Electrochemical Behaviour of First Row Transition Metal Substituted Polyoxotungstates: A Comparative Study in Acetonitrile

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Dedicated to Prof. Dr. João E. J. Simão on the occasion of his 75th birthday

Keywords: Polyoxometalates / Sandwich complexes / Transition metals / Electrochemistry

A comparative study of the electrochemical behaviour of several transition metal substituted polyoxotungstates in acetonitrile solution with tetra-*n*-butylammonium perchlorate as a supporting electrolyte is presented. Tetra-*n*-butylammonium salts of Keggin-type polyoxoanions, α-$[(C_4H_9)_4N]_4H_x[XW_{11}M(H_2O)O_{39}]\cdot nH_2O$, X = P, Si; M^{II} = Co, Ni, M^{III} = Fe, Mn, *x* = 0–2, *n* = 0–2, and sandwich-type polyoxoanions, α-B-$[(C_4H_9)_4N]_7H_3[M_4(H_2O)_2(PW_9O_{34})_2]$, M^{II} = Co, Mn, have been studied by cyclic voltammetry and spectroelectrochemistry. Under the conditions used, the tungsten-oxo framework of the metal substituted Keggin anions could accept up to three electrons in quasi-reversible one-electron consecutive processes. Comparison with the corresponding lacunary anions is presented. Redox processes at the metal centre have been detected for all metals M except Ni. For the anions α-$[XW_{11}M(H_2O)O_{39}]^{m-}$, the co-existence of species with a different degree of protonation was deduced from cyclic voltammetry results whenever protons were included in the molecular formula. The influence of the solids' composition on the electrochemical results is stressed. For the sandwich anions, cyclic voltammetry revealed redox processes occurring on the W atoms and also on the metallic belt. Two metal atoms in the belt of the α-B-$[Co^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anion could be electrochemically oxidised to Co^{III} in two separate steps. A similar result was observed for the Mn^{II} analogue, but the corresponding first step was not as well defined. Re-oxidation was only detected for the Co anion. This work is the first comparative study of the electrochemical behaviour of such transition metal substituted polyoxotungstates in an organic medium.
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Introduction

Transition metal substituted polyoxotungstates have attracted special attention over the last two decades, due to their wide range of potential applications,[1−8] especially the Keggin-type polyoxoanions α-$[XW_{11}M(L)O_{39}]^{m-}$ (X = P, Si, etc., M = transition metal and L = monodentate ligand, abbreviated as $XW_{11}M$). These may be viewed as complexes where the lacunary anion α-$[XW_{11}O_{39}]^{n-}$ (XW_{11}) coordinates the transition metal ion M^{p+} in a pentadentate fashion.[9] A labile water molecule usually occupies the sixth coordination position, giving a pseudo-octahedral environment around the metal M (Figure 1, A). The inorganic tungsten-oxo framework is inert towards oxidation but can accept reversibly up to four electrons.[5,9] The metal M may also be involved in reversible redox processes. With this in mind, several metal substituted Keggin anions have been used as electrocatalysts to reduce pollutants such as NO_2^- or NO,[10,11] and also to reduce H_2O_2 and to oxidise alcohols or cleave aryl olefins.[12−16]

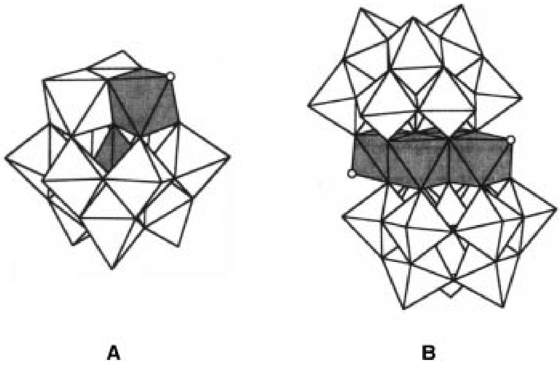

Figure 1. Structure of the complexes α-$[XW_{11}M(H_2O)O_{39}]^{m-}$ (A) and α-B-$[M_4(H_2O)_2(PW_9O_{34})_2]^{p-}$ (B). Each dashed octahedron represents a MO_6 group and the open circles represent the oxygen atom from a water molecule coordinated to M

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Another interesting type of complex of general formula α-B-$[M_4(H_2O)_2(PW_9O_{34})_2]^{p-}$, abbreviated as $M_4(PW_9)_2$, has a sandwich structure in which two sub-units α-B-$[PW_9O_{34}]^{9-}$ are linked to a belt of four metal ions[9] (Figure 1, B). Because the several metal centres in these complexes could be activated separately in redox processes, studies on their potential as electrocatalysts are certainly needed.

In addition to electrocatalysis, the above metal substituted polyoxotungstates are, in general, active in liquid-phase oxidative catalysis, and several related reviews have appeared.[2−4] Their activity and selectivity depend on the type of substrate, experimental conditions (oxidant, solvent, temperature), and on the substituting metal.[2,3] Studies on the electrochemistry of such polyoxoanions in different solvents may help in understanding their behaviour as oxidative catalysts. Numerous electrochemical studies have been made, in aqueous media, of mono-substituted Keggin polyoxotungstates with X = P, Si, such as for Mn[16−19] and Fe,[10,12,20,21] among other metals.[5,22−24] Anions with X = Zn have also been examined.[25,26] Nevertheless, studies in organic solution are scarce. Cyclic voltammetry in acetonitrile has been reported for $[PW_{11}Cu^{II}O_{39}]^{5-}$,[27] $[H_xSiW_{11}(VO)O_{39}]^{(6-x)-}$,[28] $[XW_{11}M(H_2O)O_{39}]^{m-}$, X = P, Si, Ge, B, M = Ru^{III},[29] Ir^{IV},[11,30] $[PW_{11}TcO_{40}]^{4-}$,[31] and $[XW_{11}Re^{V,VI,VII}O_{40}]^{4-}$, X = P ($Re^{V}$), Si ($Re^{VI}$), B ($Re^{VII}$).[32] Also, co-solvent effects on the redox behaviour of the $[SiW_{11}Mn(H_2O)O_{39}]^{6-}$ anion have been analysed.[19] For the sandwich-type complexes $M_4(PW_9)_2$ in acetonitrile, studies on $[Cu_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Fe_4(H_2O)_2(PW_9O_{34})_2]^{6-}$ have been published.[27,33] Studies of $Mn_4(PW_9)_2$ in aqueous solution have also been performed.[18,34] There is an obvious lack of information on the electrochemistry of these two kinds of polyoxoanions in organic solvents, considering that many redox catalysis experiments are, in fact, performed in non-aqueous media, such as acetonitrile or 1,2-dichloroethane.[2,3]

In this context, we have studied the electrochemical behaviour, in acetonitrile, of the anions $[XW_{11}O_{39}]^{n-}$ and $[XW_{11}M(H_2O)O_{39}]^{m-}$, X = P, Si, M^{II} = Co, Ni, M^{III} = Fe, Mn, and $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, M^{II} = Co, Mn. Experiments were performed using TBA salts. Determination of the diffusion coefficient in acetonitrile was attempted for several polyoxoanions. The electrochemical behaviour of the above-mentioned polyoxoanions in acetonitrile is, to our knowledge, described for the first time in a systematic way. In terms of catalysis, special interest has been paid to reactions at the metal centres (Co, Fe, Mn).

Results and Discussion

Characterisation of the Tetrabutylammonium Compounds

TBA salts with $[PW_{11}O_{39}]^{7-}$ and $[PW_{11}M(H_2O)O_{39}]^{m-}$ anions have been synthesised and characterised previously.[35−39] The compounds with the anions $[SiW_{11}M(H_2O)O_{39}]^{m-}$, M^{II} = Co, Ni, M^{III} = Fe, Mn, have four TBA cations in the molecular formula, and are isostructural. Their powder X-ray diffraction patterns were similar to those of the P analogues with metals like Co^{II}, Ni^{II} or Fe^{III},[39] indicating that the Si compounds crystallise with the same body-centred cubic structure as the P-anions.[39,40] Conversely, the X-ray diffraction powder pattern of $TBA_4H_4[SiW_{11}O_{39}]$ was identical to that of the tetragonal phase of the corresponding $TBA_4H_3[PW_{11}O_{39}]$.[39]

The infrared spectra of the compounds with the sandwich polyoxoanions, $TBA_7H_3[M_4(H_2O)_2(PW_9O_{34})_2]$, M^{II} = Co, Mn, were similar. The spectra of the present TBA salts differ from those of the corresponding potassium salts in the ν_{as}(P−O) and ν_{as}(W−O−W) region. The band due to the P−O stretching vibration, at 1030−1040 cm^{-1} for the potassium salts of the polyoxoanions $M_4(PW_9)_2$, M = Co, Mn,[41] presented a shoulder at higher wave-number in the spectra of the TBA salts (Figure 2, a,b). Therefore, the TBA counter-cations probably induce a larger distortion of the central phosphate groups of the α-B-$[PW_9O_{34}]^{10-}$ sub-units.[42,43]

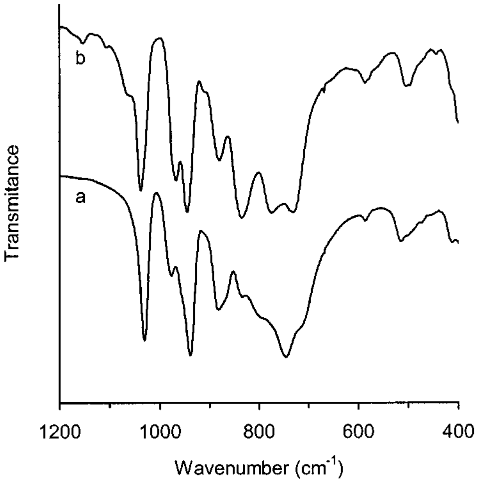

Figure 2. IR spectra of (a) $K_{10}[Mn_4(H_2O)_2(PW_9O_{34})_2]\cdot 23H_2O$ and (b) $[(C_4H_9)_4N]_7H_3[Mn_4(H_2O)_2(PW_9O_{34})_2]$

General Electrochemical Behaviour of the Keggin-Type Anions $XW_{11}M$ (X = P, Si) in Acetonitrile

Cyclic voltammograms (CV) of the $XW_{11}M$ anions in acetonitrile exhibited, in the negative potential region, one to three pairs of cathodic/anodic peaks corresponding to the redox processes of tungsten atoms (Figure 3). The substituting metal was reduced for Fe^{III} and Mn^{III} substituted anions. The voltammetric results, including those obtained for the lacunary XW_{11} anions, are summarised in Table 1. For comparison, results for $[XW_{12}O_{40}]^{3/4-}$, X = P, Si (XW_{12}), under the same experimental conditions, are included in Table 1. These are similar to previously published values.[11,29,44,45] Additionally, for M = Co^{II} (X = P, Si) and Mn^{III} (X = Si), anodic waves at positive potentials were observed, due to the oxidation of the metal M.

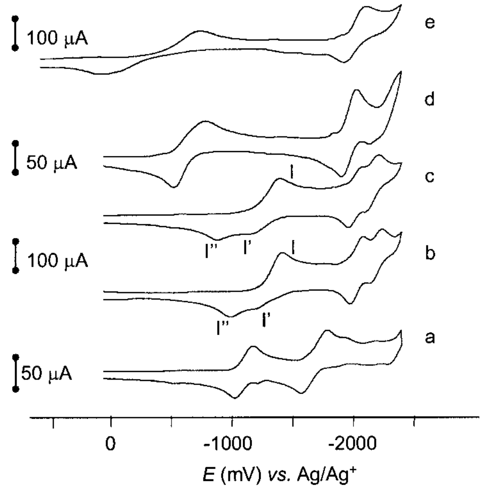

Figure 3. Cyclic voltammetry at a glassy carbon working electrode (scan rate = 100 mV/s) of acetonitrile solutions (10 mM) of (a) PW_{11}, (b) $PW_{11}Co^{II}$, (c) $PW_{11}Ni^{II}$, (d) $PW_{11}Fe^{III}$, (e) $PW_{11}Mn^{III}$

All the reduction processes of the W atoms in the metal substituted Keggin anions were quasi-reversible. The ΔE_p (anodic to cathodic peak separation) for the ferrocene/ferrocenium redox couple in acetonitrile was used as the reversibility reference (71 mV). There was an apparent decrease in the reversibility for the transition metal substituted heteropolyanions, relative to the parent structure XW_{12}. For the lacunary XW_{11} anions, the voltammetric behaviour is also consistent with W quasi-reversible reductions.

Controlled potential electrolysis revealed that each of the two first W reduction peaks corresponded to one-electron transfer processes. The number of electrons of the third W reduction (when observed) was estimated to be one, by comparison of the current of the corresponding voltammetric peak with those of the first and second reductions. Thus the tungsten-oxo framework of the heteropolyanions studied could accept one to three electrons, within the present experimental potential range.

The peak potentials of the two first W reductions were more negative for the substituted species than for the corresponding lacunary anions or for the parent Keggin anions. As found in aqueous solution,[5,21,22,46] there is no obvious correlation between the charge of lacunary or of the metal substituted anions and the reduction potentials of W (Figure 4), in contrast to the case of parent Keggin anions in aqueous[9] and non-aqueous systems[47] or for the anions $XW_{11}Ir^{IV}$, X = P, Si, Ge, B in acetonitrile.[11]

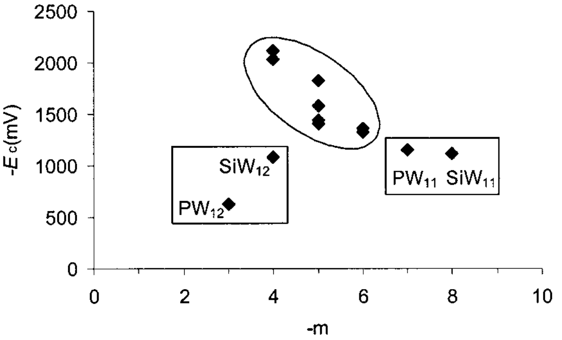

Figure 4. Potentials of the first tungsten reduction peaks of the cyclic voltammograms of XW_{12}, XW_{11}, and $XW_{11}M$ vs. the formal charge of the unprotonated anions

The redox potentials for the W atoms of the studied anions in acetonitrile were, in general, shifted towards more negative values than those reported in aqueous solution for the corresponding potassium salts.[10,18,21,22] This has been be explained by considering Lewis interactions between the polyoxoanions (bases) and the solvent molecules (acids). A correlation between the Guttmann acceptor number of the solvent[48] and the potential of the first one-electron re-

Table 1. Cyclic voltammetric data[a] for XW_{12}, XW_{11}, and $XW_{11}M$ anions in acetonitrile

Polyoxo anion		X = P				X = Si		
	$M^{III/II}$	1st W[b]	2nd W	3rd W	$M^{III/II}$ [b]	1st W	2nd W	3rd W
XW_{12}		−629 (65)	−1170 (73)	−1875 (72)		−1078 (70)	−1593 (78)	−2289 (92)
XW_{11}		−1150 (91)	−1702 (128)	−		−1119 (124)	−1626 (124)	−2284 (121)
$XW_{11}Co^{II}$		(I) −1440 (I′) −1239 (I′′) −1035	−2098 (102)	−2257 (87)		−1328 (342) -1446 (110)	−1921 (116)	−2166 (107)
$XW_{11}Ni^{II}$		(I) −1411 (I′) −1173 (I′′) −939	−2116 (105)	−2261 (93)		−1358 (409) −1452 (119)	−1959 (98)	−2148 (90)
$XW_{11}Fe^{III}$	−818 (251)	−2038 (119)			(I) −693 (I′) −504 (I′′) −233	−1584 (220)	−1964 (130)	−2199 (141)
$XW_{11}Mn^{III}$	−778 (762)	−2115 (165)			(I) −646 (I′) −103 (I′′) +228	−1828 (290)	−2052 (98)	

[a] Cathodic peak potentials and cathodic-to-anodic peak separation (in parentheses), both in mV vs. Ag/Ag⁺; working electrode: glassy carbon; polyoxoanion concentration: $1.0 \cdot 10^{-2}$ M; supporting electrolyte: $TBAClO_4$ (0.1 M); scan rate: 100 $mV \cdot s^{-1}$. [b] I′ and I′′ are the anodic counterparts of peak I.

duction has been found for α-$[SiW_{12}O_{40}]^{4-}$.[49] For redox processes at the substituting metals, the fact that the solvent may act as a donor ligand, substituting the labile water molecules coordinated to the metal M, must be considered. Recent studies have shown that for the XW_{12} anions the number of transferred electrons and the corresponding potentials are affected by various solution conditions besides the solvent, namely the acidity and the presence of different cations.[5,44,45] The influence of charge distribution on the redox behaviour of some lacunary and metal-substituted Keggin and Dawson-type species was referred by Keita et al.[46] For the $XW_{11}M$ anions the interplay of all these factors is far from being understood, preventing straightforward comparison of results obtained in different media.

Keggin-Type Anions with M^{II} = Co, Ni

The cyclic voltammograms of $XW_{11}Co$ and $XW_{11}Ni$ (X = P, Si) in acetonitrile exhibited three tungsten one-electron redox couples at negative potentials. Two anodic counterparts (I′ and I′′) were observed for the first reduction peak (Figure 3), even when the potential scan was reversed at ca. −1800 mV, i.e. after the first 1-e^- reduction of tungsten.

On increasing the scan rate (from 20 to 200 mV/s, Figure 5) the first W electron transfer with the P-anions (Figure 5, A), i.e. the first reduction peak I (around −1400 mV), was shifted to more negative potentials (ca. 38 and 50 mV, respectively, for $PW_{11}Co$ and $PW_{11}Ni$); the anodic peak I′′ became less negative and increased in intensity compared with peak I′; the position of I′ was unchanged. The W peaks at potentials more negative than −1800 mV were unchanged.

The above-mentioned splitting of the anodic counterpart of peak **I** and the observed variations with scan rate are attributed to the co-existence of distinct polyoxoanion species with different degrees of protonation. Protons were introduced in solution due to the molecular formula of the salts $TBA_4H[PW_{11}M(H_2O)O_{39}]\cdot nH_2O$. The first anodic peak (I′) corresponds to the oxidation of the less protonated species (namely $[PW_{11}M(H_2O)O_{39}]^{6-}$) whereas peak I′′, at more positive potentials, must correspond to the oxidation of a more protonated species, possibly $H[PW_{11}M(H_2O)O_{39}]^{5-}$. As the first 1-$e^-$ tungsten reduction produced a single peak it was assumed that protonation occurred after reduction. Similar behaviour has been observed previously for $SiW_{11}Mn^{II}$, in aqueous solutions,[18] i.e. depending on scan rate, reoxidation scans showed two peaks attributed to species with different degrees of protonation.

$SiW_{11}Co$ and $SiW_{11}Ni$ anions showed similar electrochemical behaviour to that of the P analogues (Figure 5, B), except that the first cathodic process was split into two peaks of approximately equal height (as found by semi derivative deconvolution) whose position did not change significantly with scan rate. Nevertheless, these first reduction processes for the Si-polyoxoanions corresponded to overall 1-e^- reductions (determined by coulometry). The observed splitting of the first cathodic W peak may indicate the existence of two stable species in the initial solutions, possibly differing in protonation degree. Protons were again introduced in solution due to the molecular formula $TBA_4H_2[SiW_{11}M(H_2O)O_{39}]\cdot nH_2O$.

Additionally, Co^{II} was oxidised at positive potentials. The voltammograms were better defined at a Pt working electrode, where the oxidation peaks occurred at E_{pa} = +954 mV for the $SiW_{11}Co$ anion and at E_{pa} = +1003 mV for $PW_{11}Co$ (100 mV/s). Bulk electrolysis with coulometric determination at a Pt working electrode, performed at +1100 mV for the $SiW_{11}Co$ and at +1200 mV for the $PW_{11}Co$ anions, gave 1.0 and 1.1 electrons transferred, respectively. The in situ visible spectra of the oxidised solutions revealed

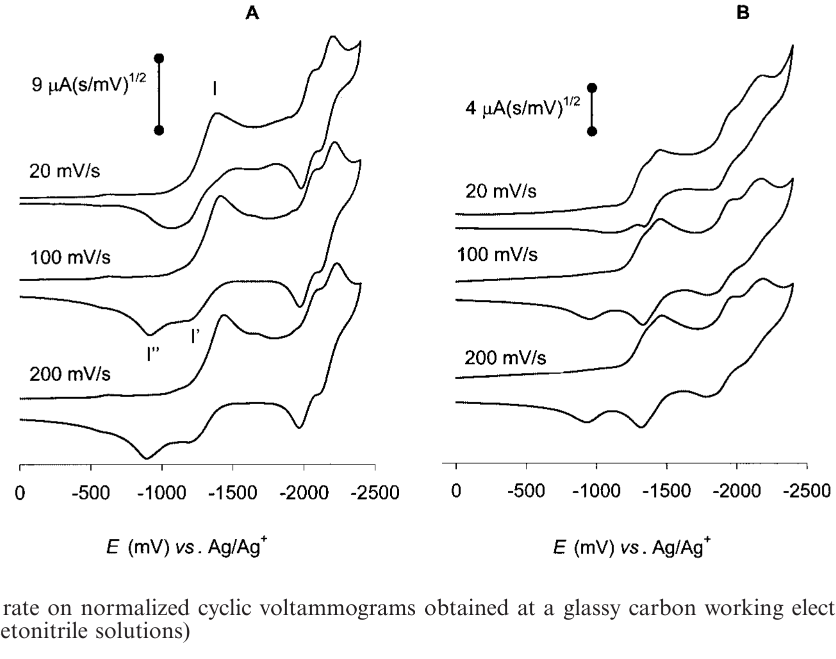

Figure 5. Effect of scan rate on normalized cyclic voltammograms obtained at a glassy carbon working electrode of (A) $PW_{11}Ni^{II}$ and (B) $SiW_{11}Ni^{II}$ (10 mM acetonitrile solutions)

a new band around 670 nm, indicating a $Co^{III}O_6$ chromophore.[50]

Different waves in the cyclic voltammograms corresponding to species with different degrees of protonation are uncommon with Keggin-type polyoxoanions, but have been reported for the anion $[H_xSiW_{11}(V^{IV}O)O_{39}]^{(6-x)-}$ in acetonitrile[28] and for $SiW_{11}Mn^{II}$ in aqueous solution.[18] Their appearance depends on the interplay of equilibrium and kinetic factors, namely acidity constants of the protonated anions, amount of protons present in solution and kinetics of proton exchange. The conditions here reported seem to favour their appearance.

Cyclic voltammograms of $PW_{11}Ni$ and $SiW_{11}Co$ in acid aqueous solutions (pH = 2.2) also show two anodic peaks as counterparts of the first cathodic wave (in this case, a 2-electron wave) that are attributed to the α-and β-isomers of the reduced anion.[22] In those voltammograms, the corresponding peak positions were not significantly altered by changing the scan rate and the intensity of the anodic peak at more positive potentials increased as the scan rate decreased. In the present study, the position of peak I′′ altered, and the variation in relative peak heights $I_{pa}(I')/I_{pa}(I'')$ with scan rate was the opposite of that in aqueous solution. These findings, together with the observation of peaks I′ and I′′ for the 1-electron reduced polyoxometalates, may indicate that the two observed anodic peaks do not correspond to different isomers. So far, for Keggin-type anions, except $[XW_{12}O_{40}]^{5-}$, X = Al, Ga,[51,52] the formation of β-isomers by spontaneous isomerization of the corresponding α-anions has been reported to occur after the uptake of, at least, two electrons.[21,22,52]

Himeno et al. have prepared β-$[PW_{12}O_{40}]^{3-}$ in water/acetonitrile solutions,[44] showing that CH_3CN, as an auxiliary solvent, stabilized markedly this isomer. Nevertheless, both α and β isomers of that anion were kinetically inert in the water/acetonitrile medium.[44] Accordingly, the results obtained here do not indicate that the organic solvent may favour α→β isomerization.

Keggin-Type Anions with M^{III} = Mn, Fe

The CV of the anions $XW_{11}M^{III}$ showed, at negative potentials, waves corresponding to the reduction of W and of the metal M^{III}. Those of $PW_{11}Fe^{III}$ and $PW_{11}Mn^{III}$ polyoxoanions exhibited two redox couples (Figure 3, d,e). Controlled potential bulk electrolysis at −1000 mV for the Fe and at −1200 mV for the Mn polyoxoanion indicated that, in both cases, the first reduction step was an one-electron reaction (0.85 and 0.90 electrons were transferred, respectively). The solution of $PW_{11}Fe^{III}$ in acetonitrile changed from yellow to purple and a band with the maximum at 536 nm appeared in the visible region spectrum (Figure 6), corresponding to the $PW_{11}Fe^{II}$ anion.[10] For the $PW_{11}Mn^{III}$ anion the characteristic bands of the $Mn^{III}O_6$ chromophore,[17,53] at 493 and 524 nm (sh), disappeared during electrolyses and the electronic spectrum of the electrolysed solution showed only a charge-transfer band extending to the UV region, indicating a $Mn^{II}O_6$ chromophore.[53,54] These results clearly show that the first reduction peak in the voltammograms of $PW_{11}Fe^{III}$ and $PW_{11}Mn^{III}$ was due to the one-electron transfer at the substituting metal centre (Fe^{III}→Fe^{II} and Mn^{III}→Mn^{II}, respectively). For the Mn^{III}/Mn^{II} couple, $E_{pa} - E_{pc}$ was quite large and increased with scan rate (ΔE_p near 760 mV at 100mV/s). As the normalised current intensity of the peaks did not vary noticeably with scan rate, the large irreversibility of the Mn^{III}/Mn^{II} couple seems to be due to slow electron transfer. This differs from aqueous solutions, in which the Mn^{III}/Mn^{II} couple for the different manganese substituted Keggin anions originated quasi-reversible waves with a peak separation in the 70−170 mV range.[16,17,19] Nevertheless, the particular kinetic inertness of the Mn^{III}/Mn^{II} couple has been referred to for other Mn complexes.[55]

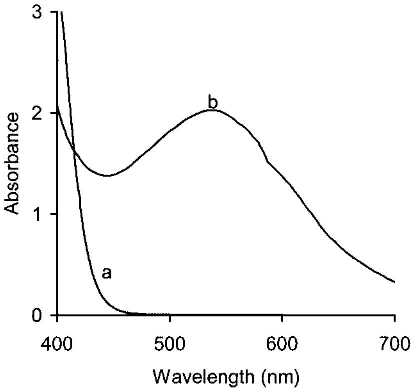

Figure 6. Visible electronic absorption spectra of the acetonitrile solution of $PW_{11}Fe^{III}$ before (a) and after bulk electrolyses at −1000 mV (b)

Except for the variation in ΔE_p corresponding to the M^{III}/M^{II} pairs (much larger for Mn than for Fe), the cyclic voltammograms of $PW_{11}Fe^{III}$ and $PW_{11}Mn^{III}$ did not change significantly with scan rate and the peaks were not split. As these polyoxoanions contain no protons in the molecular formula, no protonated species are expected. These results may further indicate that the behaviour described above for the $XW_{11}Co^{II}$ and $XW_{11}Ni^{II}$ anions is caused by protonated species.

The cyclic voltammetric data (Table 1) for the $XW_{11}Fe^{III}$ and $XW_{11}Mn^{III}$ compounds show more peaks for the Si-polyoxoanions than for the P-anions, as the tungsten atoms in the polyoxoanions containing Si are reduced at less negative potentials than the P analogues. This is another consequence of the presence of protons in solution. The voltammetric behaviour of the parent Keggin polyoxometalates in organic solvents is strongly sensitive to the presence of H^+.[45,56] In particular, the peak potentials of the W reduction waves shifted to less negative values as the amount of H^+ increased, to a point in which the one-electron reduction waves were changed into two-electron waves.[45,56] Of the compounds with metal substituted anions described in this work only $PW_{11}Fe$ and $PW_{11}Mn$ do not have protons in the molecular formula, and only for these anions is the first W reduction peak more negative than −2000 mV (Figure 3 and Table 1).

Another interesting feature in the CV of the Si anions is the unexpected splitting of the 1-e^- reduction process at the M atom. This is more clearly seen for the iron anion (Figure 7); the Mn^{III}/Mn^{II} couple gave less well-resolved waves. Thus, besides the main iron reduction peak at −693 mV (Table 1), another cathodic peak with low current intensity appeared near −1040 mV. Electrolysis at potentials near −1200 mV indicated that one 1-electron reduction took place, suggesting that both peaks correspond to one Fe atom. The observed splitting was interpreted in terms of an equilibrium between $SiW_{11}Fe(H_2O)$ and $SiW_{11}Fe(OH)$. Hydrolysis of Fe^{III} substituted Keggin anions has been reported,[20,57,58] with the formation of monomeric complexes and/or dimeric or other polynuclear species. The former seem to be obtained in the presence of non-aqueous solvents, whereas water leads to extensive dimerization. In particular, Kuznetsova et al. observed only the monomeric species $PW_{11}Fe(L)$, L = H_2O, OH^-, in acetonitrile solutions of TBA salts with Fe:PW_{11} = 1:1.[57] The CV obtained in acetonitrile of the TBA salt of $PW_{11}Fe(OH)$, prepared as previously published,[39] also showed two reduction waves, cumulatively corresponding to the 1-electron reduction of Fe. In the CV of $SiW_{11}M^{III}$ anions, the anodic counterpart of the reduction peak at less negative potentials showed the same pattern as for $XW_{11}Co$ and $XW_{11}Ni$, i.e. two anodic peaks.

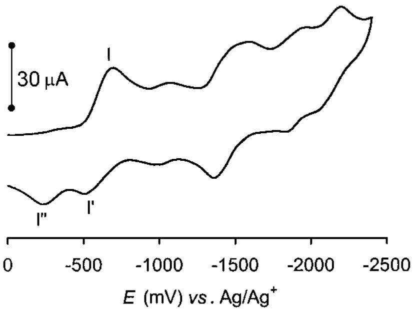

Figure 7. Cyclic voltammetry at a glassy carbon working electrode of $SiW_{11}Fe^{III}$ (10 mM acetonitrile solution, scan rate = 100 mV/s)

For the $SiW_{11}Mn^{III}$ anion, besides the $Mn^{III/II}$ redox couple, the oxidation of Mn^{III} to Mn^{IV} was observed at the Pt electrode at E_{pa} = +1046 mV (not observed for the analogue $PW_{11}Mn^{III}$). Electrolysis at +1200 mV gave 0.9 electrons transferred. Such Mn redox processes for $XW_{11}Mn^{III}$, X = P, Si, in acetonitrile are consistent with those reported for $XW_{11}Mn^{II}$ in aqueous solution.[16,17,19]

Lacunary Keggin-Type Anions

The lacunary polyoxotungstates XW_{11} (X = P, Si) gave well-defined cyclic voltammograms with two and three one-electron redox waves at negative potentials, respectively (Table 1). Under the conditions used the peak potentials of PW_{11} and SiW_{11} were similar, whereas, in the voltammogram of the parent Keggin anions, the W peak potentials in SiW_{12} were more negative than for PW_{12}, reflecting the higher charge of the anion. The different behaviour found for the parent and lacunary anions was again attributed to possible protonation of the latter, due to protons from the TBA salts (with formula $TBA_4H_3[PW_{11}O_{39}]$ and TBA_4H_4-$[SiW_{11}O_{39}]$, respectively). These protons do not exist in the salts of XW_{12} anions.

Electrochemical Behaviour of the Sandwich-Type Polyoxoanions $M_4(PW_9)_2$

Cyclic voltammetry between 1300 and −2400 mV for the TBA salts of sandwich polyoxoanions in acetonitrile revealed no significant changes upon varying the scan rate from 20 to 200 $mV \cdot s^{-1}$. For potentials < −1000 mV three quasi-reversible waves, corresponding to tungsten reductions (Table 2), were observed. Figure 8 presents the voltammogram of the $Mn_4(PW_9)_2$ anion (the Co^{II} polyoxoanion showed similar electrochemical behaviour).

Oxidation processes at the metal M were clearly observed at a Pt working electrode. For the Co sandwich polyoxoanion, two oxidation peaks of identical intensity were detected at +811 and +1123 mV (Figure 9, a). In the corresponding reduction scan, the two cathodic peaks observed at less positive potentials are the counterparts of the first oxidation process (Figure 9, b). Electrolysis of the $Co_4(PW_9)_2$ solution at the Pt electrode with coulometric determination, performed at +950 mV, indicated the transfer of 0.8 electrons, meaning that each oxidation peak corresponds to a one-electron process (total loss of two electrons). Considering the structure of the polyoxoanion,[59,60] the oxidation processes might occur at the two more external Co atoms (atoms bound to a water molecule in Figure 1, B), more accessible for the electron transfer to the electrode surface. Previous studies of two salts of oxidized derivatives of the $Mn^{II}{}_4(PW_9)_2$ anion have suggested that oxidation occurred first at the more external Mn atoms.[34] From the above considerations the cobalt oxidation processes can be described as (L = H_2O and/or CH_3CN):

$$[Co^{II}{}_2(L)_2Co^{II}{}_2(PW_9)_2]^{10-} \rightarrow [Co^{III}(L)Co^{II}(L)Co^{II}{}_2(PW_9)_2]^{9-} + e^-$$

$$[Co^{III}(L)Co^{II}(L)Co^{II}{}_2(PW_9)_2]^{9-} \rightarrow [Co_2{}^{III}(L)_2Co^{II}{}_2(PW_9)_2]^{8-} + e^-$$

We could not explain unambiguously the two reduction peaks that are the cathodic counterparts of the first oxidation process. The shape of the cyclic voltammograms was not altered either by change of scan rate or by multiple successive scans.

The Mn sandwich polyoxoanion at the Pt working electrode showed two irreversible oxidation processes at the Mn centre (Figure 9, c), with the total electron transfer of two electrons (value obtained by electrolysis with coulometric determination at +860 mV using the Pt electrode). A similar irreversible behaviour had been observed in studies in aqueous solution, and attributed to slow electron transfer, possibly due to Jahn−Teller distortion of the $Mn^{III}O_6$ octahedra, rather than to chemical irreversibility.[34]

Table 2. Cyclic voltammetric data[a] for $M^{II}_4(PW_9)_2$ anions in acetonitrile

Polyoxoanion	M[b] E_c	 E_a	1st W[c] E_c (ΔE_p)	2nd W[c] E_c (ΔE_p)	3rd W[c] E_c (ΔE_p)
$Mn_4(PW_9)_2$		500, sh; 749	−1604 (92)	−2078 (112)	−2248 (88)
$Co_4(PW_9)_2$	488; 716; 1018	811; 1123	−1593 (83)	−2045 (95)	−2219 (116)

[a] Cathodic (E_c) and anodic (E_a) peak potentials and cathodic-to-anodic peak separation (ΔE_p) in mV vs. Ag/Ag$^+$; polyoxoanion concentration: $3.0 \cdot 10^{-3}$ M; supporting electrolyte: $TBAClO_4$ (0.1 M); scan rate: 100 mV·s^{-1}. [b] Platinum foil electrode. [c] Glassy carbon electrode.

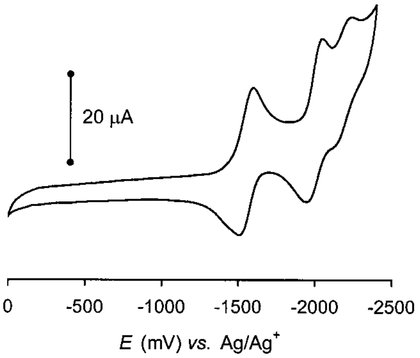

Figure 8. Cyclic voltammetry at a glassy carbon working electrode of an acetonitrile solution (3.0 mM) of $Mn^{II}_4(PW_9)_2$ (scan rate = 20 mV/s) in the negative potential region

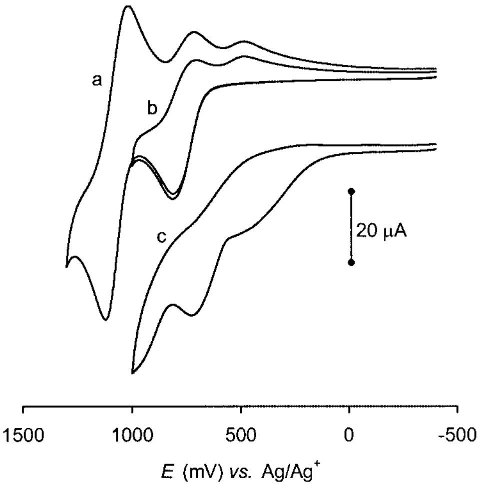

Figure 9. Cyclic voltammetry at a Pt foil working electrode of acetonitrile solutions (3.0 mM) of $Co^{II}_4(PW_9)_2$ (scan rate = 100 mV/s) (a, b) and $Mn^{II}_4(PW_9)_2$ (scan rate = 20 mV/s) (c) in the positive potential region

Diffusion Coefficients

Diffusion coefficients (*D* values) are not normally determined in mechanistic studies on electrochemical processes. However, the diffusion of species towards the electrode is important in the overall electrochemical reaction. The dependence of the cathodic and anodic peak currents on the square root of the scan rate indicates that the electrode processes are diffusion controlled. The diffusion coefficients may be estimated by applying the Randles-Sevcik equation, $|I_p| = 2.69 \cdot A \cdot n^{3/2} \cdot C \cdot D^{1/2} \cdot v^{1/2}$; where *A* is the electrode area, *C* is the concentration, *n* is the number of electrons transferred and *v* is the scan rate. Here, we determined the electrode area to be $8.58 \cdot 10^{-2}$ cm^2, by chronoamperometry with a 4 mM $K_4Fe(CN)_6$ +2 M KCl solution at 25 °C, where $D = 6.29 \cdot 10^{-6}$ cm^2·s^{-1}.[61] The diffusion coefficients were estimated only for the polyoxoanions where the reduction peak characteristics (ΔE_p and $E_p - E_{p/2}$)[61] were closer to what is expected for a reversible process. Within the scan rate range used for the Keggin-type anions (20 to 200 mV/s), all of the correlation coefficients determined were ca. 0.99. For the parent Keggin anions PW_{12} and SiW_{12} we obtained $6.0 \cdot 10^{-6}$ and $4.3 \cdot 10^{-6}$ cm^2/s, respectively. The reported $6.1 \cdot 10^{-6}$ for $[SiW_{12}O_{40}]^{4-}$ in aqueous solution (pH, 4.0),[62] is slightly higher than that obtained in acetonitrile. For the lacunary and metal substituted anions, the estimated values of $1.5 \cdot 10^{-7}$ to $1.3 \cdot 10^{-6}$ cm^2/s are lower than those reported in aqueous solution for identical anions of the same charge, e.g. $XW_{11}M$, X = P, Si, Ge, B; M = Cr, Fe, Ir,[11,14] (ca. 3−4 $\times 10^{-6}$ cm^2/s) and others.[63] However, care must be taken in making direct comparisons with these literature values, since they were obtained not only with different solvent composition, but also with different countercations, which are important factors that affect *D*.[63]

Concluding Remarks

We have performed a comparative study by cyclic voltammetry and spectroelectrochemistry of the polyoxoanions $[XW_{11}M(H_2O)O_{39}]^{m-}$, and $[XW_{11}O_{39}]^{n-}$, X = P, Si, M^{II} = Co, Ni, M^{III} = Fe, Mn, in acetonitrile solutions obtained by solubilisation of the corresponding TBA salts. In general, cyclic voltammetry in acetonitrile revealed several differences between the electrochemical behaviour of the anions and previous results in aqueous solution.[10,18,21,22] Thus, tungsten one-electron reductions were detected in acetonitrile, with corresponding reduction potentials at more negative values than those in aqueous solution. These facts were not totally unexpected, as comparable results had been previously reported for other Keggin-type anions,[5] but had not been systematically observed for the transition-metal-substituted anions here reported, for which studies in organic solvents were unknown.

The preparative methods used here led to the TBA salts $TBA_4H_x[XW_{11}M(H_2O)O_{39}]$ and $TBA_4H_x[XW_{11}O_{39}]$. Because of this, protons were introduced in solution (except for $PW_{11}M^{III}$, with $x = 0$) with important consequences for redox behaviour observed by cyclic voltammetry in acetonitrile. The degree of protonation of the anions or of the corresponding reduced species in acetonitrile solution is not known, but the fact that the results reflected the composition of the solids used is worth noting. In summary, the different effects identified in the study of these compounds are:

(1) In the presence of protons, tungsten atoms were reduced at less negative potentials. Compounds for which, due to stoichiometry, protons were not added to the solution had a CV with fewer peaks in the potential range studied.

(2) For compounds with $x = 1$ or 2, equilibria established between species with different protonation degrees changed the general pattern of the voltammograms, splitting some waves (generally those at less negative potentials). However, for the lacunary anions, for which $x = 3$ or 4, no such splitting of the re-oxidation waves was observed.

Consequently, the CV of the $PW_{11}M^{III}$, presented only one tungsten redox pair, whereas, depending on the compound studied, two or three electrons were transferred to the tungsten-oxo framework of the other heteropolyanions upon reduction.

Redox processes were detected at the metal centre for all the studied metal substituted Keggin anions, except for $XW_{11}Ni$. Two of the chosen anions included reducible substituting metal ions (Mn^{III} and Fe^{III}), and the waves corresponding to the M^{III}/M^{II} redox pairs were identified. This contrasts with reported studies on Ru^{III} and Ir^{IV} complexes in acetonitrile, in which reduction of the metals was not detected by cyclic voltammetry.[11,29] Our results indicate that the oxidation $Mn^{II} \rightarrow Mn^{III}$ is more favourable in acetonitrile than in water.[17] This accords with the slow oxidation of Mn^{II} to Mn^{III} by atmospheric O_2 that is commonly found for these anions in acetonitrile solution. Further oxidation to Mn^{IV} was only observed for $SiW_{11}Mn$. Oxidation of cobalt(II), and the corresponding reduction, was observed for both $XW_{11}Co$ anions (X = P, Si). Nevertheless, oxidations at high potentials ($Mn^{III} \rightarrow Mn^{IV}$ and $Co^{II} \rightarrow Co^{III}$) were more conveniently studied at a Pt electrode.

We have performed the first electrochemical study of the Keggin-derived sandwich complexes $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$, M^{II} = Co, Mn, in acetonitrile. Metal oxidation in two separate steps was observed for both anions, but only for cobalt could the corresponding reductions be detected by cyclic voltammetry. Thus, in acetonitrile, two atoms in the belt of the $[M^{II}_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anions (possibly the more external metal atoms) could be electrochemically oxidised in two separate steps to M^{III}.

Experimental Section

Reagents and Methods: All reagents were used as received, including tetra-*n*-butylammonium perchlorate (Sigma) and acetonitrile (Panreac, for instrumental analyses, HPLC grade). Elemental and thermogravimetric analysis, spectroscopic studies (infrared and visible), and powder X-ray diffraction analysis were performed as described previously.[64]

Electrochemical Measurements: Cyclic voltammetry measurements were carried out on a BAS 100BW electrochemical analyser using a conventional three-electrode single compartment cell supplied by BAS Inc. The working electrode was a glassy carbon disc electrode (BAS) or a homemade platinum foil electrode. The surface of the glassy carbon electrode was polished with 0.3 µm alumina and washed with distilled water and acetonitrile before each experiment. The auxiliary electrode was a Pt wire. The reference electrode comprised an Ag wire immersed in a solution of $AgNO_3$ (0.01 M) and $TBAClO_4$ (0.1 M) in acetonitrile. The Ag/Ag^+ reference electrode was calibrated against ferrocene/ferrocenium redox couple (1 mM) in the same solvent/electrolyte system. At scan rates between 20 and 200 mV/s, ferrocene presented $E_{1/2} = +0.087$ V vs. Ag/Ag^+, with a peak separation, ΔE_p, (anodic to cathodic) of 71 mV. All potentials quoted are relative to the Ag/Ag^+ reference electrode. The measurements were made at room temperature (ca. 20 °C), within the potential window +1300 to −2400 mV. The solutions were degassed with pure nitrogen for 5 minutes before use and blanketed with nitrogen gas during the voltammetric scans. Acetonitrile solutions (0.1 M $TBAClO_4$) were prepared for TBA salts of $XW_{11}M$ ($1.00 \cdot 10^{-2}$ M) or for TBA salts of $M_4(PW_9)_2$ ($3.00 \cdot 10^{-3}$ M).

Controlled potential electrolysis experiments were performed using a BAS 100BW electrochemical analyser or an AUTOLAB PGSTAT 30 Potentiostat. The reference electrode was the same as above. A carbon cloth or a platinum mesh was used as the working electrode. The counter electrode was a platinum mesh of large surface area placed in a glass tube chamber filled with the supporting electrolyte (0.2 M $TBAClO_4$ in acetonitrile) and separated from the working electrode compartment (electrolysis solution) by a porous vycor frit. To remove oxygen, nitrogen was constantly bubbled through the electrolysis solution, which was continuously stirred with a magnetic bar. All experiments were performed at room temperature.

Spectroelectrochemical experiments were performed on a UNICAM UV1 spectrophotometer connected to an AUTOLAB PGSTAT 30 potentiostat, using a quartz cuvette (4 cm optical path). The three-electrode system was inserted in the cell and kept under continuous nitrogen bubbling and stirring during electrolysis. The working electrode was a platinum foil. Experiments were performed at room temperature.

Synthesis of the Tetrabutylammonium Compounds: Published procedures were used to prepare $[(C_4H_9)_4N]_3[PW_{12}O_{40}]$,[65] $[(C_4H_9)_4N]_4[SiW_{12}O_{40}]$,[65] $[(C_4H_9)_4N]_4H_3[PW_{11}O_{39}]$,[38] $[(C_4H_9)_4N]_4H_x[PW_{11}M(H_2O)O_{39}]\cdot nH_2O$, M^{II} = Co, Ni, $x = 1$, $n = 1-2$; M^{III} = Fe, $x = 0$, $n = 0$.[38] The general procedure described in ref.[38] was also used to prepare $[(C_4H_9)_4N]_4[PW_{11}Mn^{III}(H_2O)O_{39}]$.

$[(C_4H_9)_4N]_4H_4[SiW_{11}O_{39}]$, $[(C_4H_9)_4N]_4H_2[SiW_{11}M(H_2O)O_{39}]\cdot nH_2O$, $n = 1-2$; M^{II} = Co, Ni, $[(C_4H_9)_4N]_4H[SiW_{11}M(H_2O)O_{39}]$, M^{III} = Fe, Mn, were obtained from potassium salts using a procedure adapted from the literature.[66] The potassium compounds of $SiW_{11}M$ (or SiW_{11}) were prepared by reported methods.[20,50,53,67] An aqueous solution of the potassium salt (0.5 mmol in 30 mL) and a solution of TBABr in 1,2-dichloroethane (4 mmol in 45 mL) were mixed and vigorously stirred. The organic phase was then collected and the 1,2-dichloroethane removed by evaporation. The so-obtained oil was then dissolved in acetonitrile (ca.

20 mL) and the resultant tetrabutylammonium compound was precipitated by the addition of the minimum amount of water.

$[(C_4H_9)_4N]_7H_3[M_4(H_2O)_2(PW_9O_{34})_2]$, M^{II} = Co, Mn. An aqueous solution of the potassium salt[41,68] of the $M_4(PW_9)_2$ anion (2.7 mmol in 270 mL) and a solution of TBABr (42 mmol) in an identical volume of 1,2-dichloroethane were prepared and the polyoxoanion was extracted into the organic phase. A second organic extract was collected by a further addition of TBABr organic solution. The organic extracts were then left to evaporate and the so-formed crystals were filtered off and washed with water.

The TBA salts of $SiW_{11}M$ (or SiW_{11}) and $M_4(PW_9)_2$ were re-crystallised in acetonitrile. Dissolution in the minimum amount of acetonitrile followed by the addition of water (with vigorous stirring) then afforded pure samples of TBA compounds.

$[(C_4H_9)_4N]_4H_4[SiW_{11}O_{39}]$, analytical data [found (calculated), %]: W 54.5 (55.4), C 21.68 (21.07), N 1.53 (1.53), H 4.09 (4.09). IR (cm^{-1}): 1010, $\nu_{as}(W{=}O)$, 966, $\nu_{as}(Si{-}O)/\nu_{as}(W{-}O_b{-}W)$, 919, 884, $\nu_{as}(W{-}O_c{-}W)$, 801.

$[(C_4H_9)_4N]_4H_2[SiW_{11}Co(H_2O)O_{39}].H_2O$, analytical data: W 51.9 (54.0), Co 1.38 (1.57), C 20.87 (20.55), N 1.49 (1.50), H 4.04 (4.04). IR (cm^{-1}): 1001, $\nu_{as}(W{=}O)$, 959, $\nu_{as}(Si{-}O)/\nu_{as}(W{-}O_b{-}W)$, 907, 878 (sh), $\nu_{as}(W{-}O_c{-}W)$, 808, 792 (sh), 740 (sh).

$[(C_4H_9)_4N]_4H_2[SiW_{11}Ni(H_2O)O_{39}]\cdot 2H_2O$, analytical data: W 51.2 (53.8), C 20.10 (20.45), N 1.43 (1.49), H 3.92 (4.08). IR (cm^{-1}): 1001, $\nu_{as}(W{=}O)$, 958, $\nu_{as}(Si{-}O)/\nu_{as}(W{-}O_b{-}W)$, 907, 885 (sh), $\nu_{as}(W{-}O_c{-}W)$, 807, 721, 699.

$[(C_4H_9)_4N]_4H[SiW_{11}Fe(H_2O)O_{39}]$, analytical data: W 53.5 (54.4), Fe 1.48 (1.50), C 20.38 (20.67), N 1.46 (1.51), H 3.87 (3.98). IR (cm^{-1}): 1005, $\nu_{as}(W{=}O)$, 960, $\nu_{as}(Si{-}O)/\nu_{as}$ $(W{-}O_b{-}W)$, 913, 878, $\nu_{as}(W{-}O_c{-}W)$, 796, 740 (sh).

$[(C_4H_9)_4N]_4H[SiW_{11}Mn(H_2O)O_{39}]$, analytical data: W 53.1 (54.4), Mn 1.36 (1.48), C 20.70 (20.67), N 1.57 (1.51), H 4.02 (3.98). IR (cm^{-1}): 1004, $\nu_{as}(W{=}O)$, 960, $\nu_{as}(Si{-}O)/\nu_{as}(W{-}O_b{-}W)$, 915, 894 (sh), 875, $\nu_{as}(W{-}O_c{-}W)$, 793.

$[(C_4H_9)_4N]_7H_3[Co_4(H_2O)_2(PW_9O_{34})_2]$, analytical data: W 53.3 (51.5), P 1.02 (0.96), Co 3.74 (3.67), C 20.42 (20.92), N 1.38 (1.52), H 3.99 (4.06). IR (cm^{-1}): $\nu_{as}(P{-}O)$, 1063 (sh), 1042, $\nu_{as}(W{=}O)$, 966, 946, $\nu_{as}(W{-}O_b{-}W)$, 883, $\nu_{as}(W{-}O_c{-}W)$, 832, 776, 721. Visible spectrum [acetonitrile solution, in nm (ε in $mol^{-1}dm^3cm^{-1}$)]: 502 (ε = 114); 527 sh (ε = 132); 546 sh (ε = 153); 568 (ε = 163).

$[(C_4H_9)_4N]_7H_3[Mn_4(H_2O)_2(PW_9O_{34})_2]$, analytical data: W 49.9 (51.6), P 0.95 (0.97), Mn 3.08 (3.42), C 20.81 (20.97), N 1.42 (1.53), H 4.00 (4.07). IR (cm^{-1}): $\nu_{as}(P{-}O)$, 1065 (sh), 1037, $\nu_{as}(W{=}O)$, 966, 944, $\nu_{as}(W{-}O_b{-}W)$, 879, $\nu_{as}(W{-}O_c{-}W)$, 834, 774, 730.

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