5.76

A simple correction such as that given above cannot be made when the ^{31}P NMR chemical shifts of polymolybdophosphate species dissolved in different media are compared (i.e. CD_3CN vs D_2O). Therefore, for purposes of comparison of ^{31}P NMR chemical shifts of polymolybdophosphates in acetonitrile solution to the relative abundance of ^{31}P NMR data available in the literature for these species in aqueous solution, two averaged correction factors were calculated. For polymolybdophosphate anions with chemical shifts that are not pH dependent, such as $PMo_{12}O_{40}^{3-}$ and $P_2Mo_{18}O_{62}^{6-}$, comparing literature values with those obtained in this study can be performed by utilizing the formula [δ(MeCN, CD_3CN lock solvent, TMP reference)] ppm + 2.92 ppm = [δ(aqueous, D_2O lock solvent, 85% H_3PO_4 reference)] ppm. Polymolybdophosphate anions such as $H_xP_2Mo_5O_{23}^{(6-x)-}$, $H_xPMo_9O_{31}(OH)_3^{(6-x)-}$ and $H_xPMo_{11}O_{39}^{(7-x)-}$ are capable of existing in various protonation states in solution, and consequently they have pH-dependent chemical shifts. The ^{31}P NMR chemical shifts measured for these polyoxoanions in CD_3CN can be compared to those observed from that used when converting chemical shift values that are not dependent on pH: [δ(MeCN, CD_3CN lock solvent, TMP reference)] ppm + 3.60 ppm = [δ(aqueous, D_2O lock solvent, 85% H_3PO_4 reference)] ppm. The conversion factors, δ = 2.92 and 3.60 ppm, were calculated by comparison of the literature values for ^{31}P NMR chemical shifts of aqueous solutions[17,18] of polymolybdophosphates to those obtained in acetonitrile.

(26) (a) Lebedeva, L. I.; Ptushkina, M. N. *Russ. J. Inorg. Chem.* **1972**, *17*, 1118. (b) Tsigdinos, G. A.; Hallada, C. J. *J. Less-Common Met.* **1974**, *36*, 79. (c) Kazansky, L. P.; Potapova, I. V.; Spitsyn, V. I. *Chemistry and Uses of Molybdenum, Proceedings of the International Conference, 3rd*; Barry, H. F., Mitchell, P. C. H., Eds.; Climax Molybdenum Co.: Ann Arbor, MI, 1979; p 67.

Table I. ^{31}P NMR Chemical Shifts and Line Widths of Polymolybdophosphates in Aqueous and Acetonitrile Solutions

phosphomolybdate species[a]	chem shift, ppm	$\nu_{1/2}$ line widths,[b] Hz	solvent	salt[c]	ref[d]
α-$PMo_{12}O_{40}^{3-}$	−6.07	2.9	CD_3CN	Q^+	
α-$PMo_{12}O_{40}^{4-}$	−2.29	7.2	CD_3CN	Q^+	
α-$P_2Mo_{18}O_{62}^{6-}$	−5.49	11	CD_3CN	Q^+/H^+	
$H_xP_2Mo_5O_{23}^{(6-x)-}$[e]	−1.60	11	CD_3CN	Q^+/H^+	
α-A-$H_xPMo_9O_{31}(OH)_3^{(6-x)-}$[f]	−4.77	...	CD_3CN	Q^+/H^+	
α-B-$H_xPMo_9O_{31}(OH)_3^{(6-x)-}$	−3.28	...	CD_3CN	Q^+/H^+	
α-B-$H_xPMo_9O_{31}(OH)_3^{(6-x)-}$	−3.36	...	D_2O	H^+/Li^+	
α-$H_xPMo_{11}O_{39}^{(7-x)-}$[g]	−4.86	4.5	D_2O	H^+/Li^+	
α-$H_2PMo_{11}O_{39}^{5-}$	−4.31	8.5	CD_3CN	Q^+/H^+	
α-$H_3PMo_{11}O_{39}^{4-}$ (anion of **1**)	−4.43	12	CD_3CN	Q^+/H^+	
α-$H_4PMo_{11}O_{39}^{3-}$	−5.13	11	CD_3CN	Q^+/H^+	
$PMo_{11}ZnO_{39}^{5-}$	−5.07	11	CD_3CN	Q^+/H^+	
$PMo_{11}ZnO_{39}^{5-}$	−1.2	...	D_2O	NH_4^+	14j
$PMo_{11}Cu(MeCN)O_{39}^{5-}$	−35	3300	CD_3CN	Q^+/H^+	
$PMo_{11}Cu(py)O_{39}^{5-}$	−5	3330	CD_3CN	Q^+/H^+	
$PMo_{11}Co(py)O_{39}^{5-}$	622	880	CD_3CN	Q^+/H^+	
α-$PMo_{12}O_{40}^{3-}$	−3.20	2.9	D_2O	H^+/Na^+	18
α-$PMo_{12}O_{40}^{3-}$	−3.20	<1	D_2O	H^+/Na^+	20a
α-$PMo_{12}O_{40}^{3-}$[h]	−0.4	0.1	MeCN	H^+/Na^+	20a
α-$PMo_{12}O_{40}^{4-}$[i]	+3.5	2.6	MeCN	H^+/Na^+	20a
α-$P_2Mo_{18}O_{62}^{6-}$	−2.53	2.9	D_2O	H^+/Na^+	18
$H_xP_2Mo_5O_{23}^{(6-x)-}$ ($x = 0$–2)[j]	+2.35 to +1.86	3.5–2.9	D_2O	H^+/Na^+	18
α-A-$H_xPMo_9O_{31}(OH)_3^{(6-x)-}$ ($x = 2$–3)	−1.15 to −1.00	4.3	D_2O	H^+/Na^+	18
α-B-$H_xPMo_9O_{31}(OH)_3^{(6-x)-}$ ($x = 2$–3)	+0.47 to +0.08	8.2–4.3	D_2O	H^+/Na^+	18
α-$H_xPMo_{11}O_{39}^{(7-x)-}$ ($x = 0$–2)	−0.78 to −1.20	4.3	D_2O	H^+/Na^+	18

[a] The concentrations used in this study were ~12 mM in transition-metal-substituted polyanions and ~6 mM in all other polymolybdophosphates. [b] In this study, chemical shifts of polymolybdophosphates in CD_3CN solutions are reported versus 0.1% trimethyl phosphate (TMP). The chemical shifts of the literature compounds in CD_3CN and aqueous solutions are reported versus 85% H_3PO_4; 85% H_3PO_4 is 3.76 ppm upfield of TMP in a given deuterated solvent system.[25] The line widths are measured at half peak height (peaks expanded to obtain best possible measurement). A line broadening factor of 1.0 is used in the spectra obtained for the purpose of calculating $\nu_{1/2}$. [c] Q^+ refers to the n-Bu_4N^+ cation. [d] This paper if not otherwise noted. [e] The degree of protonation, x, was not addressed in this study. [f] As in footnote *e*, the value of x for the $H_xPMo_9O_{31}(OH)_3^{(6-x)-}$ series was not determined. The ^{31}P NMR line widths were not measurable since the relative quantities of the $H_xPMo_9O_{31}(OH)_3^{(6-x)-}$ anions were quite low. [g] The degree of protonation, x, was not determined. However, if the chemical shift is reported versus the 85% H_3PO_4 reference (δ + 3.76 ppm),[25] the new value would be $\delta = -1.10$ ppm, which is close to that reported by Pettersson and co-workers[18] for the doubly protonated anion $H_2PMo_{11}O_{39}^{5-}$ ($\delta = -1.20$ ppm). [h] If the chemical shift of −0.4 ppm is corrected to the TMP reference ($\delta = -3.76$ ppm)[25] and CD_3CN locking solvent ($\delta = -2.00$ ppm),[25] then the new chemical shift would be −6.16 ppm, which is close to the value obtained in this study. [i] As in footnote *h*, the chemical shift expected under the conditions of this study is −2.26 ppm.[25] [j] When a range of chemical shift values is given in this table, the more positive value reflects the chemical shift of the least protonated polyanion species. However, the opposite trend is observed for the polymolybdophosphate α-A-$H_xPMo_9O_{31}(OH)_3^{(6-x)-}$.

The yield of **1**, after precipitation from aqueous solution with a hydrophobic cation, is a sensitive function of the concentration of initial polymolybdophosphate and base present in aqueous solution prior to precipitation. A dependence of the species present at a given pH on the overall molybdate concentration has been noted before.[14c] Data from exemplary experiments are given in Figure 3. Three different initial concentrations (0.1, 0.01, and 0.001 M) of the parent compound, α-$H_3PMo_{12}O_{40}$, plus enough base, Li_2CO_3, to adjust the pH to 4.3 in each case, gave similar spectra in water prior to precipitation (Figure 3, top). The primary species observed in all three aqueous preparations were $PMo_{11}O_{39}^{7-}$ (major product; $\delta = -4.9$ ppm vs TMP/D_2O) and α-B-$PMo_9O_{31}(OH)_3^{6-}$ (minor product; $\delta = -3.4$ ppm vs TMP/D_2O).[18] However, the products obtained after precipitation with n-Bu_4N^+, as determined directly by ^{31}P NMR in acetonitrile, are remarkably dependent on the initial concentration of α-$H_3PMo_{12}O_{40}$. At a value of $[\alpha\text{-}H_3PMo_{12}O_{40}]_0 = 0.001$ M, very little **1** is present after precipitation and the Wells–Dawson structure, $P_2Mo_{18}O_{62}^{6-}$, is the dominant polymolybdophosphate in solution. At a value of $[\alpha\text{-}H_3PMo_{12}O_{40}]_0 = 0.01$, the concentrations of $P_2Mo_{18}O_{62}^{6-}$ and **1** after precipitation are comparable, while at $[\alpha\text{-}H_3PMo_{12}O_{40}]_0 = 0.1$ M, **1** is produced with fairy high selectivity.

The infrared spectrum of **1**, $Q_4H_3PMo_{11}O_{39}$, highly purified after several recrystallizations, exhibits the general group absorbances of the parent Keggin structure but with increased complexity derived from the lowering of the molecular symmetry from T_d to C_s. The absorbances dominated by P–O, Mo–O (terminal), Mo–O–Mo (corner-shared) and Mo–O–Mo (edge-shared) stretching modes for α-$Q_3PMo_{12}O_{40}$ are at 1063, 965 and 955, 880, and 805 cm^{-1} respectively.[14b,19] When the symmetry is lowered to C_s, the greatest perturbation is observed in the P–O absorbance of **1**, which exhibits a split band of 1079 and 1052 cm^{-1}. Similar splitting of the P–O band has been observed in the infrared spectrum of the analogous tungstate complex, $PW_{11}O_{39}^{7-}$.[5h]

With conditions established under which **1** is soluble, tractable, and stable to degradation, data from a number of experiments addressing the physical and chemical properties of the complex in solution could be more readily interpreted than in previous studies. The cyclic voltammograms of both **1** and the parent Keggin complex, α-$Q_3PMo_{12}O_{40}$ (Figure 4), illustrate that for all observed redox couples, the rates of interfacial electron transfer are substantially lower for the lacunary complex than for α-$Q_3PMo_{12}O_{40}$. In contrast to the latter compound, no redox couple for **1** even approaches reversible diffusion-limited behavior. Comparison of the cyclic voltammograms of the polymolybdophosphates with those of the analogous polytungstophosphates (Figure 5) illustrates a dramatic difference in the two lacunary anions. Unlike **1**, the redox behavior of $Q_4H_3PW_{11}O_{39}$ maintains much of the reversibility of the parent complex, α-$Q_3PW_{12}O_{40}$ (Figure 5). To the best of our knowledge, **1** is the only polyoxometalate complex composed principally of type I MO_6 octahedra (one terminal M═O with minimally bonding or nonbonding LUMOs) that exhibits totally irreversible electrochemical behavior.[1e] The greater instability of the reduced forms of **1**, as suggested by the voltammograms, is in accord with the ready decomposition of **1** when this complex is treated with some reducing agents. The mild reductant $[Br_4Re^{V}{=}O]^-$ readily and satisfactorily metalates $PW_{11}O_{39}^{7-}$ in acetonitrile to form the rhenium(V)-substituted polyoxometalate.[6a,c] However, the only signal observed in the ^{31}P NMR spectrum after the addition of 1 equiv of $[n\text{-}Bu_4N][Br_4Re^{V}{=}O]$ to a CD_3CN solution of **1** corresponds to that of the one-electron-reduced Keggin anion, α-$PMo_{12}O_{40}^{4-}$ (δ −2.3 ppm versus TMP).[20b] Similar results were

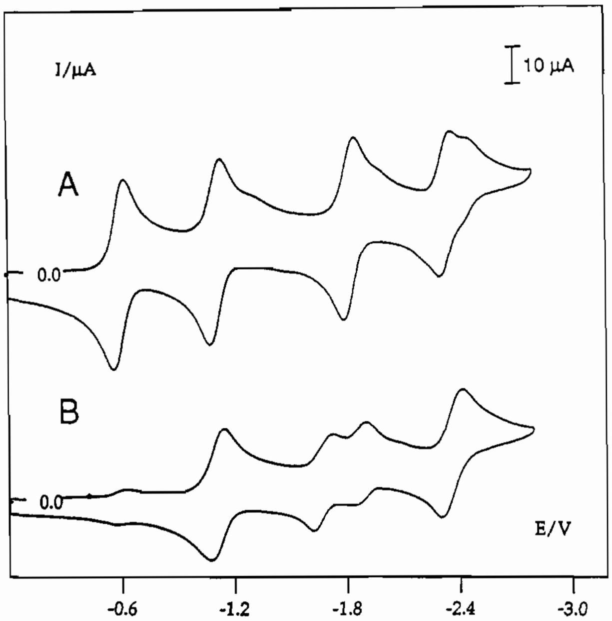

Figure 5. Cyclic voltammograms of α-$Q_3PW_{12}O_{40}$ (A) and $Q_4H_3PW_{11}O_{39}$ (B) in CH_3CN under conditions identical with those in Figure 4. The Fc/Fc$^+$ couple appears at +90 mV.

obtained, i.e. formation of a dark green product mixture composed primarily of α-$PMo_{12}O_{40}^{3-}$ and α-$PMo_{12}O_{40}^{4-}$ as determined by ^{31}P NMR, when metalation of **1** with Fe^{II} was attempted by utilizing the biphasic extraction method. Other workers have isolated a dark green product in the reaction of Fe^{II} with $PMo_{11}O_{39}^{7-}$ (generated in aqueous solution) as the *n*-Bu_4N^+ salt.[14b] They concluded the product to be the valence isomer $PMo^VMo^{VI}_{10}Fe^{III}O_{40}H_3^{4-}$, based on infrared, UV–visible, and elemental analysis. Once again, this is in sharp contrast to the lacunary polytungstophosphate, which has been successfully metalated with Fe^{II} to produce $PW_{11}Fe^{II}O_{39}^{5-}$.[14a]

Chemical Sensitivities of Kinetically Stabilized 1. The sensitivity of **1** with respect to water and heat in acetonitrile solution was evaluated. These two factors were chosen as both are of pertinence to the ultimate detailed and successful elaboration of the chemistry of **1** and its applications in catalysis.

The addition of 1% or 5% by volume of water to a CD_3CN solution of **1** has no effect on the chemical shift of **1** (no apparent decomposition) in the ^{31}P NMR spectrum after 24 h. However, the half-height line width is substantially narrowed from 12 Hz in "dry" CD_3CN to 6 Hz in the "wet" solvent. That the addition of water to the CD_3CN solutions makes the solutions more viscous is inconsistent with the line widths being dominated by the alteration of correlation times. Finke, Domaille, and co-workers[23] have attributed the narrowing of NMR line widths upon addition of water to CD_3CN solutions of $SiW_9V_3O_{40}^{7-}$ to the relative rates of H^+ exchange on the polyoxometalate surface versus the pertinent NMR time scale. The addition of water substantially increases H^+ exchange; hence, this ratio of rates also increases,[23] resulting in a sharpening of the ^{31}P NMR signal of polyoxoanions such as **1**. Alternatively, the "dry" CD_3CN might represent the slow exchange limit in which a number of discrete species of **1** exist that vary in their number and/or orientation of surface-attached protons.

Heating a CD_3CN solution of **1** for 1.5 h at 60 °C resulted in some (~33% based on relative intensities) decomposition of **1** as evidenced by the ^{31}P NMR spectrum. Two new signals, $\delta = -3.3$ and -6.6 ppm, were observed in addition to that corresponding to **1**. By comparison to a ^{31}P NMR study of aqueous solutions of polymolybdophosphates by Pettersson et al.,[18] the new species with $\delta = -3.3$ ppm versus TMP is probably α-B-$PMo_9O_{31}(OH)_3^{6-}$. This isomer has not been observed in any of our other experiments in nonaqueous media which did not require a heating step. Perhaps α-B-$PMo_9O_{31}(OH)_3^{6-}$ initially existed as α-A-$PMo_9O_{31}(OH)_3^{6-}$, which converted to the B isomer when the solution was heated. A similar isomerization has been observed in the solid-state chemistry of the corresponding nonatungstophosphates.[27] On the basis of previous work by Finke[28] and others, Knoth[27] clarified that B-$PW_9O_{34}^{9-}$ can be isolated as a solid-state thermolysis product of A-$PW_9O_{34}^{9-}$. A and B isomers each lead to different isolable TM-substituted derivatives.[27,28] The lability of these complexes in aqueous solution however is substantial.[29] Quick extraction (*n*-Bu_4NBr/CH_2Cl_2) of aqueous solutions of A-$PW_9O_{34}^{9-}$ and B-$PW_9O_{34}^{9-}$ followed by isolation and ^{31}P NMR of CD_3CN solutions of the resulting residues indicated a substantial stabilization of the respective isomers by dissolution into organic solvents (A-$PW_9O_{34}^{9-}$, $\delta = -13.87$; B-$PW_9O_{34}^{9-}$, $\delta = -13.45$ plus a trace of -13.87 ppm vs TMP).[30] These results are consistent with the thermal isomerization of A-$PMo_9O_{34}^{9-}$ to B-$PMo_9O_{34}^{9-}$ in heated aprotic solutions. The identity of the species at -6.6 ppm is as yet unknown. The fact that **1** decomposes to some extent in warm acetonitrile (60 °C) is good reason to perform all manipulations including the recrystallization (see Experimental Section) of **1** in room-temperature solutions.

Protonation and Deprotonation Chemistry of 1 in the Aprotic Medium, Acetonitrile. Acetonitrile-d_3 solutions of **1** were titrated with base, *n*-Bu_4NOH in MeOH, in an attempt to determine the number of protons associated with $PMo_{11}O_{39}^{7-}$ in solution.[23] The addition of 1 equiv of base to a CD_3CN solution of **1** resulted in the disappearance of the ^{31}P NMR peak at -4.4 ppm and the appearance of two new peaks, one with $\delta = -4.5$ ppm present as a shoulder on the major peak at -4.3 ppm. The addition of 2 or 3 equiv of base generated the species at -4.3 and -4.5 ppm in the same molar ratio but also generated two less abundant species, α-A-$PMo_9O_{31}(OH)_3^{6-}$ ($\delta = -4.8$ ppm) and α-$PMo_{12}O_{40}^{3-}$ ($\delta = -6.0$ ppm). Addition of a fourth equivalent of base resulted in the rapid and extensive decomposition of **1** as evident from the multiple lines present in the ^{31}P NMR spectrum. Unfortunately, the titration of acetonitrile solutions of **1** with base leads to decomposition side reactions, rendering it difficult to quantify the protonation state, *x*, for $H_xPMo_{11}O_{39}^{(7-x)-}$ in acetonitrile solution. To establish further the protonation chemistry of $PMo_{11}O_{39}^{7-}$ and to substantiate the apparent protonation chemistry implicated by the studies above, we sought to isolate each of the protonated forms of $PMo_{11}O_{39}^{7-}$ and spectroscopically examine each. Isolation of the complexes produced when **1** was treated with 1, 2, 3, and 4 equiv of base, *n*-Bu_4NOH in MeOH, was achieved by removing the solvent under high vacuum at room temperature after the base was allowed to react with **1** for ~5 min. The ^{31}P NMR of the resulting compounds indicated the same species to be present as were observed in the base solution titration experiment. Two significant differences were noted however. First, coupled with formation of the species with $\delta = -4.3$ ppm, decomposition of **1** to α-A-$PMo_9O_{31}(OH)_3^{6-}$ began after just 1 equiv (rather than 2 equiv) of base was added and second, in contrast to the formation of multiple products visible by ^{31}P NMR, α-A-$PMo_9O_{31}(OH)_3^{6-}$ and α-$PMo_{12}O_{40}^{3-}$ persisted with relatively high selectivity after the addition of 3 and 4 equiv of base. These differences may be attributed to the higher concentration of base and polymolybdophosphates achieved as the solvent is removed in the isolation versus the titration experiments. Changes in overall component concentrations have already been shown to significantly alter the observed product distribution in the synthesis of **1** (see section on characterization of **1**).

The addition of 1 equiv of the strong acid, concentrated H_2SO_4, per equivalent of **1** in CD_3CN resulted in the formation of a

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(27) Knoth, W. H.; Domaille, P. J.; Farlee, R. D. *Organometallics* **1985**, *4*, 62.

(28) Finke, R. G.; Droege, M.; Hutchinson, J. R.; Gansow, O. *J. Am. Chem. Soc.* **1981**, *103*, 1587.

(29) Both A-$PW_9O_{34}^{9-}$ and B-$PW_9O_{34}^{9-}$ rapidly equilibrate to a number of other phosphorus-containing polyoxoanions when dissolved in aqueous solution buffered at pH = 7.3–7.4 *in the absence of any transition metals*. The distribution of products although independent of the starting isomer, is quite dependent on the compound used as a buffer, however: Hill, C. L.; Weeks, M. S.; Schinazi, R. F. *J. Med. Chem.* **1990**, *33*, 2767.

(30) Weeks, M. S.; Hill, C. L. Unpublished results.

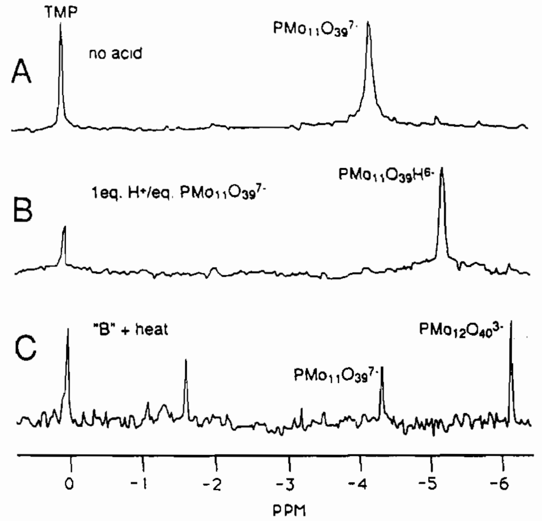
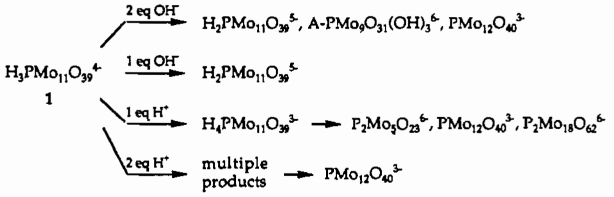


Figure 6. Effect of adding 1 equiv of acid (0.5 equiv of H_2SO_4) to a CD_3CN solution of **1** as studied by ^{31}P NMR: (A) spectrum before adding acid; (B) spectrum resulting immediately after the addition of acid; (C) spectrum observed after heating solution B at 60 °C for 1 h.

protonated form of the complex identified in part by its ^{31}P NMR spectrum (δ of the protonated species = −5.1 ppm); see Figure 6. Unlike the first three formal equivalents of H^+ associated with the purified complex $Q_4H_3PMo_{11}O_{39}$, the fourth equivalent results in a substantial change in chemical shift that can be reversed by careful addition of 1–2 equiv of base (n-$Bu_4N^+OH^-$). Heating the solution of protonated **1** at 60 °C for 1 h resulted in the production of $P_2Mo_5O_{23}^{6-}$ with a ^{31}P NMR chemical shift of δ = −1.6 ppm, the original complex (**1**, δ = −4.4 ppm), and the parent Keggin complex (δ = −6.1 ppm) with relative ^{31}P NMR signal intensities of 1:1:2 (Figure 6). Allowing an acidified solution of **1** (1 equiv of H^+/eq **1**) to sit at room temperature for 5 days results in the almost complete disappearance of **1** coupled with the appearance of $P_2Mo_5O_{23}^{6-}$, $P_2Mo_{18}O_{62}^{6-}$, and α-$PMo_{12}O_{40}^{3-}$ with relative ^{31}P NMR signal intensities of 2:1:4. Subsequent heating of this solution does not alter the appearance of the ^{31}P NMR spectrum, indicating the species are at thermal equilibrium or in deep localized kinetic minima.[31] It is clear from this experiment that **1** is greatly stabilized by placing it in an aprotic medium, thus permitting for the first time the reversible production and observation of an extensively protonated (number of $H^+ > 2$) form of the complex. This protonated complex is a likely intermediate in the acid-induced decomposition of **1** in solution.

Pettersson and co-workers[18] have studied aqueous solutions of sodium molybdate and sodium phosphate by ^{31}P NMR at [Mo]/[P] = 10.5 as a function of decreasing pH (pH = 5.5–0.5). Under these conditions, it is indicated that $PMo_{11}O_{39}^{7-}$ exists as one of the species present within the pH range of ~5.2 to ~1.5. On either side of this range, the primary polymolybdophosphate species present are $P_2Mo_5O_{23}^{6-}$ and α-B-$PMo_9O_{31}(OH)_3^{6-}$ on the basic side (pH ≤ 5.5) and α-A-$PMo_9O_{31}(OH)_3^{6-}$, $PMo_{12}O_{40}^{3-}$, and $P_2Mo_{18}O_{62}^{6-}$ on the acidic side (pH ≥ 0.5). Our observations of the decomposition of **1** in acetonitrile ([Mo]/[P] = 11) indicate a much different product distribution than that found under aqueous conditions (see Scheme I). In the presence of added base, **1** decomposes in part to α-A-$PMo_9O_{31}(OH)_3^{6-}$ and α-$PMo_{12}O_{40}^{3-}$, species usually found under acidic conditions in aqueous solutions. In the presence of 1 equiv of acid, an intermediate, protonated form of **1** initially forms and subsequently decomposes to $P_2Mo_5O_{23}^{6-}$ and α-$PMo_{12}O_{40}^{3-}$, species not normally present at the same pH for aqueous solutions in which [Mo]/[P] ≈ 11. Ultimately the acidified solution of **1** in acetonitrile also produces $P_2Mo_{18}O_{62}^{6-}$, which has been shown to form very slowly in acidified aqueous solutions of sodium molybdate and sodium phosphate ([Mo]/[P] = 10.5) as well.[18]

Scheme I. Products Generated upon Treatment of 1 with 1 or 2 equiv of OH^- or H^+ in Acetonitrile



The relative instability of the lacunary phosphomolybdate with respect to changes in pH does not permit a ready determination of the *absolute* number of protons on $PMo_{11}O_{39}^{7-}$ in solution. However, if we assume **1** exists as $H_3PMo_{11}O_{39}^{4-}$ in solution, then some tentative assignments can be made at this time. Since the addition of 1 equiv of acid results in a shift of the ^{31}P NMR signal for **1** to −5.1 ppm we may assume an additional proton is now associated with **1**, forming $H_4PMo_{11}O_{39}^{3-}$. Addition of 2 equiv of acid to a CD_3CN solution of **1** does not form the species with δ = −5.1, nor any other with a single discrete signal, but rather there is significant decomposition of **1** resulting in initial formation of multiple phosphorus-containing species and eventual (several days) formation of the parent Keggin ion, α-$PMo_{12}O_{40}^{3-}$, as the sole polymolybdophosphate species visible by ^{31}P NMR. The titration of a CD_3CN solution of **1** with 1 equiv of base results in the formation of one prominent species with δ = −4.3 ppm. This signal persists as the dominating feature of the ^{31}P NMR spectrum up through the addition of 2 to 3 equiv of base, even though some decomposition of **1** is starting to become evident. This species (δ = −4.3 ppm) is likely the doubly protonated anion $H_2PMo_{11}O_{39}^{5-}$, based on the fact that it first appears after the addition of just 1 equiv of base. Our assignment of decreasing chemical shift to increasing degree of protonation of the polyoxoanion agrees with the trend observed by Pettersson and co-workers[18] for the changes in the ^{31}P NMR chemical shift of aqueous $PMo_{11}O_{39}^{7-}$ as a function of pH.

Metalation of 1. With $PMo_{11}O_{39}^{7-}$ now kinetically stabilized, we sought high-yield, reproducible procedures to make the TM-substituted derivatives, $PMo_{11}(TM)O_{39}^{x-}$, as the latter are of potential interest in catalysis[7-13] and other applications.[2] The TM is substituted in the "hole" generated by the loss of a $(Mo{=}O)^{4+}$ unit from the parent Keggin ion, α-$PMo_{12}O_{40}^{3-}$, on formation of the lacunary anion, $PMo_{11}O_{39}^{7-}$. The lacunary anion can act as a pentadentate ligand to substituted first-row TM ions with the sixth coordination site on the TM typically occupied by a molecule of water or some other solvent molecule, denoted as "L" in this text.[1,5i,7,32] The metalation of **1** can be achieved by two methods. The first method involves a homogeneous one-phase procedure in acetonitrile, a solvent in which both **1** and the first-row TM triflate salts are readily soluble. The substitution of the first-row TM into the lacunary anion proceeds readily for ions with minimal ligand field stabilization energy and quite selectively based on ^{31}P NMR spectral studies. The main drawback of this type of synthesis is that the TM triflate salts are not always readily available. The second method obviates the need to use only TM ions soluble in organic media by employing a heterogeneous biphasic extraction technique. In this procedure, the TM salt (sulfate, nitrate, acetate, etc.) is dissolved in water and shaken with a 3:2 v/v CH_3CN–toluene solution of **1**. The organic layer is removed and allowed to evaporate slowly at room temperature until crystalline $PMo_{11}(TM)O_{39}^{n-}$ (TM = Mn^{II}, Co^{II}, Cu^{II}, Zn^{II}) precipitates from solution. The yield from this type of synthesis is typically 60–90%

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(31) Although some polyoxometalates represent local thermodynamic minima, these compounds as a whole are usually, if not always, thermodynamically unstable with respect to one of the forms of the metal oxide: MoO_3, WO_3, etc. As such, polyoxometalates, in most cases, are likely species in localized kinetic minima in context with the global potential energy surface. Since quantitative thermochemical studies of polyoxometalate to metal oxide transformations have yet to be carried out, and indeed in some cases the product(s) (the form(s) of WO_3 produced) have yet to be determined, writing balanced equations for such transformations is of questionable utility.

(32) Baker, L. C. W.; Figgis, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 3794.

based on **1**, except in the case when TM = Zn^{II} in which the yield is lower due to decomposition of **1**. (This low selectivity, $PMo_{11}Zn^{II}O_{39}^{5-}$ versus decomposition products of **1**, is observed for the homogeneous procedure as well.) Since both methods produce the same species as indicated by ^{31}P NMR (a special case, when TM = Co^{II}, will be discussed later), we have chosen, for convenience, to utilize the extraction method in our large-scale preparations. This two-phase extraction technique allows one to take advantage of the stability of **1** in organic media and the convenience of the readily available, water-soluble TM salts to form reproducibly and in high yield the corresponding TM-substituted complexes. This method works equally well for preparations of the analogous first-row TM-substituted polyoxotungstates from $(n\text{-}Bu_4N)_4H_3PW_{11}O_{39}$.

^{31}P NMR has proven to be a very useful and viable tool in determining the structure and studying the electronic effects of the paramagnetic TM-substituted polytungstophosphates.[33] Indeed we also found this spectral handle invaluable in studying not only the paramagnetic and diamagnetic TM substitution reactions of the polymolybdophosphates but also the nature of the ligand axially bound to the TM atom. In general, the magnitude and direction of the changes in the ^{31}P NMR chemical shift of the lacunary anion, **1**, upon substitution with a paramagnetic or diamagnetic TM, follow the same trend as those observed for the analogous TM-substituted polytungstophosphates (Table I).[14j,33] The identity of the axial ligand, L, in the TM-substituted polymolybdophosphates was examined by ^{31}P NMR and other techniques. The identity of L varies with the TM even when the TM-substituted polymolybdophosphates are crystallized from the same solvent under identical experimental conditions. The ^{31}P NMR of the Cu^{II} complex indicates there is only one $PMo_{11}Cu^{II}(L)O_{39}^{5-}$ species present, while the line widths are too broad for the $S = {}^5/_2$ $PMo_{11}Mn^{II}(L)O_{39}^{5-}$ complex for observation of any ^{31}P NMR signal. Acetonitrile has been shown to efficiently replace the terminally ligated water on $PW_{11}Co^{II}(H_2O)O_{39}^{5-}$;[5i] therefore, it is likely that the same process would be operable for $PMo_{11}Cu^{II}(L)O_{39}^{5-}$. The single peak observed in the ^{31}P NMR (CD_3CN) of the latter species is likely $PMo_{11}Cu^{II}(MeCN)O_{39}^{5-}$.

The ^{31}P NMR spectra for $PMo_{11}Co^{II}(L)O_{39}^{5-}$ are much more complicated. The one-phase metalation of **1** with cobalt(II) triflate initially produces only one species visible in the ^{31}P NMR spectrum in CD_3CN (δ = 345 ppm), which disappears after several days, forming three new species (δ = 521, 513, and 439) with relative intensities of 2:2:1. These three new species are also detectable in the ^{31}P NMR spectra of the cobalt complexes in CD_3CN solution obtained by using the two-phase extraction procedure. The biphasic extraction method produces four distinct $PMo_{11}Co^{II}(L)O_{39}^{5-}$ species visible in the ^{31}P NMR spectrum (δ = 521, 512, 461, and 437 ppm with relative intensities of 8:10:1:1). We propose these three to four species to have the general formula $H_xPMo_{11}Co^{II}(L)O_{39}^{(5-x)-}$, varying only in the identity of the ligand, L, and the extent of protonation, x, based on the following five lines of evidence. (1) The addition of 1 equiv of pyridine causes the four peaks in the ^{31}P NMR to coalesce to one peak with δ = 622 ppm. The pyridine-ligated complex is quite stable and may be crystallized from solution with retention of the molecule of pyridine as confirmed by ^{31}P NMR, infrared, and electronic absorption spectroscopies and elemental analysis. Isolation of the analogous tungstate complexes have been reported before[5i] although it is difficult to distinguish whether the solvent (e.g. pyridine) molecules are terminal ligands or nonassociated molecules of crystallization. Pyridine is more basic and nucleophilic than either MeCN or H_2O and has been observed by UV–visible[5i] and ^{31}P NMR[34] spectroscopy to efficiently replace the latter species terminally ligated to the cobalt atom of the analogous Co-substituted polytungstophosphate. A similar observation was made for the Cu-substituted polymolybdophosphate for which the ^{31}P NMR signal shifted downfield quantitatively upon the addition of 1 equiv of pyridine; see Table I. (2) The final products observed in the ^{31}P NMR of the cobalt complex mixture formed by metalation of **1** with cobalt(II) triflate were also obtained in the biphasic extraction preparation which utilized the cobalt(II) sulfate. Therefore, the cobalt atom in these species is not ligated by either sulfate or triflate anions, but rather by MeCN and/or H_2O, which are both present. (3) Extensive drying of the cobalt complex and the NMR solvent, CD_3CN, only slightly altered the relative intensities of the peaks in the ^{31}P NMR spectrum in favor of the two smaller peaks with δ = 459 and 434 ppm. Conversely, the brown, hydrated cobalt complex dissolved in CD_3CN has only two peaks visible in the ^{31}P NMR spectrum (δ = 518 and 509 ppm with relative intensities of ~1:1). Therefore, the species with $\delta \approx 518$ and 509 ppm are thought to be similar in that each has a molecule of water terminally ligated to the cobalt atom (L = H_2O) yet differ in the number of protons, x, associated with the complex. It follows that the two smaller peaks in the ^{31}P NMR of $H_xPMo_{11}Co^{II}(L)O_{39}^{(5-x)-}$ (δ = 434 and 459 ppm) represent species of different protonation states, x, in which the identity of L is acetonitrile. (4) The addition of 1 equiv of base, (1.1 N Q^+OH^- in MeOH), dramatically alters the ^{31}P NMR spectrum of this complex mixture. Upon addition of the base, the two more intense peaks (δ = 521 and 512 ppm) decrease in intensity by ~50%, the two smaller peaks (δ = 461 and 437 ppm) disappear, and a new peak forms (δ = 446 ppm; $\nu_{1/2}$ = 500 Hz). The relative intensity ratio of the peaks in the ^{31}P NMR for δ = 521, 512, and 446 ppm is 1:1:2. Deprotonation of the species with $x \neq 0$ could result in a decrease in ^{31}P NMR signal intensity for these species and an increase in the signal intensity of the species thought to be the deprotonated, $x = 0$. However, this did appear to be occurring in this case. Therefore, the new species with δ = 446 ppm is most likely a deprotonated, hydroxy-ligated complex that forms upon replacement of both acetonitrile and water from the substituted cobalt atom. It is not the MeOH-ligated complex since the ^{31}P NMR spectrum run in the presence of MeOH containing no Q^+OH^- is unchanged from the original spectrum. (5) Comparison of the UV–visible[5e,5i,32] and ^{31}P NMR[33] spectra of $H_xPMo_{11}Co^{II}(L)O_{39}^{(5-x)-}$ to those of the analogous tungstate complex in aqueous solution coupled with the observation of the UV–visible spectrum of the former in the presence of several oxidizing and reducing agents indicates that Co^{III} species are not formed. In summary, although the five lines of evidence above do not unequivocally establish the identity of each of the four species visible in the ^{31}P NMR of the cobalt complex, they are consistent with all being $H_xPMo_{11}Co^{II}(L)O_{39}^{(5-x)-}$, varying only in x and/or the identity of L.

Another interesting feature of $PMo_{11}Co^{II}(L)O_{39}^{5-}$ is its solvatochromism, the ability to change color with the removal or variation of the ligand L. Thorough drying of the red or brown solid under vacuum removes the axial ligand, L (MeCN and/or H_2O), changing the coordination number of the cobalt atom from six to five and the color of the complex to green (eq 1). Exposing

$$\underset{\text{red/brown}}{(n\text{-}Bu_4N)_4HPCo^{II}(L)Mo_{11}O_{39}} \rightleftharpoons \underset{\text{green}}{(n\text{-}Bu_4N)_4HPCo^{II}Mo_{11}O_{39}} + L \quad (1)$$

$$L = MeCN,\ H_2O,\ py$$

the green solid to moist air results in a reversion of the color of the cobalt complex to brown as a water molecule coordinates to the cobalt ion. Coordination of a molecule of pyridine to cobalt results in the formation of a deep red crystalline material (eq 1). These observations can best be described in eq 1. The same phenomenon has been observed for $SiW_{11}Co^{II}(H_2O)O_{39}^{6-}$ when it is transferred from water to toluene (a noncoordinating solvent), with the aid of tetra-n-heptylammonium bromide.[7]

A final phenomenon we wish to address involves the observed differences in the axial ligation chemistry of the TM-substituted

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(34) In contrast to the molybdates, using the biphasic extraction technique to synthesize the analogous polytungstate complex, $PW_{11}Co^{II}(L)O_{39}^{5-}$, produces *one* species visible by ^{31}P NMR in CD_3CN (δ = 306 ppm vs TMP, $\nu_{1/2}$ = 859 Hz), which shifts downfield by 81 ppm (δ = 387 ppm vs TMP) upon the addition of 1 equiv of pyridine.

complexes $PMo_{11}(TM^{II})(L)O_{39}^{5-}$ in the aprotic medium acetonitrile. The following observations have been made by ^{31}P NMR. First, as discussed above, the Co^{II} complex $PMo_{11}Co^{II}(L)O_{39}^{5-}$ exhibits several species in CD_3CN solution. Second, the corresponding tungsten complex, $PW_{11}Co^{II}(L)O_{39}^{5-}$, shows only one species under the same conditions. Third, the Cu^{II} complex $PMo_{11}Cu^{II}(L)O_{39}^{5-}$ shows only one peak, which narrows from ~3300 to ~2000 Hz upon addition of 15% v/v of water to the CD_3CN solution. There is no change in the observed chemical shift upon this addition of water. A caveat here is that the exceptionally large ^{31}P NMR line widths (2000–3300 Hz) of the copper species do not really permit even a semiquantitative evaluation of the relative quantities of the $Cu(NCCH(D)_3)$ and $Cu(H_2O)$ ligation isomers to be made. A workable paradigm for the axial ligand chemistry including ligand-exchange rates must satisfactorily rationalize the above facts and the literature studies of ligand-exchange rates on TM-substituted polyoxometalates in aqueous media.[5d,h,i,n]

There is more than one rationale for the presence of multiple isomers of $PMo_{11}Co^{II}(L)O_{39}^{5-}$ versus the apparently single isomer each of $PW_{11}Co^{II}(L)O_{39}^{5-}$ and $PMo_{11}Cu^{II}(L)O_{39}^{5-}$ in CD_3CN solution. One explanation is that the former complex exhibits a greater thermodynamic selectivity for binding different ligands, L (L = principally the more abundant CD_3CN or the less abundant but competitively binding H_2O), than do the latter two complexes and that axial ligation chemistry has attained equilibrium for all three complexes under the experimental conditions. A second explanation is that the observed isomers differing only in the nature of L for the three complexes above are not all at equilibrium and that the observed isomers reflect the relative rates of processes involving the axial ligands including net $H_2O \rightleftharpoons CD_3CN$ exchange. In the latter scenario, some degree of kinetic control is affecting at least the observed isomers of $PMo_{11}Co^{II}(L)O_{39}^{5-}$.

The experimental case for the former explanation is stronger than that for the latter. First, a number of experiments indicate that the distribution of isomers of $PMo_{11}Co^{II}(L)O_{39}^{5-}$ is established more rapidly than the time required to obtain the first spectra. Second, the product distributions obtained in the presence of acid, base, or pyridine discussed in the previous section appear to be quite stable for times that are long (days) relative to the time of the experiments (principally ^{31}P NMR data acquisition time). Third, it can be inferred that the rates of axial-ligand exchange should be fast based on the literature studies of axial-ligand chemistry of the divalent $3d^n$, $n \neq 0$, TM ions in Keggin and Wells–Dawson type TM-substituted polyoxometalates. The latter studies are, again, in aqueous media, and although rigorous rate measurements over a wide range of conditions have not been made in any of these studies, fairly rapid ligand-exchange rates can be inferred from reasonably thorough evaluations of axial-ligand-exchange processes, eq 2, in these studies.[5h,i,n] Fourth, the rates

$$PMo(TM{-}OH_2)O_{39}^{n-} + L \rightleftharpoons PMo(TM{-}L)O_{39}^{n-} + H_2O \quad (2)$$

of metalation of Keggin and Wells–Dawson lacunary type species, $XW_{11}O_{39}^{n-}$ and $X_2W_{17}O_{61}^{m-}$ in aqueous media, processes that should have less favorable enthalpies and entropies of activation than the exchange of L in TM–L polyoxometalates, proceed readily with Co^{II}, Cu^{II}, and all other divalent first-row d^n, $n \neq 0$, TM ions.[5] The collective evidence in this study and the literature studies in aqueous solution is most consistent with predominent, if not exclusive, thermodynamic control of axial ligation to the TM in acetonitrile solutions of the $PMo_{11}(TM{-}L)O_{39}^{5-}$ complexes (TM = Co^{II}, Cu^{II}). In context with dominant or exclusive thermodynamic control, the ^{31}P NMR spectral data, including the perturbation of observed line widths upon addition of water, are consistent with axial-ligand-exchange processes being slightly to considerably faster than the ^{31}P NMR time scale.

Despite the multiple arguments for overall thermodynamic control in axial ligation chemistry of the $PMo_{11}(TM{-}L)O_{39}^{5-}$ complexes (TM = Co^{II}, Cu^{II}) in acetonitrile (explanation 1 above), one cannot rigorously rule out explanation 2 from the data. The imposition of dominant or exclusive kinetic control in the case of $PMo_{11}Co^{II}(L)O_{39}^{5-}$ but not $PMo_{11}Cu^{II}(L)O_{39}^{5-}$ indeed is consistent with structural and electronic arguments. Arguments from classical experimental and theoretical coordination chemistry state that at parity of ligands, ligand-exchange rates will be faster at the d^9 Cu^{II} ion than at the high-spin d^7 Co^{II} ion. At nominally equivalent values of Z^2/r, the former ion has less ligand field stabilization energy and greater Jahn–Teller distortion than the latter. With these points in mind, the actual ligand environment of the TM ions imposed by the lacunary complexes must be considered. The fairly rigid chelating O_5 pentacoordinate cavity of the lacunary species binds the TM ions such that the final $TM(L)(O)_5$ coordination polyhedra are distorted to local C_{4v} symmetry by displacement of the TM toward the terminal axial ligand, the exchangeable L in this case. The O_h to C_{4v} distortion has multiple interdependent consequences. It affects all bonds lengths and strengths, but in particular those associated with the M–O(X), X = T_d central heteroatom, and M–L bonds. The weaker the M–L bond strengths, and more significantly, the greater the overall distortion from O_h symmetry, the lower will be the activation energies for exchange of the axial ligand, L. Literature data indicate that shorter and stronger M–O(X) bonds directly correlate with stronger M–L interactions. Rocchiccioli-Deltcheff and Thouvenot[14b] have demonstrated convincingly that the former can be spectroscopically assessed in the $XM_{11}(TM)(L)O_{39}^{n-}$ compounds by the magnitude of the splitting of the ν_3 PO_4 asymmetric stretch ($\Delta\nu$) in the mid-infrared region. Analysis of the infrared spectra indicates the following order for the divalent $3d^n$ TM ions: Cu (most displaced from the center of the $TM(L)O_5$ coordination polyhedron and largest splitting of the ν_3 stretch) > Zn > Mn > Fe > Co > Ni (least displaced from the center of the $TM(L)O_5$ coordination polyhedron and smallest splitting of the ν_3 stretch).[14b] In previous studies, Weakley determined the formation constants for binding of several axial ligands to the TM ions in several $PW_{11}(TM)(L)O_{39}^{n-}$ complexes in aqueous solution.[5i] Their data correlate with the displacements of the TM ions from the centers of the $TM(L)O_5$ coordination polyhedra. For example, the axial-ligand-binding constants are much greater for the $PW_{11}(TM)(L)O_{39}^{n-}$ complex for TM = Ni^{II} than those for TM = Co^{II}. Other workers[35] have noted the removal of terminally ligated water in $SiW_{11}(TM)(H_2O)O_{39}^{n-}$ compounds is more facile for TM = Cu^{II} than for TM = Ni^{II} or Mn^{II}, again correlating with the size of $\Delta\nu$ in the infrared spectra.

These lines of reasoning extend to the apparent equilibration of axial ligands on the experimental (data collection) and ^{31}P NMR time scales for $PW_{11}Co^{II}(L)O_{39}^{5-}$ but not for $PMo_{11}Co^{II}(L)O_{39}^{5-}$. Slower ligand exchange rates for the $PMo_{11}Co^{II}(L)O_{39}^{5-}$ versus the $PW_{11}Co^{II}(L)O_{39}^{5-}$ complex follow from the infrared spectral analyses,[4b] which imply that the Co^{II} ion enters more completely into the hole of the more flexible polymolybdophosphate lacunary anion relative to the corresponding polytungstophosphate, leading to stronger TM–O(P) and TM–L bonds in the former case relative to the latter. Again, the stronger TM–L bond and the lower deviation from pure O_h symmetry would both argue for slower exchange of L on $PMo_{11}Co^{II}(L)O_{39}^{5-}$ than on $PW_{11}Co^{II}(L)O_{39}^{5-}$. Our observations coupled with those of other researchers[5i,9,14b,35] leads us to conclude that the lability of the ligand terminally bound to the TM in such complexes is influenced not only by the identity of L and TM but also to a considerable extent by the polyoxoanion species.

Conclusions

(1) The 19 literature reports of the title complex, $PMo_{11}O_{39}^{7-}$, all involve aqueous solutions in which the complex is kinetically labile. The $(n\text{-}Bu_4N)_4H_3$ salt of this complex, **1**, is not labile in aprotic CH_3CN, enabling rigorous purification of the complex by repeated recrystallization and evaluation of its protonation, redox, and metalation chemistry.

(2) In the preparation of $PMo_{11}O_{39}^{7-}$, prior to precipitation with $n\text{-}Bu_4N^+$, the best yields are obtained when working in concentrated solutions of the reactant complex $\alpha\text{-}PMo_{12}O_{40}^{3-}$ (0.1 M);

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(35) Katsoulis, D. E.; Tausch, V. S.; Pope, M. T. *Inorg. Chem.* **1987**, *26*, 215.

less concentrated solutions generate $P_2Mo_{18}O_{62}^{6-}$ as the principal product.

(3) The electrochemical behavior of **1** in CH_3CN is the least reversible of any polyoxometalate constituted exclusively or primarily of type I MO_6 octahedra (those with one terminal oxo group on the d^0 TM ion) that has been reported to date. All redox couples from +0.4 to –2.4 V vs $Ag/Ag^+(AgNO_3/CH_3CN)$ are completely irreversible.

(4) Treatment of **1** with 1 equiv of OH^- in CH_3CN reversibly generates $H_2PMo_{11}O_{39}^{5-}$, whereas 2 equiv of OH^- rapidly produces A-$PMo_9O_{31}(OH)_3^{6-}$ and, interestingly, the parent Keggin structure, $PMo_{12}O_{40}^{3-}$, in addition to $H_2PMo_{11}O_{39}^{5-}$. Whereas **1** can be reversibly protonated with 1 equiv of H^+ in CH_3CN to $H_4PMo_{11}O_{39}^{3-}$ over a period of several minutes, the latter complex decomposes over a period of hours and days to three other complexes, $P_2Mo_5O_{23}^{6-}$, $PMo_{12}O_{40}^{3-}$, and $P_2Mo_{18}O_{62}^{6-}$. In the presence of 2 equiv of H^+, many products observable in the ^{31}P NMR are produced rapidly which convert more slowly to $PMo_{12}O_{40}^{3-}$ in high yield.

(5) Metalation of **1** by several divalent $3d^n$, $n \neq 0$, transition-metal (TM) ions to form the corresponding TM-substituted polymolybdophosphates, $PMo_{11}(TM)O_{39}^{5-}$, can be readily accomplished by using a homogeneous one-phase procedure (acetonitrile solvent and TM triflate salt) or by a heterogeneous two-phase procedure (treatment of 3:2 acetonitrile–toluene solution of **1** with an aqueous solution of the TM salt). The exception is for Zn^{II} which by either metalation method leads to substantial (as high as 50%) decomposition of **1**.

(6) Reversible loss of the terminal axial ligand, L, of $PMo_{11}(TM^{II}–L)O_{39}^{5-}$ is observed on drying of the solid in vacuo. Several lines of evidence are consistent with the exchange of L, on both $PMo_{11}(TM^{II}–L)O_{39}^{5-}$ and the analogous tungsten compounds in aprotic media, being thermodynamically controlled. However, some kinetic control cannot be ruled out in the complex case of $PMo_{11}(Co^{II}–L)O_{39}^{5-}$ in acetonitrile.

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Supplementary Material Available: Infrared spectra (200–4000 cm^{-1}) of **1** and the parent Keggin ion, α-$Q_3PMo_{12}O_{40}$ (Figure S1), and UV/visible spectrum of **1** in CH_3CN (Figure S2) (2 pages). Ordering information is given on any current masthead page.

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Reduced Rubredoxin Models Containing Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-X (X = MeO, H, F, CN): Electronic Influence by a Distant Para Substituent through NH- - -S Hydrogen Bonds

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Model complexes of reduced rubredoxin, $[Fe^{II}$(Z-cys-Pro-Leu-cys-Gly-NH-C_6H_4-*p*-X$)_2]^{2-}$ (X = MeO (**4**), H (**5**), F (**6**) and CN (**7**)), were synthesized by a ligand-exchange reaction of $[Fe^{II}(S\text{-}t\text{-}Bu)_4]^{2-}$ with Z-Cys(SH)-Pro-Leu-Cys(SH)-Gly-NH-C_6H_4-*p*-X. These complexes gave positively shifted redox potentials compared to other peptide model complexes such as $[Fe^{II}$(Z-cys-Pro-Leu-cys-OMe$)_2]^{2-}$ (**2**) and $[Fe^{II}$(Z-cys-Pro-Leu-cys-Gly-Val-OMe$)_2]^{2-}$ (**3**) in a weakly nonpolar solvent, e.g. 1,2-dimethoxyethane (DME). The most positively shifted redox potential at –0.24 V vs SCE was observed for **7** in DME with the strongest electron-withdrawing *p*-substituent. The strength of the NH- - -S hydrogen bonds in **4**–**7** in DME was in the order X = OMe < H < F < CN. The observed aromatic substituent effect is explained by an electronic charge flow from sulfur of the coordinated cysteine residue to the benzene ring through an NH- - -S hydrogen bond.

Introduction

Rubredoxin (Rd), which possesses an iron atom surrounded by four sulfur atoms of cysteine residues, is known to be an electron-transfer metalloprotein using a Fe(II)/Fe(III) redox couple at –0.31 V vs SCE (saturated calomel electrode) in aqueous solution.[1,2] Although many simple alkane- and arenethiolate complexes have been synthesized as model complexes of Rd,[3-5] the redox potentials of Fe(II)/Fe(III) of these model complexes, for example, $[Fe(S\text{-}Et)_4]^{2-/-}$ having a value of –1.08 V vs SCE in CH_3CN[3] and $[Fe(S_2\text{-}o\text{-}xyl)_2]^{2-/-}$ having a value of –0.99 V vs SCE in Me_2SO,[5] were substantially more negative than that of Rd.

In our continued study, we have synthesized Fe(II) complexes containing Cys–oligopeptide ligands having the invariant fragments of the rubredoxin peptide chain.[6-9] $[Fe^{II}$(Z-cys-Pro-Leu-cys-OMe$)_2]^{2-}$ (**2**) has a redox potential at –0.54 V vs SCE in CH_3CN, which is much more positive than those of simple alkane- or arenethiolate complexes. In particular, in a weakly nonpolar solvent, e.g. 1,2-dimethoxyethane (DME), the redox potential of $[Fe^{II}$(Z-cys-Pro-Leu-cys-Gly-Val-OMe$)_2]^{2-}$ (**3**) is –0.35 V vs SCE, which is the nearest value to that of native Rd. This positive shift is caused by the formation of NH- - -S hydrogen bonds from NH of the neighboring peptide residue to S of the cysteine residue as reported in previous paper.[7,8]

Instead of the conserved valine residue in a sequence Cys-Pro-Leu-Cys-Gly-Val, peptides with a para-substituted anilide residue, i.e., Z-Cys-Pro-Leu-Cys-Gly-NH-C_6H_4-*p*-X (X = MeO, H, F, CN), were synthesized. The para-substituent effect on the redox potential was examined in [Fe(Z-cys-Pro-Leu-cys-Gly-NH-C_6H_4-*p*-X$)_2]^{2-}$ in order to verify the electronic interaction through the NH- - -S hydrogen bonds. Without the NH- - -S hydrogen bond, the potential will not be susceptible to the para-substituent effect.

Previously, we and Sanders-Loehr and co-workers have reported the existence of similar NH- - -S hydrogen bonds indirectly by IR or Raman spectroscopy.[10,11] Now, ^2H NMR spectra of the

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