Synthesis, Characterization and Electrochemistry of the Novel Dawson-Type Tungstophosphate $[H_4PW_{18}O_{62}]^{7-}$ and First Transition Metal Ions Derivatives

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Following the synthesis of pure $[H_4PW_{18}O_{62}]^{7-}$ (PW_{18}), its derivatives monosubstituted with M (M = Mo^{VI}, V^{IV}, V^{V}, Mn^{II}, Fe^{III}, Co^{II}, Ni^{II} Cu^{II} and Zn^{II}) were obtained. All compounds were characterized by elemental analysis, IR, UV/visible and ^{31}P NMR spectroscopy. Their cyclic voltammetry properties were studied as a function of pH and systematically compared with those of their analogs derived from the symmetrical species, $[P_2W_{18}O_{62}]^{6-}$(P_2W_{18}). Comparison of the two unsubstituted precursors revealed that the merging of the first two waves of the monophosphate occurred in a less acidic medium than for the diphosphate. The observations point to the higher basicity of the reduced forms of PW_{18} compared with those of P_2W_{18}. The fingerprint pattern observed for α_2-$P_2W_{17}M$ derivatives in media of pH = 3 consisted of the splitting of the third W redox system into two one-electron closely spaced waves which is in contrast to the same system in α_1-$P_2W_{17}M$. This peculiarity was also obtained for several of the present α_2-$PW_{17}M$ systems in media of pH = 3 and confirmed that α_2-substituted derivatives were indeed formed. The absence of this peculiar behavior in some other derivatives is consistent with smooth variations of acid-base properties from one derivative to the next. The electrocatalytic properties of all the compounds are illustrated by the reduction of nitrite by reduced PW_{18} and of nitrate by reduced α_2-$PW_{17}Cu$.

Introduction

Heteropolyanions constitute a unique class of molecular metal-oxygen clusters which are remarkable in several respects: the variety of their properties based on their sizes, shapes, charge densities and reversible redox potentials and the enormous diversity of their structures.[1,2] Therefore, they appear as good candidates for applications in a wide range of areas, including catalysis, electrocatalysis, medicine, materials science, photochemistry, analytical chemistry and magnetochemistry.[3−6] Even though complete rationalization of the build-up of these structures is not available at present, very many of them might be recognized as being derived, at least partly, from lacunary Keggin and Dawson-type fragments. Keeping with the basic structures themselves, a formal direct relationship can be found between the Dawson structure and a tri-vacant Keggin structure. The appropriate Keggin fragment, A-$X^{V}W_9O_{34}$, is derived from the saturated $[XW_{12}O_{40}]^{n-}$ species by the removal of three MO_6 octahedra belonging to three different M_3O_{13} moieties. The Dawson structure is constructed from two half anions A-$X^{V}W_9O_{34}$, (with X = P^{V} or As^{V}).[7,8] Such "dimerization" mostly gives species in which the same heteroatom is present in the two halves. We were interested in the possibility of obtaining such "dimers" with two different central heteroatoms, with the complementary aim of studying the consequences of such asymmetry on the electrochemical and electrocatalytic properties of these heteropolyanions. To the best of our knowledge, the only example with two different heteroatoms in the +v oxidation state is an 18-tungsto monoarsenic monophosphoric acid, which was not fully characterized however.[9] In contrast, even though scarce, several examples of well-characterized heteropolyanions with two different heteroatoms and X atoms in the +III oxidation state have been reported namely $[H_nX^{III}W_{18}O_{60}]^{(9-n)-}$ (X = As or Sb, n = 2; X = Bi, n = 2).[10−12] Their X-ray crystal structures revealed them to be composed of two half-anions, B-XW_9O_{33}, connected by six oxygen atoms. For example, the two halves of $[H_2AsW_{18}O_{60}]^{7-}$ contain a trivalent As atom in one half and two hydrogen atoms in the other.[10] The two compounds $[H_2AsW_{18}O_{60}]^{7-}$ and $[H_2SbW_{18}O_{60}]^{7-}$ were found to differ only by the connectivity of their two halves.[11] In contrast, only recently has the description of $Na_7[H_2BiW_{18}O_{60}]$ confirmed the possibility that the Bi^{III} analog

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might contain two hydrogen atoms[12] instead of the three previously invoked in $(Me_4N)_6[H_3BiW_{18}O_{60}]$.[13] Finally, the present status of these asymmetric derivatives is that they are constructed from a B-XW_9O_{33} anion and a B-$H_2W_9O_{33}$ anion. To this family of asymmetric derivatives belongs the series of novel Sn^{II} substituted compounds reported recently by Krebs and co-workers.[14]

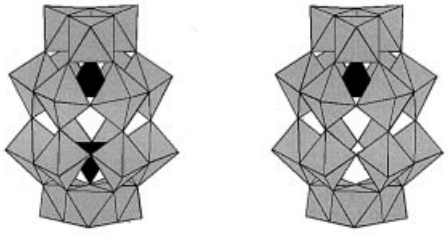
In contrast to this general situation, one of the present authors recently reported the synthesis of the novel Dawson-type tungstophosphate $[H_4PW_{18}O_{62}]^{7-}$ and its lacunary and zinc-substituted derivatives, $[H_4PW_{17}O_{62}]^{11-}$ and $[Zn(H_2O)(H_4PW_{18}O_{61})]^{9-}$, in which the two anionic halves are of the A-type with only one of them containing a central heteroatom in the +v oxidation state.[15] This pioneering report stimulated further work and, soon afterwards, our group confirmed the feasibility of this synthesis for the As^V -containing analog of the corresponding trivacant lacunary species and the synthesis of two sandwich-type derivatives, $[Zn_4(H_2O)_2(H_4AsW_{15}O_{56})_2]^{18-}$ and $[Cu_4(H_2O)_2(H_4AsW_{15}O_{56})_2]^{18-}$.[16] Finally, we have established the best experimental conditions for the synthesis of $[H_4AsW_{18}O_{62}]^{7-}$ and demonstrated that these conditions differ substantially from those necessary to obtain the well-known symmetric species $[As_2W_{18}O_{62}]^{6-}$.[17]

All of these exploratory results support the following conclusions: the putative or realized possibility of manipulating the compositions and, presumably, the acid−base and redox properties of heteropolyanions has been illustrated once more; a new family of Dawson-type heteropolyanions has been unambiguously established.

Herein we report the synthesis, characterization and electrochemistry of the hitherto unknown first-row transition metal cation-substituted heteropolyanions derived from $[H_4PW_{18}O_{62}]^{7-}$. Their electrochemistry reveals differences with the corresponding symmetric heteropolyanions. This study is completed by an evaluation of their electrocatalytic properties for the reduction of nitrate and nitrite.

Results and Discussion

All the polyanions in the present study are primarily derived from α-$[H_4PW_{18}O_{62}]^{7-}$ (abbreviated hereafter as PW_{18}) and their formulae will be written as $PW_{17}M$, with omission of oxygen atoms and overall charges when no confusion is likely to arise. M represents the substituent metal cation. The main PW_{18} isomer of interest in the following is that obtained after prolonged heating of the reaction mixture. Scheme 1 illustrates the α-structure proposed for this isomer in analogy with that of α-$[P_2W_{18}O_{62}]^{6-}$ (P_2W_{18}), an assumption based on the close resemblance of the ^{183}W NMRspectra of the two compounds.[15] In line with the numbering of tungsten atoms in α-P_2W_{18}, the IUPAC recommendations have also been followed for α-PW18. A detailed discussion[15] then shows how the results of electrochemistry, ^{31}P NMR and IR spectroscopy were combined, in this preliminary work on PW_{18}, PW_{17} and $PW_{17}Zn$, to demonstrate that the mild alkaline degradation of PW_{18} resulted in the removal of a W atom from the "cap" in the half of this molecule containing the single P atom, thus creating the first vacancy in one of the so-called α_2 positions.



Scheme 1. Schematic representations of the Dawson-type tungstodiphosohate and tungstomonophosphate

Syntheses

A number of slight modifications were introduced into the pioneering synthesis of $K_7[H_4PW_{18}O_{62}]\cdot 18H_2O$.[15] The heating duration was prolonged to at least 96 h because we found that after the formerly proposed 60 h, the reaction mixture still contained α-$K_7[H_4PW_{18}O_{62}]\cdot 18H_2O$ as the major but not the exclusive species. Even so heating at 80 °C was ultimately necessary to obtain pure α-$K_7[H_4PW_{18}O_{62}]\cdot 18H_2O$. It is worth noting that the present procedure was essential to obtain the desired product pure and in good yield (> 65% in all preparations). Also, it must be pointed out that the optimal reagent ratios were the same as those determined previously in our synthesis of α-$K_7[H_4AsW_{18}O_{62}]\cdot 18H_2O$.[17]

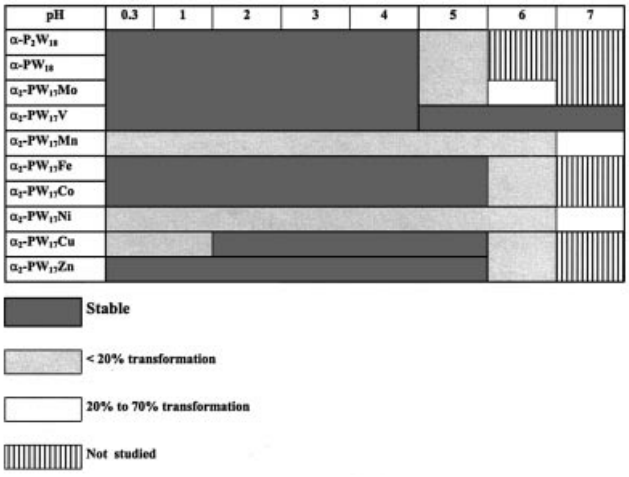
The mono-lacunary derivative was obtained under mild conditions and resulted, as indicated previously, in the creation of a vacancy in a α_2-position in the half of the molecule containing the P atom. All the metal cation-substituted species were elaborated under the same conditions as the Zn^{II}-substituted compound, sometimes with slight modifications as described in the Exp. Sect. The mild conditions of the procedure leads to isomerically pure products.

UV/Visible and IR Spectroscopic Characterization

As usual, UV/Vis spectra of these compounds cannot be considered as specific fingerprints for the polyoxoanions in this series. However, the stability of the complexes in the series as a function of pH and time was studied by monitoring the UV/Vis spectra over periods of at least 24 h. The spectra were recorded between 1300 nm and 210 nm, with the maximum absorptions being located between 240 nm and 300 nm, depending on the heteropolyanion in question. The duration of observation is larger than necessary for electrochemical characterization of the complexes but was retained in order to eventually open the way for long-lasting or preparative scale catalytic or electrocatalytic processes. For this study, in addition to the mono-vacant species itself, two groups of substituted derivatives were considered. The substituted compounds are represented by α_2-$ML(PW_{17}O_{61})$, with M representing the substituent metal cation, the ligand L = O^{2-} for M = Mo^{6+}, V^{5+} and V^{4+}, while L = H_2O for all other metal cations in this work.[1,18−20] The difference between these two groups is important in that the behavior of several of these derivatives suggests only the Mo- and V-substituted compounds fea-

ture really "saturated" substituted species while the others are close to the lacunary precursor complex. Following this classification, PW_{17} was found to be unstable regardless of the pH and to undergo fast transformation. For pH < 4, such a transformation was observed in less than one hour and the lower the pH, the faster the transformation gradually giving the saturated species PW_{18}. This behavior parallels that observed for P_2W_{17}.[1] The so-called saturated substituted compounds show stabilities close to those of unsubstituted ones: all of them were found to be stable between pH 0.3 and pH 4, with decomposition occurring to an extent of less than 20% at pH 5 and comprising between 20% and 70% at pH 6. In contrast to these results, $PW_{17}V$ remains stable up to at least pH 8. The stability domains for the other substituted complexes are shown in Table 1. Dark grey indicates the domain in which a particular derivative is stable; plain grey corresponds to a decomposition less than or equal to 20%; finally, clear grey indicates a decomposition of between 20% and 70%. Obviously, the Mn and Ni derivatives are the less stable species in the series, even though their decomposition does not reach 20% for a pH between 0.3 and 5. In contrast, Fe-, Co- and Zn-substituted complexes are stable from pH 0.3 to 5. Their transformation does not reach 20% at pH 6 and is even in the range of 6% for $PW_{17}Zn$. The case of $PW_{17}Cu$ deserves emphasis since it was observed to be stable between pH 2 and 5.

Table 1. Stability, monitored by UV/visible spectroscopy over 24 h, of α-P_2W_{18}, α-PW_{18} and the α_2-$PW_{17}M$ derivatives of the latter complex, as a function of pH. For further details, see text



The most characteristic IR band shifts in tungstophosphates are observed between 1200 and 1000 cm^{-1} and correspond to P−O vibrations. They allow a characterization of lacunary species relative to the saturated precursor. When a substituent metal cation is introduced into the vacancy, the whole symmetry of the saturated complex tends to be restored, at least as far as the IR spectra are concerned. Table 2 lists the main IR band energies for the complexes in the present study. The complex PW_{18} is characterized by two bands observed at 1066 and 1032 cm^{-1} respectively. In contrast, they are replaced mainly by a single band located at 1033 cm^{-1} in PW_{17}. Provisionally, this modification supports the location of the vacancy in the α_2 position in the half of the molecule containing the P atom. Examination of Table 2 indicates that two kinds of spectra were obtained through the series of substituted derivatives. Complexes substituted with Mo^{VI}, V^{V}, Fe^{III}, Co^{II}, Ni^{II} and Cu^{II} behave like PW_{18} itself and show two IR bands between 1200 and 1000 cm^{-1}.Complexes containing V^{IV}, Mn^{II} or Zn^{II} have only one IR band in the same energy region. These observations reflect the alteration of symmetry around the central PO_4 moiety.[21−23] This alteration clearly appears to be a function of the substituent cation. It has also been claimed that the nature of the counter-cation seems to influence the degree of restoration of symmetry in the polyanion[24] but a study and discussion of these phenomena are beyond the scope of this work. It should be noted that, in each group, the IR spectra are very similar to one another thus preventing any reliable identification of a given anion by this spectroscopic method.

^{31}P NMR Spectroscopy

Table 3 shows the ^{31}P NMR shifts and line widths for the novel Dawson-type tungsto-monophosphates and their first row transition metal ion derivatives. At least two remarks can be made regarding these results: i) as expected, the spectrum of each of these molecules displays a unique signal ii) the shifts and line widths comply with expectations from the knowledge of shifts observed for the phosphorus atom nearer to the substituent in α_2-$P_2W_{17}M$ derivatives. Further comparison of the actual shifts among the two series and also with the corresponding α_1-$P_2W_{17}M$ derivatives[25] confirms that substitution occurs in the PW_9 moiety of PW_{18} and in the α_2-position. In several instances, larger shifts were observed in the α_2-$PW_{17}M$ compounds than in the α_2-$P_2W_{17}M$ series. Further comments on this trend are, however, beyond the scope of this paper. To the best of our knowledge, Jorris et al.[26] were the first to study the NMR of paramagnetic element-containing HPA's on P_2W_{17} derivatives. Even though their syntheses resulted in mixtures of α_1 and α_2 isomers, their pioneering work constitutes a valuable basis for the interpretation of the present observations. In these complexes, it is convenient to designate the phosphorus atom nearer to the eventually paramagnetic substituent ion as P(1) and the phosphorus atom far from this element as P(2). Observations of the ^{31}P NMR spectra of several Dawson structures substituted in the α_2 position have established that the chemical shift of P(2) is practically unaffected by the nature of the substituent element. As expected, the resonance assigned to the P atom nearest to the substitution site is considerably shifted downfield in the presence of paramagnetic cations and the shift is larger for α_1 derivatives. The ^{31}P NMR line widths depend on the particular nature of the substituent atom and especially on its electronic ground state configuration. As expected[25,26] and shown in Table 3, contrasting situations are encountered for the P(1) line with respect to its line width. The signal might be narrow or relatively narrow, or become ex-

Table 2. Characteristic IR absorption bands of α-P_2W_{18}, α-PW_{18} and the α_2-$PW_{17}M$ derivatives of the latter complex. For further details, see text

Compound	Main IR absorption bands
α-P_2W_{18} [a]	1092(s); 1020(w); 960(s); 917(s); 780(vs); 600(vw); 568(w); 531(w); 476(vw); 374(ms); 328(m)
α-PW_{18}	1066(vs); 1032(s); 979(w); 949(w); 891(s); 763(w); 587(w); 522(s); 423(w)
$\alpha_2PW_{17}Mo$	1064(s); 1031(m); 978(sh); 948(m); 892(w); 795(w); 771(w); 587(w); 522(w)
$\alpha_2PW_{17}V^{5+}$	1057(s); 1039(sh); 947(m); 888(w); 767(w); 587(w); 521(m)
$\alpha_2PW_{17}V^{4+}$	1048(s); 939(m); 871(w); 768(w); 691(w); 588(w); 517(w)
$\alpha_2PW_{17}Mn$	1043(s); 932(m); 815(w); 767(w); 712(w); 590(w); 511(w); 415(m)
$\alpha_2PW_{17}Fe$	1057(s); 1025(s); 939(m); 875(w); 763(w); 587(w); 516(m); 467(w); 419(m)
$\alpha_2PW_{17}Co$	1047(s); 1025(w); 934(m); 860(w); 811(w); 755(w); 588(w); 512(m); 467(w); 415(w)
$\alpha_2PW_{17}Ni$	1050(s); 1022(s); 934(m); 871(w); 811(w); 767(w); 715(w); 587(w); 515(m); 467(w); 416(m)
$\alpha_2PW_{17}Cu$	1090(sh); 1047(s); 935(m); 871(w); 807(w); 751(w); 700(w); 590(w); 523(w); 467(w); 418(m)
$\alpha_2PW_{17}Zn$	1042(s); 934(m); 868(w); 815(w); 760(w); 711(w); 590(w); 511(m); 464(w); 419(m)

[a] NH_4^+ salt: R.Contant, R. Thouvenot; *Inorg. Chim. Acta* **1993**, *212*, 41−50

Table 3. ^{31}P NMR shifts (relative to 85% H_3PO_4) and line widths of α_2-monometalloheptadecatungstomonophosphate at 298 K

Compound	Δ(ppm)	Δν(Hz)	Medium in D_2O
H_4PW_{18}	−6.54 (−6.7)[a]	7	0.5 M Li_2SO_4
$\alpha_2PW_{17}V^{4+}$	6.77	2454	0.5 M HCl
$\alpha_2PW_{17}V^{5+}$	−5.13	7	0.5 M HCl
$\alpha_2PW_{17}Mn$	990	≈ 46000	0.05 M HCl
$\alpha_2PW_{17}Fe$	920	≈ 40000	0.05 M HCl
$\alpha_2PW_{17}Co$	424.5	368	0.5 M CH_3COOLi +0.5 M LiCl,
$\alpha_2PW_{17}Ni$	423	1864	0.5 M CH_3COOLi +0.5 M LiCl,
$\alpha_2PW_{17}Cu$	−34.87	3068	0.5 M CH_3COOLi +0.5 M LiCl,
$\alpha_2PW_{17}Zn$	−2.93 (−2.95)[a]	8	0.5 M CH_3COOLi +0.5 M LiCl,
$\alpha_2PW_{17}Mo$	−5.95	8	0.05 M HCl

[a] Ref.[15]

ceedingly broadened as exemplified by the case of the Mn^{II} derivative, the ground state of which is orbitally non-degenerate. Finally, it can be considered that a satisfactory agreement with the qualitative results from the observations of Jorris et al.[26] and other literature results[25] has been obtained in the present work. The same line of reasoning can also be applied to the interpretation of the spectra of the Zn^{II} and Cu^{II}-substituted derivatives. From the electronic configuration of Zn^{II}, no dramatic chemical shift is expected for the P atom compared with those observed with other diamagnetic substituents. The results in Table 3 validate this reasoning. In contrast, Cu^{II} is a paramagnetic d^9 ion that has a dramatic effect on the observed chemical shift, as expected.

Electrochemistry

Evidence for the Influence of the Asymmetry on the Voltammetric Behavior of PW_{18}: Comparison with P_2W_{18}

A comparison of the voltammetric characteristics of PW_{18} and P_2W_{18} is probably useful in highlighting the peculiarities of the former complex. Figure 1 shows the cyclic voltammograms (CV's) of the two complexes in a pH 0.3 sulfate medium superimposed on each other. The potential region was selected to avoid any deleterious derivatization of the electrode surface.[27] Furthermore, such an area is the most useful for the elucidation of electrocatalytic processes. Here, the voltammetric pattern is restricted to the first three waves observed for PW_{18} in this medium. Under the same conditions, the voltammetry of P_2W_{18} is known[28] and consists of two one-electron waves followed by two two-electron waves. These waves feature reversible diffusion-controlled processes. The comparison of the CV's of the two heteropolyanions (HPA's) is shown in Figure 1 (A) and is enlightening. The first wave of PW_{18} represents unambiguously a two-electron chemically reversible process. This point was checked by controlled potential coulometry. The two subsequent waves also feature two-electron processes. In short, the pattern for PW_{18} is composed of a set of three reversible diffusion-controlled waves. This observation was expanded by a brief study of the pattern as a function of pH. Figure 1 (B) illustrates this point and shows, in superimposition, the CV's of PW_{18} at pH 0.3 and 4. With the increase in pH, the formerly two-electron wave splits into

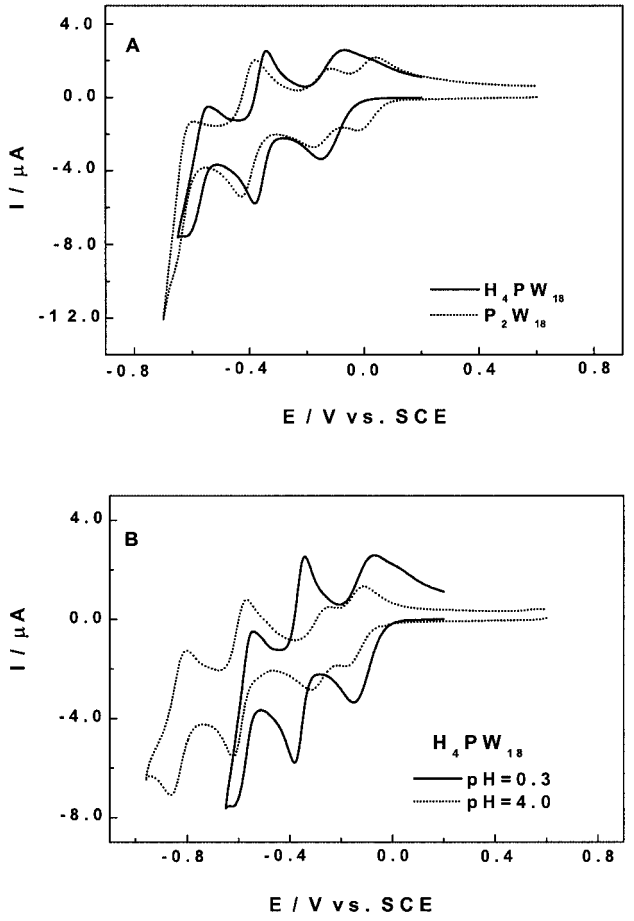


Figure 1. Cyclic voltammograms (CV's) recorded on 5×10^{-4} M solutions of the relevant polyoxometalates; scan rate: 10 $mV \cdot s^{-1}$; working electrode: glassy carbon; reference electrode: SCE; A: Comparison of the CV's observed in a pH 3 medium (0.2 M Na_2SO_4 + H_2SO_4) for the two unsubstituted tungstophosphates: PW_{18} and P_2W_{18}; B: pH Effect on the CV of PW_{18}. For further details, see text

two apparently one-electron processes. No attempt was made to ascertain quantitatively that the splitting was complete at pH 4. Turning more specifically to the comparison of the voltammetric behavior of the two HPA's, all the observations point to the higher basicity of the reduced forms of PW_{18} compared with those of P_2W_{18}. The results are consistent with the deductions which could have been forecast from their structures. Formally, PW_{18} is composed of two A-type half-anions which can be formulated as H_4W_9 and PW_9 respectively. A loose analogy might prompt us to point out the similarity between the hydrogenated fragment of PW_{18} and $[H_2W_{12}O_{40}]^{6-}$ (H_2W_{12}). This analogy should be expressed in terms of the comparable basicity between PW_{18} and P_2W_{18}, with reference to the known basicity influence in the reduction of H_2W_{12} compared with those of the corresponding species of classical Keggin-type HPA's.[28−30] In fact, polarograms (and voltammograms) of H_2W_{12} at pH < 3.5, show three waves of 2, 2 and ca. 10 electrons each,[29,30] under conditions in which the first two reductions of its analogs $[PW_{12}O_{40}]^{3-}$ and $[SiW_{12}O_{40}]^{4-}$ and even the Dawson-type P_2W_{18}, are one electron pH-independent processes. Therefore, the pH-dependent voltammetric behavior observed for PW_{18} in comparison with that of P_2W_{18} can be compared with that of H_2W_{12} vis à vis $[PW_{12}O_{40}]^{3-}$ and $[SiW_{12}O_{40}]^{4-}$. It must be concluded that PW_{18} and its first several reduced species show greater basicity compared with the corresponding P_2W_{18} species. Provisionally it is worth mentioning, in contrast, that a roughly 6 M HCl solution was necessary to make the first two waves of P_2W_{18} merge[28] and the concentration of acid reaches 7−8 M HCl in the case of $[SiW_{12}O_{40}]^{4-}$. Such merging could not be achieved for $[PW_{12}O_{40}]^{3-}$ in solution[28] and was only achieved inside polymer matrices.[31] This observation is rewarding and represents a good step in our continuous search for ways to accumulate electrons on the first or the first several waves of HPA's under mild conditions. To the best of our knowledge, this series of compounds represents the first examples in which a two-electron W-wave in a saturated species is found to appear at a relatively less negative potential and milder acidity than generally obtained in classical Dawson HPAs. This constitutes one of the favorable conditions for eventual electrocatalytic processes.

Electrochemistry of Substituted Derivatives

The lacunary precursor species PW_{17} is unstable whatever the pH of the medium which precludes a comparison of its electrochemical behavior with that of its substituted derivatives and with that of P_2W_{17}. In the study of a related series of derivatives, experimental evidence had enabled separation of the compounds into two main groups, in agreement with the discussion set down earlier in this paper.[1,18−20] Such a separation and its formerly studied electrochemical consequences should also be valid here. Following this line, the first group is composed of those derivatives that can be considered as truly saturated and include the Mo and V^V (or V^{IV})-substituted compounds; their voltammetric behavior is expected to parallel that of PW_{18} itself, in addition to the redox activity of the substituents. The second group consists of all the other derivatives and they should behave more or less like the electrochemically unknown lacunary precursor PW_{17}. Actually, we suggest that the overall electrochemical trends should be similar to those observed previously in a systematic study of α_2-$P_2W_{17}M$ derivatives[32] and should guide us toward a direct comparison of the corresponding results. The pH = 3 experiments were selected for this comparison. Figure 2 (A through C) shows representative examples of superimposed CV's. For this comparison, it is worth recalling the presence of a distinctive fingerprint for α_2-$P_2W_{17}M$ compared with α_1-$P_2W_{17}M$ at pH = 3: this peculiarity appeared in the third W-waves where a single two-electron reversible wave for the α_1 complex was replaced by two, closely spaced, presumably one-electron waves for the α_2 isomer.[32] The case of the Fe-substituted derivatives is represented in Figure 2 (A). The substituent cation is reduced within the complex more positively than the W-centers. The gross feature is that the fingerprint is present with the two one-electron waves which are more closely spaced in α_2-$PW_{17}Fe$ than in α_2-$P_2W_{17}Fe$. The presence of the fingerprint was also observed

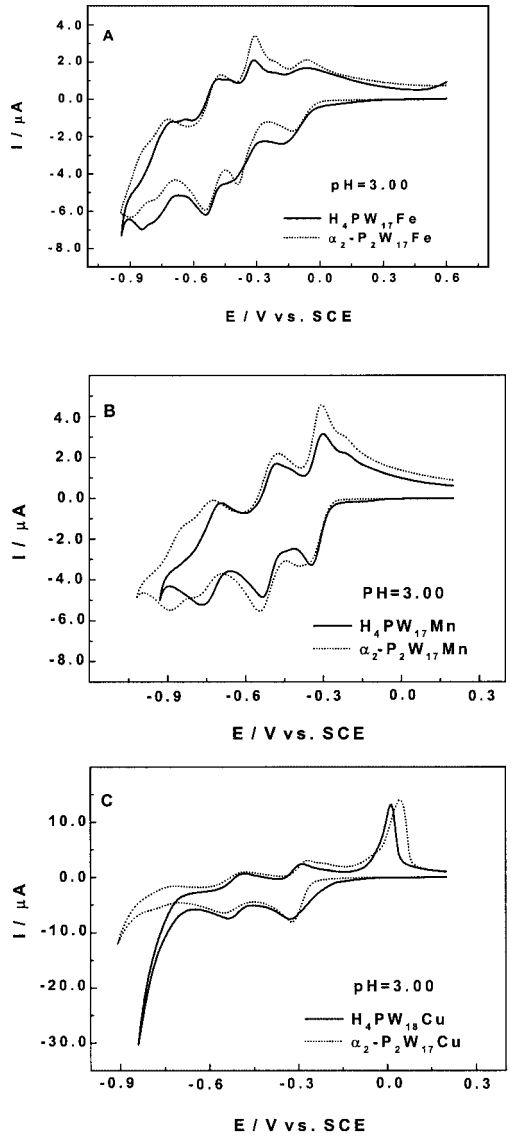


Figure 2. Comparison of the CV's observed in a pH 3 medium (0.2 M Na_2SO_4 + H_2SO_4) for representative examples of 5×10^{-4} M substituted tungstophosphates: α_2-$PW_{17}M$ and α_2-$P_2W_{17}M$; scan rate: 10 $mV.s^{-1}$; working electrode: glassy carbon; reference electrode: SCE. A: α_2-$PW_{17}Fe$ and α_2-$P_2W_{17}Fe$; B: α_2-$PW_{17}Mn$ and α_2-$P_2W_{17}Mn$; C: α_2-$PW_{17}Cu$ and α_2-$P_2W_{17}Cu$

with the V^{IV}- and Co-substituted complexes, with an almost complete merging of the waves in the latter case. In the potential region explored in Figure 2 (B), the Mn wave is not shown. The first two W-waves were observed roughly at the same potentials as the corresponding waves in α_2-$P_2W_{17}Mn$. However, the third redox system of α_2-$PW_{17}Mn$ features a single, slightly broad wave. In short, the presence of this substituent drives the third redox system in the positive potential direction and makes the fingerprint disappear. It must be pointed out that α_2-$PW_{17}Mn$ could be considered as fairly stable in the timescale of CV and the same phenomenon was seen for α_2-$PW_{17}Ni$ and α_2-$PW_{17}Zn$. Finally, the deposition of copper in Figure 2 (C) and the initiation of a probably catalytic hydrogen evolution reaction after the second W-wave precludes the observation of any possible fingerprint. In short, whatever the case, the third redox system is located at a more positive potential for α_2-$PW_{17}M$ than for α_2-$P_2W_{17}M$. Furthermore, when the fingerprint is present, the corresponding waves are more closely spaced in the former complex than in the latter. Thus, the formation of a single third W-wave is obtained through a positive move and a merging of the fingerprint waves. Such a smooth variation has not been previously observed.[32] On increasing the pH from 3 to 5, the fingerprint in the CV of α_2-$PW_{17}Fe$ becomes hardly visible. A consideration of these observations suggests that the difference in basicity between the α_2-$PW_{17}M$ and α_2-$P_2W_{17}M$ reduced forms is the basis for the splitting or otherwise of the third W-redox systems in the CV's. Such a difference in basicity is expected as a parallel to that observed between α-PW_{18} and α-P_2W_{18}. However, its intensity seems to depend critically on the substituent cations. Another outcome of this comparison is the confirmation that α_2-substituted derivatives were indeed formed.

The main other voltammetric characteristics of α_2-$PW_{17}M$ are gathered for pH 3 and pH 5 values in Table 4 for the potential locations of the first two W-waves and in Table 5 for those of the electroactive substituent cations. The values in Table 5 speak for themselves and do not call for particular comments. Even though subtle differences exist from one substituent cation to the next, a rough conclusion can be drawn from Table 4. The nature of the cation seems to induce a uniform influence on the potential locations of the two W-waves, except for the remarkable examples of Mo and Cu. The small differences are more pronounced at pH 3 than at pH 5 and more on the first wave than on the second. A combined Cu and W-wave is observed for α_2-$PW_{17}Cu$. No net separation of these two processes was obtained on going from pH 3 to 5. Controlled potential coulometry just past the peak location of this composite wave consumes four electrons per molecule for complete reduction at pH 3. Electrolysis conducted at half wave potential indicates, by spectroelectrochemistry or even by simple inspection of the solution color, that the two-electron reduction of the Cu^{2+} centre is completed before that of the W^{6+}-centres begins.

Electrocatalytic Reductions of Nitrite and Nitrate

Complexes were selected on the basis of their stability as a function of pH. Their behavior towards the electrocatalytic reductions of nitrite and nitrate in cyclic voltammetry was examined. In the potential regions explored, no direct reduction of nitrite or nitrate on the glassy carbon electrode surface could be observed.[33,34] The catalytic current intensity enhancement on the first wave or the first several waves of each HPA is preferable, with the aim of saving energy and to avoid derivatization of the electrode surface.[27] Conclusions from our previous work[16,34] are confirmed here which indicate only Cu and Ni-substituted species catalyze the reduction of nitrate, while most derivatives catalyze the reduction of nitrite. Therefore, two representative examples were selected. Figure 3 (A) illustrates the voltammetric behavior of PW_{18} towards the reduction of nitrite. For this

Table 4. Potential locations in pH = 3.00 and pH = 5.00 media of the first two W-waves of α-H_4PW_{18} and α_2-$H_4PW_{17}M$. Cyclic voltammetry: scan rate: 10mV·s^{-1}; working electrode: glassy carbon; reference electrode: SCE; E_{pc} = cathodic peak potential, $E^\circ = (E_{pc} + E_{pa})/2$. pH = 3.00 (0.2 M Na_2SO_4 + H_2SO_4); pH = 5.00 (0.4 M CH_3COONa + CH_3COOH)

HPA	pH = 3.00				pH = 5.00			
	$-E^1_{pc}$	$-E^\circ_1$/V	$-E^2_{pc}$	$-E^\circ_2$/V	$-E^1_{pc}$	$-E^\circ_1$/V	$-E^2_{pc}$	$-E^\circ_2$/V
H_4PW_{18}	0.174	0.144	0.294	0.266	–	–	–	–
$H_4PW_{17}Mo$	0.316	0.264	0.492 0.544	0.458 0.584	–	–	–	–
$H_4PW_{17}V^{4+}$	0.418	0.390	0.588 broad	0.563	0.546	0.509	0.720	0.695
$H_4PW_{17}V^{5+}$	0.430	0.400	0.594	0.574	0.558	0.522	0.722	0.700
$H_4PW_{17}Mn$	0.346	0.324	0.536	0.507	0.568	0.513	0.656	0.628
$H_4PW_{17}Fe$	0.438	0.375	0.546	0.515	0.566	0.537	0.660	0.631
$H_4PW_{17}Co$	0.400	0.357	0.548	0.517	0.559	0.526	0.650	0.627
$H_4PW_{17}Ni$	0.420	0.357	0.552	0.521	0.548	0.517	0.664	0.639
$H_4PW_{17}Cu$	0.330 (merged with Cu wave)	0.309 (with Cu oxidation at −0.014)	0.536	0.512	0.468 (merged with Cu wave)	0.442	0.656	0.629
$H_4PW_{17}Zn$	0.396	0.365	0.540	0.515	0.554	0.527	0.664	0.641

Table 5. Potential locations in pH = 3.00 and pH = 5.00 media of the cations which may be reduced or oxidized within α_2-$H_4PW_{17}M$

Reducible cations	pH = 3.00		pH = 5.00	
	$-E_p$/V	$-E^\circ$/V	$-E_p$/V	$-E^\circ$/V
Fe^{3+}	0.188	0.123	0.250	0.166
Cu^{2+}	merged with the first W-wave	desorptive wave at +0.014	merged with the first W-wave	desorptive wave at 0.00 (single)
V^{4+}	−0.252	−0.296	−0.218	−0.276
Mo^{6+}	−0.060	−0.094	−0.060	−0.094
Oxidizable cations	E_{pa}/V	E_{pc}/V	E_{pa}/V	E_{pc}/V
V^{4+}	broad 0.394 to 0.418	0.238	0.314	broad cathodic 0.230 to 0.252
Mn^{2+}	1.106	one reduction clearly visible at 0.818	0.974	two reduction peaks observed at +0.604 and −0.082 on potential reversal
Co^{2+}	–	–	1.406	–

experiment, a medium of pH 1 was selected to obtain a complete merging of the first two waves of PW_{18}. Addition of NO_2^- [35] induced a large current intensity enhancement. No anodic trace was observed on potential reversal, even for small values of the excess parameter γ ($\gamma = C_{NO2}^-/C_{HPA}$). Increasing the concentration of nitrite still enhanced the cathodic current. It must be concluded that an efficient catalysis of the reduction of nitrite[35] can be achieved during the reduction of PW_{18}. It is worth pointing out that the catalytic process is carried out on a two-electron first wave obtained under mild conditions in the tungsten series. Provisionally, similar observations were made with the first wave of P_2W_{18}, except that this wave features a one-electron process in the medium of pH 1.

While electrocatalysis by PW_{18} is triggered by reduced W centers within the HPA, a multi-step process must be considered in the case of $PW_{17}Cu$. The phenomena will be described in terms of the example of electrocatalytic reduction of nitrate which is not common among substituted HPA's.[16,34] For example, electrocatalytic reduction of nitrate was not expected and was not observed with PW_{18}. In contrast, Figure 3 (B) shows the electrocatalytic reduction of nitrate by $PW_{17}Cu$ at pH 3. The composite nature of the first wave of $PW_{17}Cu$, described above, combines the reduction of Cu^{2+} within the complex and the first reduction of the W centers. Upon addition of increasing amounts of nitrate, a high intensity catalytic wave was observed starting just negative of the peak potential of the combined first wave. For a selected potential in the catalytic wave domain, increasing the concentration of nitrate still enhanced the cathodic wave. In the present case, electrocatalysis of nitrate was triggered by the electrodeposited copper as well as the reduced W centers. The electrocatalysis remains efficient at pH 5. Whatever the pH, the electrocatalysis of nitrate was observed at more negative potentials than for nitrite. Furthermore, in order to observe catalytic activity, larger values of the excess parameter were necessary for the former substrate than for the latter.

Conclusions

First-row transition metal cations were introduced as mono-substituents in the framework of the novel Dawson-

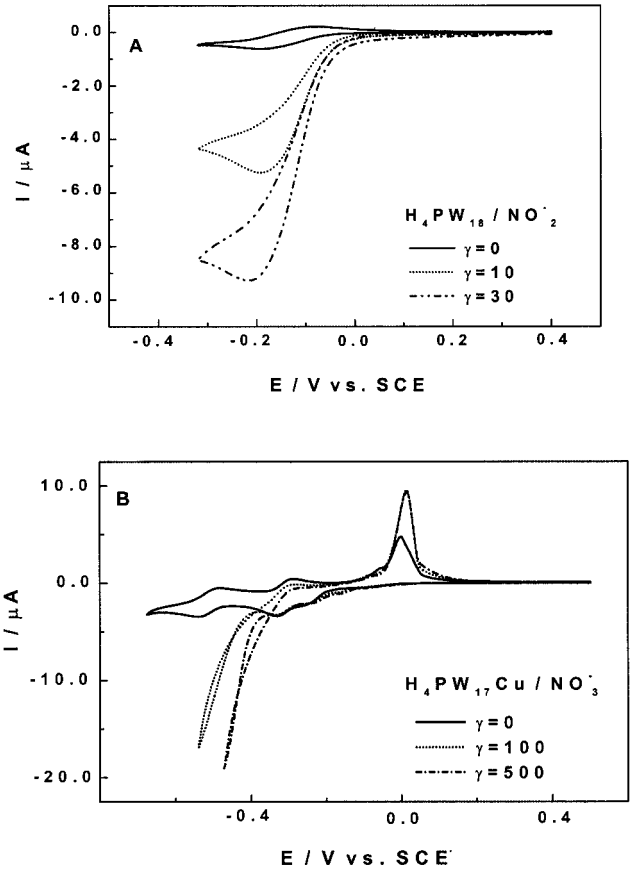


Figure 3. Cyclic voltammograms showing the catalytic activity of PW_{18} towards nitrite and α_2-$PW_{17}Cu$ towards nitrate respectively. Scan rate: 2 $mV \cdot s^{-1}$; working electrode: glassy carbon; reference electrode: SCE; A: Cyclic voltammograms at pH 1 (0.2 M Na_2SO_4 + H_2SO_4) of 2×10^{-4} M PW_{18} in the presence of increasing amounts of nitrite; the excess parameter $\gamma = C_{NO2}^{-}/C_{HPA}$ is indicated in the figure; B: Cyclic voltammograms at pH 3 (0.2 M Na_2SO_4 + H_2SO_4) of 5×10^{-4} M α_2-$PW_{17}Cu$ in the presence of increasing amounts of nitrate; the excess parameter $\gamma = C_{NO3}^{-}/C_{HPA}$ is indicated in the figure

type tungstomonophosphate PW_{18}. During this work, more prolonged heating times than used previously proved helpful in obtaining pure PW_{18} as a starting material. Comparison of the CV properties of PW_{18} and P_2W_{18} as a function of pH shows that the first two W-waves merge in less acidic solution in the former than in the latter complex. This observation leads to the conclusion that the first reduced forms of PW_{18} are more basic than the corresponding forms of P_2W_{18}. The result is interesting in at least two respects: the merging of the W-waves was obtained here through the manipulation of the acid base properties of the molecule by assembling two different building blocks; the association of such "putative" building blocks might constitute an important step in designing polyoxometalates with pre-selected properties. Another aspect of the observed basicity of PW_{18} deserves emphasis i.e. the facile formation of a two-electron first W-wave in mildly acidic media is uncommon in the classical saturated Dawson HPAs and might constitute a favorable first step in electrocatalytic processes that require several electrons in order to be effective. Concerning monosubstituted derivatives, several lines of experimental evidence converge to indicate that the substitution occurs in the α_2 position. Among them, the splitting of the third W redox system in pH 3 media was observed in several substituted derivatives. It deserves particular attention because it confirms that α_2-substituted derivatives were formed. Indeed the extent of splitting also varies smoothly from one derivative to the next, thus suggesting a simple explanation based on small basicity variations for this phenomenon.

Experimental Section

Preparations: All chemicals were of reagent grade and were used as received. The yields of finally isolated pure products ranged constantly from 60 to 95% in all the preparations.

$K_7[H_4PW_{18}O_{62}]\cdot 18H_2O$: The literature method was followed[15] with slight modifications. A sample of $Na_2WO_4\cdot 2H_2O$ (240 g, 0.73 mol) was dissolved in Millipore water (300 mL). The solution was acidified under vigorous stirring by 4 M HCl (160 mL). A mixture of 1 M H_3PO_4 (38 mL) and 4 M HCl (100 mL) was then added. The pH was adjusted to a value slightly less than 2, and the solution was heated to reflux for at least 96 h. After cooling, the solution was treated with solid KCl (100 g). The precipitate was redissolved in H_2O (150 mL) and heated at 80 °C for at least 48 h. After cooling, the clear solution was treated with solid KCl (30 g) to give a fine yellow crystalline powder. $K_7[H_4PW_{18}O_{62}]\cdot 18H_2O$ (4934.2): calcd. K 5.55, P 0.63, W 67.07; found K 5.96, P 0.63, W 66.62.

$K_{11}[H_4PW_{17}O_{61}]\cdot 18H_2O$: A sample of $K_7[H_4PW_{18}O_{62}]\cdot 18H_2O$ (8 g, 1.62 mmol) was dissolved in Millipore water (20 mL) with stirring. To the clear solution, was added a 1 M $KHCO_3$ solution (17 mL) and a white precipitate formed. Stirring was continued for roughly one more hour. The solid was then left to settle and was filtered, washed twice with ethyl alcohol, twice with diethyl ether and was air-dried by suction through a flask with a water pump. $K_{11}[H_4PW_{17}O_{61}]\cdot 18H_2O$ (4890.6): calcd. K 8.76, P 0.63, W 63.67; found K 9.66, P 0.63, W 62.80.

$K_9[H_4Zn(H_2O)PW_{17}O_{61}]\cdot 19H_2O$ (abbreviated as $PW_{17}Zn$): A sample of $Zn(NO_3)_2\cdot 6H_2O$ (0.30 g, ≈ 1 mmol) was dissolved in Millipore water (45 mL) and $K_{11}[H_4PW_{17}O_{61}]\cdot 18H_2O$ (4 g, 0.82 mmol) was added. The mixture was filtered while hot and the clear filtrate left in a beaker. A white crystalline material appeared during cooling. This material was filtered and left to dry in the open air. $K_9[H_4Zn(H_2O)PW_{17}O_{61}]\cdot 19H_2O$ (4913.8): calcd. K 7.16, P 0.63, W 63.61, Zn 1.33; found K 8.88, P 0.62, W 63.54, Zn (1.52). ^{183}W NMR: δ = −98 (2 W), −135 (2 W), −147 (2 W), −176 (2 W), −195 (2 W), −200 (2 W), −205 (2 W), −208 (2 W), −222 (1 W) ppm.

$K_9[H_4Cu(H_2O)PW_{17}O_{61}]\cdot 17H_2O$ (abbreviated as $PW_{17}Cu$): A sample of $Cu(NO_3)_2\cdot 3H_2O$ (0.25 g, ≈ 1 mmol) was dissolved in Millipore water (45 mL) and $K_{11}[H_4PW_{17}O_{61}]\cdot 18H_2O$ (4 g, 0.82 mmol) was added in small portions while heating the mixture on a water bath (≈ 60 °C). After half an hour, the mixture was filtered hot and the green clear filtrate left in a beaker. A pale green crystalline material appeared during cooling. This material was filtered and left to dry in the open air. $K_9[H_4Cu(H_2O)PW_{17}O_{61}]\cdot 17H_2O$ (4875.9): calcd. K 7.22, P 0.64, W 64.10, Cu 1.30; found K 7.11, P 0.62, W 63.42, Cu 1.44.

$K_9[H_4Ni(H_2O)PW_{17}O_{61}]\cdot 20H_2O$ (abbreviated as $PW_{17}Ni$): A sample of $Ni(NO_3)_2\cdot 6H_2O$ (0.30 g, ≈ 1 mmol) was dissolved in Millipore water (45 mL) and $K_{11}[H_4PW_{17}O_{61}]\cdot 18H_2O$ (4 g, 0.82 mmol) was added in small portions while heating the mixture on a water bath (≈ 60 °C). After half an hour, the mixture was filtered hot and the green clear filtrate left in a beaker. A pale green yellow crystalline material appeared during cooling. This material was filtered and left to dry in the open air. $K_9[H_4Ni(H_2O)PW_{17}O_{61}]\cdot 20H_2O$ (4925): calcd. K 7.15, P 0.63, W 63.46, Ni 1.19; found K 7.40, P 0.63, W 64.11, Ni 1.29. W NMR: δ = +468 (2 W), +386 (2 W), −140 (2 W), −164 (2 W), −167 (2 W), −187 (2 W), −245 (1 W) ppm.

$K_9[H_4Co(H_2O)PW_{17}O_{61}]\cdot 20H_2O$ (abbreviated as $PW_{17}Co$): A sample of $Co(NO_3)_2\cdot 6H_2O$ (0.30 g, ≈ 1 mmol) was dissolved in Millipore water (45 mL) and $K_{11}[H_4PW_{17}O_{61}]\cdot 18H_2O$ (4 g, 0.82 mmol) was added in small portions while heating the mixture on a water bath (≈ 60 °C). After half an hour, the mixture was filtered hot and the clear dark red filtrate left in a beaker. A "terre claire'' crystalline material appeared during cooling. This material was filtered and left to dry in the open air. $K_9[H_4Co(H_2O)PW_{17}O_{61}]\cdot 20H_2O$ (4925.3): calcd. K 7.14, P 0.63, W 63.46, Co 1.20; found K 7.39, P 0.65, W 63.94, Co 1.34.

$K_8[H_4Fe(H_2O)PW_{17}O_{61}]\cdot 19H_2O$ (abbreviated as $PW_{17}Fe$): A sample of $Fe(NO_3)_3\cdot 9H_2O$ (0.40 g, ≈ 1 mmol) was dissolved in Millipore water (45 mL) and $K_{11}[H_4PW_{17}O_{61}]\cdot 18H_2O$ (4 gm, 0.82 mmol) was added in small portions while heating the mixture on a water bath (≈ 60 °C). After half an hour, the mixture was filtered hot and the yellow clear filtrate transferred to a beaker. Upon treatment of this filtrate with KCl (10 g), a pale yellow crystalline material appeared. This material was filtered and left to dry in the open air. $K_8[H_4Fe(H_2O)PW_{17}O_{61}]\cdot 19H_2O$ (4865): calcd. K 6.43, P 0.64, W 64.24, Fe 1.15; found K 6.79, P 0.64, W 63.96, Fe 1.34.

$K_9[H_4Mn(H_2O)PW_{17}O_{61}]\cdot 20H_2O$ (abbreviated as $PW_{17}Mn$): A sample of $Mn(NO_3)_2\cdot 4H_2O$ (0.25 g, ≈ 1 mmol) was dissolved in Millipore water (45 mL) and $K_{11}[H_4PW_{17}O_{61}]\cdot 18H_2O$ (4 g, 0.82 mmol) was added in small portions while heating the mixture on a water bath (≈ 60 °C). After half an hour, the mixture was filtered hot and the dark beige clear filtrate left in a beaker. A chestnut colored crystalline material appeared during cooling. This material was filtered and left to dry in the open air. $K_9[H_4Mn(H_2O)PW_{17}O_{61}]\cdot 20H_2O$ (4921.3): calcd. K 7.15, P 0.63, W 63.51, Mn 1.12; found K 7.22, P 0.62, W 65.90, Mn 1.08.

$K_9[H_4PV^{(4+)}W_{17}O_{62}]\cdot 18H_2O$ [abbreviated as $PW_{17}V^{(4+)}$]: A sample of $VOSO_4\cdot 5H_2O$ (0.42 g, 1.7 mmol) was dissolved in Millipore water (90 mL) and acidified with 4 M HCl (8.5 mL). $K_{11}[H_4PW_{17}O_{61}].18H_2O$ (8 g, 1.64 mmol) was then added in small portions with stirring. The black solution was stirred for roughly half an hour and then, treated with KCl (10 g). The grey black precipitate that resulted was recrystallized from a minimum of acidified water (HCl solution pH < 1). $K_9[H_4PV^{(4+)}W_{17}O_{62}]\cdot 18H_2O$ (4879.3): calcd. K 7.21, P 0.64, W 64.06, V 1.04; found K 7.13, P 0.62, W 64.7, V 1.05.

$K_8[H_4PV^{(5+)}W_{17}O_{62}]\cdot 18H_2O$ [abbreviated as $PW_{17}V^{(5+)}$]: To Millipore water (90 mL) was added a solution of 0.5 M HVO_4^{2-} (3.5 mL) with 4 M HCl (8.5 mL). $K_{11}[H_4PW_{17}O_{61}]\cdot 18H_2O$ (8 g, 1.64 mmol) was then added in small portions whilst stirring. The yellow solution was stirred for roughly half an hour, filtered and then treated with KCl (10 g). The yellow precipitate that resulted was recrystallized from a minimum of acidified water (HCl solution pH < 1). $K_8[H_4PV^{(5+)}W_{17}O_{62}]\cdot 18H_2O$ (4840.2): calcd. K 6.46, P 0.64, W 64.57, V 1.05; found K 5.95, P 0.63, W 65.10, V 0.95.

$K_7[H_4PMoW_{17}O_{62}]\cdot 18H_2O$ (abbreviated as $PW_{17}Mo$): A sample of $Na_2MoO_4\cdot 2H_2O$ (0.40 g, 1.7 mmol) was dissolved in Millipore water (90 mL) and acidified with 4 M HCl (8.5 mL). $K_{11}[H_4PW_{17}O_{61}]\cdot 18H_2O$ (8 g, 1.64 mmol) was then added in small portions with stirring. The clear yellow solution was stirred for roughly half an hour and then filtered and treated with KCl (10 g). The fine yellow precipitate that resulted was recrystallized from a minimum of acidified water (HCl solution pH < 1). $K_7[H_4PMoW_{17}O_{62}]\cdot 18H_2O$ (4846.1): calcd. K 5.65, P 0.64, W 64.49, Mo 1.98; found K 5.76, P 0.66, W 64.51, Mo 2.01.

General Methods and Materials: Pure water was used throughout and was obtained by passing through an RiOs 8 unit followed by a Millipore-Q Academic purification set. All reagents were of high-purity grade and were used as purchased. Elemental analyses were performed by Kanti Labs Ltd. in Mississauga, Canada. The IR spectra were recorded in KBr pellets with a Perkin−Elmer Spectrum One FT-IR spectrophotometer. The UV/Vis spectra were recorded with a Perkin−Elmer Lambda 19 spectrophotometer on 2.5 × 10^{-5} M solutions of the relevant polyanion. Matched 1.000-cm optical path quartz cuvettes were used. The compositions of the various media were as follows: for pH 0.33: 0.5 M H_2SO_4; for pH 1 to 3: 0.2 M Na_2SO_4 + H_2SO_4; for pH 4 and 5: 0.4 M CH_3COONa + CH_3COOH; for pH 6 and 7: 0.4 M NaH_2PO_4 + NaOH.

Electrochemical Experiments: The same media used for UV/visible spectroscopy were also used for electrochemistry except that the polyanion concentration was 5 × 10^{-4} M. All cyclic voltammograms were recorded at a scan rate of 10 mV·s^{-1} unless otherwise stated.

The solutions were de-oxygenated thoroughly for at least 30 min with pure argon and kept under a positive pressure of this gas during the experiments. The source, mounting and polishing of the glassy carbon electrodes (GC, Tokai, Japan) has been described.[36] The glassy carbon samples had a diameter of 3 mm. The electrochemical set-up was an EG & G 273 A system controlled by a PC with M270 software. Potentials are quoted relative to the saturated calomel electrode (SCE). The counter electrode was a platinum gauze of large surface area. All experiments were performed at room temperature.

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