Iron-Substituted Dawson-Type Tungstodiphosphates: Synthesis, Characterization, and Single or Multiple Initial Electronation Due to the Substituent Nature or Position

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Isomerically pure α_1- and α_2-$[Fe(OH_2)P_2W_{17}O_{61}]^{7-}$ and $\alpha_2[Fe(OH_2)P_2Mo_2W_{15}O_{61}]^{7-}$ were synthesized as aqueous-soluble potassium salts. The iron-substituted complexes as well as their immediate lacunary precursors have been characterized by IR, UV−visible, and ^{31}P NMR spectroscopies. The acid−base equilibria were studied for the iron-substituted complexes. The hydroxo compound α_2-$[Fe(OH)P_2W_{17}O_{61}]^{8-}$ has also been synthesized, and its elemental analysis is correct. Its further characterization and study will be published elsewere. For a given pH value, the comparisons of the cyclic voltammograms reveal the influence of the location of the iron-filled site in the framework. This influence is strong in the α_1 isomer and makes its electrochemistry clearly different from that of the α_2 isomer. This observation is ascribed mainly to the large framework distortion induced by the vacancy in the α_1 site, to subtle variations in the detailed protonation events which ensue, and to the nature of the iron substituent, which can be considered not to fill "completely" the vacancy. The distortion effect is found to favor the coalescence of waves, as also do lower and lower pH media. The combination of these parameters appears to be beneficial for the observation of multiple electronation processes on the first wave of heteropolyanions under very mild conditions.

Introduction

The research on the catalytic abilities of transition metal substituted polyoxometalates based on the Keggin or Dawson frameworks continues unabated. This impetus for studying, for example, their synthesis, NMR characterization, and catalytic atom transfer chemistry[1] and their electrocatalytic or redox chemistry[2] toward other substrates like nitrite anion relies mainly on the remark of Baker:[3] he noted as early as 1973 that, in substituted monolacunary polyoxotungstates such as the monosubstituted Keggin anion $[(M^{n+}\cdot OH_2)PW_{11}O_{39}]^{(n-9)}$, the (M^{n+}) heterometal is ligated in a pseudo porphyrin environment. This "ligand" framework is nonoxidizable, and can be expected to remain stable during a catalytic process. Then, its presence will mainly modulate the catalytic properties known for the transition metal cations in related organometallic compounds.

The possibility of synthesizing such substituted polyoxotungstates was demonstrated even earlier and continues steadily.[4] But the first breakthroughs in "inorganic-porphyrin"-like polyoxometalate-based catalysis had to await the work of Katsoulis and Pope[5] in nonaqueous solvents, followed by work of a few others.[6] Electrochemistry studies, from our group and others, demonstrated the existence of catalytic properties even in water.[2] Turning more specifically to the classically used catalysts, several difficulties exist as to their synthesis and unequivocal characterization, in the Keggin as well as in the Dawson series.

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These problems concern mainly the following: (i) the purity of the compounds; (ii) the location(s) of the substituent(s), especially when several substituents of different nature are present in the molecule; (iii) the identity of the ligand present in the sixth coordination site of the heterometal. Thus, complete characterization of the substituted polyoxometalate is a necessary prerequisite for a reliable study of its catalytic properties, and this remains a challenge.

In this context, we have been interested for several years in the synthesis and physical characterization of a series of substituted Dawson-type heteropolytungstates with the goal of exploring their redox chemistry and catalytic and electrocatalytic abilities.[2a−c,4h,k,7] In general, parameters which favor multiple electronation retain our attention.[7b,d,9j] Also, it came out from the scrutiny of a large number of variously substituted compounds that, not unexpectedly, the location of the "catalytic" substituent in the framework constitutes an important parameter of its reactivity. For instance, the reduced forms of α_1-[Fe(OH$_2$)P$_2$W$_{17}$O$_{61}$]$^{7-}$ and α_2-[Fe(OH$_2$)P$_2$W$_{17}$O$_{61}$]$^{7-}$ [2a−c] differ in their electrocatalytic behaviors toward the reduction of nitrite. (In the following, the negative charges as well as all of the water molecules will be omitted when no confusion seems possible. Then, the preceding compounds should be abbreviated as α_1-FeP$_2$W$_{17}$ and α_2FeP$_2$W$_{17}$, respectively. The same convention will be used throughout). To our knowledge, the electrochemical implications of the position of the substituent in heteropolyanions have not been studied.

Herein, we focus on three substituted Wells−Dawson-type tungstodiphosphates and on their lacunary precursors (Figure 1).[8] We report the synthesis, isolation, characterization, and electrochemical behaviors of α_1FeP$_2$W$_{17}$ and α_2FeP$_2$W$_{17}$ along with those of α_2FeP$_2$Mo$_2$W$_{15}$, in which the three substituents are in the "cap". These complexes have been characterized by elemental analysis, ^{31}P NMR spectroscopy, and IR spectroscopy. Also, α_2Fe(OH)P$_2$W$_{17}$ has been synthesized.

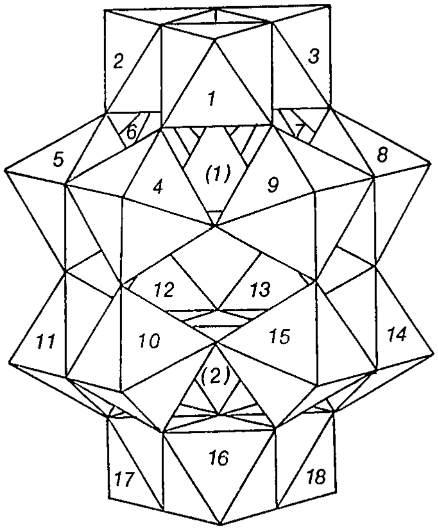

Figure 1. Numbering scheme for αP$_2$W$_{18}$ (Dawson structure).

To our knowledge, α_1FeP$_2$W$_{17}$ and α_2FeP$_2$Mo$_2$W$_{15}$ and especially their electrochemical properties have not been described. In particular, we are interested in single or apparently multiple electronation processes due to the nature, number, and/or position of substituents. Furthermore, we are interested in obtaining these multiple electronation processes in a potential domain where no derivatization of the electrode surface could be encountered. As a matter of fact, such a derivatization, which has been discovered and studied in some detail by our group[9] along with other behaviors of heteropolyanions, could limit severely the selectivity and hence the yield of certain catalytic processes.[2d]

Experimental Section

Preparation. The potassium salts of αP$_2$W$_{18}$, P$_2$W$_{17}$ (α_2), P$_2$W$_{17}$ (α_1), and 2,3-P$_2$Mo$_2$W$_{15}$ (α_2) were prepared by published methods.[7,4k]

K$_7$Fe(OH$_2$)(P$_2$Mo$_2$W$_{15}$O$_{61}$)·19H$_2$O. A sample of 2.43 g (6 mmol) of Fe(NO$_3$)$_3$·9H$_2$O was dissolved in 65 mL of water, and 23 g (4.9 mmol) of K$_{10}$P$_2$Mo$_2$W$_{15}$O$_{61}$·21H$_2$O was added with stirring. The mixture was heated at 35 °C, and then the clear solution was cooled at 5 °C overnight. The yellow crystals that appeared were filtered (18 g) and dried in air. Anal. Calcd for K$_7$Fe(OH$_2$)(P$_2$Mo$_2$W$_{15}$O$_{61}$)·19H$_2$O: K, 5.85; P, 1.32; Fe, 1.19; Mo, 4.10; W, 58.96; H$_2$O, 7.70. Found: K, 5.79; P, 1.35; Fe 1.16; Mo, 4.2; W, 59.2; H$_2$O, 7.71.

K$_7$-α_2-Fe(OH$_2$)(P$_2$W$_{17}$O$_{61}$)·19H$_2$O. A sample of 2.43 g (6 mmol) of Fe(NO$_3$)$_3$·9H$_2$O was dissolved in 65 mL of water, and 23 g (4.7 mmol) of (α_2) K$_{10}$P$_2$W$_{17}$O$_{61}$·20H$_2$O was added with stirring. The whole dissolution occurs at 30 °C, and the solution was left at 6 °C overnight. The yellow crystals that appeared were filtered (17 g) and dried in air. Anal. Calcd for K$_7$Fe(OH$_2$)(P$_2$W$_{17}$O$_{61}$)·19H$_2$O: K, 5.6; P, 1.28; Fe, 1.15; W, 64.4; H$_2$O, 7.42. Found: K, 5.46; P, 1.29; Fe, 1.16; W, 65.2; H$_2$O, 7.41.

K$_8$-α_2-Fe(OH)(P$_2$W$_{17}$O$_{61}$)·19H$_2$O. A sample of 2.43 g (6 mmol) of Fe(NO$_3$)$_3$·9H$_2$O and 20 g (4.1 mmol) of α_2-K$_{10}$P$_2$W$_{17}$O$_{61}$·20H$_2$O were dissolved in 65 mL of water with stirring. To this mixture was added 60 mL of KCl saturated solution. The yellow precipitate was filtered (16.5 g) and poured into 35 mL of water, and the mixture was treated with 3.5 mL of 1 M KOH. The maroon mixture was heated at 50 °C, and the maroon solid was filtered off. Yellow green crystals that appeared on cooling were filtered and dried in air. Anal. Calcd for K$_8$Fe(OH)(P$_2$W$_{17}$O$_{61}$)·19H$_2$O: K, 6.40; Fe, 1.14; W, 63.9; H$_2$O, 7.18. Found: K, 6.46; Fe, 1.16; W, 63.6; H$_2$O, 7.14.

K$_7$-α_1-Fe(OH$_2$)(P$_2$W$_{17}$O$_{61}$)·19H$_2$O. A sample of 2.43 g (6 mmol) of Fe(NO$_3$)$_3$·9H$_2$O was dissolved in 90 mL of water, and 23 g (4.9 mmol) of α_1-K$_9$LiP$_2$W$_{17}$O$_{61}$·20H$_2$O was added with stirring. To the solution was added 90 mL of KCl saturated solution. The pale yellow crystals that appeared were filtered off (16.5 g) and dried in air. Anal.

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(8) In Figure 1, the tungsten atoms in αP$_2$W$_{18}$O$_{62}$$^{6-}$ are numbered according to the IUPAC recommendations (Jeannin, Y.; Fournier, M. *Pure Appl. Chem.* **1987**, *59*, 1529). The two phosphorus 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 the α_2 positions and those in the "belt" the 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. Contant and Ciabrini were the first to propose the difference between α_1 and α_2 lacunary isomers of the Wells−Dawson derivatives and discovered the way to make α_1 derivatives (Contant, R.; Ciabriani, J. R. *J. Chem. Res., Synop.* **1977**, 222; *J. Chem. Res., Miniprint* **1977**, 2601).

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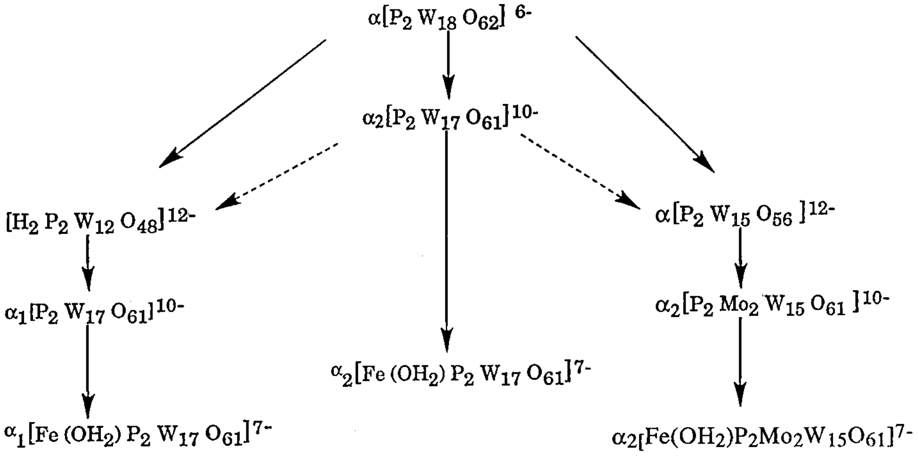
Scheme 1



Calcd for $K_7Fe(OH_2)(P_2W_{17}O_{61})\cdot 19H_2O$: K, 5.64; P, 1.28; Fe, 1.15; W, 64.4; H_2O, 7.42. Found: K, 5.56; P, 1.29; Fe, 1.21; W, 64.6; H_2O, 7.48.

NMR, IR, UV−Visible, and Potentiometric Measurements. ^{31}P NMR spectra were recorded in 10 mm optical density tubes on a Brucker 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−visible spectra were recorded on a 555 Perkin-Elmer spectrophotometer.

Potentiometric measurements were made on a Tacussel LPH 430T pH meter. The apparent formation constants $\beta_{1\mathrm{app}}$ were determined potentiometrically[10] in 1 M HNO_3. In this medium, the lacunary polyoxometalates of this work have three titratable protons; furthermore, they do not complex Fe^{2+} ions.Then, the true β_1 formation constants ensue. The potential measurements that give the Fe^{3+}/Fe^{2+} ratio ($E°_{Fe^{3+}/Fe^{2+}} = 0.770$ V (ENH), $E°_{Fe^{3+}/Fe^{2+}}) = 0.528$ V (SCE)) were carried out under a nitrogen stream.

Electrochemical Experiments. Chemicals, Equipment, and Apparatus. Pure water was used throughout. It was obtained by passing water through a Milli-RO4 unit and subsequently through a Millipore Q water purification set. All of the chemicals were of high-purity grade and were used as received. H_2SO_4 and Na_2SO_4 were commercial products (Prolabo). The pH = 2 electrolyte was made up of 0.2 M $Na_2SO_4 + H_2SO_4$. Other pH values were adjusted by addition of H_2SO_4 or NaOH (Prolabo), respectively.

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.[9p] The glassy carbon samples had a diameter of 3 mm. The electrochemical setup was an EG & G273 A driven by a PC with the 270 software. The data were recorded in the computer and then printed, when necessary, on a HP DeskJet 560 C printer. Potentials are quoted against a saturated calomel electrode (SCE). The counter electrode was a platinum gauze of large surface area. Experiments were performed at the laboratory temperature.

Results

The species studied in the work are all of the Dawson-type. They derive from αP_2W_{18} through the sequence shown in Scheme 1.

All of the iron-substituted anions have been characterized by ^{31}P NMR, IR, and UV−visible spectroscopies and acid−base equilibria. The electrochemical studies also included their immediate lacunary precursors. All these points will be introduced at appropriate places in the following section.

Discussion

Syntheses. The three iron-substituted species were obtained from P_2W_{18}, in two steps for α_2-$[Fe(OH_2)P_2W_{17}]$ and three steps for the others. The point of interest is to obtain isomerically pure anions. For this purpose, mild methods, avoiding boiling and high temperatures, are to be preferred. We have followed this general idea and selected suitable conditions for the synthesis of $\alpha_1P_2\square W_{17}$ and $\alpha_2P_2\square_3W_{15}$. It has been necessary to modify the preparation method for $[Fe(OH_2)P_2W_{17}O_{61}]^{10-}$ proposed by Zonnevijlle et al.[4f] These authors start from $P_2\square W_{17}$ without stating specifically that it was actually the α_2 isomer, and they raise the temperature of the reaction mixture to 90 °C. Under such conditions, it has been shown by Jorris, Kozik, et al.[1] that the isomerization of the α_2 into the α_1 isomer could happen in the presence of a metallic ion. Also, the synthesis of $P_2\square Mo_2W_{15}$ is carried out under mild conditions, which allows the selective addition of two molybdenum atoms in an apical site of $[P_2\square_3W_{15}O_{56}]^{12-}$. The location of the molybdenum atoms was confirmed during the ^{31}P and ^{183}W NMR structural study of complexes such as $[P_2Mo_3W_{15}O_{62}]^{6-}$ and $[P_2Mo_2VW_{15}O_{62}]^{7-}$ obtained by addition of a third heterometal into the vacancy of $[P_2Mo_2\square W_{15}O_{61}]^{10-}$.

IR and UV−Visible Characterization. Figure 2 allows a comparison of the IR spectra of the main species appearing in the synthesis sequences of Scheme 1. In tungstophosphates, the most characteristic IR band shifts correspond to P−O vibrations situated between 1200 and 1000 cm^{-1}, and these shifts characterize lacunary species. With an iron atom added into the vacancy, the whole symmetry is restored, at least as far as IR spectra are concerned. This results in IR spectra which are very close to that of $[P_2W_{18}O_{62}]^{6-}$ thus preventing any reliable identification of a given anion.

In UV−visible spectra, the Fe−O band remains very close to the W−O bands and it is not possible to distinguish one FeP_2W_{17} isomer from the other. With Mo present in the molecule, the Fe−O and Mo−O charge transfer bands are mixed and the whole spectrum is shifted in the yellow direction, but without separating from the W−O group of bands. As a result, just like IR spectroscopy, UV−visible spectroscopy does not allow the identification of a ferric complex.

^{31}P NMR Characterization. In ^{31}P NMR measurements on Dawson-type heteropolyanions substituted by a paramagnetic ion like Fe(III), the chemical shifts are much more influenced for the band corresponding to the P atom close to the iron atom than for that of the other P atom. As a consequence, the spectra

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(10) Tézé, A. Thesis, University of Paris, 1973.

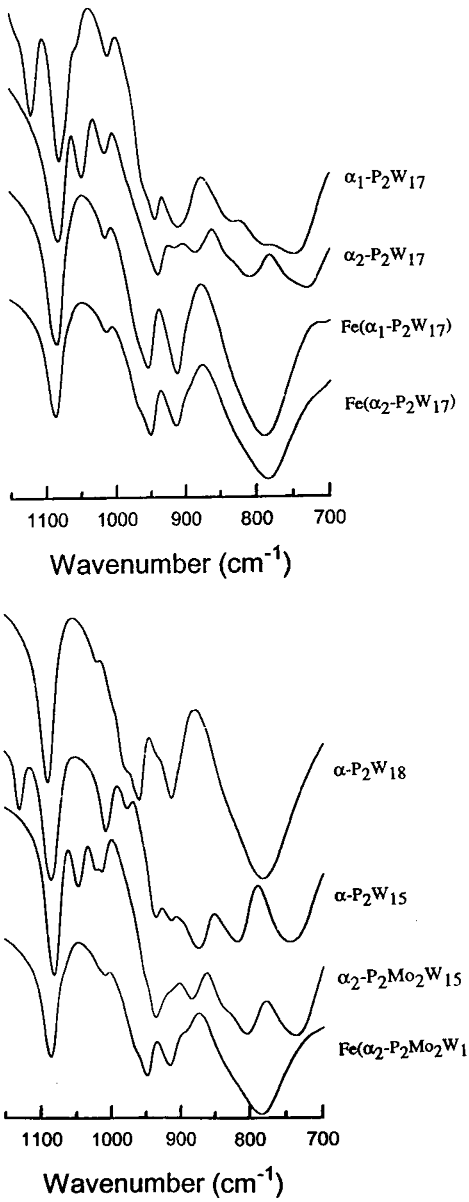

Figure 2. IR spectra (KBr) of the hydrated heteropolyanions studied in this work.

for ferric complexes exhibit only one peak corresponding to the P(2) atom, which is farther from the heterometal. Table 1 gives the measured chemical shifts for all of the species in Scheme 1. For those species in which the iron atom occupies the 1-position (α_2), the chemical shift remains close to that of the corresponding lacunary precursor. However, broader bands are usually observed for the paramagnetic substituted compounds. For the other isomer, with the iron atom in the 4-position (α_1), being thus farther from the P(2) atom, the NMR band is considerably broadened and shifted. As appears in Figure 3, the two spectra for the α_1 and α_2 isomers are sufficiently different to allow for the characterization of each isomer and the determination of their respective proportions in a mixture.

Stability Domain. Ferric complexes have large formation constants (Table 2) and are, thus, stable in a wide pH domain. Tézé[11] has shown that alkalinization of $[Fe(OH_2)(\alpha\ SiW_{11}O_{39})]^{5-}$ by one equiv of OH^- results in the formation of a hydroxo complex and, then, of a μ-oxo complex. Ciabrini[12] also synthesized an analogous compound, $[Fe_2O(\alpha_2P_2W_{17})_2]$, but did not succeed in obtaining the corresponding hydroxo monomer or any basic species with the α_1 isomer possibly due to high ionic strength. Basic and condensed compounds will be described elsewhere. For the ferric complexes of the present work, alkalinization curves (Figure 4) of the aqua complexes do not depend on the concentration in the range 10^{-3} M $\leq C \leq 4 \times 10^{-3}$ M, and they show obviously the deprotonation of the water molecule. The acido basic character of the curves is confirmed as follows: (i) for $0.1 < x < 0.9$ (x being the number of moles base per mole of heteropolyanion), we show that $\mathrm{pH} + \log(x/(1-x)) = \mathrm{p}K_a$; (ii) the protonation curve of the hydroxo complex corresponds to that of the conjugate base of the aqua species. Table 2 summarizes the main results. For concentrations smaller than 4×10^{-3} M in aqueous solutions, the acid form prevails for $\mathrm{pH} < \mathrm{p}K_a$, and the hydroxo basic form for $\mathrm{p}K_a < \mathrm{pH} < \mathrm{p}K_a + 2$. The aqua and hydroxo complexes are faint yellow. The brown dimers have μ-oxo structures and constitute the stable species in high-concentration media. Perhaps higher basicity species exist ($x = 2$) as suggested by $A = f(x)$ curves in Figure 4 (A is the absorbance of the solution).

Table 1: ^{31}P NMR Chemical Shifts for all Polyoxometalates in Scheme 1

	δP(1), ppm	δP(2), ppm	$\Delta\nu_{1/2}$, Hz
P_2W_{18}	−12.4	−12.4[a]	
	−12.44	−12.44[c]	
P_2W_{15}	+0.9	−14.1[a]	
	+0.1	−13.3[d,e]	
P_2W_{12}	−8.45	−8.45[a]	
	−7.8	−7.8[b,e]	
$FeP_2W_{17}(\alpha_1)$	not obsd	−4.6	700[a]
$FeP_2W_{17}(\alpha_2)$	not obsd	−12.6	160[a]
$FeP_2Mo_2W_{15}(\alpha_2)$	not obsd	−13.3	160[a]
$P_2W_{17}(\alpha_1)$	−8.6	−12.9[a]	
	−9.0	−13.1[b]	
P_2W_{17} (α_2)	−6.9	−13.7[a]	
	−7.1	−13.6[b]	
$P_2Mo_2W_{15}$ (α_2)	−4.95	−13.8[a]	
	−5.09	−13.9[c]	

[a] This work. [b] Reference 4m. [c] Reference 4k. [d] Reference 7a. [e] 1 M lithium acetate buffer.

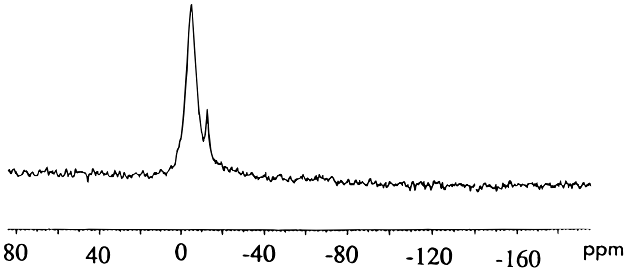

Figure 3. ^{31}P NMR spectrum of a mixture of α_1- (95%) and α_2-$Fe(OH_2)P_2W_{17}$ (5%).

Table 2. Acidity and Formation Constants for the Iron-Substituted Dawson-Type Tunsgtodiphosphates of This Work[a]

	pK_a	log β_{1app} (1 M HNO_3)	log β_1
FeP_2W_{17} (α_1)	7.55	12.4	23.0
FeP_2W_{17} (α_2)	5.85	7.6	19.0
$FeP_2Mo_2W_{15}$ (α_2)	5.84	6.6	17.2

[a] For further details, see text.

It must be noted that the hydroxo complex has been obtained under conditions very close to those in which Zonnevijlle *et al.* claimed that dimers are formed: they describe a yellow-green compound analogous to that synthesized here by us, but substantially different from maroon compound $K_{12}[Fe_2O(SiW_{11}O_{39})_2]$, the structure of which has been resolved by Tézé

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(11) Tézé, A. Personal communication, 1997.
(12) Ciabrini, J. P. Thesis, University of Paris, 1982.

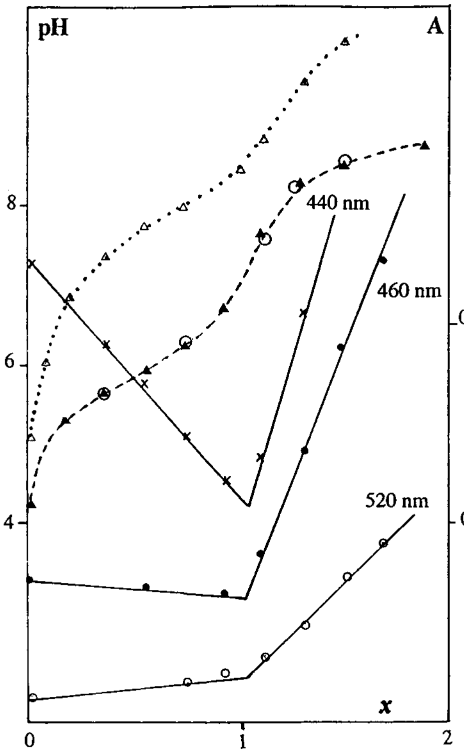

Figure 4. Potentiometric and spectrophotometric titrations of the iron-substituted complexes studied in this work; for further details, see text. Upper: potentiometric curve for $\alpha_1FeP_2W_{17}$. Lower: potentiometric curves for $\alpha_2FeP_2W_{17}$ and $\alpha_1FeP_2Mo_2W_{15}$ (the two curves are superimposable). All spectrophotometric curves pertain to $\alpha_2FeP_2Mo_2W_{15}$ at the λ values indicated on each curve.

and Hervé,[11] and from $[Fe_2O(P_2W_{17}O_{61})_2]^{16-}$ studied by Ciabrini.[12] Taking into account the whole paper by Zonnevijlle et al.,[4f] it appears that no unambiguous demonstration of the condensation of species is given, and that the different techniques used by these authors allow only to correlate analogous species.

Electrochemistry

Our ultimate goal for the synthesis of the substituted heteropolyanions is to study their ability to perform catalytic redox or electrocatalytic transformations on a series of small molecules. Therefore, the present electrochemical experiments are designed to find out their fundamental behaviors, which could be helpful in designing and understanding the planned catalytic processes. In the following, our studies are restricted mainly to the first or first several redox processes of the substituted anions and, eventually, to their evolution with pH. The descriptions are made essentially at pH = 2, in which all of them proved to be stable. For lower or higher pH values, long term stability tests were also carried out, in addition to the acid−base equilibria studied previously.

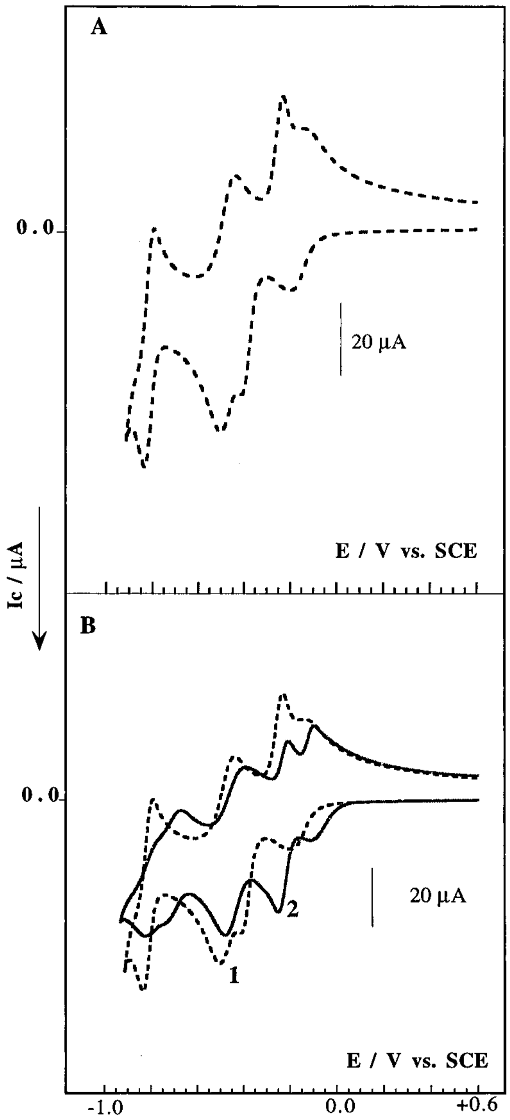

Figure 5. Comparison of the cyclic voltammograms observed in a pH = 2 medium (0.2 M Na_2SO_4 + H_2SO_4) for a 5×10^{-4} M solution of the two iron-substituted heteropolyanions; scan rate: 100 mV/s. (A) $\alpha_1FeP_2W_{17}$. (B) $\alpha_1FeP_2W_{17}$ (curve 1) and $\alpha_2FeP_2W_{17}$ (curve 2).

Electrochemistry of α_1-$[Fe(OH_2)\ P_2W_{17}O_{61}]^{7-}$ and α_2-$[Fe(OH)P_2W_{17}O_{61}]^{7-}$. Curve 1 of Figure 5A represents the cyclic voltammogram of $\alpha_1FeP_2W_{17}$ in a pH = 2 medium at a scan rate of 100 mV/s. The first wave, which is attributed mainly to the reduction of Fe^{3+} to Fe^{2+}, is, however, composite and broad. It must, therefore, be concluded that, at least, a coalescence of the iron wave with part of a tungsten wave occurs. This assumption is confirmed by two independent experiments. On the one hand, the comparison of the composite first wave of $\alpha_1FeP_2W_{17}$ with the known monoelectronic wave of P_2W_{18} indicates that the former process involves 1.73 electrons/molecule. On the other hand, controlled potential electrolysis carried out on $\alpha_1Fe\ P_2W_{17}$ at −0.350 V vs SCE under continuous argon bubbling consumes 1.8 electrons/molecule. This value is close to that obtained above by direct evaluation from cyclic voltammograms and indicates clearly that the first wave of $\alpha_1FeP_2W_{17}$ cannot be ascribed solely to the reduction of Fe^{3+} to Fe^{2+}. This conclusion is reinforced by the gradually important blue color which develops during controlled potential electrolysis. Turning now to the remaining waves of the cyclic voltammogram of $\alpha_1FeP_2W_{17}$, the second wave is very close to the third one and, in the pH = 2 medium, seems to have grown partially at the expense of the latter. There is no doubt that protonation processes following reduction control the observations. It has been checked, by limiting the cathodic potential scan just negative of the peak location of the second wave, that the corresponding anodic return trace is indeed very close to that of the first wave. These conclusions will be reinforced by the pH effects studied in the following on the present complex. Finally, the fourth wave of the α_1 isomer features a two-electron process.

Figure 5B compares the cyclic voltammograms of α_1- and $\alpha_2FeP_2W_{17}$ in a pH = 2 medium at a scan rate of 100 mV/s. The voltammetric pattern of α_2FeP2W17 has been run prevoiusly as part of our work on the catalytic reduction of nitrite and nitric oxide by a large series of unsubstituted and substituted heteroplyanions.[2a,b] Curve 2 of Figure 5B is first the subject of our focus. It shows a set of four voltammetric waves, the last one being obviously composite. Here again, the first wave is attributed mainly to the redox reaction of the Fe^{3+}/Fe^{2+} moiety in the substituted complex. The peak intensity is comparable to that of the first wave of P_2W_{18}, which is monoelectronic under the same conditions. This estimate has been confirmed by controlled potential coulometry. The other waves are attributed to the reduction of W^{VI} centers in the framework. The gross features of our observations may appear to be much the same as published recently by Dong et al.,[2g] but the electrochemical details mentioned here are lacking completely. The authors do not mention even the identity of the isomer they were studying. However, it is clear from their preparation method, taken from ref 1b, and from the potential locations of their voltammetric waves that the α_2 isomer was indeed under investigation.

Figure 5B speaks by itself and shows that the voltammograms of the α_1 and α_2 isomers differ notably. The first wave of α_1-FeP_2W_{17} is distinctly more negative in potential than that of the α_2 isomer. In particular, we focus on the numbers of electrons consumed for the respective first waves: 1.0 electron for the α_2 isomer and 1.8 electrons for the α_1 isomer at pH = 2. Among the reasons which induce multiple electron transfers in large molecules at the same potential, we retain, in the present case, framework distortion[7a,d] and protonation processes.[9j] These parameters may act independently, or the second one may be a consequence of the first one.

As a whole, the change in symmetry in the PO_4 tetrahedron in the α_1- and $\alpha_2FeP_2W_{17}$ isomers is first taken into account:[13] its symmetry is C_{3v} in αP_2W_{18}; in $\alpha_2FeP_2W_{17}$, a general reduction in local symmetry appears and makes the PO_4 symmetry close to T_d. In this case, little perturbation is to be expected from the addition of a heterometal atom in the α_2 position, which is actually observed. On the contrary, the corresponding PO_4 tetrahedron in $\alpha_1P_2\square W_{17}$ assumes a C_s symmetry, which would favor a stronger coupling of the heterometal with the tungsten atoms in the "belt" of the heteropolyanion. Whether this difference in symmetry is sufficient alone to explain the difference in the electrochemistry of the α_1- and $\alpha_2FeP_2W_{17}$ isomers is not known at present. In any case, this difference in symmetry must induce subtle variations in the detailed protonation events, thus ending in the differences observed above in the cyclic voltammograms.

The morphologies of the first three waves of $\alpha_1FeP_2W_{17}$ induce us to study the cyclic voltammetry behaviors of this compound as a function of pH. The idea behind this set of experiments is that a decrease in pH should, in particular, favor the merging of waves, possibly by EEC type mechanisms as demonstrated by us on other examples (SiW_{12}, P_2W_{18}).[9j] Correlatively, an increase in pH should separate the voltammetric waves and make them tend toward one-electron processes. Provisionally, we also note the following observation: whatever the pH dependence of the "iron" wave in substituted heteropolyanions,[2e,g] this wave involves one electron, as expected. Figure 6 shows a set of three typical cyclic voltammograms for $\alpha_1FeP_2W_{17}$ as a function of pH. Starting from our standard pH = 2 solution, the other acidity values are adjusted by addition of small volumes of concentrated H_2SO_4 solution and the pH is measured accurately. The pH domain has been explored between 3 and 0.16. The stability of α_1-FeP_2W_{17} in this domain has been checked by running its cyclic voltammogram just after the preparation of the solution, waiting, at the very least, overnight, and running it again. No variation in current intensities nor in potential locations of the various waves was observed, which we consider as a sufficient test of stability of this substituted heteropolyanion under the present experimental conditions. Curves 1−3 of Figure 6 represent the cyclic voltammograms obtained at pH = 2, 1.03, and 0.16, respectively. Clearly, the reduction peak current intensity of the "iron" wave becomes larger with a small positive potential shift as the pH decreases. The current of the first "tungsten" wave of $\alpha_1FeP_2W_{17}$ diminishes while that of the second "tungsten" wave increases. This observation is perfectly in line with our previous interpretation of the cyclic voltammetric pattern at pH = 2, concerning the partial coalescence of the "iron" and "tungsten" waves on the one hand; on the other hand, the partial coalescence of two "tungsten" waves is also confirmed, and these waves are still clearly separated at pH = 1.03 as expected. It must be noted that, at pH = 1.03, all of the "tunsgten" waves in Figure 6 are substantially more positive than the corresponding waves at pH = 2. Turning now to the reoxidation waves, the immediate notice is the almost complete coalescence of the "iron" and the first "tungsten" traces. Finally, at sufficiently high proton concentration, for a pH value between 1.03 and 0.16, the "iron" wave reaches its maximum peak current intensity and the first "tungsten" wave no longer appears. Note that we did not attempt, in the present experiments, to find out with accuracy the pH value for which the complete merging of the "iron" and "tungsten" waves occurs, even though intermediate evolutions have been studied. Curve 3 in Figure 6 has been run at pH = 0.16 (curve 3). The evolution in current intensities, in morphologies, and in peak potential locations is obvious. Coulometry performed at the peak potential of the first wave for each pH value confirmed the observed effects. Values of 1.31, 2.25, and 3.0 electrons/molecule were obtained

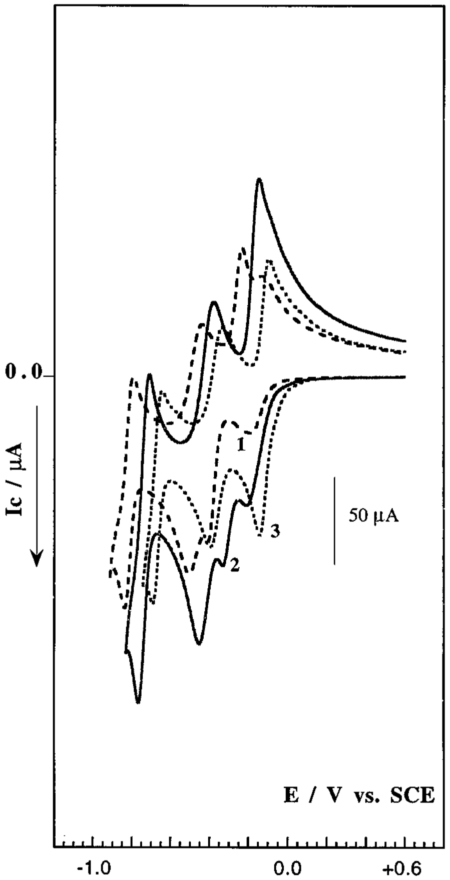

Figure 6. pH effect on the cyclic voltammogram of $\alpha_1FeP_2W_{17}$. Curve 1: pH = 2. Curve 2: pH = 1.03. Curve 3: pH = 0.16.

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(13) Rocchiccioli-Deltcheff, C.; Thouvenot, R. *Spectrosc. Lett.* **1979**, *12*, 127.

at pH = 2, 1, and 0.16, respectively, in perfect agreement with the current intensities of cyclic voltammograms.

The consequences of this apparently multielectron process at the same potential vis-à-vis a series of electrocatalytic and redox catalytic reactions are under investigation.

Starting with the pH = 0.16 solution, we found that the gradual addition of NaOH up to pH = 2 makes the first wave of $\alpha_1FeP_2W_{17}$ diminish and the "W" wave reappears. The cyclic voltammogram goes back through the intermediate evolutions observed previously. Therefore, the pH effect appears reversible. This, again, underscores the stability of $\alpha_1FeP_2W_{17}$ in the pH = 0.16 medium.

In summary, a clear difference in their electrochemical behaviors is observed for the α_1- and $\alpha_2FeP_2W_{17}$ isomers. To our knowledge, this constitutes the first example in which the position of the heterometal in a substituted heteropolyanion is clearly shown to have a profound influence on the electrochemical behaviors of the framework.

The same trend toward the merging of the iron and the molybdenum waves is observed for $\alpha_2FeP_2Mo_2W_{15}$ at pH = 2. This result suggests that apparently multiple electronation processes, suitable for efficient redox or electrocatalytic reactions, should be readily obtained by substitution of the W framework by selected ensembles of different heterometals. Detailed results will be published elsewhere.

Concluding Remarks and Future Directions

The synthesis and full characterization of α_1- and $\alpha_2FeP_2W_{17}$ from their corresponding lacunary species have permitted a comparison of their main electrochemical behaviors. It is worth noting that NMR spectroscopy was the main technique to discriminate between these complexes. Electrochemistry proves, in the present case, to be also very valuable in this issue. In these complexes, which can be symbolized as α_1- and α_2-ZL-($P_2W_{17}O_{61}$) with Z ≡ Fe^{3+} and L ≡ H_2O, it appears that the location of the iron substituent in the framework and the pH of the electrolyte influence the number of electronations observed on the first wave. The effect is stronger in the α_1 than in the α_2 isomer. It can be ascribed, at least partly, to the important frame distortion associated with that of the PO_4 tetrahedron close to the α_1 vacancy, and to subtle protonation events which ensue. As a fact, it is observed that the α_1 substituted isomer is also more sensitive to pH effects than the α_2 species. Finally, it can be concluded that the present study helps to identify at least two parameters: the framework distortion and the pH effect, which converge to favor multiple electronation on the first wave of these heteropolyanions. Such a clear comparison was made possible and easy due to the synthesis of isomerically pure α_1 and α_2 isomers.

Preliminary studies with $\alpha_2FeP_2Mo_2W_{15}$ show analogous trends.

Various combinations of these parameters will be investigated, by varying essentially the nature, number, and locations of the substituents, in the pH range of stability of these compounds.

Transposition of these studies to nonaqueous media, without or with acidification, is also under investigation.

Finally, catalytic processes, which could benefit from the multiple electronation behaviors of substituted heteropolyanions, will be studied.

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