Investigation of Multi-Nickel-Substituted Tungstophosphates and Their Stability and Electrocatalytic Properties in Aqueous Media

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Several sandwich-type polyoxometallates based on the trivacant $[PW_9O_{34}]^{9-}$ fragment with different Ni nuclearities were selected. Their stability and redox behaviour in aqueous media were evaluated by UV/Vis spectroscopy and cyclic voltammetry as a function of pH with the aim of finding the conditions under which these compounds could be suitable candidates for electrocatalytic processes. Two polyoxoanions — $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$ and (to a lesser extent) $[Ni_4Mn_2P_3W_{24}O_{94}]^{17-}$ — were found to be stable over a wide pH domain, while $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ requires the pH to be greater than 4 for its stability. The other derivatives are only suitable for solid-state studies. The stable polyoxoanions were tested for their activity in the electrocatalytic reduction of nitrate. The results suggest unambiguously that an increase in the number of Ni centres within these sandwich-type polyanions has a beneficial effect on the electrocatalytic process.

Introduction

Polyoxometallate ions are gaining widespread attention owing to their possible applications in catalysis, electrocatalysis, medicine, materials science, photochemistry, analytical chemistry and magnetochemistry.[1−5] The impetus was partly triggered by the pioneering remark by Baker[6] that monosubstituted heteropolyanions can be considered as the analogues of metallated porphyrins, and used in catalytic processes with the advantage, over their organic counterparts, of thermal stability, robustness and inertness toward oxidizing environments. With regard to their electrochemistry and, correspondingly, their use in electrocatalysis, we are currently studying the parameters, which eventually in conjunction with pH effects, could improve the catalytic properties of heteropolyanions (HPAs). The incentive behind this search is to trigger those energetically favourable cathodic processes that require several electrons for their effectiveness by reduced HPAs.[7−11] Among several possibilities, substitution effects on the polyoxometallates are considered with attention: the location of the metal atom in the framework; the nature and number of substituents are expected to influence more or less the interactions between the electroactive centres within the HPA molecule.

The present paper is devoted to a study of the effects of the accumulation of nickel centres in HPAs on their stability and electrocatalytic behaviour. Several reasons have dictated this choice. Recently, we have demonstrated, for the first time to the best of our knowledge, that Cu^{2+}- or Ni^{2+}-containing HPAs are the only monosubstituted polyoxoanions to be effective in the electrocatalytic reduction of nitrate in mildly acidic aqueous media.[12] Also, we have shown that the accumulation of Cu^{2+} centres within HPAs is useful in enhancing the catalytic properties of the polyoxometallate.[13] Specifically, a comparison of the catalytic activity of $\alpha\beta\beta\alpha$-$(Cu^{II}OH_2)_2Cu^{II}{}_2(H_4AsW_{15}O_{56})_2{}^{18-}$ based on the novel Wells−Dawson complex $H_4AsW_{18}O_{62}{}^{7-}$ [14] with those of the analogous monosubstituted Cu-HPAs demonstrated a favourable effect of the accumulation of Cu centres in the electrocatalytic reduction of nitrate; hence the idea that multi-nickel derivatives might be interesting in this respect. A large family of Ni-substituted tungstophosphates with a sandwich-type structure is known[15] and some other structures exist as well.[16−19] Novel polyoxoanions are often difficult to obtain owing to the fact that the mechanism of formation is far from well understood. Numerous sandwich-type compounds have been synthesised and characterised since the pioneering work of Weakley et al.,[20] but the nickel-containing Keggin derivative $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ has been isolated only recently under severely controlled experimental conditions to avoid or minimize other side products.[18] The synthesis con-

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ditions suggest strongly that some species might be stable only in narrow pH domains in solution. Our choice of (PW_9O_{34})-based derivatives allows us to study several species with different nuclearities. However, there are also complications that have been reviewed recently, for example the existence of multiple isomers and their transformation pathways.[21] It has been demonstrated recently that the triferric sandwich-type complex $[Fe_2(FeOH_2)(NaOH_2)(P_2W_{15}O_{56})_2]^{14-}$ is significantly more stable than its diferric and tetraferric analogues.[22] The unique coordination environment of its single external iron site and the incorporated sodium ion most likely play an important, stabilizing role. This observation suggests that the nuclearity and the geometry of the incorporated transition metal centres might also influence the stability of other sandwich-type polyanions. Finally, the aforementioned catalytic activity of a monosubstituted Ni-HPA towards nitrate[12] and the diversity of multi-nickel HPAs available at present justify the search for a unified view of their behaviour in aqueous media.

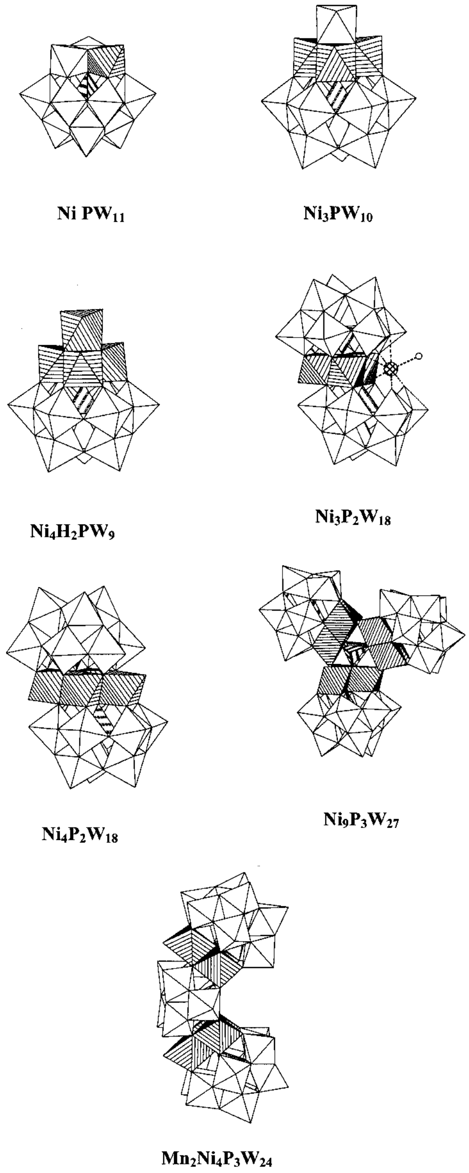
Results and Discussion

Selection of Relevant Heteropolyanions

All polyanions studied here are derived from the Keggin fragment $[PW_9O_{34}]^{9-}$. The trilacunary $[A,\beta\text{-}PW_9O_{34}]^{9-}$ (A,β-PW_9) and the monolacunary $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ (PW_{11}) were synthesised according to literature procedures.[23,24] Preparation of $[B,\alpha\text{-}PW_9O_{34}]^{9-}$ (B,α-PW_9) was accomplished from A,β-PW_9 by heating according to the procedure first reported by Finke and co-workers[25] and then by Domaille.[24] The solution behaviour of the various isomers of the mono- and trilacunary Keggin species can be helpful for understanding possible transformation pathways of the Ni-containing compounds of interest. The following polyoxoanions were synthesised by literature methods and thoroughly characterised as pure samples. The mixed nickel/manganese-substituted $[Ni_4Mn_2P_3W_{24}O_{94}]^{17-}$ constitutes a novel polyanion:[27] $[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]^{2-}$ ($Ni_4H_2PW_9$);[19] $[Ni_3(H_2O)_3PW_{10}O_{39}H_2O]^{7-}$ (Ni_3PW_{10});[18] $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ ($Ni_4P_2W_{18}$);[18] $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ ($Ni_9P_3W_{27}$);[18] $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$ ($Ni_3P_2W_{18}$);[15,26] $[Ni_4Mn_2P_3W_{24}O_{94}]^{17-}$ ($Mn_2Ni_4P_3W_{24}$).[27] Also $[Ni_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ ($Ni_4P_4W_{30}$)[28] will be considered for a brief comparison. The structures of $Ni_4H_2PW_9$, Ni_3PW_{10}, $Ni_4P_2W_{18}$, $Ni_9P_3W_{27}$, $Ni_3P_2W_{18}$, $Mn_2Ni_4P_3W_{24}$, and $Ni_4P_4W_{30}$ are shown in Scheme 1.

Cyclic Voltammetry (CV) Study of Selected Multi-Nickel HPAs in pH 3 Sulfate Medium

The cyclic voltammograms of the various electroactive species were monitored as a function of time. Therefore, their recording was started shortly after addition of the relevant HPA to the previously deaerated supporting electrolyte. The choice of CV in this issue stems from our primary interest to detect stable electroactive species that constitute the sole useful candidates for electrocatalysis. Three main classes will be discussed: two compounds — $Ni_3P_2W_{18}$ and $Mn_2Ni_4P_3W_{24}$ — are stable over a wide pH domain; $Ni_4P_2W_{18}$ requires pH values higher than 4 for its stability; no pH domain could be found for an appreciable stability of $Ni_4H_2PW_9$, Ni_3PW_{10} and $Ni_9P_3W_{27}$.



Scheme 1. Structures of polyanions $Ni_4H_2PW_9$, Ni_3PW_{10}, $Ni_4P_2W_{18}$, $Ni_9P_3W_{27}$, $Ni_3P_2W_{18}$, $Mn_2Ni_4P_3W_{24}$, and $Ni_4P_4W_{30}$

$[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]^{2-}$ ($Ni_4H_2PW_9$)

The very first voltanmmogram of $Ni_4H_2PW_9$ shows a composite reduction wave located between −0.600 V and

−0.900 V vs. SCE. (Figure 1A). The proton reduction wave which followed this immediately is not shown. Roughly 10 min after the addition of $Ni_4H_2PW_9$ to the solution a modification of the voltammetric pattern was observed, characterised by two main features: (i) the whole voltammogram experiences a shift to positive potential; (ii) the two waves become better and better defined and separated. For the sake of clarity, only the "initial" cyclic voltammogram and those recorded after 30 min and 4 h are shown in Figure 1A. The two waves are attributed to the reduction of W^{VI} centres. This hypothesis was confirmed by controlled potential electrolysis. The cyclic voltammograms recorded after more than 4 h are nearly identical to that recorded after 4 h, except for a small increase of the second wave at the expense of the first one. It should be noted that the first wave remains slightly composite. The next issue concerns the nature of the new product(s). In particular, the possibility that one or several Ni^{2+} ions are lost from the new complexes should be considered. As a matter of fact, the present transformations resemble those of B,α-PW_9. In the supporting electrolyte used here, it was checked that B,α-PW_9 is rapidly converted into a species whose cyclic voltammogram is identical to that of PW_{11}, in agreement with the literature.[21] In contrast, Figure 1B indicates a difference of 58 mV between the potentials of the first reduction peaks of the transformation products of $Ni_4H_2PW_9$ and B,α-PW_9, the former complex being the more negative of the two. Finally, Figure 1C shows that the new complex from $Ni_4H_2PW_9$ has a cyclic voltammogram very close to that of $[PW_{11}O_{39}Ni(H_2O)]^{5-}$ ($PW_{11}Ni$).

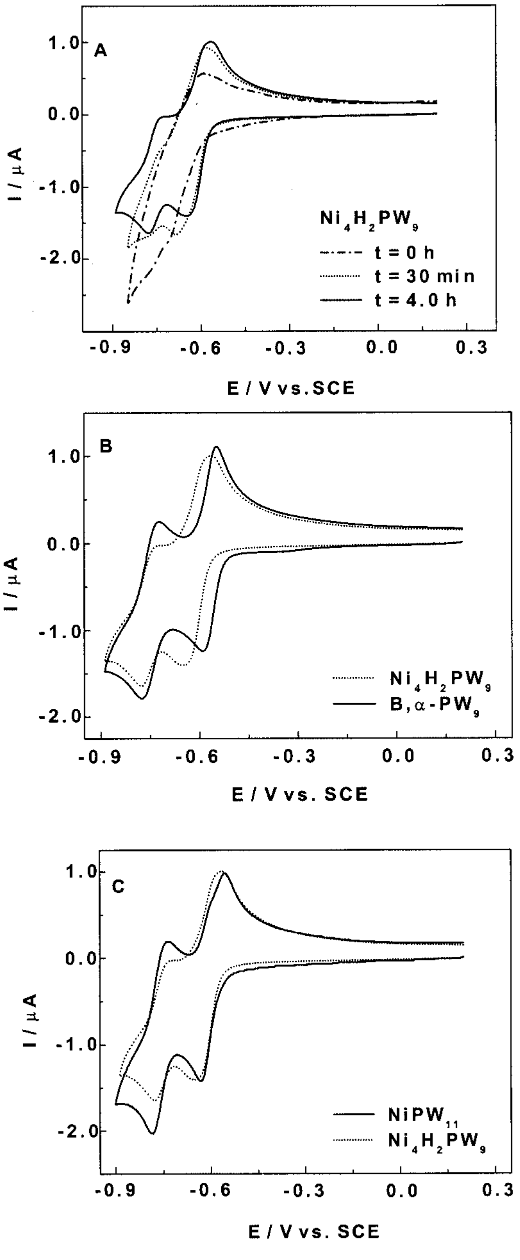


Figure 1. A: Cyclic voltammetry monitoring of the transformations of 2×10^{-4} M $Ni_4H_2PW_9$ as a function of time; medium 0.2 M Na_2SO_4 + H_2SO_4 (pH = 3); scan rate: 10 $mV{\cdot}s^{-1}$; working electrode: polished glassy carbon; reference electrode: SCE; B: superimposition of the final cyclic voltammetry patterns for $Ni_4H_2PW_9$ and B,α-PW_9; the experimental conditions are the same as in A; C:) superimposition of the final cyclic voltammetry patterns for $Ni_4H_2PW_9$ and $NiPW_{11}$; the experimental conditions are the same as in A; for further details see text

Comparison with Other Multi-Nickel Derivatives

The "initial" cyclic voltammogram of Ni_3PW_{10} is different from that of $Ni_4H_2PW_9$; its conversion ends up in $NiPW_{11}$ in roughly 5 h (Figure 2A). The trimeric $Ni_9P_3W_{27}$ is also unstable in the pH 3 medium (0.2 M Na_2SO_4 + H_2SO_4) and its conversion is relatively fast. The first-wave current increases at the expense of the second one, which has a larger current intensity than the first wave and which is composite. Figure 2B shows, in superimposition, the "initial" cyclic voltammogram of $Ni_9P_3W_{27}$ and that recorded after 1.5 h. A longer duration does not bring about substantial changes in this cyclic voltammogram. The final pattern is different from that of $NiPW_{11}$, except for the first wave, which shows a peak located at the same potential in the two systems. However, no conclusion can be drawn at this stage (vide infra UV/Vis studies). For $Ni_4P_2W_{18}$, the "initial" cyclic voltammogram comprises a first composite wave, followed by a second wave close to the reduction of protons (Figure 2C). This pattern does not resemble any of the preceding ones. However, a very slow and gradual transformation of the cyclic voltammogram is observed as a function of time; in particular, the current intensity of the second wave decreases significantly, while the wave itself becomes better and better defined, with a gradual move of its reduction peak potential in the negative direction. In Figure 2C the "initial" cyclic voltammogram and those recorded after 3 h and 9 h are compared. Even after 9 h of transformation of $Ni_4P_2W_{18}$ the first wave remains slightly composite, which could indicate the presence of a mixture of products. No attempt was made to identify these other products but it is likely that the mixture contains $Ni_3P_2W_{18}$. This assumption is supported by Figure 2D, which compares the last cyclic voltammogram recorded with $Ni_4P_2W_{18}$ to that of $Ni_3P_2W_{18}$. Such a possibility is reminiscent of the aforementioned higher stability of the triferric

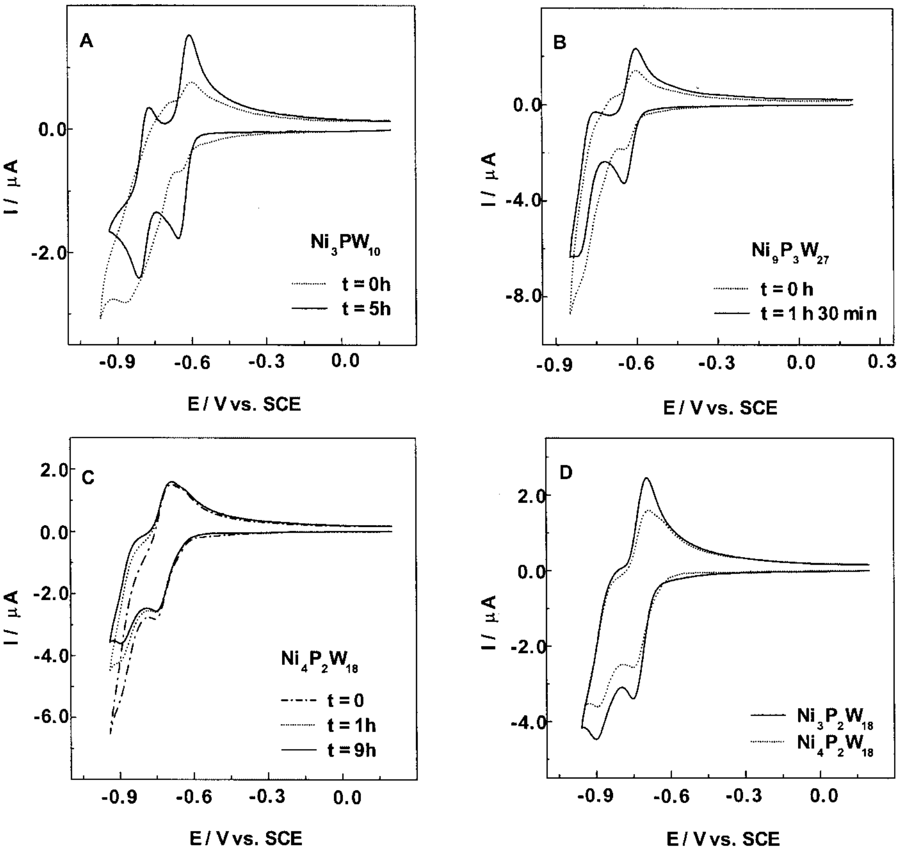


Figure 2. A: Comparison of the "initial" and "final" cyclic voltammograms of 2×10^{-4} M Ni_3PW_{10}; medium 0.2 M Na_2SO_4 + H_2SO_4 (pH = 3); scan rate: 10 mV·s^{-1}; working electrode: polished glassy carbon; reference electrode: SCE; B: superimposition of the "initial" cyclic voltammogram of $Ni_9P_3W_{27}$ and that recorded after 1.5 h; the experimental conditions are the same as in A; C: cyclic voltammetry monitoring of the transformations of 2×10^{-4} M $Ni_4P_2W_{18}$ as a function of time; the experimental conditions are the same as in A; for further details see text; D: superimposition of the "final" cyclic voltammogram of $Ni_4P_2W_{18}$ with that of the stable $Ni_3P_2W_{18}$; the experimental conditions are the same as in A

sandwich complex $[Fe_2(FeOH_2)(NaOH_2)(P_2W_{15}O_{56})_2]^{14-}$ than its diferric and tetraferric analogues.[22] These complexes show remarkable differences in their junction connectivities. The tetrairon-substituted $[Fe_2(FeOH_2)_2(P_2W_{15}O_{56})_2]^{12-}$ has two β-junctions, the diiron-substituted $[Fe_2(NaOH_2)_2(P_2W_{15}O_{56})_2]^{16-}$ has two α-junctions and the triiron-substituted $[Fe_2(FeOH_2)(NaOH_2)(P_2W_{15}O_{56})_2]^{14-}$ has one β-junction and one α-junction.[22,29−31] The junction connectivity of the Keggin-based $Ni_3P_2W_{18}$ is ααβα[15] and therefore in complete agreement with the triiron Wells−Dawson derivative of Hill et al.[22] The unique coordination environment of the single external Ni site and the incorporated sodium ion seem to enhance the stability of the trinickel species, in analogy with the triiron derivative. Provisionally, it is worth recalling that $Ni_3P_2W_{18}$ is stable in the present medium, as reported previously.[15,26]

In summary, all of the above Ni-substituted tungstophosphates can be distinguished from each other, provided their very first cyclic voltammograms are recorded shortly after dissolution in the supporting electrolyte. With the exception of $Ni_3P_2W_{18}$ and $Mn_2Ni_4P_3W_{24}$ all polyoxoanions studied here are unstable upon standing in the pH 3 sulfate medium.[15,27] The slow transformation of $Ni_4P_2W_{18}$ in this pH 3 medium is also worth noting.

Influence of Counteranions

In the case of $Ni_4H_2PW_9$ it was checked that replacement of the countercation Na^+ by Li^+ in the supporting electrolyte has a negligible influence on the observed electrochemical processes. Therefore, in the following study of the influence of the counteranion and the pH of the electrolyte we selected the sodium counterion in all cases. This study was performed with $Ni_4H_2PW_9$ as a representative polyoxometallate. The choice of anions was restricted to those classically used in the electrochemistry of HPAs, namely ClO_4^-, $H_2PO_4^-$, CH_3COO^- and Cl^-; SO_4^{2-} has already been studied above. For easier comparisons, all the experiments were carried out at pH = 3 with 0.4 M Na^+.

The cyclic voltammogram of $Ni_4H_2PW_9$ also changes as a function of time for $H_2PO_4^-$ and CH_3COO^-, resulting in a mixture of electroactive products, and $NiPW_{11}$ appears to be the main product. To illustrate this conclusion, Figure 3A shows in superimposition the so-called "final state" cyclic voltammograms recorded in the presence of these two

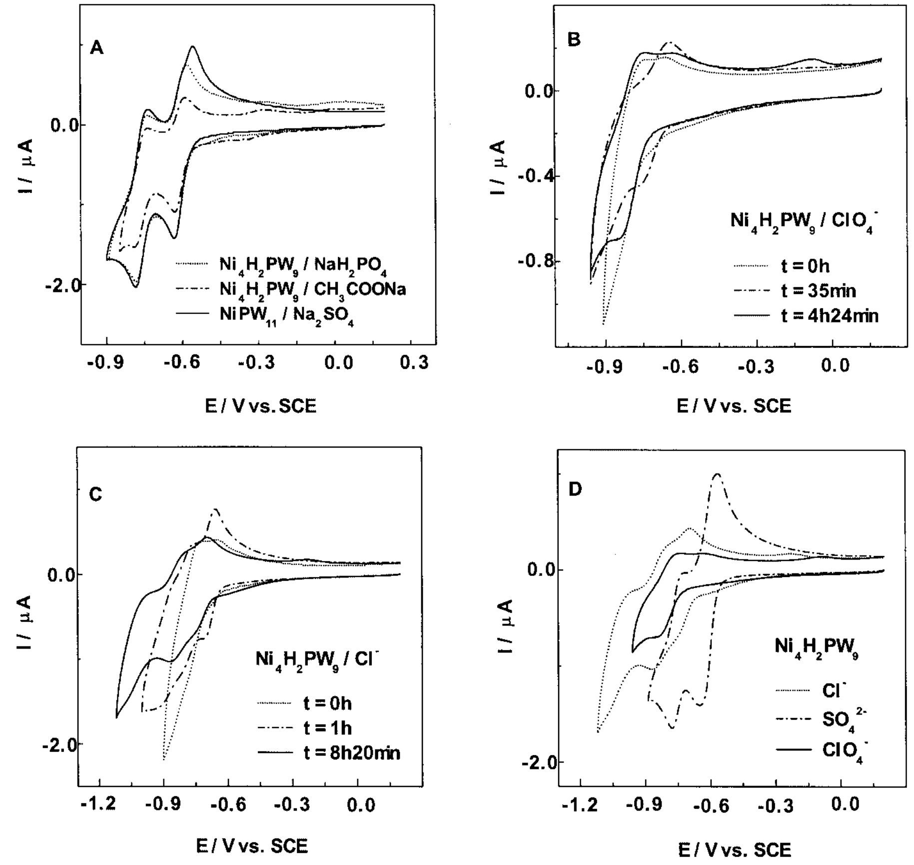


Figure 3. A: Superimposition of the so-called "final state" cyclic voltammograms recorded for 2×10^{-4} M $Ni_4H_2PW_9$ in pH 3 phosphate (0.4 M NaH_2PO_4 + H_3PO_4) and acetate (0.4 M CH_3COONa + CH_3COOH) media (pH = 3), respectively, and the cyclic voltammogram of $NiPW_{11}$ in sulfate medium (pH = 3); scan rate: 10 mV·s^{-1}; working electrode: polished glassy carbon; reference electrode: SCE; B: cyclic voltammetry monitoring of the transformations of 2×10^{-4} M $Ni_4H_2PW_9$ as a function of time in the presence of 0.4 M $NaClO_4$ + $HClO_4$ (pH = 3); the experimental conditions are the same as in A; C: cyclic voltammetry monitoring of the transformations of 2×10^{-4} M $Ni_4H_2PW_9$ as a function of time in the presence of 0.4 M NaCl + HCl (pH = 3); the experimental conditions are the same as in A; D: superimposition of the "final" cyclic voltammograms of 2×10^{-4} M $Ni_4H_2PW_9$ observed in the presence of sulfate, chloride and perchlorate anions (pH = 3), respectively; the experimental conditions are the same as in A; for further details see text

anions and the cyclic voltammogram of $NiPW_{11}$ in sulfate medium. The transformation yield into $NiPW_{11}$ is smaller with CH_3COO^-. The presence of this anion induces an important formation of secondary species, as could be detected by their electroactivity between 0 and −0.4 V. It should also be noted that these "final states" were obtained after 2 h and 3 h for CH_3COO^- and $H_2PO_4^-$, respectively.

More intricate observations are made for $Ni_4H_2PW_9$ in the presence of ClO_4^- or Cl^- as illustrated in Figure 3B and C, respectively. These figures represent the "initial" cyclic voltammogram in superimposition with two other selected states; as a matter of fact, even after more than 6.5 h of standing, no "final state" could be reached. It is clear, however, that several electroactive species are formed irrespective of which of the two anions is present. Figure 3D compares the cyclic voltammograms recorded after 6.5 h in the presence of ClO_4^- and Cl^- with that recorded as a "final state" in sulfate medium. The remarkable influence of the two counteranions is obvious. The more marked effect is seen in the presence of ClO_4^- for which a small composite wave is observed, followed by the proton reduction wave (not shown).

In short, $Ni_4H_2PW_9$ is converted into respectable amounts of $NiPW_{11}$ in the presence of SO_4^{2-}, $H_2PO_4^-$ and CH_3COO^-. The transformation yield is similar for SO_4^{2-} and $H_2PO_4^-$, but is smaller for CH_3COO^-. No attempt was made to identify the secondary products. In contrast to this first group of anions, more complex observations are made in the presence of ClO_4^- and Cl^-; in their presence, $Ni_4H_2PW_9$ is gradually converted into various products with decreased overall electroactivity. This trend is representative of the main observations in the series of unstable multi-nickel compounds, except for $Ni_4P_2W_{18}$. The behaviour of the latter is illustrated in Figure 4, where the voltammograms obtained in the presence of SO_4^{2-}, ClO_4^- and Cl^- are compared. Unlike the other compounds of the series, no new electroactive species is detected in the explored potential domain. The two well-behaved waves recorded in the pH 3 sulfate medium undergo a general move in the negative potential direction, with a slight distortion of the second wave. Such behaviour has been observed previously for a large selection of stable Keggin and Wells−Dawson HPAs and has been ascribed to the buffer capacity of the electrolytes as a function of the coun-

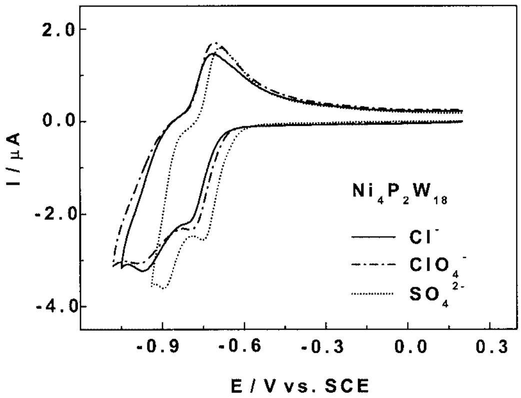


Figure 4. Superimposition of the “final” cyclic voltammograms of 2×10^{-4} M $Ni_4P_2W_{18}$ observed in the presence of sulfate, chloride and perchlorate anions (pH = 3), respectively; scan rate: 10 mV·s^{-1}; working electrode: polished glassy carbon; reference electrode: SCE; for further details see text

teranion present in the medium.[32] Again, the clear observation of this phenomenon indicates a relatively large stability of $Ni_4P_2W_{18}$ in the pH 3 media.

UV/Vis Investigations

This study was performed as a function of pH. $Ni_4H_2PW_9$ was selected as a representative example showing the main UV/Vis features repeatedly encountered with all the other compounds. Only the observations at pH = 3 (0.2 M Na_2SO_4 + H_2SO_4) are shown. Typically, a 4.3×10^{-5} M solution of $Ni_4H_2PW_9$ in a 1.00-cm optical-path quartz cuvette was monitored as a function of time by UV/Vis spectroscopy between 380 and 200 nm. Figure 5A shows the evolution of the spectrum over 10 h. The general variation trends of the absorbance are sketched by arrows and indicate a transformation of the complex. The very first spectrum recorded does not go through the apparent isosbestic point in Figure 5A. It was checked that the variation of absorbance remains negligible from 10 h to 24 h, thus indicating that a complex stable in the pH 3 medium is already obtained. Figure 5B shows the initial spectrum of $Ni_4H_2PW_9$ and the final spectrum recorded after 24 h of standing. This last spectrum peaks at 252 nm. As it was checked previously that B,α-PW_9 is rapidly converted, in the supporting electrolyte used here, into a species whose cyclic voltammogram is identical to that of PW_{11}, we wondered whether the final complex from $Ni_4H_2PW_9$ could be the lacunary species PW_{11}, the UV/Vis spectrum of which peaks at 248 nm. However, this peak is preceded by a shoulder located between 280 and 260 nm, which rules out the presence of this lacunary complex. In contrast, the spectrum of an authentic sample of $NiPW_{11}$, which is stable in the pH 3 medium, peaks at 252 nm and has exactly the same shape as the spectrum recorded after 24 h shown in Figure 5B. These observations are in complete agreement with the conclusions from the CV investigations.

In short, the initial spectrum observed with each of the multi-nickel-substituted tungstophosphates of this work was clearly different from those of $NiPW_{11}$ or $[PW_{11}O_{39}]^{7-}$. Long-term UV/Vis spectra and CV experiments on solutions aged for appropriate durations converge to indicate that the transformations of $Ni_4H_2PW_9$ and Ni_3PW_{10} end up, at least partly, in $NiPW_{11}$. Also, UV/Vis spectroscopy confirms the presence of $NiPW_{11}$ as a decomposition product of $Ni_9P_3W_{27}$, a conclusion already suggested by CV experiments.

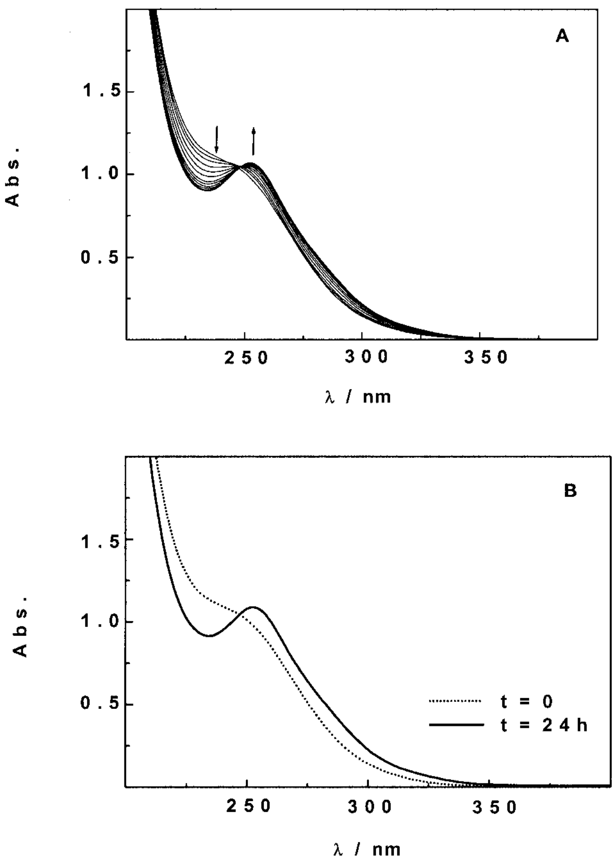


Figure 5. UV/Vis spectra of 4.3×10^{-5} M $Ni_4H_2PW_9$, recorded in a pH 3 medium (0.2 M Na_2SO_4 + H_2SO_4) with a 1.00-cm optical-path quartz cuvette; A: evolution of the spectrum with time; the arrows indicate the direction of variation of the absorbance with time; B: the initial spectrum and that recorded after 24 h of standing; for further details see text

Influence of pH

The pH influence was studied for all selected HPAs All solutions, except for the 0.5 M H_2SO_4 (pH = 0.33) solution, contained Na^+ at a concentration of 0.4 M as the major cation, in order to avoid any possibility of cation effect. The compositions of these media are indicated in the Exp. Sect.

Unstable HPAs

The polyanions $Ni_4H_2PW_9$, Ni_3PW_{10}, and $Ni_9P_3W_{27}$ are unstable at all pH values studied in this work. Occasionally, identification of a major transformation product by CV was achieved.

Media of pH ≤ 3

In 0.5 M H_2SO_4 (pH = 0.33) $Ni_4H_2PW_9$ is not stable and precipitates gradually. In pH 1 and 2 media (0.2 M Na_2SO_4 + H_2SO_4), its current intensity for the whole pattern decreases steadily, without any other significant modifications of the CV characteristics, nor any appearance of significant new waves. The decomposition products are probably not electroactive in these two media. The decomposition is noted to be faster the higher the proton concentration. Also, the decompositions of Ni_3PW_{10} and $Ni_9P_3W_{27}$ are so fast at pH = 2 that further studies at lower pH were not carried out. For instance, CV monitoring of the transformation of Ni_3PW_{10} shows its concentration to decrease by a factor of two in less than 2 h; no new wave was observed, which indicates that the decomposition products do not show any electrochemical activity in this medium. In contrast, the decomposition of $Ni_9P_3W_{27}$ is characterised by several new waves indicating the presence of various electroactive species.

Media of pH ≥ 3

In pH 4 or 5 buffer media $Ni_4H_2PW_9$, Ni_3PW_{10} and $Ni_9P_3W_{27}$ are converted into $PW_{11}Ni$ as the major product, with Ni_3PW_{10} being by far the most unstable. At pH = 6, only $Ni_4H_2PW_9$ is slowly converted (7 h) into $NiPW_{11}$ as the major product. Compounds resulting from decomposition of Ni_3PW_{10} and $Ni_9P_3W_{27}$ have cyclic voltammograms with characteristics close to those of $NiPW_{11}$; these cyclic voltammograms might feature isomers of $NiPW_{11}$. At pH = 7, the three complexes and $NiPW_{11}$ exhibit ill-defined cyclic voltammograms, with a steady decrease in current and no new waves appearing.

The preceding sections have revealed that $Ni_4P_2W_{18}$ must be considered as a special case among the series of unstable multi-nickel species. Figure 6 illustrates the evolution of the cyclic voltammograms of $Ni_4P_2W_{18}$ as a function of pH. As expected, this polyanion behaves differently from the other three unstable HPAs as a function of pH variation. The transformation at pH < 3 leads to the same (not fully identified) product as observed in the pH 3 medium. The only difference is the faster kinetics at lower pH. The steady decrease of the transformation kinetics with increasing pH values could explain why $Ni_4P_2W_{18}$ is stable at pH > 4. The tendency for separation of waves with decreasing pH is not unusual in polyoxometallate electrochemistry.[33] Anyhow, despite the limited pH stability domain for $Ni_4P_2W_{18}$, the behaviour of this polyanion is distinctly more favourable than that of the Wells−Dawson analogue $[Ni_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ ($Ni_4P_4W_{30}$) described by Ruhlmann and co-workers, for which slow degradation was observed during any titration between pH = 1 and 6.[28]

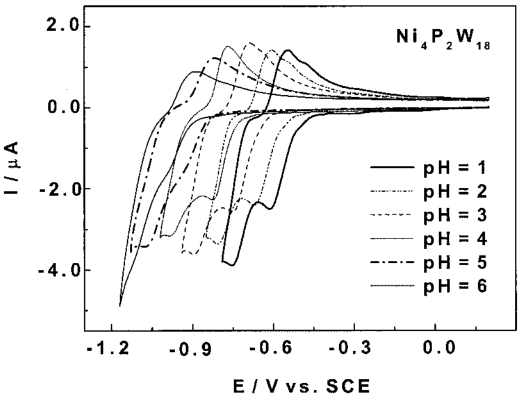


Figure 6. Superimposition of the "final" cyclic voltammograms of 2×10^{-4} M $Ni_4P_2W_{18}$ observed as a function of pH; scan rate: 10 mV·s^{-1}; working electrode: polished glassy carbon; reference electrode: SCE; for further details see text

Stable Multi-Nickel HPAs: Preliminary Evaluation of Electrocatalytic Processes

The representatives of this group are $Ni_3P_2W_{18}$ and $Mn_2Ni_4P_3W_{24}$, to which $Ni_4P_2W_{18}$ can be added at pH > 4. The electrochemistry of the two "fully" stable species at pH = 3 and 5 has been described in detail previously.[15,27] However, in order to envision electrocatalytic applications we decided to investigate the stability and redox behaviour of these polyanions from pH = 0 to 7 by UV/Vis spectroscopy and CV. The stability conclusions were deduced from the comparison of the UV/Vis spectra run on the freshly prepared solution and on the same solution after standing for 24 h. This duration is much longer than necessary for an electrochemical characterisation, but was considered useful to envision electrocatalytic applications. The results indicate that $Ni_3P_2W_{18}$ is very stable from pH = 1 to 6. The stability domain of $Mn_2Ni_4P_3W_{24}$ ranges from pH = 2 to 6. However, even at pH = 7 its decomposition is not very fast and reaches only 34% of the starting complex after 24 h. The characteristics of the W centres within the complexes were monitored by cyclic voltammetry as a function of time and pH. The results confirm the stability of the two HPAs. In agreement with previous observations at pH = 3 and 5,[15,27] the redox behaviour of the W centres is pH-dependent. Figure 7A shows the evolution of the cyclic voltammogram of $Ni_3P_2W_{18}$ for pH = 1−6. The curve for pH = 3 fits perfectly in the scheme, but it has been published previously[15] and is therefore omitted here for clarity. Coulometric determinations have also already been performed at pH = 3 and 5 and indicate that the first wave features an overall four-electron/four-proton process.[15] From a more qualitative point of view, the evolution of cyclic voltammograms with pH is illustrative of a behaviour frequently encountered in multi-electron/multi-proton processes. The distribution of the formal potentials and pK_a values of the various intermediate species will determine the broadness of the corresponding waves (and the current intensity of the wave). The same parameters will favour the merging of waves (or eventually their splitting) when their displacements as a function of pH are different. A remarkable example of such behaviour has been described recently in the electrochemistry of the tetrameric polyanion $[H_7P_8W_{48}O_{184}]^{33-}$.[33]

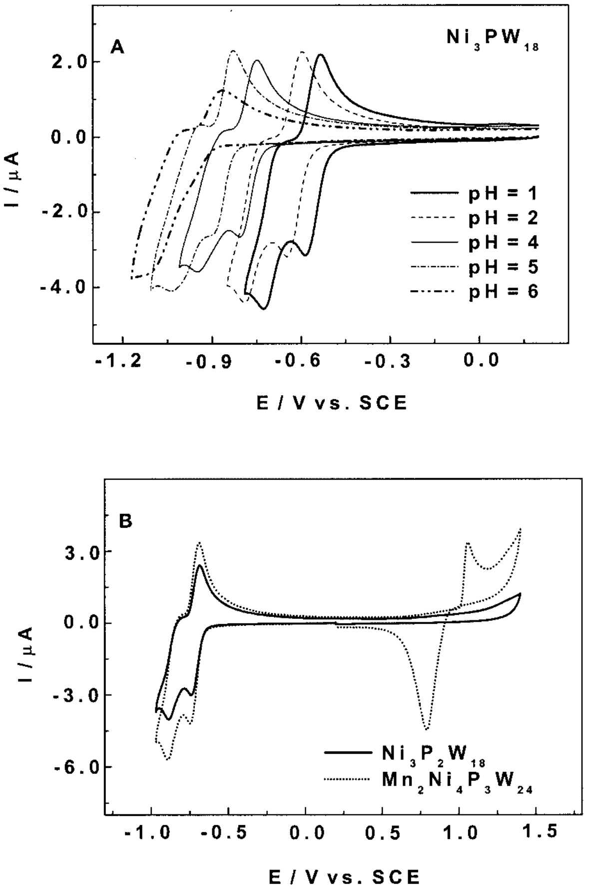


Figure 7. A: Superimposition of the cyclic voltammograms of 2 × 10^{-4} M $Ni_3P_2W_{18}$ observed as a function of pH; scan rate: 10 mV·s^{-1}; working electrode: polished glassy carbon; reference electrode: SCE; B: comparison of the cyclic voltammograms of 2 × 10^{-4} M $Ni_3P_2W_{18}$ and $Mn_2Ni_4P_3W_{24}$ at pH = 3 (0.2 M Na_2SO_4 + H_2SO_4); for further details see text

Figure 7B compares the cyclic voltammograms of $Ni_3P_2W_{18}$ and $Mn_2Ni_4P_3W_{24}$ at pH = 3. The redox processes of the Mn centres in the latter complex do not require further comments. For both polyanions the W-centred redox processes are very similar in shape, with the current intensities being larger for $Mn_2Ni_4P_3W_{24}$ than for $Ni_3P_2W_{18}$. Coulometry in the pH 3 sulfate medium indicates a six-electron process for the first W wave of $Mn_2Ni_4P_3W_{24}$. These trends comply with expectations if it is assumed that all relevant parameters in the electrochemistry of the two complexes are close or even equal, except for their different diffusion coefficients.

Cyclic voltammetry was used to evaluate the activity of $Ni_3P_2W_{18}$ and $Mn_2Ni_4P_3W_{24}$ in the electrocatalytic reduction of nitrate. The choice of the substrate is tricky, as nitrate is difficult to reduce. To the best of our knowledge, the only examples where HPAs have proven to be useful in this system have been described recently by our group.[12,13,34] For this purpose, the excess parameter is an operational parameter defined as $\gamma = C^{o}_{NO_3^-}/C^{o}_{HPA}$ where C° designates the concentration of the relevant species. The electrocatalysis is characterised by the catalytic efficiency, CAT, defined as: $CAT = 100 \times [I_{(HPA+NO_3^-)} - I^{d}_{(HPA)}]/I^{d}_{(HPA)}$, where $I_{(HPA+NO_3^-)}$ is the peak current for reduction of the heteropolyanion (HPA) in the presence of NO_3^- and $I^{d}_{(HPA)}$ is the corresponding diffusion peak current for the HPA alone. CAT values are sufficient to compare the efficiencies for a given electrocatalytic process either for one compound as a function of pH or for two compounds under the same experimental conditions. However, it must be recognized that a more detailed comparison would necessitate determination of the nature and yields of the final products, which is beyond the scope of this work. As a first example, CAT values were measured in the presence of $Ni_3P_2W_{18}$ for the electrocatalytic reduction of nitrate in a pH 2 sulfate medium. CAT was measured at −0.840 V and varied from 2098 to 2733 for $\gamma = 500$ and 1000, respectively. These values indicate an efficient electrocatalysis of the reduction of nitrate by $Ni_3P_2W_{18}$ at pH = 2. Furthermore, several tests with NO_2^- and/or with NO under the aforementioned conditions confirm that these species are easily reduced electrocatalytically at substantially less negative potentials than nitrate.[35] Insofar as nitrite and NO are known to appear as intermediates in the reduction of nitrate by various metals, the present results suggest that highly reduced species should be obtained in the electrocatalytic reduction of nitrate in the presence of $Ni_3P_2W_{18}$. Also, the number of accumulated electrons in the polyoxoanion framework at the potential where the transformation of nitrate takes place is large enough for a complete reduction, which supports also the assumption of reduction of intermediates.

The media of pH = 3 and 5 were selected to compare the efficiencies of $Ni_3P_2W_{18}$ and $Mn_2Ni_4P_3W_{24}$, respectively, in the electrocatalytic reduction of nitrate because the latter complex is not very stable at pH = 2. Whatever the pH, $Mn_2Ni_4P_3W_{24}$ was found to be the more efficient of the two complexes: its CAT values were four and seven times larger at pH = 3 and 5, respectively, than those measured for $Ni_3P_2W_{18}$ under the same conditions.

The results for these two complexes were compared with the efficiencies obtained with $Ni_4P_2W_{18}$ and $NiPW_{11}$ in the pH 5 medium where all these complexes are stable. The efficiencies for $Ni_3P_2W_{18}$ and $Ni_4P_2W_{18}$ turned out to be comparable. In contrast, $NiPW_{11}$ shows a negligibly small activity toward the electrocatalytic reduction of nitrate in this medium.

Finally, comparisons of the efficiencies of several Ni-substituted tungstophosphates vis-à-vis the catalytic electroreduction of nitrate suggest that an increase of the number of Ni centres incorporated in stable sandwich-type polyoxoanions has a very beneficial effect.

Concluding Remarks

Several conclusions emerge from this work. The stability of a large variety of Ni-containing sandwich-type polyoxoanions has been investigated by electrochemistry in aqueous media. Such an evaluation is necessary in order to detect those species suitable for solid-state studies. Simultaneously, such a study permits the selection of good candidates for electrocatalysis applications along with the appropriate pH conditions. At least two complexes turned out to be stable over a fairly wide pH domain. To the best of our knowledge such a broad, comparative overview has not been performed previously. The remarkable stability of the Keggin-based $Ni_3P_2W_{18}$ must be emphasised and is reminiscent of that demonstrated by Hill and co-workers for the Wells−Dawson-based triiron analogue.[22] Concerning electrocatalysis perspectives, it is worth noting that reduction of the W centres in the present complexes provides an appreciable electron reservoir under conditions where modification of electrode surfaces does not take place. The accumulated electrons in the HPA framework might therefore be useful for various electrocatalytic processes.

Experimental Section

General Methods and Materials: Pure water was used throughout. It was obtained by passing through a RiOs 8 unit followed by a Millipore-Q Academic purification set. H_2SO_4, Na_2SO_4, HCl, NaCl, $HClO_4$, $NaClO_4$, CH_3CO_2H, CH_2ClCO_2H, CH_3CO_2Na, H_3PO_4, NaH_2PO_4 were of high-purity grade and were used as purchased (Prolabo) without further purification. The UV/Vis spectra were recorded with a Perkin−Elmer Lambda 19 spectrophotometer from 600 to 200 nm using solutions that contained 2.5×10^{-5} M or 4.3×10^{-5} M of the relevant HPA. The measurements were performed in matched 1.000-cm optical-path quartz cuvettes. The preparation and characterisation of $Ni_4H_2PW_9$, Ni_3PW_{10}, $Ni_4P_2W_{18}$, $Ni_9P_3W_{27}$, $Ni_3P_2W_{18}$, and $Ni_4P_4W_{30}$ have already been described in detail.[15,18,19,26,28] The synthesis and characterisation of the novel polyanion $Mn_2Ni_4P_3W_{24}$ are described elsewhere.[27]

Electrochemical Experiments: The same media as for UV/Vis spectroscopy were used for electrochemistry, but the HPA concentration was at least 2×10^{-4} M. All cyclic voltammograms were recorded at a scan rate of 10 mV·s^{-1}, unless otherwise stated. The solutions were deaerated 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 (GC, Tokai, Japan) electrodes has been described previously.[36] The glassy carbon samples had a diameter of 3 mm. The electrochemical setup was an EG & G 273 A driven by a PC with the M270 software. Potentials are quoted against a saturated calomel electrode (SCE). The counter electrode was a platinum gauze of large surface area. All experiments were performed at laboratory temperature.

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