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Highly Oxidation Resistant Inorganic-Porphyrin Analogue Polyoxometalate Oxidation Catalysts. 1. The Synthesis and Characterization of Aqueous-Soluble Potassium Salts of α_2-$P_2W_{17}O_{61}(M^{n+}\cdot OH_2)^{(n-10)}$ and Organic Solvent Soluble Tetra-*n*-butylammonium Salts of α_2-$P_2W_{17}O_{61}(M^{n+}\cdot Br)^{(n-11)}$ ($M = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$)

David K. Lyon,[1] Warren K. Miller,[1] Thomas Novet,[1] Peter J. Domaille,[2] Eric Evitt,[3] David C. Johnson,[1] and Richard G. Finke*,[1]

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403, Catalytica, Incorporated, Mountain View, California, 94043, and Central Research and Development, The Du Pont Company Experimental Station, Wilmington, Delaware 19898.

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Abstract: The synthesis and characterization of isolated, *isomerically pure* α_2-$P_2W_{17}O_{61}(M^{n+}\cdot L)^{y-}$ ($M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}$, and Cu^{2+}) as aqueous-soluble potassium salts ($L = H_2O$) and organic-soluble tetra-*n*-butylammonium salts ($L = Br^-$) are reported. These complexes have been characterized by ^{31}P NMR, elemental analysis, sedimentation equilibrium molecular weight, thermal gravimetric analysis (TGA), temperature-varied solid-state magnetic susceptibility studies, UV-visible spectroscopy, infrared spectroscopy (IR), and ^{183}W NMR. These compounds constitute the first *isolated* monosubstituted Dawson α_2-isomer complexes that have been prepared free of the α_1-isomer. Preliminary axial-base binding studies for α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn\cdot Br)$ are reported and demonstrate that the "pocket" around the transition metal is actually somewhat hindered, but less so than in sterically congested porphyrins. Further studies show that α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn\cdot Br)$ is not oxidatively degraded by 1500 equiv of PhIO even over 48 h. In an accompanying paper, oxidation catalysis by α_2-$P_2W_{17}O_{61}(M\cdot L)^{y-}$ is reported yielding olefin epoxidations and aliphatic and aromatic hydroxylations.

Introduction

The ability of heme-based enzymes, such as cytochrome P_{450},[4] and non-heme enzymes, such as dopamine β-hydroxylase,[5] to catalytically oxygenate both saturated and unsaturated hydrocarbons has led to substantial interest in catalytic homogeneous oxidations in recent years.[6] Mn(III) and Fe(III) porphyrins have been found to be especially good catalysts for the monooxygenation of hydrocarbons by various oxygen atom donors, such as iodosylarenes,[7,8] hypochlorite,[9] amine *N*-oxides,[10] H_2O_2,[11] peracids,[12] and dioxygen in the presence of various reducing agents.[13] Systems using metallotetraarylporphyrins bearing halogen substituents in the ortho position of the *meso*-aryl groups have led to very high rates of epoxidation (up to 300 turnovers per second in the case of iodosylarenes[14]) and high yields based on the starting oxygen atom donors.[15]

Simple iron and manganese salts also catalyze the epoxidation of alkenes by PhIO,[16] indicating that the presence of a porphyrin ligand is not required for such monooxygenation reactions. However, in most cases, these non-porphyrin catalysts gave lower yields, selectivities, and rates than the porphyrin catalysts.[16f]

As early as 1973, Baker[17] noted that substitued monolacunary polyoxotungstates,[18] such as the monosubstituted[19] Keggin[20] anion

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(1) Department of Chemistry, University of Oregon.

(2) The Du Pont Company, Contribution Number 5708.

(3) Catalytica, Inc.

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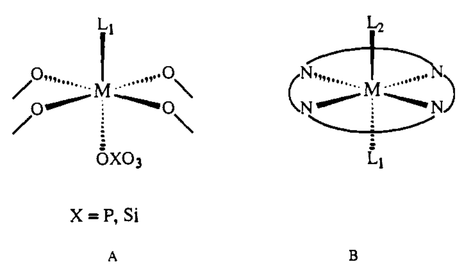


Figure 1. Schematic representations of the primary coordination spheres of M in (A) monosubstituted Keggin- and Dawson-type polyoxometalates and (B) metalloporphyrin complexes.

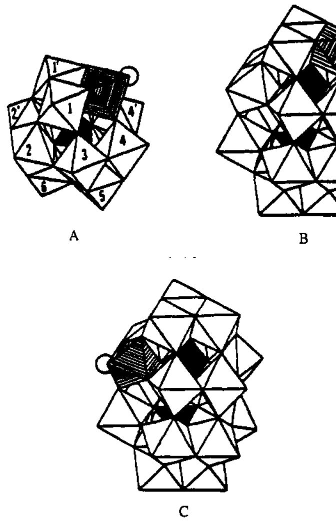
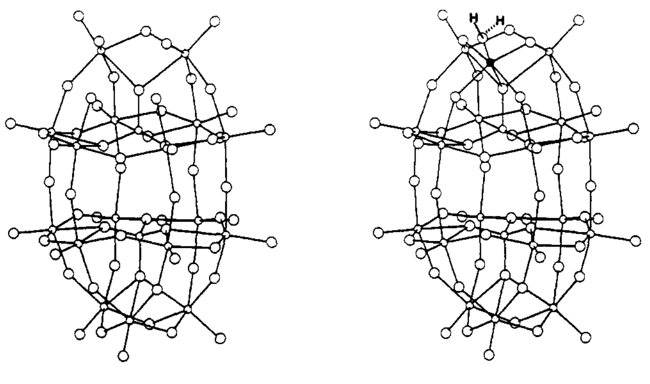


Figure 2. Polyhedral representations of (A) the monosubstituted Keggin-type polyoxometalate and the two possible isomers [(B) α_2 and (C) α_1] of the monosubstituted Dawson-type polyoxometalate. The internal black tetrahedra represent the PO_4^{3-} (or SiO_4^{4-}) core, while the white octahedra represent WO_6 fragment with a tungsten atom in the center of the octahedra and oxygen atoms at each corner. The hatched octahedra represent the heterometal (in the center of the octahedra) with oxygen atoms at the vertices except for the open circle, which represents L (L = H_2O for aqueous-soluble salts; L = Br^- for the $[(n\text{-}C_4H_9)_4N]^+$ salts reported in this paper).

$[PW_{11}O_{39}(M^{n+}\cdot OH_2)]^{(n-9)}$, ligate the heterometal (M^{n+}) in a pseudo-porphyrin environment, Figure 1. In addition, the framework of the polyoxometalate is composed of *nonoxidizable* d^0 W^{6+} atoms bound to formally O^{2-} ligands and as such should be highly oxidation resistant, if not nearly inert. However, very little heterometal coordination chemistry was demonstrated at the time since only aqueous-soluble forms of these polyoxometalates were known, with water dominating the coordination chemistry of the sixth coordination site of the heterometal.[21]



$\alpha_2\text{-}P_2W_{17}O_{61}{}^{10-}$ $\alpha_2\text{-}P_2W_{17}O_{61}(Co\cdot OH_2)^{8-}$

Figure 3. Ball and stick representations of the structures determined by X-ray crystallography by Weakley,[34] $\alpha_2\text{-}P_2W_{17}O_{61}{}^{10-}$ and $\alpha_2\text{-}P_2W_{17}O_{61}\text{-}(Co\cdot OH_2)^{8-}$ (the darker Co and its attached OH_2 are shown).

Katsoulis and Pope[22] initiated the first major advances in "inorganic-porphyrin"-like polyoxometalate-based catalysis by demonstrating that the sixth coordination site on the heterometal could be dehydrated by extracting monosubstituted polyoxometalates into organic solvents. This extraction technique leaves the heterometal unsaturated and quite reactive. Katsoulis and Pope[23] have also shown that the chromium(III) monosubstituted polyoxotungstate "$SiW_{11}O_{39}(Cr^{III})^{7-n}$", Figure 2, could be oxidized to a solution-stable chromium(V)–oxo species by oxygen transfer from iodosylbenzene. This stable species, analogous to chromium(V)–oxo porphyrins,[24] does not perform atom-transfer reactions.

Hill and Brown[25] have demonstrated the catalytic epoxidation of olefins with iodosylarenes and the monosubstituted Keggin anions $[(n\text{-}C_4H_9)_4N]_4HPW_{11}O_{39}(M^{2+}\cdot L)^{4-}$ (M^{2+} = Mn^{2+}, Co^{2+}; L = unknown), Figure 2. Alkane hydroxylation has also been demonstrated by Faraj and Hill[26] using monosubstituted Keggin anions *as the precatalysts* with *tert*-butylhydroperoxide as the oxidant, although metals leached from the polyoxoanions by the peroxide were not ruled out as the true catalysts.

Lyons and co-workers have demonstrated propane oxidation *with dioxygen* and precatalysts such as $PW_{11}O_{39}(M\cdot N_3)^{x-}$ (M = Cr^{3+}, Mn^{2+}, others[27b]) at 100–175 °C and 100–2000 psig of O_2 for 3–6 h.[27] Unclear aspects of this important work include the composition of the actual catalyst, the role of N_3^-, and the detailed oxidation mechanism. Most recently, Neumann and Abu-Gnim[28] have demonstrated hydrocarbon oxidation starting with a polyoxotungstate having the composition of $SiW_{11}O_{39}(Ru^{III}\cdot OH_2)^{5-}$ and a variety of oxidants. Rather clearly, a rich but still relatively little explored area—transition-metal-substituted polyoxometalate-based oxidation catalysis—is beginning to unfold.

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In mid-1983, our own collaborative efforts[29] examining polyoxotungstates as oxidation catalysts also initially focused on the synthesis, characterization, and catalytic oxidation capabilities of organic-soluble Keggin anion derivatives, such as $XW_{11}O_{39}(M^{n+}\cdot L)^{x-}$ (X = P, Si; $M^{n+} = Fe^{2+}$; Mn^{2+}; L = H_2O), Figure 2. However, this effort was abandoned due to characterization problems caused by the decreased effectiveness, and in some cases the nearly complete loss, of direct analytical techniques such as ^{31}P and ^{183}W NMR when M^{n+} is paramagnetic.[30] More importantly, our interest in eventually understanding the *mechanism* of these novel oxidation catalysts required us to emphasize systems that can be well characterized; hence, we chose to examine the potentially superior $P_2W_{17}O_{61}(M^{n+}\cdot L)^{(n-10)}$ system in which the sample's homogeneity and integrity following catalysis can readily be established by observation, for example, of the two phosphorus[31] resonances by ^{31}P NMR.

Herein we report the synthesis, isolation, and characterization of a series of monosubstituted[19c,32] Dawson[33] anion complexes, Figure 2, α_2-$P_2W_{17}O_{61}(M^{n+}\cdot L)^{(n-10)}$ [$M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$], as both their aqueous- (potassium salts, L = H_2O) and organic-soluble (tetra-*n*-butylammonium salts, L = Br^-) salts. These complexes have been characterized by full elemental analysis, ^{31}P NMR and IR, UV-vis, HPLC, sedimentation equilibrium molecular weight measurements, and temperature-varied magnetic susceptibility studies. We also report the partially observable ^{183}W NMR spectra of α_2-$K_7P_2W_{17}(M^{3+}\cdot OH_2)O_{61}$ (M = Mn^{3+}, Fe^{3+}), of α_2-$K_8P_2W_{17}(Cu^{2+}\cdot OH_2)O_{61}$, and of α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn\cdot Br)$. ^{183}W NMR studies of the potassium salts of α_2-$P_2W_{17}MO_{61}^{8-}$ (M = Co^{2+}, Ni^{2+}) were obtained and reported previously.[30] X-Ray crystallographic structural data for both the precursor polyoxoanion α_2-$P_2W_{17}O_{61}^{10-}$ and the monosubstituted Co^{2+} compound α_2-$P_2W_{17}O_{61}(Co\cdot OH_2)^{8-}$ have been reported by Weakley (see Figure 3).[34]

Although these complexes are based on the well-known monosubstituted Dawson anion and important prior work from several research groups,[32] and although monosubstituted Keggin ion polyoxometalates were first reported as oxidation catalysts four years ago,[25] the present work is the first report with the following: (i) where a designed system (the Dawson ion based system) is reported, one that has both ^{31}P and ^{183}W NMR spectroscopic handles, and one that is more optimized toward making the needed mechanistic studies possible; (ii) where *pure, isolated* α_2-$P_2W_{17}O_{61}(M\cdot L)^{y-}$ is reported in both water-soluble and organic-soluble forms [pure α_2-isomers have been prepared and isolated (free of the α_1-isomer) for the first time];[30] (iii) where the resultant polyoxometalate precatalysts are fully characterized by nearly all applicable physical methods; (iv) where the full synthetic and characterization details are reported; (v) where the unequivocal identity of the ligand, L, at the heterometal in α_2-$P_2W_{17}O_{61}(M\cdot L)^{y-}$ is reported (this is important since replacing this L by an oxo ligand (M=O) is a key for oxidation catalysis); (vi) where added L base-binding equilibria are reported,[19g] studies that suggest that the steric demands of α_2-$P_2W_{17}O_{61}(M\cdot L)^{y-}$ are minimal (approximately similar to the steric demands of tetraphenylporphyrin); and (vii) where evidence is provided that the monosubstituted polyoxometalate α_2-$P_2W_{17}O_{61}(Mn\cdot L)^{7-}$ remains intact under oxidation catalysis conditions.[35]

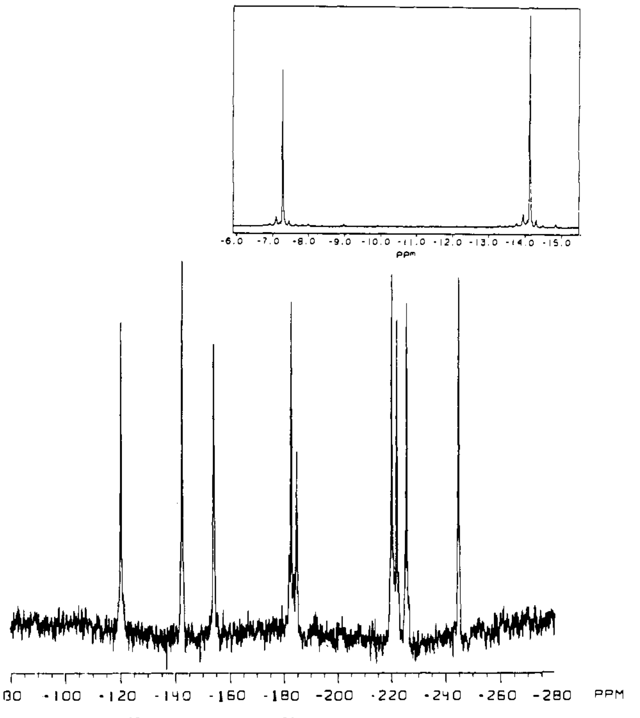

Figure 4. The ^{183}W NMR and ^{31}P NMR (inset) of pure (≥98%) α_2-$P_2W_{17}O_{61}\cdot 15H_2O$ as its Li^+ salt following metathesis with $LiClO_4$ (−$KClO_4$).

In an accompanying paper,[35] catalysis by α_2-$P_2W_{17}O_{61}(M\cdot L)^{y-}$ is reported, yielding olefin epoxidations and hydrocarbon (aliphatic and aromatic) hydroxylations.

Results

The ultimate goal of these synthesis and characterization studies is to prepare pure α_2-$P_2W_{17}O_{61}(M\cdot L)^{10-}$ as their organic solvent soluble $[(n\text{-}C_4H_9)_4N]^+$ salts. Keys to the strategy that allowed us to obtain the results described below include (i) the use of crystalline, isomerically pure α_2-$P_2W_{17}O_{61}^{10-}$ lacunary precursor; (ii) the strategy of purification via recrystallization at *the aqueous-soluble K^+ salt stage* for each α_2-$P_2W_{17}O_{61}(M\cdot L)^{10-}$ (purification at the $[(n\text{-}C_4H_9)_4N]^+$ stage is difficult, if not impossible); (iii) careful control of the solution pH when performing the metathesis to the $[(n\text{-}C_4H_9)_4N]^+$ salt (a general problem exists: knowing what pH is best to yield the desired *x* and *y* values in $[(n\text{-}C_4H_9)_4N]_xH_y[\alpha_2\text{-}P_2W_{17}O_{61}(M^{n+}\cdot L)]^{(x+y+n-10)}$); (iv) use of a CH_2Cl_2/CH_3CN extraction method that avoids lengthy filtration steps of some precipitated $[(n\text{-}C_4H_9)_4N]^+$ salts; and (v) extensive use of the ^{31}P NMR handle in the Dawson-type $P_2W_{17}M$ system to survey different conditions for the best route to pure $P_2W_{17}M$ products. Generally, even 2–4% of impurities (e.g., the α_1-isomer of $P_2W_{17}M$) proved detectable by ^{31}P NMR.

α_2-$P_2W_{17}O_{61}^{10-}$.[36] This synthesis is based on the fact that α_2-$P_2W_{17}O_{61}^{10-}$ is the first product formed by base degradation of[37,38] α-$P_2W_{18}O_{62}^{6-}$. The monolacunary polyoxometalate is

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[29] (a) These studies were initiated as a cooperative University of Oregon/Catalytica, Inc. investigation.[29b,c] (b) Evitt, E.; Finke, R. G.; Miller, W. K. Unpublished results. (c) Oral Presentations of parts of this work include (i) Finke, R. G. Conference on Oxidation Chemistry, California Institute of Technology, February 25–27, 1986. (ii) Mansuy, D.; Lyon, D. K.; Miller, W. K.; Finke, R. G. *Abstracts of Papers*, 197th National Meeting of the American Chemical Society, Dallas, TX; American Chemical Society: Washington, DC, 1989; INORG 96. (iii) Finke, R. G. *Abstracts of Papers*, 1989 International Chemical Conference of Pacific Basin Societies, Honolulu, HI, 1989; INORG 731.

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[31] For the purposes of this paper, the established nomenclature[30] will be used to define the phosphorus atoms. In this nomenclature, the phosphorus closest to the site of substitution will be designated P(1) and the phosphorus furthest from the site of substitution will be designated P(2).

[32] We wish to clearly and specifically point out important, prior work in the $P_2W_{17}M$ area (see also ref 42): (a) Weakley, T. J. R.; Malik, S. A. *J. Inorg. Nucl. Chem.* **1967**, *29*, 2935. (b) Malik, S. A.; Weakley, T. J. R. *J. Chem. Soc. A* **1968**, 2647. (c) Tourné, C. M.; Tourné, G. F.; Malik, S. A.; Weakley, T. J. R. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3875. (d) Massart, R.; Contant, R.; Fruchart, Ciabrini, J.-P.; Fournier, M. *Inorg. Chem.* **1977**, *16*, 2916.

[33] (a) Dawson, B. *Acta Crystallogr., Sect. B* **1953**, *6*, 113. (b) D'Amour, H. *Acta Crystallogr.* **1976**, *B32*, 729.

[34] Weakley, T. J. R. *Polyhedron* **1987**, *6*, 931.

[35] Mansuy, D.; Bartoli, J. F.; Battioni, P.; Lyon, D. K.; Finke, R. G. *J. Am. Chem. Soc.*, the following paper in this issue.

[36] (a) Although the preparation of the monolacunary Dawson-type polyoxometalates is well-documented,[32] this is the first report in which the pure α_2-isomer complexes α_2-$P_2W_{17}O_{61}(M\cdot L)^{y-}$ are *isolated* and *characterized*. (b) During the construction of this paper, a publication appeared describing the synthesis and isolation of pure α_1- and α_2-$K_{10}P_2W_{17}O_{61}$.[36c] (c) Contant, R. *Inorg. Synth.* **1990**, *27*, 107.

isolated as the potassium salt and is recrystallized once to yield isomerically pure α_2-$P_2W_{17}O_{61}{}^{10-}$. This preparation yields consistently 70–85% of α_2-isomer, greater than 98% pure (as determined by ^{31}P NMR, Figure 4, inset). Confirmation that the preparation yields the α_2-isomer (and not the α_1-isomer) was obtained by ^{183}W NMR (the expected nine-line spectrum, Figure 4).[39]

General Route to α_2-$K_{(10-n)}P_2W_{17}O_{61}(M^{n+}\cdot OH_2)$ (M^{n+} + Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}). These compounds were prepared by an adaptation of synthesis routes described in the literature.[32] As noted above, use of isomerically pure α_2-$P_2W_{17}O_{61}{}^{10-}$ as the isolated, recrystallized material, rather than generating the lacunary anion in situ,[30,32] avoids a mixture of α_1 and α_2 products and is one simple but important key to the synthetic work reported herein. The heterometal was then added in stoichiometric amounts as a solution to facilitate incorporation of the metal into the lacunary site, rather than precipitation of the starting lacunary polyoxometalate with the heterometal as a counterion. The α_2-$P_2W_{17}O_{61}(M^{n+}\cdot OH_2)^{(n-10)}\cdot xH_2O$ complexes were precipitated as their potassium salts and recrystallized from hot water (pH 6–7) to remove any minor impurities. Each complex was then characterized by ^{31}P NMR, HPLC, IR, UV-vis, and elemental analysis to confirm the homogeneity of the product and the clean incorporation of the heterometal. Yields are good, falling between 70 and 90%.

The ^{31}P NMR provides a sensitive probe of M^{n+} incorporation, showing a broadened peak between −10 and −30 ppm. This peak is due to P(2),[31] the phosphorus atom farthest from the substitution site. The phosphorus atom closest to the site of incorporation, P(1), has been observed but is radically shifted and broadened by the paramagnetic incorporated metal and typically appears 500–1000 ppm downfield. Furthermore, several P(1) resonances have line widths as broad as 30 000 Hz.[31] Owing to the broadness and difficulty of observing P(1), only the P(2) resonance was routinely used to determine purity. These results demonstrate the value of the Dawson-type $P_2W_{17}O_{61}(M^{n+})$ system with its "close (north)" and "far (south)" P(1) and P(2) atoms, respectively, in comparison to the Keggin system $PW_{11}O_{39}(M^{n+})$ with only a close phosphorus atom.

Visible spectra are consistent with the literature reports,[32] exhibiting maxima attributable to the heterometal and a sharp rise into the UV, due to the tungstate framework. Thermal gravimetric analysis was done on each of the compounds to determine the number of waters of hydration (±1.0 water).

α_2-$K_7P_2W_{17}O_{61}(Mn^{3+}\cdot OH_2)$. This particular compound has been successfully prepared by three separate methods: (i) direct incorporation of the Mn^{3+} heterometal into the lacunary polyoxometalate; (ii) direct incorporation of Mn^{2+} followed by the isolation and characterization of α_2-$K_8P_2W_{17}O_{61}(Mn^{2+}\cdot OH_2)$ (^{31}P NMR: δ [P(2)] −12.1, at 0.04 M, literature[30] δ [P(2)] −13.4, at 0.01 M), and then subsequent oxidation of the isolated Mn^{2+} complex to the Mn^{3+}-polyoxometalate complex with persulfate; and (iii) in situ preparation and subsequent persulfate oxidation of the Mn^{2+} complex. Each synthesis gives identical products and similar yields of ca. 70%. Option iii is the method reported in the Experimental Section due primarily to the ease of preparation.

^{31}P NMR of the α_2-$P_2W_{17}O_{61}(Mn^{3+}\cdot OH_2)^{7-}$ confirms the presence of a single product exhibiting a single resonance in the NMR at δ −12.3. The visible spectrum shows a maximum at 484 nm with ϵ_{484} = 400 cm^{-1} M^{-1} at 1 × 10^{-3} M.[40] The infrared absorbances are listed in the Experimental Section and confirm the incorporation of the heterometal into the lacunary polyoxometalate. Thermal gravimetric analysis, of material prepared and dried as detailed in the Experimental Section, shows a weight loss of 4.87% between 40 and 240 °C corresponding to 13 H_2O.

α_2-$K_7P_2W_{17}O_{61}(Fe^{3+}\cdot OH_2)$. The monosubstituted iron–polyoxometalate was prepared by the addition of a solution of Fe^{3+} to a solution of α_2-$K_{10}P_2W_{17}O_{61}\cdot 15H_2O$, which yielded a dark yellow-orange solution. It is important in this synthesis to allow the reaction solution to cool to room temperature, prior to addition of the KCl, to allow an unidentified dark orange impurity to precipitate and to be removed by filtration. After the addition of KCl and recrystallization, the desired product was obtained in high yield (78%) as a yellow crystalline material. Isomeric purity of α_2-$P_2W_{17}O_{61}(Fe\cdot OH_2)^{7-}$ was confirmed by ^{31}P NMR (a single resonance at δ −12.4). The visible spectrum contained no discernible maxima, rather only a shoulder trailing into the ultraviolet region. The infrared absorbances are reported in the Experimental Section and are consistent with incorporation of the heterometal into the polyoxometalate framework. Thermal gravimetric analysis shows a loss of 3.48%, consistent with nine waters of hydration.

We note here that "$P_2W_{17}O_{61}(Fe^{3+})^{7-}$" (i.e., presumable a mixture of α_1- and α_2-isomers?) is reported[42] to form hydroxy-bridged dimers at pH values above 4–5 on the basis of good evidence (cryoscopic molecular weight, paper electrophoresis, gel filtration, and UV–visible experiments) and with an apparent formation constant of ca. 20. In fact, the dimerization reaction is said to be general for "all Fe(III) heteropolytungstates".[42] Our ultracentrifugation molecular weight experiments detected only a monomer of α_2-$K_7P_2W_{17}O_{61}(Fe^{3+})$, but this is the expected result for the conditions of our molecular weight experiment (water, pH ca. 4, 0.2 M LiCl, and low ca. 1 × 10^{-5} M polyoxoanion where only monomer should exist given the low dimer-formation constant; see the Experimental Section for further details).

Very recently we were able to address this monomer vs dimer question by X-ray crystallography. Crystals of $K_7[\alpha_2$-$P_2W_{17}O_{61}(Fe\cdot H_2O)]\cdot nH_2O$ were grown from a solution of ca. 5 g of sample in 100 mL of 0.2 M LiCl concentrated to ca. 15 mL. The resultant crystals are rhombohedral, with a trigonal (nonprimitive) cell of dimensions (diffractometer) a = 19.682 (4) Å, c = 15.608 (6) Å, and V = 5236 (3) Å^3. The Laue symmetry is $\bar{3}$. Several other potassium salts of monosubstituted Dawson anions with −7 or −8 charge have similar cell dimensions.[19c] The primitive rhombohedral cell of volume 1745 Å^3 can contain just one Dawson-type anion (i.e., a monomer is present). The probable space group is $R3$, with the anion on a 3-fold crystallographic axis and the Fe atom necessarily disordered over three or all six cap positions (the alternative, centrosymmetric, space group $R\bar{3}$ would require the anion to be grossly disordered). Because of the expected disorder, the structure was not studied further.

α_2-$K_8P_2W_{17}O_{61}(Co^{2+}\cdot OH_2)$. This complex was prepared by us five times by the addition of Co^{2+} to a solution of the monolacunary polyoxometalate. Yields are reasonable for this reaction, varying from 55 to 75%. The ^{31}P NMR of the twice recrystallized compound shows a single peak at δ −22.6. If the crude compound is only recrystallized once, an unassigned resonance (less than 5%) is observed at δ −34.0. (Note, again, the importance of the recrystallization step prior to making the desired $[(n\text{-}C_4H_9)_4N]^+$ salt.) The visible spectrum (1 × 10^{-2} M) shows a maximum at 544 nm with ϵ_{544} = 108 cm^{-1} M^{-1}. Infrared data are listed in the Experimental Section and are consistent with the incorporation of the heterometal into the lacunary polyoxometalate. Thermal gravimetric analysis shows a loss of 6.43% corresponding to 17 H_2).

α_2-$K_8P_2W_{17}O_{61}(Ni^{2+}\cdot OH_2)$. This complex was prepared by the addition of Ni^{2+} to a solution of the lacunary polyoxometalate. Yields are good (75%) and can be improved to as high as 95% by the addition of (solid) KCl to the mother liquor. However, such addition of excess KCl tends to give products 1–2% high in the potassium analysis. The product is determined to be isomerically pure by ^{31}P NMR, which shows a single resonance at δ −14.0. The visible spectrum (1.8 × 10^{-2} M) shows a flat broad absorbance between 650 and 750 nm (ϵ_{680} = 10 cm^{-1} M^{-1}). Infrared data are listed in the Experimental Section and confirm the incorporation of the heterometal into the lacunary polyoxo-

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(37) Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886.

(38) Wu, H. *J. Biol. Chem.* **1920**, *43*, 189.

(39) Acerete, R.; Harmalker, S.; Hammer, C. F.; Pope, M. T.; Baker, L. C. W. *J. Chem. Soc., Chem. Commun.* **1979**, 777.

(40) The concentrations at which the UV–vis spectra were obtained are reported since it has been previously noted that ϵ is concentration dependent (i.e., deviations from Beer's law are observed) in similar compounds.[32c]

Table I. ^{31}P NMR, IR, and UV–Vis Data for α_2-$K_{10}P_2W_{17}O_{61}\cdot15H_2O$ and Its Transition-Metal-Substituted Derivatives α_2-$P_2W_{17}O_{61}(M^{n+}\cdot Br)^{(n-11)}$ as Their $[(n\text{-}C_4H_9)_4N]^+$ Salts

	^{31}P NMR	IR (KBr disc)	UV–vis
α_2-$P_2W_{17}O_{61}{}^{10-}$ [a]	−7.3, −14.1	740, 805, 880, 905, 940, 985, 1022, 1084	
α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$ [b]	−10.0[c,d]	791, 888, 945, 956, 1016, 1089	478 (380),[d] 453 (250)[e]
α_2-$P_2W_{17}O_{61}(Fe\cdot L)^{8-}$ [b] (L = 0.75 H_2O, 0.25 Br^-)	−12.7[c,d]	791, 888, 945, 956, 1016, 1089	
α_2-$P_2W_{17}O_{61}(Co\cdot Br)^{9-}$ [b]	−26.4[c,d]	816, 914, 947, 956, 1017, 1087	484 (325),[d] 574 (76)[e]
α_2-$P_2W_{17}O_{61}(Ni\cdot Br)^{9-}$ [b]	−12.0[c,d]	812, 909, 945, 958, 1028, 1087	671 (12),[d] 699 (11)[e]
α_2-$P_2W_{17}O_{61}(Cu\cdot Br)^{9-}$ [b]	−9.9[c,d]	820, 916, 952, 962, 1017, 1087	706 (35),[d] 706 (38)[e]

[a] Physical properties determined for the Li^+ salt (^{31}P NMR) and K^+ salt (IR). [b] Physical properties determined for the $[(n\text{-}C_4H_9)_4N]^+$ salt. The compound listed (the Br^-–containing material) was dissolved in the indicated[d,e] solvent for the measurement. On the basis of the nearly complete dissociation of Br^- from α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$ in CH_2Cl_2, it is probable that the Br^- is nearly quantitatively displaced by solvent for all of the compounds. Therefore, all solution measurements should be for α_2-$P_2W_{17}O_{61}(M\cdot L)^{y-}$, where L is solvent. [c] The P(1) resonance, if determined, is available in the Experimental Section or elsewhere.[30] [d] Measured as a CH_3CN solution. [e] Measured as a CH_2Cl_2 solution.

metalate. Thermal gravimetric analysis shows a loss of 6.75%, which corresponds to 18 H_2O.

α_2-$K_8P_2W_{17}O_{61}(Cu^{2+}\cdot OH_2)$. Identical with the preparation of the other monosubstituted compounds, this complex was prepared by the addition of the heterometal Cu^{2+} to a solution of α_2-$K_{10}P_2W_{17}O_{61}$. This synthesis, which is similar to that of the monosubstituted Ni^{2+} complex, gives good yields of ca. 70%. The yields can be improved by KCl addition. Multiple recrystallization is required since, without it, samples tend to analyze slightly high for potassium. The resultant product is isomerically pure by ^{31}P, which shows a single resonance at δ −13.0. The visible spectrum (1.8×10^{-2} M) shows a broad absorbance with a maximum at 885 nm (ϵ_{885} = 55 cm^{-1} M^{-1}), which then trails into the far-IR. Infrared data (listed in the Experimental Section) confirm the incorporation of the heterometal into the lacunary polyoxometalate. Thermal gravimetric analysis shows a loss of 6.26%, which is consistent with 17 waters of hydration.

General Synthetic Route to the Organic-Soluble Compounds α_2-$[(n\text{-}C_4H_9)_4N]_{(11-n)}P_2W_{17}O_{61}(M^{n+}\cdot Br)$, $P_2W_{17}M$ (M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}). One subtle but crucial unknown in such polyoxometalate syntheses is the initial question of what pH to work at, and what pH as a function of each different M^{n+}, to yield the desired $[(n\text{-}C_4H_9)_4N]^+/H^+$ counterion combination, $P_2W_{17}O_{61}(M\cdot OH_x)^{y-}$ (x = the degree of protonation). The synthesis of the $[(n\text{-}C_4H_9)_4N]^+$ salts and their full characterization are *not* trivial.[41]

The synthetic route to each of these compounds involves a metathetical exchange by addition of a stoichiometric amount of $[(n\text{-}C_4H_9)_4N]Br$ to an aqueous solution of the potassium salt of the polyoxometalate *with stringent control of the solution pH*—a key also to avoiding α_2-$P_2W_{17}O_{61}(M^{n+})^{y-}$ degradation at too low or too high a pH. A stoichiometric amount of the $[(n\text{-}C_4H_9)_4N]^+$ salt must be used to avoid having excess $[(n\text{-}C_4H_9)_4N]Br$ in the final product, which proved difficult to remove. Optimizing the pH (and then maintaining it) throughout the reaction also must minimize possible alkaline solution hydrolysis of the heterometal,[42] or degradation of the complexes in too acidic solutions, to yield α_2-$P_2W_{17}O_{61}{}^{10-}$ and the free heterometal. The tetra-n-butylammonium salts of the monosubstituted Dawson complexes are then isolated by extraction into CH_2Cl_2 (in several cases, addition of CH_3CN was necessary to minimize frothing) and evacuation of the solvent. (This method avoids slow filtration steps.) The complexes were then reprecipitated from CH_3CN with ether to give an oily product, which yields fine powders upon repeated trituration with diethyl ether. In all cases (except where M = Fe), the C, H, N, and Br analyses demonstrate that the isolated complexes contain 1 extra equiv of $[(n\text{-}C_4H_9)_4N]Br$ (a result that could well extend to some[22,23,28] earlier studies of less well characterized materials).[22,23,25,26] Evidence for the coordination of the bromide anion to the heterometal is presented in a following section.

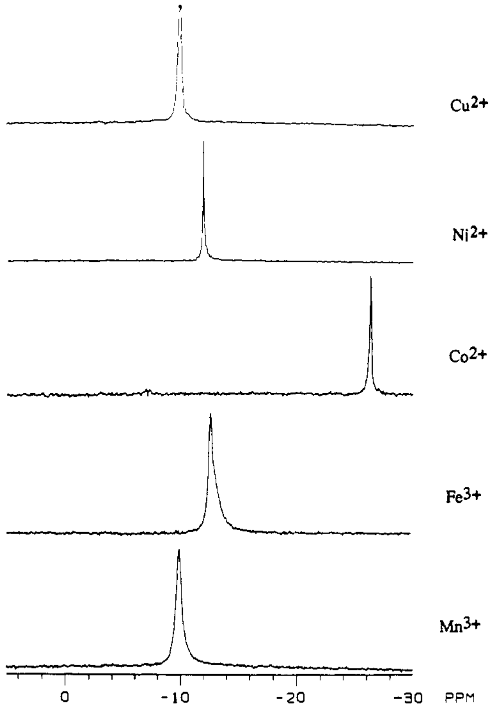

Figure 5. Stacked plot of the (temperature-dependent)[65b] ^{31}P spectra at 20 °C of the P(2) resonances of α_2-$[(n\text{-}C_4H_9)_4N]_{(11-n)}P_2W_{17}O_{61}(M^{n+}\cdot L)$ (M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}) as 0.04 M CH_3CN/CD_3CN solutions.

The yields of the tetra-n-butylammonium salts of the monosubstituted Dawson anions are moderate [in most cases, ca. 50% yields were obtained although high yields (80%) were obtained for $P_2W_{17}Mn(III)$] owing to the low partition coefficient for the extraction when only stoichiometric amounts of $[(n\text{-}C_4H_9)_4N]^+$ are used. Each complex was characterized by ^{31}P NMR, UV–vis, and IR, data that are summarized in Table I, as well as sedimentation equilibrium molecular weight, TGA, and complete elemental analysis. Only the P(2) ^{31}P NMR resonances (vide supra) were observed and appear between δ −10 and −30, Figure 5. The sedimentation equilibrium molecular weights are atypically high (see the Experimental Section and supplementary material, especially for M^{n+} = Mn^{3+} and Co^{2+}) but can be used to satisfactorily characterize the products as monomeric and not dimeric polyoxometalates, at least under the conditions of the molecular

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(41) (a) A knowledge of the pH-dependent *solution* chemistry of the M^{n+} cation is, of course, crucial.[41b] (b) Baes, C. F., Jr.; Mesmer, R. E. *The Hydrolysis of Cations*; Wiley-Interscience: New York, 1976. (c) Although the synthesis of these precatalysts might appear to be no more than a simple metathetical exchange on well-known compounds, it becomes readily apparent, especially in light of the present work, that this is not true. In fact, our experience shows *that each metathetical exchange becomes the synthesis and nontrivial characterization of a new polyoxoanion.* Drawing analogy to the better developed organic synthesis literature, each countercation exchange and *subsequent characterization* for a polyoxometalate can involve the same amount of work necessary to prepare a new derivative of a moderate-sized organic system.

(42) Zonevijille, F.; Tourné, C. M.; Tourné, G. F. *Inorg. Chem.* **1982**, *21*, 2751 and ref 7 therein. Tourné and Tourné have shown that aqueous-soluble iron(III)-substituted polyoxometalates can be hydrolyzed to hydroxo and μ-oxo dimer species. However, the instability of their iron species to the aqueous reaction conditions may make it difficult if not impossible to access oxidized species of these compounds.

weight experiments. Thermogravimetric analyses (TGA) show no solvates (40–240 °C), as is generally observed for other organic-soluble polyoxometalates,[43] and exhibit the appropriate weight decrease (over the 240–940 °C temperature range) due to the thermal degradation of the tetra-*n*-butylammonium cations and to volatile P_2O_5 formation.[44]

$\alpha_2\text{-}[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn^{3+}\cdot Br)$, $P_2W_{17}Mn(III)$. This compound has been prepared six different times at several concentrations and pH's. If the $\alpha_2\text{-}K_7P_2W_{17}O_{61}(Mn\cdot OH_2)$ is metathesized at a pH of less than 4 the compound partially degrades (10–20%, as judged by ^{31}P NMR) to the starting materials $\alpha_2\text{-}P_2W_{17}O_{61}{}^{10-}$ and an unidentified manganese-containing compound—again showing the importance of a ^{31}P NMR handle. At pH more than 8, $P_2W_{17}Mn$ appears to hydrolyze to either an oxo- or hydroxomanganese polyoxometalate (which could prove very valuable in later mechanistic studies, if electrochemically oxidizable), although the presence of a Mn═O or Mn—OH species has not been unambiguously determined.[45] The homogeneity of $\alpha_2\text{-}P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$ is demonstrated by its ^{31}P NMR spectrum of the P(2) phosphorus, which shows a resonance at δ -10.0 ($\Delta\nu_{1/2} = 90 \pm 1$ Hz). We were unable to observe the P(1) resonance (closest to the paramagnetic center) in this *Bu_4N^+ salt in CH_3CN* (perhaps not surprisingly, since it is 9000 Hz wide for the K^+ salt in H_2O).[30] The ^{183}W NMR spectrum of this compound exhibits six of the nine possible resonances due to the effects of the paramagnetic manganese(III). (The ^{183}W NMR data are tabulated in the Experimental Section.) Evidence for the counterion composition was obtained by elemental analysis and the number of $[(n\text{-}C_4H_9)_4N]^+$ confirmed by TGA. The complex has been demonstrated to be monomeric under the conditions of the molecular weight experiment (1×10^{-5} M CH_3CN/0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$). $\bar{M}_r$ ($\bar{M}_r$ = weight-average molecular weight) calculated for $[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn\cdot Br)$ (found): 6069 (6500 ± 600).

$\alpha_2\text{-}[(n\text{-}C_4H_9)_4N]_{6.75}H_{0.5}P_2W_{17}O_{61}(Fe^{3+}\cdot L)$, $P_2W_{17}Fe(III)$, (L = $^3/_4$ H_2O, $^1/_4$ Br^-). The iron-containing organic-soluble complex has been prepared twice at ca. pH 6.5 and once at pH 5. In neither of the preparations was degradation to $\alpha_2\text{-}P_2W_{17}O_{61}{}^{10-}$ and free heterometal observed. The reaction was not examined under alkaline conditions. The homogeneity of the complex was demonstrated by a single resonance in the ^{31}P NMR at δ -12.7 ($\Delta\nu_{1/2} = 100 \pm 5$ Hz). Elemental analysis and TGA are consistent with 6.75 $[(n\text{-}C_4H_9)_4N]^+$, with the one-half proton being added for charge balance (the 0.25 equiv of Br^- is required by analysis). Solution molecular weight measurements demonstrate that $P_2W_{17}Fe$ is monomeric, at least under the conditions of the molecular weight experiment (1×10^{-5} M CH_3CN/0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$). $\bar{M}_r$ calculated for $[(n\text{-}C_4H_9)_4N]_{6.75}H_{0.5}P_2W_{17}O_{61}(Fe\cdot L)$ (found); 5876 (6000 ± 600).

$\alpha_2\text{-}[(n\text{-}C_4H_9)_4N]_9P_2W_{17}O_{61}(Co^{2+}\cdot Br)$, $P_2W_{17}Co(II)$. The cobalt-containing polyoxometalate has been prepared eight times at a variety of pH's and concentrations. If the metathesis of $\alpha_2\text{-}K_8P_2W_{17}O_{61}(Co\cdot OH_2)$ is carried out below pH 5, small amounts of decomposition begin, yielding $\alpha_2\text{-}P_2W_{17}O_{61}$ (by ^{31}P NMR) and an undetermined cobalt-containing product. At pH less than 4.5, the decomposition is observed to be as high as 50%. Interestingly, this compound appears to be relatively insensitive to basic hydrolysis conditions, with no decomposition products apparent by ^{31}P NMR up to pH 9. The isomeric purity of the compound is demonstrated by a single resonance in the ^{31}P NMR at δ -26.4 (25 ± 1 Hz). Elemental analysis and TGA were consistent with the presence of 9 $[(n\text{-}C_4H_9)_4N]^+$ counterions.

Curiously, we have had great difficulty obtaining reliable tungsten analyses for $P_2W_{17}Co$. Four separate analyses (two different preparations) gave results that were not only incorrect for our formulation but internally inconsistent (three samples analyzed between 2 and 3% low in W and one sample analyzed 2% high in W). Although it is difficult to reconcile why only this compound has not given reliable tungsten analyses, we believe that the stated formulation is correct since it is clean by ^{31}P NMR, all of the other elements analyze satisfactorily, plus the fact that thermogravimetric analysis confirms the expected volatile and residual matter.

Sedimentation equilibrium molecular weight analysis of $\alpha_2\text{-}[(n\text{-}C_4H_9)_4N]_9P_2W_{17}O_{61}(Co\cdot Br)$ gave an acceptable value. $\bar{M}_r$ calculated for $[(n\text{-}C_4H_9)_4N]_9P_2W_{17}O_{61}(Co\cdot Br)$ (found): 6479 (6500 ± 500; four experiments).

$\alpha_2\text{-}[(n\text{-}C_4H_9)_4N]_9P_2W_{17}O_{61}(Ni^{2+}\cdot Br)$, $P_2W_{17}Ni$, and $\alpha_2\text{-}[(n\text{-}C_4H_9)_4N]_9P_2W_{17}O_{61}(Cu^{2+}\cdot Br)$, $P_2W_{17}Cu(II)$. These compounds have been prepared at pH's varying between 4 and 8.5. However, in contrast to $P_2W_{17}Mn$ and $P_2W_{17}Co$, the Ni^{2+} and Cu^{2+} complexes show almost no tolerance to a wide variety of pH conditions for their preparation. At pH's between 5.5 and 6, decomposition begins (about 5%, as judged by ^{31}P) and reaches as high as 50% by pH 5. At pH's greater than 7, the compounds appear to form different types of hydrolysis products depending upon the concentration and pH of the solution. As with the "hydrolysis" products of $P_2W_{17}Mn^{3+}$, no $P_2W_{17}Ni^{2+}$ and $P_2W_{17}Cu^{2+}$ hydrolysis products have been unambiguously characterized, but they do show unique ^{31}P NMR and UV–vis spectra.[46] The homogeneity of the $\alpha_2\text{-}P_2W_{17}O_{61}(Ni\cdot Br)^{9-}$ and $\alpha_2\text{-}P_2W_{17}O_{61}(Cu\cdot Br)^{9-}$ compounds prepared as described in the Experimental Section is confirmed by their respective ^{31}P NMR resonances [δ -12.0 ($\Delta\nu_{1/2} = 21 \pm 1$ Hz) and δ -9.9 ($\Delta\nu_{1/2} = 53 \pm 1$ Hz)]. Again, the elemental analysis and TGA are consistent with the proposed formulation of these complexes.

The visible spectrum of $P_2W_{17}Ni$ varies somewhat in coordinating vs noncoordinating solvents, while that for $P_2W_{17}Cu$ shows almost no difference between coordinating and noncoordinating solvents (see the Experimental Section for λ_{max} and ϵ data). This suggests that the Cu^{2+} polyoxometalate is five-coordinate or pseudo-four-coordinate (i.e., the L_1 position is extremely weakly ligated) as expected for Jahn–Teller distorted, d^9 Cu^{2+}. This conclusion is identical with Pope's following his extraction of $[SiW_{11}O_{39}(Cu\cdot OH_2)]^{6-}$ into toluene.[22] Sedimentation equilibrium molecular weight studies have been done on both the $P_2W_{17}Ni$ and $P_2W_{17}Cu$ compounds and confirm that they are both monomeric under the experimental conditions. $\bar{M}_r$ calculated for $[(n\text{-}C_4H_9)_4N]_1P_2W_{17}O_{61}(Ni\cdot Br)^{8-}$ (found): 4447 (4700 ± 500). $\bar{M}_r$ calculated for $[(n\text{-}C_4H_9)_4N]_5P_2W_{17}O_{61}(Cu\cdot Br)^{4-}$ (found): 5437 (5500 ± 500).

$\alpha\text{-}[(n\text{-}C_4H_9)_4N]_4HPW_{11}O_{39}(Mn^{2+}\cdot OH_2)$, $PW_{11}Mn(II)$. $PW_{11}Mn(II)$ was synthesized as part of our early[29] survey work into monosubstituted polyoxometalates as oxidant-resistant catalysts. The complex was characterized by a complete analysis and TGA to determine cation composition; however, further spectroscopic characterization was not attempted in light of Hill and Brown's work.[25] (Our synthesis and partial characterization are detailed in the Experimental Section to aid other researchers in reproducing both our synthesis and catalysis results.[35])

K_{eq} Studies of $\alpha_2\text{-}P_2W_{17}O_{61}(Mn^{3+}\cdot Solvent)^{8-} + Br^- \rightleftharpoons \alpha_2\text{-}P_2W_{17}O_{61}(Mn^{3+}\cdot Br)^{8-}$ in the Presence of Added $[(n\text{-}C_4H_9)_4N]Br$. The metathesis of the potassium salts of the monosubstituted polyoxometalates with tetra-*n*-butylammonium bromide results in organic-soluble products *that each contain 1 extra equiv of $[(n\text{-}C_4H_9)_4N]Br$* (except in the case of $\alpha_2\text{-}P_2W_{17}O_{61}(Fe\cdot L)^{7-}$, which only contains a partial equivalent). Because this result has not been previously reported,[47] and because a strongly binding Br^-

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(43) Finke, R. G.; Rapko, B.; Saxton, R. J.; Domaille, P. J. *J. Am. Chem. Soc.* **1986**, *108*, 2947.

(44) (a) $x[(n\text{-}C_4H_9)_4N]^+$ cations are lost as $x/2$ $[(n\text{-}C_4H_9)_4N]_2O$ (presumably as volatile H_2O + 2 Bu_3N + butene), and the two $PO_4{}^{3-}$ cores are lost as volatile P_2O_5.[44b] (b) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. *Inorg. Chem.* **1983**, *22*, 207.

(45) (a) This putative hydrolysis of the manganese heterometal is based on the observation of a different chemical shift in the ^{31}P NMR and a different UV–vis spectrum. Polyoxometalates are known to stabilize Mn(IV).[45b–d] (b) Baker, L. C. W.; Weakley, T. J. R. *J. Inorg. Nucl. Chem.* **1966**, *28*, 447. (c) Dale, B. W.; Buckley, J. M.; Pope, M. T. *J. Chem. Soc. A* **1969**, 301. (d) Ichida, H.; Nagai, K.; Sasaki, Y.; Pope, M. T. *J. Am. Chem. Soc.* **1989**, *111*, 586.

(46) (a) Flynn and Pope have reported the stabilization of Ni(IV) by a polyoxometalate.[46b] (b) Flynn, C. M., Jr.; Pope, M. T. *J. Am. Chem. Soc.* **1970**, *92*, 85.

Table II. Association Equilibrium Constants for α_2-$P_2W_{17}O_{61}(Mn^{3+}\cdot Br)^{8-}$ in CH_2Cl_2 [α_2-$P_2W_{17}O_{61}(Mn^{3+}\cdot Solvent)^{7-}$] and Various Bases

$$\alpha_2\text{-}P_2W_{17}O_{61}(Mn^{3+}\cdot \text{solvent})^{7-} + B \rightleftharpoons \alpha_2\text{-}P_2W_{17}O_{61}(Mn^{3+}\cdot B)^{7-}$$

B (base)	K_{assoc} (M^{-1})
N-methylimidazole	3600 ± 1700
pyridine	4100 ± 1700
triphenylphosphine	6 ± 3
Br^-	48 ± 9

ligand would directly affect the ability of the heterometal to coordinate either the oxidant or the substrate *during catalysis*, we felt it crucial to determine the dissociation constant of bromide for the most reactive catalyst[35] α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$. This was done by determining the association equilibrium constant for Br^- binding to α_2-$P_2W_{17}O_{61}(Mn\cdot L)^{7-}$ (L = solvent) in CH_2Cl_2, K_{eq} = 48 ± 9 M^{-1} (see the Experimental Section for details). Thus, with 1 equiv of Br^- initially present, less than 3% of it is bound to the manganese center in CH_2Cl_2 at 2 × 10^{-3} M α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$. Therefore, we conclude that the bromide is *not* coordinated under the more polar conditions employed for catalysis (1:1 CH_2Cl_2/CH_3CN), and that bromide *does not* hinder access to the heterometal during catalysis. Restated, the Br^- adducts α_2-$P_2W_{17}O_{61}(M\cdot Br)^{y-}$ serve as excellent, isolable *yet reactive* precatalysts.

K_{eq} Comparisons for α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$ and Selected Bases. There is relatively little substitution or other coordination chemistry for polyoxometalate-incorporated metals[19b,g,21] and no quantitative K_{eq} values like those reported in Table II for α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$. The association constants obtained for α_2-$P_2W_{17}O_{61}(Mn\cdot solvent)^{7-}$, especially those for *N*-methylimidazole and pyridine (3600 and 4100 M^{-1}, respectively), suggest a less hindered access to the manganese than in sterically demanding porphyrins. This conclusion is corroborated by comparison to the smaller association constant (245 ± 45 M^{-1}) obtained by Bruice and co-workers[48] for the *sterically congested* $Mn(Me_8TPP)(Cl)$[49] + imidazole (Im) $\rightleftharpoons$ $Mn(Me_8TPP)(Cl)(Im)$. [Unfortunately, few other Mn(porphyrin) axial-base values are available, presumably due to the complication of the presence of both five- and six-coordinate (mono- and bis(axial-base) forms).[47]] Overall, the "pocket" around Mn in P_2W_{17}Mn(III) appears to be somewhat hindered, a result independently demonstrated by the catalytic studies using P_2W_{17}Mn(III).[35]

Spectrophotometric Titration of α_2-$P_2W_{17}O_{61}(Mn^{3+}\cdot Br)^{8-}$ with OH^-. The possibility of accessing high-valent manganese intermediates, such as oxo and hydroxo species, is interesting especially in light of the facts that polyoxometalates are already known to stabilize high-valent manganese(IV) species.[45] Since polyoxometalates are frequently more stable under nonaqueous conditions, the synthesis of Mn(III)-OH in CH_3CN was examined via spectrophotometric titration with hydroxide of Mn(III)-containing α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$. A plot of absorbance vs equivalents of OH^- added shows only a single break point at 1.0 equiv of OH^-, with no further break point up to 4.5 equiv of OH^- (i.e., Mn(III)-OH, but not deprotonated Mn(III)-O^-, is observed). These results indicate that the Mn(III)-OH hydroxo species is rapidly formed and that the hydroxo ligand is stable to further deprotonation (an alternative possibly is that Mn(III)-OH is actually being deprotonated to yield Mn(III)-O^- species, but that little difference exists between their visible spectra). An important future experiment is electrochemical or other oxidation of P_2W_{17}(Mn—OH) to possibly independently generate the desired hypervalent, polyoxoanion-stabilized Mn(IV or V)=O species.

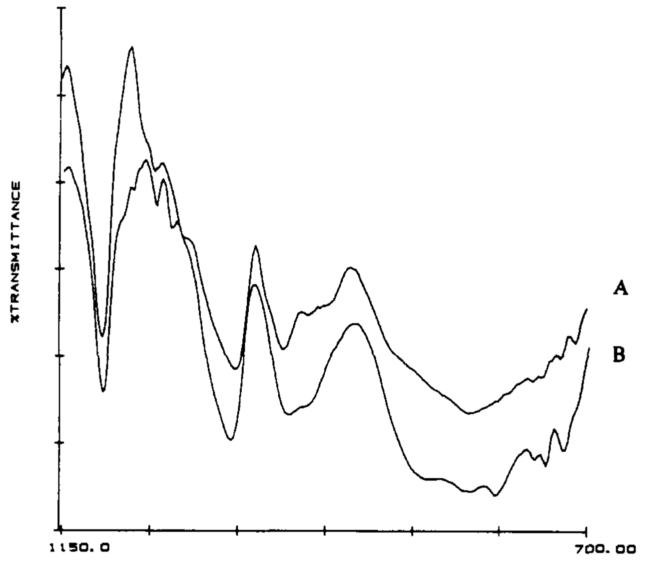

Figure 6. Stacked plot of the IR spectrum of α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn^{3+}\cdot Br)$ (A) before and (B) after treatment with 1500 equiv of PhIO for 48 h. This plot shows the substituted polyoxometalate's complete resistance within experimental error to oxidative degradation by PhIO.

Stability of α_2-$P_2W_{17}O_{61}(Mn^{3+}\cdot Br)^{8-}$ in the Presence of Excess PhIO. An important issue in studying the monosubstituted Dawson-type polyoxometalates as oxidation catalysts is whether the metal remains incorporated in the framework under the conditions effecting oxidation catalysis. One of the best methods for probing this issue is infrared spectroscopy, which is very sensitive to whether the polyoxometalate framework remains intact and whether the heterometal remains incorporated.[50] As a background spectrum, the KBr IR spectrum of the $P_2W_{17}O_{61}(Mn^{3+}\cdot Br)^{8-}$ starting material was obtained, Figure 6A. For this experiment, a CH_3CN/1,2-DCE (1:1) (dark red) solution of α_2-$P_2W_{17}O_{61}(Mn^{3+}\cdot Br)^{8-}$ of ca. 2 × 10^{-3} M (catalysis conditions[35]) was prepared. Approximately 1500 equiv of solid PhIO was added to this solution, and then the heterogeneous reaction mixture was stirred for 48 h. Within 5 min, the dark red reaction solution turned bright yellow.

The yellow reaction solution was isolated from the unreacted solid oxidant and separated into two halves. As a control, the solution IR spectrum of the first half of the sample was obtained. The second half was evacuated to dryness, washed with diethyl ether, and dried for 2 h. The IR spectrum of this solid was then obtained as a KBr disc, Figure 6B; it was indistinguishable from the starting material's spectrum in Figure 6A. Furthermore, both the solution and KBr spectra of the yellow product were identical (superimposible) within experimental error, consistent with the maintenance of the Dawson framework. [Quantification of the spectra by comparison with a control solution of α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$ in 1:1 CH_3CN/CH_2Cl_2 (no oxidant added) show that 100 ± 10% present of the substituted polyoxometalate remained intact.] Therefore, we conclude that α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$ is completely oxidation *inert* (within experimental error), even after 48 h in the presence of 1500 equiv of PhIO and without substrate present, conditions that oxidatively degrade the bulk of an analogous solution of Mn(TPP)Cl *and* Mn(TDCPP)Cl.[35,51]

The interesting dark red to yellow color change remains to be specifically accounted for, although the only possibility is a change

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(47) This result is consistent with the fact that Katsoulis and Pope[22b] report that extraction of their compounds into toluene in the presence of Cl^- salts inhibits the binding of SO_2 or O_2 to their compounds, a qualitative demonstration suggesting (but not proving) Cl^- binding.

(48) (a) Wong, W.-H.; Ostović, D.; Bruice, T. C. *J. Am. Chem. Soc.* **1987**, *109*, 3428. (b) The above paper fully describes the experimental and computational difficulties associated with calculating the association equilibrium constants for a system, like Mn-porphyrins, which contain multiple ligand-binding equilibria.

(49) Me_8TPP = 5,10,15,20-tetrakis(2,6-dimethylphenyl)porphyrin dianion.

(50) (a) Rocchiccioli-Deltcheff, C.; Thouvenot, R. *Spectrosc. Lett.* **1979**, *12*, 127. (b) ^{31}P NMR would also be adequate for determining whether the heterometal remains incorporated; however, it is not possible to obtain high signal-to-noise spectra at low (10^{-3} M) concentrations.

(51) As noted elsewhere,[35] solutions of Mn(TPP)Cl and Mn(TDCPP)Cl stirred in the presence of 1000 equiv of PhIO are 65% and 50% degraded over 24 h (by UV-visible spectroscopy), respectively.

Table III. Listing of the Magnetic Susceptibility Data for α_2-$[(n\text{-}C_4H_9)N]_{(11-n)}P_2W_{17}O_{61}(M^{n+}\cdot Br)$ ($M^{n+} = Mn^{3+}$ and Cu^{2+}) and α_2-$K_{(10-n)}P_2W_{17}O_{61}(M^{n+}\cdot OH_2)$ (M = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+})

sample[a]	$C/(T + \Theta)$	Θ	μ_{eff}	$\mu_{lit.}$[b]
$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}$-$(Mn^{3+}\cdot Br)$	3.38 (0.05)	1.6 (0.1)	5.2	5.1–5.3
$[(n\text{-}C_4H_9)_4N]_9P_2W_{17}O_{61}$-$(Cu^{2+}\cdot Br)$	0.61 (0.01)	4.0 (0.3)	2.2	1.7–2.2
$K_7P_2W_{17}O_{61}(Mn^{3+}\cdot OH_2)$	3.41 (0.03)	2.0 (0.1)	5.2	5.1–5.3
$K_7P_2W_{17}O_{61}(Fe^{3+}\cdot OH_2)$	4.7 (0.1)	2.5 (0.2)	6.1	5.9
$K_8P_2W_{17}O_{61}(Co^{2+}\cdot OH_2)$[c]	2.47 (0.03)	1.1 (0.1)	4.4	4.1–5.2
$K_8P_2W_{17}O_{61}(Ni^{2+}\cdot OH_2)$	1.46 (0.02)	3.2 (0.1)	3.4	2.8–4.0
$K_8P_2W_{17}O_{61}(Cu^{2+}\cdot OH_2)$	0.51 (0.01)	1.3 (0.3)	2.03	1.7–2.2

[a] The samples are all the pure α_2-isomer as described in the text. Plots of the experimental data and fits are available as supplementary material. Error bars are reported in parentheses. [b] Ranges reported in the literature as taken from ref 54. [c] Magnetic susceptibility data for $K_8P_2W_{17}O_{61}(Co^{2+}\cdot OH_2)$ had to be modeled by $C/(T + \Theta + \chi_o)$ ($\chi_o = 6.5 \times 10^{-3}$) to obtain an adequate fit.

in the ligand, L, in $P_2W_{17}(Mn{-}L)$, where L = O, PhIO, or PhI(X)O adducts. (Identification of the possible Mn=O stretch,[52] expected when such a manganese compound has been treated with an oxygen atom transfer reagent such as iodosylbenzene, was not possible due to interfering W=O absorbances.)

Magnetic Susceptibility Studies. Although some magnetic measurements exist for these monosubstituted polyoxometalates,[32a,b] high-precision magnetic susceptibility measurements over a wide temperature range have not been previously reported. Magnetic measurements were taken from 2 to 300 K. The values and their fitting parameters are summarized in Table III. These studies were undertaken to confirm the oxidation states of the monosubstituted polyoxometalates and the degree of interaction between the heterometal in the solid state. We note that the oxidation state of $K_7P_2W_{17}O_{61}(Mn^{III}\cdot OH_2)$ was previously a point of contention.[53]

The data were analyzed by using a Curie–Weiss law [$\chi = C/(T + \Theta)$] to obtain a fit between the calculated curves. For α_2-$K_8P_2W_{17}O_{61}(Co^{2+}\cdot OH_2)$, an additional temperature-independent paramagnetic term was required to fit the data [$\chi = C/[T + \Theta + \chi_o)$]. The Weiss constants ($\Theta$) obtained were all less than 5 K, indicating as expected, that there are no strong inter-polyoxometalate interactions. All of the compounds examined have a high-spin configuration (the observed magnetic moments all are within the expected ranges[54]), consistent with the known weak-field ligating ability of polyoxoanions like α_2-$P_2W_{17}O_{61}^{10-}$. In addition, there is no difference (within experimental error) between the potassium and tetra-*n*-butylammonium salts of the compounds containing the same transition metal. The fitted curves are available as supplementary material.

HPLC Studies. HPLC studies using the methods we developed[55] were originally undertaken with the ultimate goal of purifying any metastable catalytic reaction intermediates. However, consistent with our original report where the length of the $R_{4-x}NH_x^+$ alkyl chain can be a key, we were unable to find conditions where the *tetra-n-butylammonium salts* of the polyoxometalates were retained on the column. However, we were successful in chromatographing *the potassium salts* of the polyoxometalates using hexylammonium counterions and other conditions as described elsewhere.[55] The HPLC purity of each compound prepared in this study is greater than 99%, consistent with the ^{31}P NMR findings and elemental analyses. The chromatographs are presented as supplementary material (Figure L).

Preliminary Electrochemical Studies. Understanding the influence of the α_2-$P_2W_{17}O_{61}^{10-}$ "ligand" on the M^{n+} and its oxidation potential should prove crucial to understanding reactivity and catalysis by α_2-$P_2W_{17}O_{61}(M^{n+})^{y-}$ compounds. Most importantly, we were interested in the oxidation potential of what proved to be the best catalyst[35] α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$, in organic solvents and the direct comparison of the results to the analogous metalloporphyrins. Unfortunately, four preliminary attempts toward obtaining voltammagrams of α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$ in CH_3CN yielded complicated results and not readily interpretable voltammograms. (Added ferrocene gave the expected clean, reversible electrochemistry in a control experiment.) We suspect that the nonaqueous electrochemistry of α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$ is complicated by the presence of Br^- and H^+; further electrochemical studies have been delayed to coincide with in-depth mechanistic studies.

Our electrochemical studies of the potassium salt of α_2-$P_2W_{17}Mn^{II/III}O_{61}^{8-/7-}$ in pH 4.5 *aqueous buffer* have verified the reported literature[32b] value of $E_{1/2}$ (vs SCE) = 0.47 ± 0.05 V. The value we observe for $PW_{11}Mn^{II/III}O_{39}^{5-/6-}$ in pH 4.3 aqueous buffer is 0.65 ± 0.05 V (vs SCE), again consistent with the literature.[32c]

Discussion

The above results demonstrate that isolated, isomerically pure potassium and tetra-*n*-butylammonium salts of the monosubstituted Dawson-type polyoxometalates α_2-$P_2W_{17}O_{61}(M\cdot L)^{y-}$ can be prepared. One key to these syntheses is the use of *isomerically pure*[30,38] α_2-$K_{10}P_2W_{17}O_{61}\cdot 15H_2O$. The synthesis and characterization of the potassium salts are then straightforward following literature procedures[32] and result in the series of isomerically pure complexes α_2-$K_{(10-n)}P_2W_{17}O_{61}(M^{n+}\cdot OH_2)\cdot xH_2O$ ($M^{n+} = Mn^{3+}$, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}). These complexes have been characterized by ^{31}P NMR, TGA, elemental analysis, IR, and UV–vis. The previously unreported ^{183}W NMR spectra for the potassium salts of the Mn^{3+}, Fe^{3+}, and Cu^{2+} complexes were also provided.

The pure potassium salts were metathesized to the corresponding tetra-*n*-butylammonium salts with *stoichiometric* amounts of $[(n\text{-}C_4H_9)_4N]Br$. Careful control of the solution pH during these metatheses must be maintained—between ca. pH 6 and 7 at all times. If the aqueous reaction solution has an acidic pH (less than ca. 5–6), decomposition of the polyoxometalate complexes ensues, yielding α_2-$P_2W_{17}O_{61}^{10-}$ (by ^{31}P NMR) and an unidentified heterometal product. Conversely, metathesis at a more alkaline pH appears to give unidentified polyoxometalate hydrolysis products (except for the $P_2W_{17}Co$, which is stable from pH 5.5–9). These Bu_4N^+ salt precatalysts have been characterized by ^{31}P NMR, TGA, complete elemental analyses, IR, UV–vis, and ^{183}W NMR for α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$.

An interesting result from the metathesis experiments was the appearance of exactly *1* extra equiv of $[(n\text{-}C_4H_9)_4N]Br$ in four of the five complexes prepared by this method. (The Fe^{3+} complex contained only a partial equivalent.) This excess Br^- caused us to examine Br^- binding to α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}$-$(Mn\cdot Br)$, demonstrating that even in CH_2Cl_2 less than 3% of the Br^- remains ligated to the Mn(III) center, *even* in the "noncoordinating"[56] solvent CH_2Cl_2. Hence, under our more polar catalysis conditions[35] (1:1 CH_3CN/CH_2Cl_2), Br^- cannot be hindering the access of the oxidant to the metal center. Base binding experiments using pyridine, 1-methylimidazole, and triphenylphosphine provide the first quantitative K_{eq} data available for Mn(III) in the inorganic-porphyrin ligand α_2-$P_2W_{17}O_{61}^{10-}$ and

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(52) (a) Collins, T. J.; Gordon-Wylie, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 4511. (b) Collins, T. J.; Powell, R. D.; Slebodnick, C.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 899. (c) Czernuszewicz, R. S.; Su, Y. O.; Stern, M. K.; Macor, K. A.; Kim, D.; Groves, J. T.; Spiro, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 4158.

(53) Maslov, L. P.; Bosik, I. I.; Rykov, A. G. *Russ. J. Inorg. Chem.* (Engl. Transl.) **1985**, *30*, 1745.

(54) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; J. Wiley & Sons: New York, 1980; pp 625–628.

(55) Kirk, A. D.; Riske, W.; Lyon, D. K.; Rapko, B.; Finke, R. G. *Inorg. Chem.* **1989**, *28*, 792.

(56) (a) There are reports of CH_2Cl_2[56b,c] and other halocarbons[56d–g] coordinating to metal centers. (b) Winter, C. H.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7560. (c) Mattson, B. M.; Graham, W. A. *Inorg. Chem.* **1981**, *20*, 3186. (d) Burk, M. J.; Segmuller, B.; Crabtree, R. *Organometallics* **1987**, *6*, 2241 and references therein. (e) Czech, P. T.; Gladysz, J. A.; Fenske, R. F. *Organometallics* **1989**, *8*, 1806 and references therein. (f) Winter, C. H.; Veal, W. R.; Garner, C. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 4766. (g) Cutler, A. R.; Todaro, A. B. *Organometallics* **1988**, *7*, 1782.

suggest that the pocket around the manganese center is slightly hindered.

Exposure of α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn{\cdot}Br)$ to excess oxidant for extended periods of time shows that the framework of the polyoxometalate remains intact. Furthermore, these experiments confirm that the manganese heterometal remains securely ligated by the polyoxometalate in organic solvents like CH_3CN and CH_2Cl_2 as determined by infrared spectroscopy. This is as expected, since even in aqueous solution the $P_2W_{17}O_{61}{}^{10-}$ ligand binds Mn^{3+} with a K_{eq} of about 10^5;[19h] in organic solvents, where free Mn^{3+} solvation should be smaller and H-bonding stabilization of any $P_2W_{17}O_{61}{}^{10-}$ would be absent, an ever higher K_{eq} for Mn^{3+} binding (by probably several powers of 10) is expected.

Summary and Future Directions

The synthesis and characterization of the aqueous-soluble α_2-$K_{10-n}P_2W_{17}O_{61}(M^{n+}{\cdot}OH_2)^{(n-10)}$ and the organic-soluble α_2-$[(n\text{-}C_4H_9)_4N]_{11-n}P_2W_{17}O_{61}(M^{n+}{\cdot}Br)^{(n-11)}$ ($M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$) complexes provide a more optimized system than heretofore available, one allowing for full characterization prior to reactivity and mechanistic studies. The $[(n\text{-}C_4H_9)_4N]^+$ salts are clean, well-characterized, robust, and as oxidation resistant as any porphyrin-like ligand prepared to date. These features and the other results described make α_2-$P_2W_{17}O_{61}(M^{n+}{\cdot}L)^{y-}$ an ideal system for detailed catalytic and mechanistic studies of inorganic-porphyrin analogue[22,23,25-28] chemistry. In the following paper,[35] the catalytic activity for the α_2-$P_2W_{17}O_{61}(M^{n+}{\cdot}L)^{y-}$ series is investigated in comparison to prototype metalloporphyrin catalysts.

Additional studies of polyoxoanion "inorganic-porphyrin analogues" are also in progress in our labs[57,58] and elsewhere.[59,25b]

Experimental Section

General Procedures. The following reagents were used as received unless noted otherwise: $Na_2WO_4{\cdot}2H_2O$, KCl, KBr, NaOH, $Ni(NO_3)_2{\cdot}6H_2O$, $K_2S_2O_8$, $MnCl_2{\cdot}4H_2O$, CH_3CN, CH_2Cl_2, anhydrous diethyl ether, 37% HCl, 85% H_3PO_4, 96% H_2SO_4, HPLC grade water, HPLC grade MeOH, and toluene (Baker); 95% EtOH (Punctilius), hexylamine, Br_2, *N*-methylimidazole, triphenylphosphine, 4-(dimethylamino)pyridine, iodobenzene diacetate (Aldrich); $Cu(SO_4){\cdot}5H_2O$, Davison molecular sieves [3 or 4 Å] (Fisher); $Fe(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ (Mallinckrodt); CD_3CN, D_2O (Cambridge Isotopes); pyridine (MCB); Ag_2O (Aesar); and $[(n\text{-}C_4H_9)_4N]Br$ (Fluka). Distilled water was used throughout the study. Iodosylbenzene[60] was prepared as described in the literature. An aqueous $[(n\text{-}C_4H_9)_4N]OH$ solution was prepared according to the literature[61] and titrated the the methyl red and phenolpthalein end points immediately prior to use. All preparations were performed at the University of Oregon except the synthesis of $[(n\text{-}C_4H_9)_4N]_4HPW_{11}O_{39}(Mn{\cdot}OH_2)$, which was performed at Catalytica, Inc., Mountain View, CA.

Instrumentation/Analytical Procedures. Ultraviolet and visible spectra were recorded on a Beckman DU-7 spectrophotometer using 1-cm quartz cells. Solvents used during the UV–vis studies were dried over 3-Å molecular sieves for at least 7 days prior to use and are referred to in the text as "dry" solvents. Infrared (IR) spectra were recorded as 0.2% w/w KBr discs or as solutions by using a Wilmad reflectance cell on a Nicolet 50XB FT-IR. Elemental analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY, and Mikroanalytisches Labor Pascher, Remagen, West Germany.

Thermal gravimetric analyses (TGA) were performed at Catalytica, Inc., Mountain View, CA, by using a Perkin-Elmer TGS-2 thermogravimetric analyzer equipped with a System 7/4 Perkin-Elmer thermal analysis controller. Samples were heated under air from 40 to 940 °C at a rate of 10 °C/min. Solution pH was monitored with a Corning Model 125 pH meter using a Corning calomel combination electrode, calibrated with a pH 4.0, 0.5 M, potassium biphthalate solution, a pH 7.0 sodium phosphate/potassium phosphate/sodium hydroxide buffer, and a pH 10.0 boric acid/potassium hydroxide buffer (Baker). Solution molecular weight measurements were performed by using a Beckman Instruments Spinco Model E ultracentrifuge equipped with a scanning photoelectric system by the sedimentation equilibrium method as previously described.[62]

Nuclear Magnetic Resonance Studies (NMR). ^{31}P and ^{183}W NMR spectra at 30 °C at Du Pont were obtained (on the K^+ salts) as previously described.[30,63a] Briefly, some specific details are Nicolet NT-360WB spectrometer with 12-mm broad-band probe for ^{31}P and 20-mm sideways probe for ^{183}W. Phosphorus spectra were always run with a concentric capillary for field/frequency lock, and were referenced to the same configuration of 85% H_3PO_4. Tungsten spectra were referenced to 2 M Na_2WO_4 in the sidways tube configuration.

^{31}P NMR. ^{31}P NMR spectra obtained at Oregon were recorded on a Nicolet Technology NTC-360NB FT-NMR spectrometer system at a nominal frequency of 146.21 MHz and a temperature of 20 ± 1 °C. All spectra were digitized by using 8192 data points, giving spectral resolution of 2.4 Hz/data point. The spectrometer was locked on the H resonance of the internal deuterated solvent. Spectra were obtained by using 12-mm-o.d. tubes (Spectra Tech) and are referenced to external 85% H_3PO_4 by the substitution method. Chemical shifts upfield of H_3PO_4 are reported as negative. Line widths were determined by Lorentzian fit. Samples were prepared at concentrations of 0.04 M in 1:1 D_2O/H_2O for the Li^+ salts ($+LiClO_4$, $-KClO_4$) and in 1:1 CD_3CN/CH_3CN for the tetra-*n*-butylammonium salts. Typical parameters for the diamagnetic polyoxoanions were pulse width 14 μs, delay time, 2.0 s, spectral width ±10 000 Hz. Typical parameters for paramagnetic polyoxoanions were pulse width 30 μs, delay time 1.0 s, spectral width ±10 000 Hz.

^{183}W NMR. ^{183}W NMR spectra obtained at Oregon were recorded on a Nicolet Technology NTC-360NB at a nominal frequency of 15.04 MHz and a temperature of 20 ± 1 °C. All spectra were digitized by using 16 384 data points with a spectral resolution of 0.6 Hz/data point for diamagnetic species and spectral resolution of 2.4 Hz/data point for paramagnetic species. The spectrometer was locked on the H resonance of the deuterated solvent. Spectra were obtained with 10-mm-o.d. tubes (Spectra Tech) and are referenced to external pD 8 Na_2WO_4 (2 M) in D_2O. Chemical shifts upfield of the resonance are reported as negative. The broad-band power amplifier was attenuated by 6 dB to prevent probe arching. Typical parameters for diamagnetic polyoxoanions such as $P_2W_{18}O_{62}{}^{6-}$ or α_2-$P_2W_{17}O_{61}{}^{10-}$ were sample concentration 0.1 M, pulse width 70 μs, delay time 1.0 s, spectral width ±2500 Hz. Typical parameters for paramagnetic metal containing polyoxoanions were sample concentration 0.1 M, pulse width 65 μs, delay time 3.5 s, spectral width ±20 000 Hz.

Some of the later ^{183}W NMR (for the $P_2W_{17}Cu(II)$ and $P_2W_{17}Fe(III)$) were obtained at Oregon on a NT-360 wide bore (operating at 27.0 ± 0.5 °C) because of the increased sample volume and better probe performance leading to higher S/N spectra on the wide bore.

α/β-$K_6P_2W_{18}O_{62}{\cdot}10H_2O$.[37] In a 1000-mL Erlenmeyer flask, 100 g (0.303 mol) of $Na_2WO_4{\cdot}2H_2O$ was dissolved in 350 mL of refluxing H_2O. Phosphoric acid (150 mL of 85% H_3PO_4, 0.772 mol) was added dropwise over 30 min, and the resulting light green solution was refluxed for 8 h. The crude product was precipitated by the addition of 100 g (1.34 mol) of solid KCl and recrystallized by dissolving the precipitate in about 500 mL of boiling H_2O and cooling to 5 °C overnight. If cloudiness remained upon the dissolution of the crude product, the hot solution was filtered through a Celite pad before continuing. The final

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(57) Areas worthy of future or additional emphasis include detailed mechanistic studies, substitution of other metal fragments into this framework (including Ru═O[28,59a] and Re═O[59b,c]), plus attempts at isolation and identification of hypervalent intermediates that are expected in oxidative catalytic cycles. It would also be interesting to extend this chemistry to solvent systems such as benzene or toluene by preparing and isolating the tetra-*n*-hexylammonium salts of α_2-$P_2W_{17}O_{61}(M^{n+})^{(n-10)}$.[58]

(58) Interestingly, our initial attempts to prepare these tetra-*n*-hexylammonium salts have been frustrated by the *high solubility* of the resulting complexes of these 7^- and 8^- ions in a variety of solvents including pentane/tetramethylsilane mixtures at 0 °C. Further cooling of these mixtures leads only to congealed oils.

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product was collected on a medium frit and washed with 150 mL (3 × 50 mL) of H_2O, 150 mL (3 × 50 mL) of 95% EtOH, and 150 mL (3 × 50 mL) of anhydrous diethyl ether. The solid was dried under vacuum at room temperature for 8 h. Yield: 75 g (0.016 mol, 92%). NMR of the Li^+ salt ($^+LiClO_4$, $-KClO_4$), isomeric impurities of the products determined by ^{31}P NMR: (α) δ −12.7; (β) δ −11.0 and −11.6. ^{183}W NMR: (α) δ −125 and −170; (β) −112, −131, −171 and −191.[64a]

α-$K_6P_2W_{18}O_{62}\cdot 14H_2O$.[37] The synthesis of the pure α-isomer takes advantage of Wu's observation[38] that base-degraded β-$P_2W_{18}O_{62}^{6-}$ yields α_1-$P_2W_{17}O_{61}^{10-}$. The α_1-$P_2W_{17}O_{61}^{10-}$ then, in the presence of WO_4^{2-} and acid, reforms *only* α-$P_2W_{18}O_{62}^{6-}$ (≥99%). α/β-$K_6P_2W_{18}O_{62}\cdot 10H_2O$ (70 g, 0.015 mol) was dissolved in 250 mL of 80 °C water, contained in a 1500-mL flask, with magnetic stirring. A drop of bromine was added to oxidize the small amount of heteropoly blue that forms, causing the light green solution to turn bright yellow. $KHCO_3$ (400 mL of a 1 M solution, 0.4 mol) was added over 5 min, causing a white precipitate of $P_2W_{17}O_{61}^{10-}$. (This precipitate continues to evolve over about 30 min.) HCl (150 mL of a 6 M solution, 0.9 mol) was then added over about 10 min, regenerating a clear yellow solution of α-$P_2W_{18}O_{62}^{6-}$. Any insoluble impurities were removed by filtering over a Celite pad. Solid KCl (100 g, 1.34 mol) was then added to the solution, and it was cooled to 5 °C overnight. The compound was then recrystallized from a minimum of boiling H_2O (about 150 mL) and again cooled to 5 °C overnight. Yield: 52.4 g (0.0108 mol, 72%). NMR of the Li^+ salt ($^+LiClO_4$, $-KClO_4$), ^{31}P NMR: δ −12.7. ^{183}W NMR: δ −125 and −170. Infrared spectrum (cm^{-1}): 780 (s), 912 (s), 960 (s), 975 (s), 1022 (m), and 1090 (s).

α_2-$K_{10}P_2W_{17}O_{61}\cdot 15H_2O$. In a 1000-mL Erlenmeyer flask, 135 g (0.0293 mmol) of α-$K_6P_2W_{18}O_{62}\cdot 14H_2O$ was dissolved in 300 mL of 40 °C H_2O. $KHCO_3$ (500 mL of a 1 M solution, 0.5 mol) is added with vigorous stirring. A white precipitate begins to form after about 50 mL of the base has been added. After the base addition was complete, the mixture was stirred for an additional 30 min. The white precipitate is collected on a coarse glass frit. The crude white solid was recrystallized by dissolving it in 200 mL of boiling H_2O (if any insoluble material remained, it was removed by hot filtration through a Celite pad) and cooling to 5 °C overnight. The resulting white crystals were collected on a medium glass frit and washed with 150 mL (3 × 50 mL) of H_2O, 150 mL (3 × 50 mL) of 95% EtOH, and 150 mL (3 × 50 mL) of anhydrous diethyl ether. The solid is dried under vacuum at room temperature for 8 h. Yield: 108 g (0.022 mol, 75%). NMR of the Li^+ salt ($^+LiClO_4$, $-KClO_4$), ^{31}P NMR in 1:1 H_2O/D_2O at 20 °C indicates greater than 98% purity as the single α_2-P_2W_{17} isomer: δ (Li^+ salt, $+LiClO_4$, $-KClO_4$) −7.27, −14.11 [literature[32d] δ (Li^+ salt in H_2O) −7.1, −13.6; presumably these values should be corrected[63b] by ca. +0.7 ppm for comparison to the data herein obtained on a superconducting magnet geometry (vertical $\mathbf{B}_0$ field)]. ^{183}W NMR: δ −120, −143, −154, −183, −185, −220, −222, −226, and −245. [Note that the exact chemical shifts for lacunary polyoxoanions like $P_2W_{17}O_{61}^{10-}$ can be sensitive to which counterion (e.g., K^+, Li^+) is available to fill the lacunary site.[64b]] Infrared spectrum (cm^{-1}): 740 (s), 805 (s), 880 (m), 905 (sh), 940 (s), 985 (m), 1022 (m), 1084 (s). TGA (40–240 °C): calculated weight loss for 15 H_2O 5.66% (observed weight loss 5.60%).

α_2-$K_7P_2W_{17}O_{61}(Mn^{3+}\cdot OH_2)\cdot 12H_2O$. This preparation is based on the literature[32b] with modifications that include the use of isomerically pure α_2-$K_{10}P_2W_{17}O_{61}\cdot 15H_2O$. In a 500-mL flask, 52.0 g (10.8 mmol) of α_2-$K_{10}P_2W_{17}O_{61}\cdot 15H_2O$ was dissolved in 150 mL of 90 °C H_2O. A solution of 2.40 g (12.1 mmol) of $MnCl_2\cdot 4H_2O$ in 40 mL of H_2O was added with vigorous stirring, giving a dark brown solution. When dissolution of the $MnCl_2$ was complete, 1.64 g (6.07 mmol, 12.1 mequiv) of $K_2S_2O_8$ in 25 mL of H_2O was added. The solution was maintained at 90 °C for 60 min. The oxidation is complete (by visible spectroscopy) after 60 min. Solid KCl (20 g, 0.268 mol) was added to the hot solution, and the solution was cooled to room temperature. The solution was then placed at 5 °C overnight. The resultant purple crystals were collected on a coarse glass frit and recrystallized from 50 mL of boiling H_2O. The crystals were collected on a medium frit, washed with 50 mL of H_2O, and vacuum dried for 6 h. Yield: 36.5 g (7.6 mmol, 70%). Elemental analysis calculated (found): K, 5.72 (5.71); Mn, 1.15 (1.16); P, 1.29 (1.10); W, 65.38 (65.51) (a full analysis is reported for the organic-soluble $[(n\text{-}C_4H_9)_4N]^+$ salt). NMR of the K^+ salt obtained at Du Pont, ^{31}P NMR at 30 °C: δ ($\Delta\nu_{1/2}$) P(2) resonance −12.3 (66 Hz), P(1) resonance +564 (12 300) [literature[30] at 24 °C −12.5 (60) and +575 (~9000)[65]]. ^{183}W NMR in D_2O at 30 °C: δ ($\Delta\nu_{1/2}$ (Hz)) of nine possible (total) resonances are observed −74 (26), −128 (32), −238 (12), −412 (30), −531 (56), −653 (68); at Oregon on the NT-360 wide bore at 27 °C in 1:1 H_2O/D_2O of the Li^+ salt ($+LiClO_4$, $-KClO_4$) δ ($\Delta\nu)_{1/2}$)) −77.4 (10), −132.2 (6), −243.8 (9), −423.1 (14), −524.2 (27), −666.3 (23). Infrared spectrum (cm^{-1}): 780 (s), 915 (s), 948 (s), 970 (sh), 1020 (m), 1085 (s). Visible spectrum: (1 × 10^{-2} M) λ_{max} = 484 nm, ϵ_{484} = 400 cm^{-1} M^{-1} (literature[32b] λ = 502 nm, ϵ = 403 cm^{-1} M^{-1}). TGA (40–240 °C): calculated weight loss for 13 H_2O 4.87% (observed weight loss 5.21%).

α_2-$K_7P_2W_{17}O_{61}(Fe^{3+}\cdot OH_2)\cdot 8H_2O$. α_2-$K_{10}P_2W_{17}O_{61}\cdot 15H_2O$ (100 g, 20.7 mmol) was dissolved in 300 mL of 90 °C H_2O (pH 6.4). A solution of 8.6 g (21.3 mmol) of $Fe(NO_3)_3\cdot 9H_2O$ in 40 mL of H_2O (pH <1.0) was added with vigorous stirring, giving a dark yellow-orange solution (pH 4.0). Bromine (3 drops) was pipetted into the solution to ensure a fully oxidized product. The solvent volume was reduced to 200 mL and then allowed to cool to room temperature. A small amount of an unidentified dark orange solid precipitated and was removed by filtration through a Celite pad. Solid KCl (50 g, 670 mmol) was added to the filtrate, and the solution was warmed (about 60 °C) until it became homogeneous. The solution was then cooled to 5 °C for 4 h. The resulting fine yellow crystals were collected on a medium glass frit. The product was recrystallized from a minimum of boiling H_2O (about 70 mL) and cooled to 5 °C overnight. The yellow product was collected on a medium frit, washed with 50 mL of H_2O, and dried under vacuum at room temperature for 6 h. Yield: 75.7 g (16.0 mmol, 78%). This synthesis has also been successfully completed on a half scale. Yield: 39.6 g (8.37 mmol, 81%). Elemental analysis calculated (found): K, 5.88 (6.10); Fe 1.20 (1.22) (a full analysis is reported on the organic-soluble $[(n\text{-}C_4H_9)_4N]^+$ salt). NMR of the Li^+ salt ($+LiClO_4$, $-KClO_4$), ^{31}P NMR at 20 °C: P(2) resonance δ ($\Delta\nu_{1/2}$) −11.9 (65). ^{183}W NMR at 27 °C (obtained on the NT-360 wide bore at Oregon) in 1:1 H_2O/D_2O on the Li^+ salt ($+LiClO_4$, $-KClO_4$): δ ($\Delta\nu_{1/2}$ (Hz)) −144.6 (2), −146.3 (3), −151.8 (5), −190.7 (7), −445.9 (41). Infrared spectrum (cm^{-1}): 800 (s), 914 (s), 945 (s), 965 (sh), 1012 (m), and 1083 (s). The visible spectrum shows no maxima. TGA (40–240 °C): calculated weight loss for 9 H_2O 3.48% (observed weight loss 3.43%). Since hydroxy-bridged dimer formation is reported as "general for all Fe(III) heteropolyoxoanions",[42] we checked for this under the conditions of an ultracentrifugation molecular weight experiment [ca. 1 × 10^{-5} M polyoxoanion in water, 0.2 M LiCl, pH(obsd) of 4 (by Hydrion paper), and using an independently measured $\bar{\nu}$ of 0.123].[62] Only monomer was found, MW 5300 ± 600, as expected for reasons discussed in the text.

α_2-$K_8P_2W_{17}O_{61}(Co^{2+}\cdot OH_2)\cdot 16H_2O$. In a 500-mL flask, α_2-$K_{10}P_2W_{17}O_{61}\cdot 15H_2O$ (51.0 g, 10.6 mmol) was dissolved in 200 mL of 90 °C H_2O. A solution of 3.36 g (11.5 mmol) of $Co(NO_3)_2\cdot 6H_2O$ in 40 mL of H_2O was added with vigorous stirring, giving a dark red solution. After 15 min, solid KCl (30 g, 0.40 mmol) was added, and the solution was cooled to room temperature. The resulting light red crystals were collected on a medium glass frit and recrystallized twice from a minimum amount (about 50 mL) of boiling H_2O. The product was collected on a medium glass frit, washed with 50 mL of H_2O, and dried under vacuum at room temperature for 6 h. Yield: 36.2 g (7.5 mmol, 71%). Elemental analysis calculated (found): K, 6.46 (6.35); W, 64.56 (64.43); Co, 1.22 (1.22) (a full analysis is reported on the organic-soluble $[(n\text{-}C_4H_9)_4N]^+$ salt). NMR of the Li^+ salt ($+LiClO_4$, $-KClO_4$), ^{31}P NMR at 20 °C: P(2) resonance δ −22.6 (literature[30] δ −23.7). ^{183}W NMR: see the literature.[30] Infrared spectrum (cm^{-1}): 796 (s), 912 (s), 942 (s), 965 (sh), 1010 (m), and 1082 (s). Visible spectrum: (1 × 10^{-2} M) λ_{max} = 544, ϵ_{544} = 108 cm^{-1} M^{-1} (literature[32b] λ = 546 nm, ϵ = 113 cm^{-1} M^{-1}). TGA (40–240 °C): calculated weight loss for 17 H_2O 6.32% (observed weight loss 6.75%).

α_2-$K_8P_2W_{17}O_{61}(Ni^{2+}\cdot OH_2)\cdot 17H_2O$. In a 250-mL flask, α_2-$K_{10}P_2W_{17}O_{61}\cdot 15H_2O$ (50.1 g, 10.4 mmol) was dissolved in 100 mL of 90 °C H_2O. A solution of 3.45 g (11.9 mmol) of $Ni(NO_3)_2\cdot 6H_2O$ in 40 mL of H_2O was added with vigorous stirring, giving a light green solution. After stirring for 15 min, the solution was cooled to 5 °C overnight. The light green crystals were collected on a medium frit and recrystallized by dissolving them in a minimum amount (about 100 mL) of boiling H_2O and cooling to 5 °C overnight. The product was collected on a medium glass frit, washed with 50 mL of H_2O, and dried under vacuum for 6 h.

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(65) (a) Literature values are reported for ^{31}P NMR and UV–vis spectra for comparison purposes. However, these values are for mixtures of α_1- and α_2-isomers. Therefore, the values reported in this paper need not necessarily correspond with those previously reported. (b) Small changes in temperatures are probably responsible for the chemical shift differences seen in these paramagnetic species (which show temperature-dependent magnetic susceptibilities, see the supplementary material). Baker has previously shown, however, that the ^{31}P NMR chemical shifts "*do not* have large concentration or ionic strength dependencies."[30]

Yield: 37.9 g (7.8 mmol, 75%). Elemental analysis calculated (found): K, 6.44 (6.52); Ni, 1.21 (1.23); P, 1.28 (1.27) (a full analysis is reported on the organic-soluble $[(n\text{-}C_4H_9)_4N]^+$ salt). NMR of the Li^+ salt (+$LiClO_4$, −$KClO_4$), ^{31}P NMR at 20 °C: P(2) resonance δ −14.0 (literature[29] δ −14.0). ^{183}W NMR: see the literature.[30] Infrared spectrum (cm^{-1}): 800 (s), 910 (s), 947 (s), 960 (sh), 1007 (m), and 1080 (s). Visible spectrum: (1.8×10^{-2} M) λ = 680 nm (due to a broad flat absorbance between 650 and 750 nm, 680 nm was chosen for the extinction coefficient determination), $\epsilon_{680} = 10\ cm^{-1}\ M^{-1}$ (literature[32b] λ = 699 nm, $\epsilon = 14.3\ cm^{-1}\ M^{-1}$). TGA (40–240 °C): calculated weight loss for 18 H_2O 6.32% (observed weight loss 6.75%).

α_2-$K_8P_2W_{17}O_{61}(Cu^{2+}\cdot OH_2)\cdot 16H_2O$. In a 500-mL flask, α_2-$K_{10}P_2W_{17}O_{61}\cdot 15H_2O$ (75.0 g, 15.6 mmol) was dissolved in 150 ml of 90 °C H_2O. A solution of 4.5 g (18.0 mmol) of $CuSO_4\cdot 4H_2O$ in 40 mL of H_2O was added with vigorous stirring, giving a green solution. After stirring for 15 min, the solution is cooled to 5 °C overnight. The light green crystals were collected on a medium frit and were recrystallized by dissolving them in a minimum amount (about 75 mL) of boiling H_2O and cooling the solution to 5 °C overnight. The product was collected on a medium frit, washed with 100 mL (2 × 50 mL) of H_2O, and vacuum dried for 6 h. Yield: 54.7 g (11.3 mmol, 72%). Elemental analysis calculated (found): K, 6.45 (6.57); W, 64.50 (64.93); Cu, 1.31 (1.20); P, 1.27 (1.38) (a full analysis is reported on the organic-soluble $[(n\text{-}C_4H_9)_4N]^+$ salt). NMR of the Li^+ salt (+$LiClO_4$, −$KClO_4$), ^{31}P NMR at 20 °C: δ ($\Delta\nu_{1/2}$) −13.0 (11), −35 (900). ^{183}W NMR at 27 °C (obtained on the NT-360 wide bore at Oregon) in 1:1 H_2O/D_2O on the Li^+ salt (+$LiClO_4$, −$KClO_4$): δ ($\Delta\nu_{1/2}$ (Hz)) −151.5 (3), −198.1 (9), −205.0 (3), −220.5 (11), −230.7 (3). Infrared spectrum (cm^{-1}): 788 (s), 905 (s), 942 (s), 962 (sh), 1005 (m), and 1074 (s). Visible spectrum: (1.8×10^{-2} M) λ_{max} = 855 nm, $\epsilon_{885} = 55\ cm^{-1}\ M^{-1}$ (literature[32c] λ = 870 nm, $\epsilon = 57\ cm^{-1}\ M^{-1}$). TGA (40–240 °C): calculated weight loss for 17 H_2O 6.31% (observed weight loss 6.26%).

α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn^{3+}\cdot Br)$. In a 1500-mL flask, α_2-$K_8P_2W_{17}O_{61}(Mn\cdot OH_2)\cdot 16H_2O$ (10.4 g, 2.32 mmol) was dissolved in 500 mL of H_2O. $[(n\text{-}C_4H_9)_4N]Br$ (4.9 g, 15.2 mmol, 7 equiv) was added in 250-mg portions concurrently with 0.18 M H_2SO_4 to keep the pH of the solution between 6 and 7 at all times. The final pH was 6.1. CH_2Cl_2 (200 mL) and CH_3CN (200 mL) were added to the slurry, causing the dissolution of the small amount of precipitate. The mixture was vigorously stirred for 5 min and allowed to separate into a cloudy aqueous layer (pH 6.5) and a dark purple organic layer. The organic layer was rotovapped to dryness. The resulting solid was dissolved in a minimum amount of CH_3CN (less than 15 mL). Anhydrous diethyl ether (200 mL) was added, precipitating a small amount of brown solid and a purple oil. The supernatant ether was passed through a medium frit to remove the small amount (less than 500 mg) of brown solid. The purple oil was treated with 75 mL of fresh ether and triturated until a fine powder was obtained (approximately 3 × 75 mL ether and 1–2 h were needed to complete this step). This brown solid is collected on the same frit as the original solid and washed with 75 mL (3 × 25 mL) of anhydrous diethyl ether. The powder was then air-dried on the frit until it was easily manipulated and then vacuum dried for 24 h at 50 °C. Yield: 11.4 g (1.81 mmol, 81% based on $P_2W_{17}O_{61}(Mn\cdot OH_2)^{7-}$ added). Elemental analysis calculated (found): C, 23.12 (23.32, repeat 23.12, 23.06); H, 4.38 (4.37); N, 1.83 (1.72); P, 1.02 (0.84); W, 51.5 (50.0, repeat 51.4); Mn, 0.90 (0.85); Br, 1.32 (1.00); O, 16.1 (15.5); total 100.17 (98.8). ^{31}P NMR at 20 °C: P(2) resonance δ ($\Delta\nu_{1/2}$) −10.0 (90 ± 1 Hz). ^{183}W NMR at 20 °C: −64, −116, −136, −202, −295. Infrared spectrum (cm^{-1}): 791 (s), 888 (s), 945 (s), 956 (sh), 1016 (m), and 1089 (s). Visible spectrum: (2.6×10^{-3} M solution in CH_3CN) λ_{max} = 478 nm, $\epsilon_{478} = 380\ cm^{-1}\ M^{-1}$; ($2.6 \times 10^{-3}$ M in CH_2Cl_2) λ_{max} = 453 nm, $\epsilon_{453} = 250\ cm^{-1}\ M^{-1}$. TGA (240–940 °C): calculated weight loss for 3.65 $[(n\text{-}C_4H_9)_4N]_2O + P_2O_5$ 32.7% (observed weight loss 32.4%). Molecular weight (sedimentation equilibrium method) calculated for α_2-$[(n\text{-}C_4H_9)_4N]_9P_2W_{17}O_{61}$-$(Mn\cdot Br)$ (observed): 6069 (6500 ± 600), supplemental material, Figure A.

α_2-$[(n\text{-}C_4H_9)_4N]_{6.75}H_{0.5}P_2W_{17}O_{61}(Fe^{3+}\cdot L)$ (L = 0.75 H_2O, 0.25 Br^-). In a 1500-mL Erlenmeyer flask, α_2-$K_7P_2W_{17}O_{61}(Fe\cdot OH_2)\cdot 8H_2O$ (9.64 g, 2.07 mmol) was dissolved in 500 mL of H_2O. The pH of the solution was adjusted to 6.25 by the addition of 1 mL of 0.4 M aqueous $[(n\text{-}C_4H_9)_4N]OH$. $[(n\text{-}C_4H_9)_4N]Br$ (4.68 g, 14.5 mmol, 7 equiv) was added to the solution, causing the pH to rise to 6.5 and the solution to become cloudy. CH_2Cl_2 (200 mL) was added to the solution, and the solution was shaken vigorously for 5 min. Upon standing, the mixture separates into a clean yellow organic layer and a cloudy white aqueous layer (pH 8.2 by pH meter, pH 6–7 by pH paper). The organic layer was rotovapped to dryness at 60 °C. The resulting yellow oil was dissolved in 30 mL of CH_3CN. Anhydrous diethyl ether (200 mL) was added to the solution, causing immediate precipitation of a yellow oil. The yellow oil was repeatedly triturated in ether (about 75 mL total) until a fine yellow/green solid was obtained. The solid was collected on a medium glass frit and air-dried until it was easily manipulated. The solid was then vacuum dried for 24 h at 60 °C. Yield: 6.72 g (1.13 mmol, 54.6%). Elemental analysis calculated (found): C, 22.07 (22.02, repeat 22.00); H, 4.18 (4.08, repeat 4.29); N, 1.61 (1.64, repeat 1.80); P, 1.05 (0.95); W, 53.2 (50.8, repeat 53.1); Br, 0.34 (0.30); Fe, 0.95 (0.86); O, 16.6 (16.8); total, 99.91 (99.75). ^{31}P NMR at 20 °C: P(2) resonance δ ($\Delta\nu_{1/2}$) −12.7 (100 ± 5). The visible spectrum shows no maxima. Infrared spectrum (cm^{-1}): 791 (s), 888 (s), 945 (s), 956 (sh), 1016 (m), and 1089 (s). TGA (240–940 °C): calculated weight loss for 3.375 $[(n\text{-}C_4H_9)_4N]_2O + P_2O_5$ 31.1% (observed weight loss 30.6%). Molecular weight (sedimentation equilibrium method) $\bar{M}_r$ calculated for α_2-$[(n\text{-}C_4H_9)_4N]_{6.75}H_{0.5}P_2W_{17}O_{61}(Fe\cdot L)$ (L = 0.75 H_2O, 0.25 Br^-) (found): 5876 (6200 ± 600), supplementary material, Figure B. Note that no dimer[42] is present under the stated conditions of the molecular weight experiment.

α_2-$[(n\text{-}C_4H_9)_4N]_9P_2W_{17}O_{61}(Co^{2+}\cdot Br)$. α_2-$K_8P_2W_{17}O_{61}(Co\cdot OH_2)\cdot 15H_2O$ (15.2 g, 3.13 mmol) was dissolved in 150 mL of H_2O (pH 6.6). The pH was adjusted to 5.6 by the addition of one drop of 0.18 M H_2SO_4. $[(n\text{-}C_4H_9)_4N]Br$ (7.91 g, 24.5 mmol, 8 equiv) was added to the solution, causing the pH to rise to 5.9. CH_2Cl_2 (200 mL) and CH_3CN (100 mL) were added to the aqueous solution, and the solution was vigorously shaken for 5 min. The mixture separated into two layers upon standing. The aqueous layer was pink and cloudy (pH is 9.7 by pH meter, pH is between 6 and 7 by pH paper), while the organic layer is a clear dark red. The organic layer was rotovapped to dryness at 60 °C. The resulting light brown solid was dissolved in a minimum amount (about 20 mL) of CH_2Cl_2. This solution was then treated with 75 mL of anhydrous diethyl ether, which caused a deep brown oil to form. The oil was then triturated in ether until a light brown powder was obtained. The product was collected on a medium glass frit and washed with 25 mL of anhydrous diethyl ether. The product was then air-dried until it was easily manipulated and vacuum dried at 50 °C for 24 h. Yield: 11.7 g (1.88 mmol, 60.1%). Elemental analysis calculated (found): C, 26.67 (26.88); H, 5.03 (5.23); N, 1.94 (2.01); P, 0.96 (0.74); W, 48.2 (45.1, repeat 44.5, 46.2 and 50.0); Co, 0.87 (0.91); Br, 1.23 (1.11); O, 15.0 (13.9, repeat 15.0); total, 99.9 (96.98). ^{31}P NMR at 20 °C: P(2) resonance δ ($\Delta\nu_{1/2}$) −26.4 (25 ± 1). IR (cm^{-1}): 816 (s), 914 (2), 947 (s), 956 (sh), 1017 (m), 1087 (s). Visible spectrum: (2.20×10^{-3} M in CH_3CN) λ_{max} = 484.0 nm, $\epsilon_{484} = 325\ cm^{-1}\ M^{-1}$; ($2.00 \times 10^{-3}$ M in CH_2Cl_2) λ_{max} = 574.0 nm, $\epsilon_{484} = 76\ cm^{-1}\ M^{-1}$. TGA (240–940 °C): calculated weight loss for $^9/_2$ $[(n\text{-}C_4H_9)_4N]_2O + P_2O_5$ 36.9% (observed weight loss 36.5%). Molecular weight (sedimentation equilibrium method) calculated for α_2-$[(n\text{-}C_4H_9)_4N]_9P_2W_{17}O_{61}(Co\cdot Br)$ (found): 6479 (6500 ± 500), supplementary material, Figure C.

α_2-$[(n\text{-}C_4H_9)_4N]_9P_2W_{17}O_{61}(Ni^{2+}\cdot Br)$. α_2-$K_8P_2W_{17}O_{61}(Ni\cdot OH_2)\cdot 17H_2O$ (4.0 g, 0.823 mmol) was dissolved in 200 mL of H_2O (pH 6.55). $[(n\text{-}C_4H_9)_4N]Br$ (2.11 g, 6.5 mmol, 8 equiv) was added concurrently with 0.18 M H_2SO_4 to maintain the pH between 6 and 7. CH_2Cl_2 (200 mL) was added, and the solution was stirred vigorously for 5 min. Upon standing, the solution separated into a cloudy, white aqueous layer (pH 6.5) and a yellow organic layer. The organic layer was then rotovapped to dryness at 60 °C. The yellow solid was dissolved in a minimum amount (20 mL) of CH_3CN. The resulting yellow solution was then treated with 50 mL of anhydrous diethyl ether, which caused a small amount of yellow solid and a yellow oil to form. The supernatant ether layer was passed through a medium frit to collect the small amount of solid (less than 400 mg). The oil was triturated with fresh ether (3 × 50 mL) until a fine light yellow powder was obtained. The powder was collected on the same frit as the initial solid that was collected and washed with 75 mL (3 × 25 mL) of anhydrous diethyl ether. The resulting yellow solid was air-dried until it was easily manipulated and then dried under vacuum at 50 °C for 24 h. Yield: 2.54 g (0.39 mmol, 47.4%). Elemental analysis calculated (found): C, 26.67 (26.75); H, 5.04 (4.79); N, 1.94 (2.09); P, 0.95 (0.84); W, 48.2 (47.1, repeat 47.4); Ni, 0.91 (0.78); Br, 1.23 (0.88); O, 15.0 (14.3, repeat 15.0); total, 99.94 (98.53). ^{31}P NMR at 20 °C: P(2) resonance δ ($\Delta\nu_{1/2}$) −12.0 (21 ± 1). Infrared spectrum (cm^{-1}): 812 (s), 909 (s), 945 (s), 958 (sh), 1028 (m), and 1087 (s). The visible spectrum is somewhat sensitive to coordinating vs less donating solvents: (1.3×10^{-2} M in CH_3CN) λ_{max} = 671 nm, $\epsilon_{671} = 12.4\ cm^{-1}\ M^{-1}$; ($9.6 \times 10^{-3}$ M in CH_2Cl_2) λ_{max} = 699.5 nm, $\epsilon_{699.5} = 10.9\ cm^{-1}\ M^{-1}$. TGA (240–940 °C): calculated for $^9/_2$ $[(n\text{-}C_4H_9)_4N]_2O + P_2O_5$ 36.9% (observed weight loss 36.1%). Molecular weight (sedimentation equilibrium method) calculated for $[(n\text{-}C_4H_9)_4N]_2P_2W_{17}O_{61}(Ni\cdot Br)^{8-}$ (found): 4736 (4700 ± 400), supplementary material, Figure D.

α_2-$[(n\text{-}C_4H_9)_4N]_9P_2W_{17}O_{61}(Cu^{2+}\cdot Br)$. α_2-$K_8P_2W_{17}O_{61}(Cu\cdot OH_2)\cdot 16H_2O$ (10.24 g, 2.11 mmol) was dissolved in 500 mL of 40 °C H_2O (pH 6.2). $[(n\text{-}C_4H_9)_4N]Br$ (5.43 g, 16.9 mmol, 8 equiv) was added, causing a slight precipitate to form. CH_2Cl_2 (200 mL) and CH_3CN (200 mL) were added and vigorously stirred for 5 min. The solution formed an emulsion that slowly (15–30 min) separated into a cloudy aqueous layer (pH 9.4 by pH meter; pH 6.5 by pH paper) and a bright green organic layer. The layers were separated, and the organic layer was rotovapped to dryness. The green solid was then dissolved in a minimum of CH_3CN (less than 30 mL), and the solution was treated with 100 mL of anhydrous diethyl ether. The ether treatment caused a small amount of light green precipitate and a dark green oil to form. The supernatant ether was passed through a medium glass frit to collect the solid material. The oil was then triturated with 150 mL (3 × 50 mL) until a fine light green powder was formed. The powder was then collected on the same frit as the solid that formed initially and washed with 75 mL (3 × 25 mL) of anhydrous diethyl ether. The solid was air-dried until it was easy to manipulate and then further dried under vacuum at 50 °C for 24 h. Yield: 9.56 g (1.47 mmol, 69.8%). Elemental analysis calculated (found): C, 26.65 (26.08); H, 5.03 (4.88); N, 2.04 (2.06); P, 0.95 (0.86); W, 48.2 (48.1); Cu 0.98 (0.79); Br, 1.23 (1.04); O, 15.0 (14.4); total, 100.08 (98.21). ^{31}P NMR at 20 °C: P(2) resonance) δ ($\Delta\nu_{1/2}$) −9.9 (53 ± 1). Infrared spectrum (cm^{-1}): 792 (s), 820 (s), 916 (s), 952 (s), 962 (sh), 1017 (m), 1087 (s). The visible spectrum is *not* sensitive to changes in coordinating vs less donating solvent: (2.3×10^{-3} M in CH_3CN) $\lambda_{max} = 706.0$ nm, $\epsilon_{706} = 35.0\ cm^{-1}\ M^{-1}$; ($2.6 \times 10^{-3}$ M in CH_2Cl_2) $\lambda_{max} = 706.0$ nm, $\epsilon_{706} = 38.0\ cm^{-1}\ M^{-1}$. TGA (240–940 °C): calculated weight loss for $^9/_2$ $[(n\text{-}C_4H_9)_4N]_2O + P_2O_5$ 37.0% (observed weight loss 37.2%). Molecular weight (sedimentation equilibrium method) calculated for $[(n\text{-}C_4H_9)_4N]_5P_2W_{17}O_{61}(Cu\cdot Br)^{4-}$ (found): 5437 (5500 ± 500), supplementary material, Figure E.

$[(n\text{-}C_4H_9)_4N]_4HPW_{11}O_{39}(Mn^{2+}\cdot OH_2)$. This preparation is based on the literature with minor modifications.[32c] In a 500-mL round-bottom flask, $H_3PW_{12}O_{40}\cdot xH_2O$ (98.64 g, 34.3 mmol if $x = 0$) was stirred in 250 mL of warm H_2O. To this mixture a few drops of aqueous 0.5 M $KHCO_3$ was added. The entire mixture was then transferred to a 1000-mL round-bottom flask, and the volume was increased to 500 mL. The mixture was heated to 80 °C, and aqueous $KHCO_3$ (0.5 M) was added until the mixture became homogeneous (pH 5.3). Solid $MnCl_2\cdot 4H_2O$ (6.79 g, 34.3 mmol) was then added, causing the solution to turn deep amber while remaining homogeneous. In a separate 1000-mL flask, $[(n\text{-}C_4H_9)_4N]Br$ (149.75 g, 464.5 mmol) was dissolved in about 500 mL of H_2O and heated to 80 °C. The amber polyoxometalate solution was then added to the stirring $[(n\text{-}C_4H_9)_4N]Br$ solution, causing an immediate brown precipitate. The precipitate was then collected on a medium frit and washed with approximately 1 L of hot H_2O. The damp precipitate was then dissolved in 400 mL of CH_3CN and filtered to remove a small amount of solid residue. The filtrate was warmed, and diethyl ether (300 mL) was added until a small amount of precipitate was noted. The mixture was warmed until the precipitate redissolved, and then the flask was placed into the freezer overnight. Yield: 10.1 g (2.70 mmol, 7.9% based on $MnCl_2\cdot 4H_2O$). Elemental analysis calculated (found): C, 20.66 (20.45); H, 3.98 (4.16); N, 1.51 (1.6); P, 0.83 (0.79); W, 54.35 (54.1); Mn, 1.48 (1.38); O, 17.2 (17.1); total, 100.0 (99.58). TGA (Du Pont 1090 Instrument) (25–940 °C under N_2): calculated weight loss for 4 $[(n\text{-}C_4H_9)_3N]$ + 4 $n\text{-}C_4H_8$ + 3 H_2O + 0.5 P_2O_5 29.6% (observed weight loss 29.5%). Note that the Br^- adduct is *not* formed in *this* preparation. perhaps since Mn(II) and not Mn(III) is present.

Determination of the Br^- Association Equilibrium Constant for α_2-$P_2W_{17}O_{61}Mn(III)^{7-}$. Caution was taken to employ dry solvents since H_2O could significantly influence the extent of Br^- dissociation/association. A solution of α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn\cdot Br)$ was prepared by placing 92.98 mg (1.53×10^{-5} mol) in a 25.0-mL volumetric flask and diluting to the line with dry CH_2Cl_2. A $[(n\text{-}C_4H_9)_4N]Br$ solution was prepared by dissolving 9.85 g (0.0306 mol) of white, multiply recrystallized (from ethanol) $[(n\text{-}C_4H_9)_4N]Br$ (then dried, under vacuum at 50 °C) in about 10 mL of dry CH_2Cl_2 in an 18 × 150 mm disposable test tube. This solution was pipetted into a 25.0-mL volumetric flask and diluted to the line with dry CH_2Cl_2. For each sample, 0.50 mL (3.06×10^{-7} mol) of the polyoxometalate solution was syringed into a 3.0-mL volumetric flask. Into this polyoxometalate solution was syringed 0, 0.10, 0.25, 0.50, 1.00, and 2.00 mL of the $[(n\text{-}C_4H_9)_4N]Br$ solution (0, 398, 995, 1990, 3980, and 7691 equiv of Br^-, respectively), and then the solution was diluted to the line with dry CH_2Cl_2 to reach 3.0-mL total volume in each case: the final polyoxometalate concentration was 1.0×10^{-4} M. The concentrated $[(n\text{-}C_4H_9)_4N]Br$ solutions are yellow (i.e., are not transparent in the visible region); our guess for the yellow color is ion pair (possibly triple ion) formation, which is expected in lower dielectric constant solvents (the probability of triple ions like $\{[(n\text{-}C_4H_9)_4N]^+(Br^-)[(n\text{-}C_4H_9)_4N]^+\}^+$ and $\{Br^-[(n\text{-}C_4H_9)_4N]^+Br^-\}^-$ increases as $1/D^3$, D equaling the dielectric constant of the solvent). Therefore, individual background (reference) solutions containing the same $[(n\text{-}C_4H_9)_4N]Br$ concentrations were prepared identically with the sample solutions except that dry CH_2Cl_2 was substituted for the polyoxometalate solution. The sample and background solutions were allowed to equilibrate at 25.0 ± 0.2 °C for 5 min prior to the measurement of the spectrum. Evaluation of the absorbance increase at $\lambda = 520$ nm vs added $[Br^-]$ by Drago's method[66] yielded an association constant of 48 ± 9, supplementary material, Figure F. The spectrum contains only approximate isobestic points (there is some experimental error due to the dilution of the multiple samples).

Determination of Equilibrium Constants for Selected Bases and α_2-$P_2W_{17}O_{61}(Mn^{3+}\cdot L)$ (L = Solvent), General Procedure. For example, a 0.256 mM solution of α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn\cdot Br)$ was prepared by placing 293.39 mg of the compound in a 50-mL volumetric flask and diluting to the line with dry CH_2Cl_2. Each sample was made by syringing 1.0 mL of the polyoxometalate solution into a 3.0-mL volumetric flask. The appropriate amount of the base solution was then added by syringe, and the solution was diluted to the line with dry CH_2Cl_2. (The final polyoxometalate concentration was 2.56×10^{-4} M.) The bases could not be treated as being completely transparent in the visible region. Therefore, an individual background solution was prepared for each sample by syringing the appropriate amount of base solution into the volumetric flask and diluting to the line with dry CH_2Cl_2. Each sample (and its background reference of $[(n\text{-}C_4H_9)_4N]Br$ in dry CH_2Cl_2) was allowed to equilibrate to 25.0 ± 0.2 °C in the sample chamber of the spectrometer prior to obtaining the spectrum. Some of the spectra contained only approximate isobestic points (there is some experimental error due to the dilution of the multiple samples).

Titration of α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn\cdot Br)$ with *N*-Methylimidazole (*N*-MeIm). Solutions (2.56×10^{-4} M) of the polyoxometalate, prepared as above, were treated with 0, 1.0, 5.1, 10.2, and 51.2 equiv of *N*-MeIm, which was prepared as follows: *N*-MeIm (1614.92 mg, 19.67 mmol) was weighed into a 25.0-mL volumetric flask and diluted to the line with dry CH_2Cl_2 to give a 0.787 mM solution (1024.5 equiv/mL). Attempts to titrate the polyoxometalate solution with more than 51.2 equiv of *N*-MeIm caused a pink precipitate to form. Determination of K_{eq} from the absorbance increase at 496 nm as a function of [*N*-MeIm] by the Drago method gave an equilibrium constant of 3600 ± 1700 and $\epsilon(\alpha_2\text{-}P_2W_{17}O_{61}(Mn\cdot N\text{-}MeIm)^{7-}) = 580 \pm 20\ cm^{-1}\ M^{-1}$, supplementary material, Figure G.

Titration of α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn\cdot Br)$ with Pyridine (py). This titration was performed as described above on a 2.56×10^{-4} M $P_2W_{17}Mn$ solution with a pyridine solution prepared by dissolving pyridine (1523.12 mg, 19.26 mmol) in dry CH_2Cl_2 in a 25.0-mL volumetric flask (1003.1 equiv/mL). To the polyoxometalate solutions were added 0, 2.0, 5.0, 10.0, 501.5, and 1003.1 equiv of pyridine. The absorbance increase at $\lambda = 491$ nm vs [py] yielded $K_{eq} = 4100 \pm 1700$, $\epsilon(\alpha_2\text{-}P_2W_{17}O_{61}(Mn\cdot py)^{7-}) = 521 \pm 9\ cm^{-1}\ M^{-1}$, supplementary material, Figure H.

Titration of α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn\cdot Br)$ with Triphenylphosphine (PPh_3). This titration was again performed as described above on a 2.56×10^{-4} M $P_2W_{17}Mn$ solution with a PPh_3 solution prepared by dissolving PPh_3 (5163.8 mg, 19.69 mmol) in dry CH_2Cl_2 in a 25.0-mL volumetric flask (1025.5 equiv/mL). To the polyoxometalates solutions were added 0, 500, 1500, and 2000 equiv of the PPh_3 solution. The absorbance increase at $\lambda = 500$ nm vs $[PPh_3]$ yielded $K_{eq} = 6 \pm 3$, $\epsilon(\alpha_2\text{-}P_2W_{17}O_{61}(Mn\cdot PPh_3)^{7-}) = 409 \pm 46$, supplementary material, Figure I.

Spectrophotometric Titration of a_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn^{3+}\cdot Br)$ with $[(n\text{-}C_4H_9)_4N]OH$. α_2-$[(n\text{-}C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn\cdot Br)$ (101.84 mg, 1.68×10^{-5} mol) was placed in a 50.0-mL volumetric flask and diluted to the line with dry CH_3CN. In a 25.0-mL volumetric flask, 1.0 mL of a 0.38 M (3.80×10^{-4} mol) $[(n\text{-}C_4H_9)_4N]OH(aq)$ solution was diluted to the line with dry CH_3CN to give a 1.52×10^{-2} M solution. For each sample, 1.0 mL of the 3.36×10^{-4} M polyoxometalate solution was syringed into a 3.0-mL volumetric flask. The appropriate amount of base was added (0, 10, 20, 30, 40, 50, 60, 80, 100, 150, 200, and 1000 μL; 0.227, 0.453, 0.680, 0.907, 1.13, 0.136, 1.81, 2.27, 3.40, 4.54, and 22.7 equiv of OH^-, respectively), and the solution was diluted to the line with dry CH_3CN; the resultant $[P_2W_{17}Mn]$ was 1.1×10^{-4} M. The plot of absorbance loss at 475 nm vs equivalents of OH^- shows a break point at about 1.0 equiv of OH^- added. No degradation was apparent below 4.54 equiv of OH^- (based on the observation that no polyoxoanion-free Mn was observed in the visible region nor was any decrease noted for the UV absorbance that arises from the polyoxometalate framework). The 22.7-equiv point did not pass through the isosbestic point, and there was an observable decrease in the polyoxometalate framework UV absorbance; thus, it is likely that some degra-

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[66] Drago, R. S. *Physical Methods in Chemistry*; Saunders: Philadelphia, 1977.

dation of the complex had occurred by this point, supplementary material, Figure J.

Stability of α_2-[$(n$-$C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn^{3+}\cdot Br)$ in the Presence of Excess PhIO. Throughout this experiment, the following two vials were treated identically except for the addition of oxidant. α_2-[$(n$-$C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn\cdot Br)$ (53.35 mg, 8.79×10^{-3} mmol) was dissolved in 5.0 mL of 1:1 CH_2Cl_2/CH_3CN. The polyoxometalate solution was split into two equal 2.50-mL fractions and syringed into separate vials. To one of the vials was added 1492.8 mg (6.79 mmol, 1545 equiv) of PhIO, and the heterogeneous mixture was vigorously stirred for 48 h. Within 5 min, the red solution had changed to a bright yellow. The white-yellow solid (presumably a mixture of unreacted PhIO and the disproportion product $PhIO_2$) that remained at the end of the reaction period was removed by filtration through Whatman No. 2 paper and washed with 1.0 mL of CH_3CN. Infrared spectrum: (CH_3CN, cm^{-1}) 785 (s), 870 (s), 946 (s), 958 (sh), 1014 (m), and 1092 (s); (KBr pellet, cm^{-1}) 793 (s), 869 (s), 948 (s), 958 (sh), 1012 (m), and 1069 (s).

Magnetic Susceptibility Experiments. Magnetic susceptibility data were obtained between 2 and 300 K at fields ranging from 5.5 to 19.5 kG by using a high-sensitivity automated Faraday balance described in detail elsewhere.[67] The error in the measured susceptibility is less than 0.5% with the standard sample size of ca. 20 mg. Fitted curves are available as supplementary material, Figures K–Q.

HPLC Studies. High-performance liquid chromatography (HPLC) studies were conducted as previously described.[55] The samples were chromatographed on a Waters HPLC system containing dual Model 510 pumps and an automated gradient controller. The samples were detected at 280 nm with a Lambda-Max LC spectrophotometer, and the chromatograms were plotted with a Model 740 data module. The samples were prepared as 1 mM solution in HPLC grade H_2O and filtered through Alltech 0.45 μ disposable syringe filters. If the samples were not immediately chromatographed, they were stored (less than 24 h) at 0 °C to minimize decomposition.[68] The samples were chromatographed on a Chromatographic Sciences Co. CSC-S ODS2 25 × 0.46 cm C-18 reverse-phase column that had more than 40000 theoretical plates. The eluent was a 85:15 pH 6.5 hexylamine and citric acid buffer/MeOH prepared as previously described.[55] The chromatograms are available as supplementary material, Figure R.

Electrochemical Studies. Electrochemical experiments were performed by using a Princeton Applied Research (PAR) electrochemical station including a Model 175 universal programmer, a Model 173 potentiostat–galvanostat and Model 174A polarographic analyzer and a Model 179 Coulometer. The recordings were made with a Gould Model 3054 *XY*-recorder. The auxilliary electrode consisted of a Pt wire coiled around a Pt bead electrode. The samples were analyzed as ~1 mM α_2-[$(n$-$C_4H_9)_4N]_{7.3}H_{0.7}P_2W_{17}O_{61}(Mn\cdot Br)$ in 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6/CH_3CN$ solutions and referenced to the standard calomel electrode (SCE). Variations on this experiment included replacing the Pt bead electrode with a glassy carbon electrode or preoxidizing either electrode by holding the potentiostat at +1.5 V for 5 min prior to conducting the experiment. The cyclic voltammagram of ferrocene (as a control) gave the expected full electrochemically reversible voltammogram.

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Supplementary Material Available: Sedimentation–equilibrium molecular weight plots (ln *A* vs r^2) for the tetra-*n*-butylammonium salts of $P_2W_{17}M$ ($M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$) (Figures A–E), spectrophotometric titrations and UV–vis plots of α_2-$P_2W_{17}O_{61}(Mn\cdot Br)^{8-}$ titrated with $[(n\text{-}C_4H_9)_4N]Br$, *N*-methylimidazole, pyridine, triphenylphosphine, and $[(n\text{-}C_4H_9)_4N]OH$ (Figures F–J), temperature-varied magnetic susceptibility plots of $P_2W_{17}M$ ($M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$) (Figures K–Q), a stacked plot of the HPLC traces for the potassium salts of $P_2W_{17}M$ ($M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$) (Figure R) (18 pages). Ordering information is given on any current masthead page.

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(67) The Faraday balance used in these experiments is based on the design found in Johnson, D. C. Ph.D. Dissertation, Cornell University, 1983.

(68) In our original HPLC work, storing the solutions at 0 °C was used to avoid decomposition of the samples, hence, this same protocol was initially followed herein. However, decomposition at neutral pH appears not to be a problem with the compounds synthesized in this paper, since they all show identical chromatograms either immediately after dissolution or after 24 h in solution.