Synthesis, Characterization and Electrochemistry of Complexes Derived from $[(1),2,3\text{-}P_2Mo_2W_{15}O_{61}]^{10-}$ and First Transition Metal Ions

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The complexes formed by $[(1)\text{-}2,3\text{-}P_2Mo_2W_{15}O_{61}]^{10-}$ with vanadium(IV), manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) were synthesized. They were characterized by elemental analysis, IR, UV/Vis and ^{31}P NMR spectroscopy. Their electrochemical studies are complemented by those of the previously synthesized iron(III)- and Mo(VI)-substituted complexes. Among the main conclusions from the electrochemistry of all these compounds, it can be pointed out that only the iron(III) and the copper(II) ions within the complexes are reducible in the same potential domain as the molybdenum(VI) moieties. In the case of the iron(III) complex, it has been possible to obtain a reversible overall three-electron process on the first wave of the oxometalate by varying the pH of the solution. In contrast, copper can be deposited from the corresponding complex. Substitution of $[(1)\text{-}2,3\text{-}P_2Mo_2W_{15}O_{61}]^{10-}$ with vanadium(IV), manganese(II), iron(III), cobalt(II), nickel(II), copper(II), zinc(II) and molybdenum(VI) gives a series of complexes in which the trimetallic moiety constituting one of the "caps" of the polyoxometalate contains cations different from the remaining tungsten skeleton. The electrochemical properties of these complexes are modulated by this particular constitution.

Introduction

In recent articles,[1,2] we described the syntheses, characterization and the electrochemical properties of some monoferro-heptadecatungsto-diphosphates and pentadecatungsto-dimolybdo-diphosphates. This work constitutes a first step in our systematic examination of parameters and combination of parameters which could favor or counteract the merging of the first several waves in heteropolyanion (HPA) electrochemistry. As a matter of fact, it turns out that most energetically favorable electro-reductive catalytic processes triggered by HPAs require more than one electron and are thus, usually accomplished at fairly negative potentials where the necessary number of electrons could be accumulated and delivered by the framework. In the above-mentioned articles from this group, three complexes of the present series have already been studied, with M = Mo^{VI}, V^{V}, Fe^{III}. The electrochemistry of $\alpha_2P_2Mo_3W_{15}$ has been described briefly.[2,3] In a pH = 2 medium, its cyclic voltammogram begins with three well-behaved one-electron diffusion waves. In contrast, with V^{V} as a substituent instead of Mo^{VI}, the molybdenum centers are easily reduced through an apparently direct two-electron process. Still more striking, the substitution by Fe^{III}, combined with pH effects, allows for an approach to an overall three-electron process on the first voltammetric wave of the corresponding complex in a pH = 2 medium. Such results stimulated the need for the present study. Furthermore, as another incentive, it is anticipated that the presence of two molybdenum atoms in the "cap" near the substituent heterocation might substantially influence the electronic communication between the various sites in this trimetallic moiety, especially during redox processes. In this context, we describe here the syntheses, characterization and electrochemical properties of the complexes formed by $[(1)\text{-}2,3\text{-}P_2Mo_2W_{15}O_{61}]^{10-}$ with some first transition metal ions and with the Zn dication.

Results and Discussion

All the polyanions to be studied here can be considered as being primarily derived from $[\alpha P_2W_{18}O_{62}]^{6-}$, abbreviated as P_2W_{18}. In Figure 1, the tungsten atoms in αP_2W_{18} are

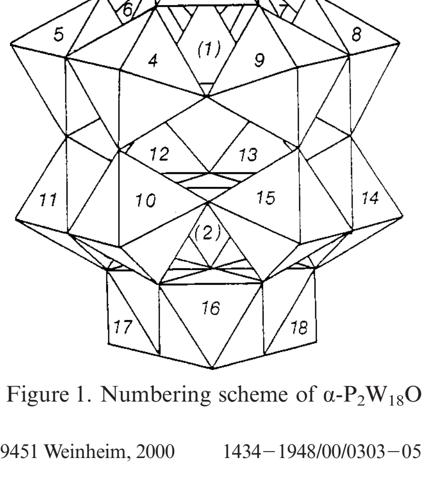

Figure 1. Numbering scheme of $\alpha\text{-}P_2W_{18}O_{62}^{6-}$ (Dawson structure)

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Table 1. Selected IR data for $(M^{(x)}(H_2O)(P_2Mo_2W_{15}O_{61})^{10-x}$. The assignments follow from the results of references 9 through 11 (ν_{as}: $\nu_{asymmetric}$; vs.: very strong; s: strong; m: medium; sh: shoulder; w: weak).

	ν_{as} **PO$_a$**W	ν_{as} **PO$_a$**Mo	ν_{as}W**O$_d$**	ν_{as}Mo**O$_d$**
α-$K_6P_2W_{18}O_{62}$	1091(vs.)		959(s)	
	1021(w)		911(s)	
α2-$K_{10}P_2W_{17}O_{61}$	1084(vs.)		938(s)	
	1051(m)		910(m)	
	1014(m)		867(w)	
α-$Na_{12}P_2W_{15}O_{56}$	1131(s)		935(w)	
	1087(vs.)			
	1008(s)			
	977(w)		913(w)	
α2-$K_{10}P_2Mo_2W_{15}O_{61}$	1082(vs.)		936(vs.)	
	1022(w)	1047(m)	922(sh)	885(m)
α2-$K_8(VOP_2Mo_2W_{15}O_{61})$	1084(vs.)		945(vs.)	
	1016(m)	1062(w)	918(w)	888(w)
α3-$K_8(Mn(OH_2)P_2Mo_2W_{15}O_{61})$	1083(vs.)		939(m)	
	1012(m)	1054(m)	916(w)	896(sh)
α2-$K_8(Co(OH_2)P_2Mo_2W_{15}O_{61})$	1083(vs.)		941(vs.)	
	1010(m)	1060(w)	915(m)	892(sh)
α2-$K_8(Ni(OH_2)P_2Mo_2W_{15}O_{61})$	1083(vs.)		942(vs.)	
	1009(m)	1059(sh)	916(m)	893(sh)
α2-$K_8(Cu(OH_2)P_2Mo_2W_{15}O_{61})$	1083(vs.)		940(vs.)	
	1015(w)	1056(m)	918(w)	890(w)
α2-$K_8Zn(OH_2)P_2Mo_2W_{15}O_{61})$	1083(vs.)		940(vs.)	
	1014(m)	1055(m)	918(w)	890(sh)

numbered according to the IUPAC recommendations.[4] The two P atoms are numbered (1) and (2) for the upper and the lower halves of the molecule, respectively. Considering the upper half of the molecule and taking into account the numbering, the metal atoms in the "cap" occupy what will be termed α_2 positions and those in the "belt", α_1 positions. In the lacunary species, the vacancies (missing W atoms) are numbered in the same way and represented by ☐ in the formula of the anion. Any heterometal filling the vacancy will keep the same index.

Syntheses

The metal cation substituted species were elaborated under the same conditions as the iron(III)-substituted one. However, the ^{31}P NMR spectra have shown that there was an isomerically pure compound with V, Ni and Cu, but two compounds with Mn, Co and Zn. With heated Co sample, two main compounds and several isomeric impurities were observed. Such a behavior has been described by T. L. Jorris et al.[5] on metallo-heptadecatungsto-diphosphates. and was interpreted as $\alpha_2 \rightarrow \alpha_1$ isomerization. In our case the migration of molybdenum atoms may give numerous other isomers. The number and the nature and the ratio of isomers depend on preparation conditions. To obtain more than 90% of the α_2 isomer, the synthesis must be performed in acidic solution without heating.

UV/Vis and IR Characterization

The formation constants of the complexes have been measured. The logβ values are fairly large; they are shown in brackets for the various substituent metal cations: V^{IV} (>18); Mn^{II} (6.5); Fe^{III} (17.2); Co^{II} (7.4); Ni^{II} (7.5); Cu^{II} (7.9); Zn^{II} (7.5). The electrochemical behavior to be discussed in a subsequent section, has been studied essentially at pH 3 and 5 for all the complexes. Their stability in these media and, occasionally in others when necessary, has been checked by monitoring their UV/Vis spectra at least over a period of 24 h. The only slight instability was detected with the cobalt-substituted compound, which shows decreasing absorbance, even though the decrease is not fast enough to preclude an electrochemical study.

^{31}P NMR

The NMR study of paramagnetic elements containing HPAs was performed by Jorris et al.[5] on P_2W_{17}. They found no isomerically pure compound but a mixture of α_1 and α_2 isomers. They observed with the α_2 isomer that the chemical shifts of the P atom far from the paramagnetic elements were unaffected by the nature of the element. There is an exception: Co^{II}. The same observation, with the same exception, appears in Table 2 and in Figure 2. This

Table 2. ^{31}P NMR chemical shifts (from 85% H_3PO_4) and line widths of α_1- and α_2-monometallo-dimolybdo-pentadecatungsto-diphosphates at 298 K (0.01 M solutions of K^+ salts in LiCl 1 M, in 20% D_2O)

Species	δ(P1) ppm	Δν(P1) Hz	δ (P2) ppm	Δν(P2) Hz
$V^{IV}P_2Mo_2W_{15}$[a]	8.3	2500	–13.7	15
$Mn^{II}P_2Mo_2W_{15}$[a]	not observed		–13.0	150
$Fe^{III}P_2Mo_2W_{15}$[a]	ca. 900	ca.>30000	–13.6	100
$Co^{II}P_2Mo_2W_{15}$[a]	350	80	–17.7	6
$Ni^{II}P_2Mo_2W_{15}$[a]	ca. 230	1100	–14.1	80
$Cu^{II}P_2Mo_2W_{15}$[a]	–27.2	1100	–13.0	60
$Zn^{II}P_2Mo_2W_{15}$[a]	–6.3	3	–13.65	3
P_2Mo_2W15[b]	–4.93	2	–13.75	2
$P_2Mo_3W_{15}$[b]	–9.7	2	–12.24	2
$Mn^{II}P_2Mo_2W_{15}$[c] (α_1)	not observed		–4.1	200
$Co^{II}P_2Mo_2W_{15}$[c] (α_1)	300	100	–20.8	6
$Zn^{II}P_2Mo_2W_{15}$[c] (α_1)	–7.21	3	–13.6	2

[a] Pure isomer or main product. – [b] See ref.[4] – [c] Minor product.

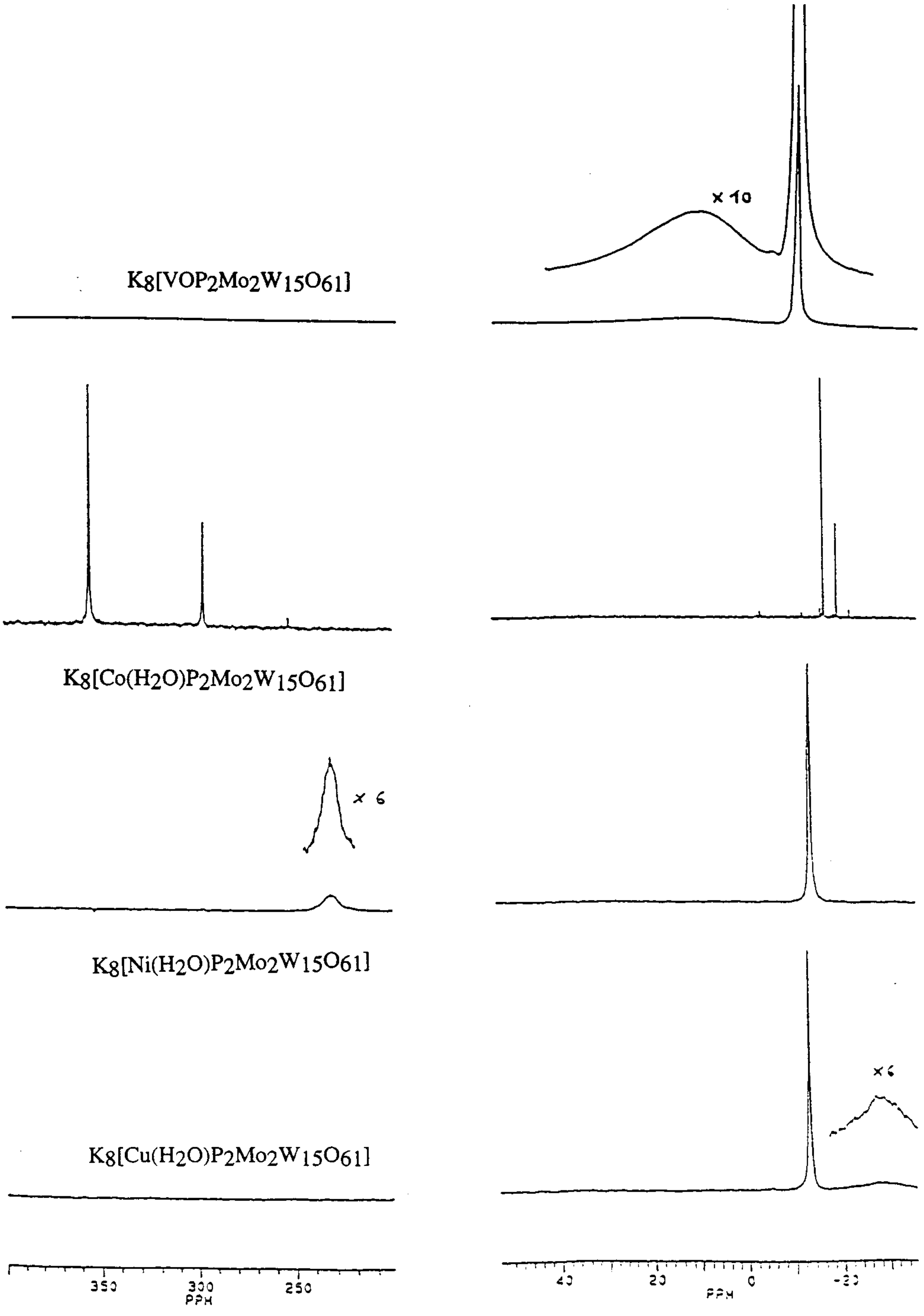

Figure 2. Selected representative ^{31}P NMR spectra. The appropriate compound formula is indicated on each spectrum

Figure shows spectra representative of the whole series. Such an observation confirms the stereospecificity of the syntheses. Under the same standard conditions used for all the other compounds, only one ^{31}P NMR line is observed for the V^{IV}-substituted species. Therefore, particular attention has been exercised to obtain a satisfactory ^{31}P NMR spectrum for this complex. A fairly concentrated solution of the lithium salt of this compound was prepared. With such a solution, it has been possible to observe the NMR line corresponding to the phosphorus atom in the close vicinity of the magnetic atom. This line appears at around $\delta = 8.3$ ppm and is roughly 2500 Hz broad.

Electrochemistry

The following studies are restricted either to the first or to the first few chemically reversible redox processes of the substituted complexes, and to their changes with pH. As a matter of fact, we are interested in controlling the number of electrons which could be accumulated on the first wave of HPAs. This restriction also avoids any derivatization of the electrode surface as observed previously, albeit under different conditions.[9] In this study, the focus will be directed mainly on the reduction of molybdenum centers up to the first wave corresponding to the reduction of the tungsten framework. The redox behavior of the "substituent" metallic center will be considered simultaneously when it happens to appear in the potential domain of interest for the reduction of molybdenum centers. Otherwise, this behavior will be described separately.

Well-separated redox behaviors for the substituent cation and for the HPA framework: This situation is encountered with V^{IV}-, Mn^{II}-, Co^{II}-, Ni^{II}-, and Zn^{II}-substituted compounds. Figure 3 shows representative examples of the main features observed, throughout this work, for most of the complexes at pH = 3 and pH = 5. The Ni^{II} and V^{IV} complexes have been chosen. The cyclic voltammogram of the parent lacunary complex has been added for comparison. In Figure 3A, two well-behaved redox systems are observed. In line with previous work,[1,2,10] the first wave is assigned to the reduction of the molybdenum centers. Whatever the substituted complex, only very modest peak potential and peak current intensity variations are observed compared to the same parameters for the lacunary species, provided comparable concentrations are used. It must be concluded that for the pH = 3 medium, the Ni^{II}- and V^{IV}-substituted complexes behave in the same way as the lacunary compound, at least where the reduction of the molybdenum centers is concerned. No reduction of the substituent "heterometallic" cation has been detected in the potential domain studied. In Figure 3A, the wave corresponding to the reduction of the tungsten framework appears to be more discriminating among the complexes. Starting with the lacunary compound, the potential location of this "tungsten wave" is pushed to more and more negative values when passing to the Ni^{II}- and the V^{IV}-substituted complexes. It is worth noting that the trend is the same, but much more pronounced here than for the reduction of molybdenum centers. In this pH = 3 medium, exactly the same general behavior as observed for the Ni^{II}- and V^{IV}-substituted complexes is seen with Mn^{II}, Co^{II}, and Zn^{II} as substituents.

Figure 3B, obtained at pH = 5 for the lacunary species and for the Ni^{II}- and V^{IV}-substituted complexes displays more contrasted behaviors. We focus first on the cyclic voltammogram of the lacunary species. The cathodic pattern is composed of a system of drawn-out, presumably close-spaced two waves, followed by a well-defined two-electron wave. By continuity with the observations performed in the pH = 3 and the pH = 4 (not shown) media, the first system should be attributed to the reduction of molybdenum centers, while the last wave should feature the reduction of the tungsten framework. It is worth noting that on potential reversal, the respective anodic traces are well-behaved. In particular, a single anodic wave is observed for the reoxidation of the molybdenum centers. This result would suggest that no intrinsic electron-transfer "slowness" should actually exist for the reduction of molybdenum moieties. So, the observation might be traced to one or several of the following effects: condensation, pH and/or cation effects in the solution. The cyclic voltammetric patterns for Ni^{II}- and V^{IV}-substituted compounds can be considered as featuring a modulation, to different extents, of the observed sluggishness in the lacunary complex. For the V^{IV} complex, the first wave remains peak-shaped while a rather plateau current is obtained for the Ni^{II} complex. It must be noted that the "slowness" is less pronounced for these complexes than for the lacunary compound. Also, the tungsten wave can no longer be considered as a fingerprint to distinguish between the Ni^{II} and V^{IV} compounds, as their potential locations are now roughly the same.

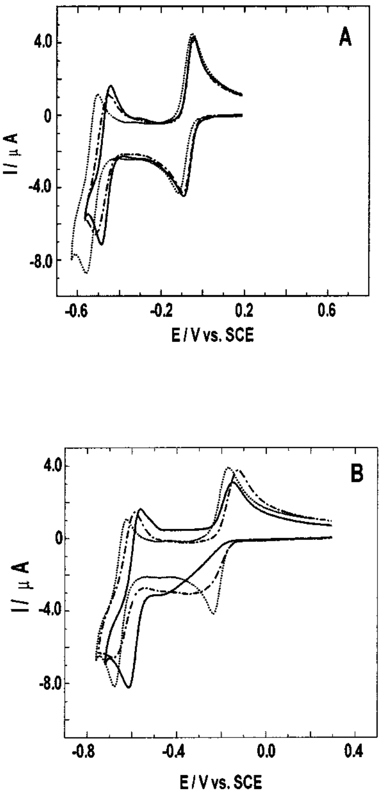

Figure 3. Comparison of the cyclic voltammograms observed for 5 × 10^{-4} M solutions of the lacunary heteropolyanion $[(1)\text{-}2,3\text{-}P_2Mo_2W_{15}O_{61}]^{10-}$ and the corresponding Ni^{II}- and V^{IV}-substituted complexes. Scan rate: 10 mV s^{-1} .(A) pH = 3 (0.2 M Na_2SO_4 + H_2SO_4): *solid line curve*: $P_2\square Mo_2W_{15}$; *dot and dash curve*: $P_2W_{15}Mo_2Ni$; *short dot curve*: $VP_2Mo_2W_{15}$. (B) pH = 5 (0.2 M CH_3COONa + CH_3COOH): *solid line curve*: $P_2\square Mo_2W_{15}$; *dot and dash curve*: $P_2W_{15}Mo_2Ni$; *short dot curve* $P_2VMo_2W_{15}$. For further details, see text.

The observations in the pH = 4 medium show a smooth transition of wave shapes and potential locations from the pH = 5 medium. The complexes substituted by the other metallic cations selected in this work, have also been examined in the same pH media. Due to the smooth evolution already mentioned, emphasis is put here only on the pH = 5 medium. The main qualitative difference is the extent of "slowness" observed from one complex to the next. In this series, it was found that the first wave of the V^{IV}-substituted complex has kept a sharp peak shape. All other complexes show plateau currents, with the same limiting current. For this purpose, due care has been exercised concerning the reproducibility of the working electrode surface area and the concentrations of the complexes in solution. Incidentally, the results for pH = 3 prove that the diffusion coefficients remain very close to each other in these complexes. We arbitrarily chose the only well-defined peak potential value as the reference point for which the current intensities are measured for all the other complexes. Then, as no current crossing is observed between the various ”polarograms“ up to their common limiting value, the measured current intensities feature a qualitatively good index of the relative ”slowness“ among complexes. In the order of increasing slowness, the scale is then: V^{IV}(0.62), Ni^{II}(0.69), Co^{II}(0;72), Zn^{II}(0.74), Mn^{II}(0.80) and □, where this symbol represents the vacancy. Provisional crystal ionic radii of the various ions in Å are given in brackets.[11]

Considering all the results together, it becomes evident that a large number of parameters or combinations of parameters govern the electrochemical behaviors of the present complexes as revealed by cyclic voltammetry. Only qualitative aspects can be considered here as possible guidelines in an attempt at rationalization of the observed behaviors. Despite this really entangled situation, a simple electrostatic consideration might explain qualitatively the difference between the metal cation substituted complexes and the lacunary species. The substitution lowers the negative charge on the heteropolyanion and facilitates its reduction. Then, the differences between the potential locations of the various substituted complexes are more difficult to rationalize. As a matter of fact, it is probably more difficult to take several possible parameters into account. The size of each ion, its electronic configuration, its favorite geometry, should contribute to fix the extent of its penetration in the vacancy of the lacunary HPA. The possibility and extent of the Jahn–Teller effect should not be neglected. Furthermore, there is no change in the oxidation state of the heterometallic cation during the redox processes studied in this section, which could have modified the abovementioned considerations substantially. Also, it must be anticipated that the presence of the two MoO_6 octahedra next to the vacancy should render the latter more flexible than in a skeleton comprised totally of tungsten. The interplay of these various influences should determine the extent of “effective” lowering of the negative charge on the heteropolyanion due to substituent metallic cation, relative to the initial charge of the lacunary species. It should also determine, at least partly, the possibility and extent of electronic “communication” between neighbor redox centers in the complex, and, more specifically, between the heterometal substituent and the molybdenum moieties. A more important parameter in this last issue is the distribution of the redox potentials of the possibly interacting centers. Although no clear conclusions can be drawn, it is worth noting provisionally that it is now widely accepted that P_2W_{18} is initially reduced at one of the twelve equivalent tungsten atoms.[3,12,13] Here, the molybdenum centers, which are more easily reducible than the tungsten moieties, are situated in the "cap". On the basis of the foregoing discussion, no simple correlation is expected unless a single parameter overrides all others and/or several parameters show the same trend. However, the results in Figure 3B and the corresponding results for the other complexes would suggest that the “slowness” observed for the reduction of molybdenum centers is strictly larger as the crystal ionic radius of the substituent cation increases. But such an explanation would not include the results in Figure 3A, in which such a possible size effect could not be distinguished. Finally, in the present qualitative discussion, the pH appears as a decisive parameter. As a matter of fact, ECE-type mechanisms are known to intervene frequently in the redox behaviors of heteropolyanions.[14,15]

The redox behaviors of the substituent metal cations have been studied briefly. In the potential domains explored, no electrochemical activity has been detected for Ni^{II} or Zn^{II}. The Co^{II} center is oxidized to Co^{III}, with a peak potential observed at +1.120 V vs. SCE during the first positive potential scan. This wave disappears on subsequent runs. Even during the very first run, no reduction of Co^{III} back to Co^{II} is obtained. Such a behavior should be traced to the abovementioned lability of the cobalt-substituted complex rather than to an electrode material effect. In contrast, a well-behaved, reversible one-electron wave is observed for the oxidation of V^{IV} to V^{V} and the subsequent reduction of V^{V} to V^{IV} with E_0 around +0.412 V vs. SCE at pH = 5. This wave seems slightly pH-dependent. The case of Mn^{II} is more striking, as at least two fairly stable states are obtained, featuring the Mn^{II}/Mn^{III} and Mn^{III}/Mn^{IV} steps.

Mixed redox behaviors for the substituent cation and for the HPA framework: This situation, encountered with Fe^{III} and Cu^{II} as substituents in the present work, is the one likely to make the first wave of the corresponding HPAs involve *n* electrons (*n* □ 2). The case of the Fe^{III} complex has been described briefly,[1,2] and is mentioned here for completeness and for the sake of comparison with the Cu^{II} complex. Typically, the presence of the Fe^{III} cation in $[\alpha_2Fe(OH_2)P_2Mo_2W_{15}]^{7-}$, abbreviated as $\alpha_2FeP_2Mo_2W_{15}$, modifies substantially the electrochemical behavior of this heteropolyanion compared to the behavior of $\alpha_2P_2Mo_3W_{15}O_{62}^{6-}(\alpha_2P_2Mo_3W_{15})$. In a pH = 2 medium, the cyclic voltammogram of $\alpha_2P_2Mo_3W_{15}$ begins with three diffusion-controlled one-electron waves. In contrast, the iron(III)-substituted complex displays a cyclic voltammogram nearly identical in potential locations to that of the corresponding lacunary species. Comparison of current intensities as well as controlled potential coulometry indicate the consumption of roughly three electrons per molecule on the first wave of $\alpha_2FeP_2Mo_2W_{15}$. This result is consistent with the merging of the molybdenum and iron waves at pH = 2. The combined wave remains chemically reversible upon cycling. A study of this pattern as a function of pH allows the Fe^{III} wave to be separated from the molybdenum reduction, thus confirming the merging mechanism.

Figure 4 shows representative examples of the cyclic voltammograms obtained with the Cu^{II} substituted complex. In Figure 4A, the “first” wave of the system is displayed for pH = 3 and pH = 5. The pH-dependence is obvious for

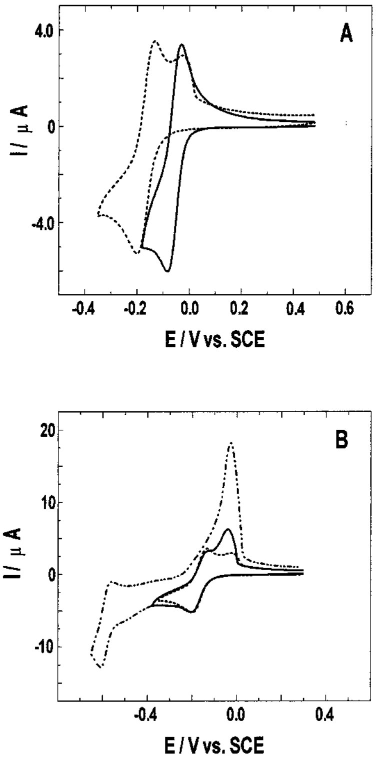

Figure 4. Cyclic voltammograms observed for [1,2,3-$P_2CuMo_2W_{15}$) under various conditions. Scan rate: 10 mV s^{-1}. – (A) *Solid line curve*: pH = 3 (0.2 M Na_2SO_4 + H_2SO_4). Use of an acetate medium does not modify the results. – *Short dot curve* pH = 5 (0.2 M CH_3COONa + CH_3COOH). The voltammograms are restricted to the "first" wave of the system. – (B) pH = 5 (0.2 M CH_3COONa + CH_3COOH): The negative going scan is reversed at different potential values.

the cathodic wave, concerning its potential location as well as its current intensity. A rough estimate would indicate a peak potential shift of 52 mV/pH-unit. These observations must be traced mainly to the electrochemical behavior of molybdenum centers. On potential reversal, two well-defined and well-separated oxidation peaks are observed at pH = 5. The same pattern is obtained at pH = 3, but with poorer separation. This result suggests that one of the two oxidation components is hardly pH-dependent, if at all. It has been checked that no splitting of the oxidation wave associated with the reduced molybdenum centers is observed at pH = 3 and at pH = 5 for the lacunary species α_2P_2 Mo_2W_{15}. A reasonable outcome is the hypothesis that the reduction of the Cu^{II} center mixes up, at least partly, with that of the molybdenum moieties. Support for such a possibility appears in Figure 4B. The well-behaved cathodic trace of the "molybdenum wave" is followed by an ill-defined series of waves. The potential excursion is reversed just past the first other well-behaved wave. Comparison of the cyclic voltammogram of Figure 4B with that of $\alpha_2P_2Mo_2W_{15}$ indicates that this last wave must be associated with the first tungsten-centered redox process of the heteropolyanion framework. The anodic trace associated with the ill-defined zone and the molybdenum wave is clearly composite. The more anodic wave of this composite trace is the larger and the sharper, the more cathodic is the value selected to reverse the potential during the negative going scan. In short, the anodic trace reveals the reduction of copper within the heteropolyanion. The electrochemical behavior of the Cu^{II} in $\alpha_2CuP_2Mo_2W_{15}$ deserves some comments. In the pH domain which could be explored in the present experiments, the copper reduction mixes up partly with the molybdenum reduction. A controlled potential coulometry is performed at $E = -0.176$ V vs. SCE, a potential just negative of the peak of the "molybdenum wave" in a pH = 3 medium, where no obvious reduction of Cu^{II} is observed on the cyclic voltammogram. Substantially more than two electrons per molecule of complex are consumed. Provisionally, it is worth noting that this electrolysis results in a red deposit, visible to the naked eye on the electrode surface. Preliminary XPS analyses indicate mainly the presence of copper in the deposit.

Concluding Remarks

One of the main ideas behind the present work is to take a further step in our systematic study of parameters which could favor several electron processes on the first wave of HPAs. The introduction of two molybdenum atoms in the "cap" of the framework of $\alpha P_2W_{18}O_{62}^{6-}$, with the possibility of varying the nature of the third metallic atom in the corresponding trimetallic moiety, has given interesting results. The molybdenum centers are reducible in a fairly positive potential domain, and their redox behaviors are pH-dependent. Another outcome worth noting is the importance of those heterometallic centers which are easily reduced in the same potential domain as the molybdenum centers. The Fe^{III}- and Cu^{II}-substituents appear to be two excellent illustrations of this conclusion. In the case of Fe^{III}, the interplay between the potential location of the iron-centered reduction and the pH effect on the potential location of the molybdenum moieties reduction, has permitted the observation of a three-electron first wave for $\alpha_2FeP_2Mo_2W_{15}$. For the Cu^{II} complex, a deposition process has been demonstrated, and further details are under scrutiny. For the other metallic cations used in this work, the comparison of their cyclic voltammograms with that of $\alpha_2P_2Mo_2W_{15}$ indicates unambiguously that the influence of all these substituents, in combination with the known pH effect, favors the two-electron reduction of the molybdenum centers. However, the first redox process of the corresponding heteropolyanion remains, at most, limited to the two-electron uptake of the molybdenum centers. Furthermore, some of the metallic substituents do not show any electrochemical activity within the heteropolyanion. Possibly, substitution at the α_1 position rather than at the α_2 position explored here, might be beneficial to circumvent some of the present difficulties. Work is in progress in this direction.

Experimental Section

Preparations: The potassium salt of $[(1)\text{-}2,3\text{-}P_2\square Mo_2W_{15}O_{61}]^{10-}$ was prepared by published methods.[1,3,16,17]

$K_8[VOP_2Mo_2W_{15}O_{61}]\cdot 16H_2O$: A sample of $K_{10}[P_2Mo_2W_{15}O_{61}]\cdot 19H_2O$ (9.4 g, 2 mmol) was dissolved in a stirred solution of LiCl (6.8 g), glacial acetic acid (3.7 mL) and lithium hydroxide (1.64 g) in water (220 mL). A sample of vanadyl sulfate, $VOSO_4\cdot 5H_2O$ (0.51 g, 2 mmol), was added and the whole solution was treated with saturated KCl solution (170 mL). After 30 min, the precipitate was filtered on a sintered glass frit, washed with ethanol and diethyl ether, and dried in air. $K_8[VOP_2Mo_2W_{15}O_{61}]\cdot 16H_2O$: calcd. K 6.72, V 1.10, Mo 4.12, W 59.2, H_2O 6.19; found: K 6.64, V 1.09, Mo 4.1, W 59.0, H_2O 6.25.

$K_8[Mn(H_2O)P_2Mo_2W_{15}O_{61}]\cdot 16H_2O$: To a stirred solution of $Mn(NO_3)_2\cdot 6H_2O$ (0.63 g, 2.2 mmol) in water (80 mL), acidified with HNO_3 (1 M, 0.5 mL), was added $K_{10}[P_2Mo_2W_{15}O_{61}]\cdot 19H_2O$ (9.4 g, 2 mmol). The solution was treated with saturated KCl solution (40 mL). The precipitate was filtered on a sintered glass frit, washed with ethanol and diethyl ether and air-dried. $K_8[Mn(H_2O)P_2Mo_2W_{15}O_{61}]\cdot 16H_2O$: calcd. K 6.71, Mn 1.18, Mo 4.12, W 59.2, H_2O 6.56; found: K 6.65, Mn 1.16, Mo 4.06, W 59.0, H_2O 6.49.

$K_8[CO(H_2O)P_2Mo_2W_{15}O_{61}]\cdot 15H_2O$: Prepared by the same method as the manganese(II) salt. $K_8[Co(H_2O)P_2Mo_2W_{15}O_{61}]\cdot 15H_2O$: calcd. K 6.73, Co 1.27, Mo 4.12, W 59.1, H_2O 6.20; found: K 6.60, Co 1.27, Mo 4.35, W 59.5, H_2O 6.19.

$K_8[Zn(H_2O)P_2Mo_2W_{15}O_{61}]\cdot 14H_2O$: Prepared by the same method as the manganese(II) salt. $K_8[Zn(H_2O)P_2Mo_2W_{15}O_{61}]\cdot 14H_2O$: calcd. K 6.75, Zn 1.41, Mo 4.12, W 59.2, H_2O 5.82; found: K 6.74, Zn 1.37, Mo 4.1, W 59.5, H_2O 5.71

$K_8[Ni(H_2O)P_2Mo_2W_{15}O_{61}]\cdot 15H_2O$: A sample of $Ni(NO_3)_2\cdot 6H_2O$ (0.73 g, 2.5 mmol) was added to water (80 mL) with stirring, and $K_{10}[P_2Mo_2W_{15}O_{61}]\cdot 19\ H_2O$ (9.4 g, 2 mmol) was added. The mixture was warmed up until dissolution occurred, and the solution was then left at 5 °C for a few hours. The pale yellow crystals were filtered off, washed with ethanol and diethyl ether, and then air-dried. $K_8[Ni(H_2O)P_2Mo_2W_{15}O_{61}].15H_2O$: calcd. K 6.73, Ni 1.25, Mo 4.12, W 59.2, H_2O 6.20; found: K 6.65, Ni 1.26, Mo 4.06, W 59.0, H_2O 6.12.

$K_8[Cu(H_2O)P_2Mo_2W_{15}O_{61}]\cdot 15.5H_2O$: Prepared by the same method as the nickel(II) salt. $K_8[Cu(H_2O)P_2Mo_2W_{15}O_{61}].15.5H_2O$: calcd. K 6.71, Cu1.36, Mo 4.12, W 59.2, H_2O 6.37; found: K 6.65, Cu 1.34, Mo 4.07, W 59.9, H_2O 6.34.

NMR, IR and UV Visible and Potentiometric Measurements: ^{31}P NMR spectra were recorded in 10 mm optical density tubes on a Bruker VM 250 apparatus operating at 101.2 MHz, in the Fourier transform mode. The ^{31}P chemical shifts were measured on 0.02 M solutions of the polyanions in aqueous 1 M LiCl (10% D_2O) solutions, and were referenced to external 85% H_3PO_4 by the substitution method. – IR spectra were recorded on a Bio-Rad FTS 165 FTIR spectrophotometer. – UV/Vis spectra were recorded on a 555 Perkin–Elmer spectrophotometer. – Potentiometric measurements were made on a Tacussel LPH 430T pH meter. The apparent formation constant β_{app} for the Fe^{III}-substituted compound was determined potentiometrically in 1M HNO_3, considering that in this medium, the lacunary polyoxometalates of this work do not complex Fe^{2+} ions.[1] The formation constant for the V^{IV}-substituted complex has been evaluated by comparison with the value obtained for the iron complex. For all the other compounds, a procedure derived from that described in detail for the stability constant measurements of Ce^{III} and Ce^{IV} complexes of both the α_1 and α_2 $[P_2W_{17}O_{61}]^{10-}$ isomers[18] was used. A detailed account of these measurements for each complex will be given elsewhere.[19] In the present work, the Co^{II} derivative of α_2 $[P_2W_{17}O_{61}]^{10-}$ was selected as the central species worked out in detail in an acid medium, and with which all the others are then compared. In an acid medium, the lacunary species is known[20] to be in the protonated form α_2 $[H_3P_2W_{17}O_{61}]^{7-}$. The determination of the three acidity constants of this species and that of the substituted complex are the main sources of error. An average estimation of the total error on the $\log\beta$ values is in the range of ± 0.3.

Electrochemical Experiments; Chemicals, Equipment and Apparatus: Pure water was used throughout. It was obtained by passing through a Milli-RO_4 unit and subsequently through a Millipore Q water purification set. All the chemicals were of high-purity grade and were used as received. H_2SO_4, Na_2SO_4, CH_3COONa, CH_3COOH and NaOH were commercial products (Prolabo). The appropriate compositions of the various supporting electrolytes are indicated in the figure captions.

The solutions were purged 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.[21] The glassy carbon samples had a diameter of 5 mm. The electrochemical set-up was an EG G 273 A driven by a PC with the 270 software. The data were recorded in the computer. Potentials are quoted against a saturated calomel electrode (SCE). The counter electrode was a platinum gauze of large surface area. Spectroelectrochemical experiments were performed in a three-compartment cell comprising a 1 cm optical path quartz cuvette. The working electrode was a sheet of glassy carbon (V25, Le Carbone Lorraine). The whole cell remained inserted in the spectrometer cavity and kept under continuous argon bubbling and stirring during the electrolysis. A second 1 cm quartz cell was matched with that of the electrochemical cell and served as a reference. The UV/Vis spectra were recorded with a Perkin–Elmer Lambda 19 spectrophotometer. All experiments were performed at the laboratory temperature.

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[1] R. Contant, M. Abbessi, J. Canny, A. Belhouari, B. Keita, L. Nadjo, *Inorg. Chem.* **1997**, *36*, 4961–4967.

[2] B. Keita, A. Belhouari, L. Nadjo, R. Contant, *J. Electroanal. Chem.* **1998**, *442*, 49–57.

[3] J. P. Ciabrini, R. Contant, J. M. Fruchart, *Polyhedron* **1983**, *2*, 1229–1233.

[4] Y. Jeannin, *Chem. Rev.* **1998**, *98*, 51–76.

[5] T. L. Jorris, M. Kozik, N. Casan-Pastor, P. J. Domaille, R. G. Finke, W. K. Miller, L. C. W. Baker, *J. Am. Chem. Soc.* **1987**, *109*, 7402–7408.

[6] C. Rocchiccioli-Deltcheff, R. Thouvenot, *Spectroscopy Letters* **1979**, *12*, 127–138.

[7] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem.* **1983, 22**, 207–216.

[8] R. Thouvenot, M. Fournier, R. Franck, C. Rocchiccioli-Deltcheff, *Inorg. Chem.* **1984**, *23*, 598–605.

[9] B. Keita, L. Nadjo, *Mater. Chem. Phys.* **1989**, *22*, 77–103.

[10] M. Abbessi, *Thesis*, **1989**, Université Paris VI, France.

[11] Handbook of Chemistry and Physics, 66th edition, p. F164.

[12] G. M. Varga, E. Papaconstantinou, M. T. Pope, *Inorg. Chem.* **1970**, *9*, 662–667.

[13] R. Acerete, S. Harmalker, C. F. Hammer, M. T. Pope, L. C. W. Baker, *J. Chem. Soc., Chem. Commun.* **1979**, 777–779.
[14] B. Keita, L. Nadjo, *Topics in Current Electrochem*. **1993**, *2*, 77–106.
[15] B. Keita, L. Nadjo, *J. Electroanal. Chem*. **1987**, *227*, 77–98.
[16] M. Abbessi, R. Contant, R. Thouvenot, G. Hervé, *Inorg. Chem*. **1991**, *30*, 1695–1702.
[17] R. Contant, *Inorg. Synth*. **1990**, *27*, 104–111.
[18] [18a] J. P. Ciabrini, R. Contant, *J. Chem. Res., Miniprint* **1993**, 2720. [18b] J. P. Ciabrini, R. Contant, *J. Chem. Res.,Synop.* **1993**, 391.
[19] R. Contant *et al., to be published*.
[20] [20a] R. Contant, J. P. Ciabrini, *J. Chem. Res., Miniprint* **1982**, 641–660. [20b] R. Contant, J. P. Ciabrini, *J. Chem. Res., Synop.* **1982**, 50–51.
[21] B. Keita, K. Essaadi, L. Nadjo, *J. Electroanal. Chem.* **1989**, *259*, 127–146.

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