Compared Behaviours of Dawson-Type Tungstodiarsenates and -diphosphates

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The lacunary α_2-$[As_2W_{17}O_{61}]^{10-}$ derived from the Dawson molecule α-$[As_2W_{18}O_{62}]^{6-}$ was used as a ligand for the following metal cations: Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}. The cyclic voltammograms of this lacunary precursor species, as well as those of the substituted complexes were run in a medium at pH = 3. A systematic comparison was carried out with the electrochemical characteristics of the corresponding complexes derived from α-$[P_2W_{18}O_{62}]^{6-}$, with the aim of highlighting the differences in their behaviour, which could be ascribed to the identity of the central atoms. The study was also extended to the Fe^{3+} species of the α_1 series. The comparisons reveal that whatever the series, the first several voltammetric waves are driven in the positive potential direction by the presence of As as the central atom in the heteropolyanions. These results agree with those from crystallographic evaluations, and with the knowledge of the stability constants of the complexes, indirectly reveal a coherent picture of the behaviour of the vacant sites in the diarsenates and diphosphates. In particular, the influence of the central heteroatom on the redox and/or acid-base properties could be assessed and compared. Steric effects, expected on geometrical grounds, and already reflected in the values of the stability constants of the metal ion substituted compounds, also influence the cyclic voltammograms.

1. Introduction

Much work has been devoted to Dawson-type tungstodiphosphates. In particular, their ability to generate lacunary species, and hence metal cation substituted derivatives has received extensive attention.[1−10] The impetus was triggered by the pioneering remark that monosubstituted heteropolyanions can be considered as the analogues of metallated porphyrins, and can be used in catalytic processes with the advantage, over their organic counterparts, of their thermal stability, robustness and inertness toward oxidising environments.[11] In contrast, the corresponding diarsenates have been the subject of very few papers,[12−14] presumably owing to the assumption that a complete analogy should be expected between the two series of species. Actually, such an assumption would ignore the possibility that the change in the central heteroatom might bring about new physical, and correlatively, electronic, chemical and redox behaviours. Several papers[2,4] have shown the linear dependence of the first one-electron reduction potentials (under conditions of no protonation) on the overall negative charge of the heteropolyanions, in conjunction with the charge on the central heteroatom. Further, the influence of the central heteroatom (Si^{IV}, Ge^{IV}, P^{V}, As^{V}) on the stabilities of the metal(II) and alkaline ion complexes of selected heteropolytungstates[12,15] was published. However, most of these studies were performed in the Keggin series.

In our systematic study of the parameters which could modify the redox properties of heteropolyanions, and hence their electrocatalytic behaviour, several possibilities were identified. The pH of the solution is one obvious parameter. A rich series of possibilities is opened up by the substituent effect; the location of the heterometal in the framework, the nature, and the number of substituents may influence the interactions between the electroactive centres within the molecule.[6,9,16] Furthermore, a recent paper from our group[17] has stressed the change in symmetry of the charge distribution in lacunary species and in their first transition metal ion substituted derivatives, thus justifying the comparison between these two series of compounds, and not with the saturated precursors.[6,9,16,17]

Until now the influence of the central heteroatom in Dawson-type anions on their cyclic voltammograms was not explored. In this context, we are interested in comparing saturated and metal ion monosubstituted diarsenates with diphosphates. Particular attention will be paid to the location of the vacant site in the framework, to steric effects (in other words the ability of the vacant site to accommodate the substituent metal cation), and the physical and chemical behaviour.

2. Results

2.1. The Selection of Relevant Heteropolyanions

All the polyanions studied here can be considered as being primarily derived from α-$[P_2W_{18}O_{62}]^{6-}$ (abbreviated as

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α-P_2W_{18} in the following) and α-$[As_2W_{18}O_{62}]^{6-}$ (abbreviated as α-As_2W_{18}). Although it has become classical, Figure 1 is shown for clarity. The tungsten atoms are numbered according to the IUPAC recommendations. The two P atoms are numbered 1 and 2 for the upper and the lower halves of the molecule, respectively. For example, 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, when necessary, by □ in the formula of the anion. Any metal atom occupying the vacancy will keep the same index.

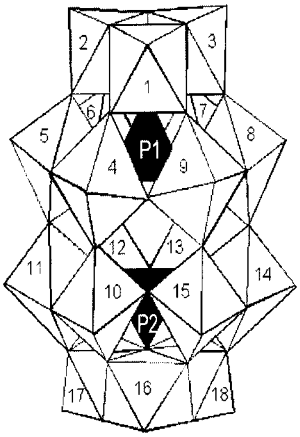

Figure 1. Idealised structure of α-$[P_2W_{18}O_{62}]^{6-}$ and its substitution derivatives

The following heteropolyanions were used: α-$[As_2W_{18}O_{62}]^{6-}$ (abbreviated as α-As_2W_{18}), α_1- and α_2-$[As_2W_{17}O_{61}]^{10-}$ (α_1- and α_2-As_2W_{17}), α_2-$[Mn(H_2O)(As_2W_{17}O_{61})]^{8-}$ (α_2-$As_2W_{17}Mn$), α_1- and α_2-$[Fe(H_2O)(As_2W_{17}O_{61})]^{7-}$ (α_1- and α_2-$As_2W_{17}Fe$), α_2-$[Co(H_2O)(As_2W_{17}O_{61})]^{8-}$ (α_2-$As_2W_{17}Co$), α_2-$[Ni(H_2O)(As_2W_{17}O_{61})]^{8-}$ (α_2-$As_2W_{17}Ni$), α_2-$[Cu(H_2O)(As_2W_{17}O_{61})]^{8-}$ (α_2-$As_2W_{17}Cu$), α_2-$[Zn(H_2O)(As_2W_{17}O_{61})]^{8-}$ (α_2-$As_2W_{17}Zn$), α-$[P_2W_{18}O_{62}]^{6-}$ (abbreviated as α-P_2W_{18}), α_1- and α_2-$[P_2W_{17}O_{61}]^{10-}$ (α_1- and α_2-P_2W_{17}), α_2-$[Mn(H_2O)(P_2W_{17}O_{61})]^{8-}$ (α_2-$P_2W_{17}Mn$), α_1- and α_2-$[Fe(H_2O)(P_2W_{17}O_{61})]^{7-}$ (α_1- and α_2-$P_2W_{17}Fe$), α_2-$[Co(H_2O)(P_2W_{17}O_{61})]^{8-}$ (α_2-$P_2W_{17}Co$), α_2-$[Ni(H_2O)(P_2W_{17}O_{61})]^{8-}$ (α_2-$P_2W_{17}Ni$), α_2-$[Cu(H_2O)(P_2W_{17}O_{61})]^{8-}$ (α_2-$P_2W_{17}Cu$), α_2-$[Zn(H_2O)(P_2W_{17}O_{61})]^{8-}$ (α_2-$P_2W_{17}Zn$). Their preparation and characterisation have already been described in detail.[6,8,9,12−15,18,19]

2.2. Electrochemistry

The main features of the electrochemical data are presented in Table 1, which allows a pertinent comparison of the reduction peak potentials pertaining to the first W wave for the As and P derivatives. The ΔE_p values can be considered as a self-consistent parameter, using the appropriate precursor lacunary species as a reference. Most of our study is devoted to derivatives that are substituted in the α_2 position. Strictly, the changes in acid-base properties from the lacunary precursor to the substituted species preclude the direct use of the ΔE_p values in obtaining reliable values for the stability constants of the complexes. As previously with tungstodiphosphates, the location of the vacant site, and subsequently of the substituent metal cation, is revealed by the characteristic fingerprint associated with the α_2 compounds in a medium with pH = 3,[10] where the first two two-electron W-centred processes are followed by two one-electron processes. From the two pH values studied (pH = 3 and 5), the first W wave is shifted roughly by 74 mV/pH, irrespective of the type of substituted tungstodiarsenate.

Table 1. Reduction peak potential vs. SCE for the first tungsten wave in α_2-$X_2W_{17}M$ complexes (X = As or P; M represents the substituent metal cation) and comparison with the appropriate lacunary species; supporting electrolyte: 0.2 м Na_2SO_4 + H_2SO_4 (pH = 3); scan rate 10 mV·s^{-1}; the results for the diphosphates were published previously in ref.[10], but here, for composite waves in this series, only the most negative peak potential was retained for clarity

Compound	$-E_p$ [mV] vs. SCE	$\delta\Delta E_p$ [mV][a]
α-As_2W_{18}	−18	–
α-P_2W_{18}	22	–
α_2-As_2W_{17} o	298	0
α_2-P_2W_{17} o	320	0
α_2-$As_2W_{17}Mn$	324	26
α_2-$P_2W_{17}Mn$	394	74
α_2-$As_2W_{17}Fe$	360	62
α_2-$P_2W_{17}Fe$	402	82
α_2-$As_2W_{17}Co$	346	48
α_2-$P_2W_{17}Co$	392	72
α_2-$As_2W_{17}Ni$	358	60
α_2-$P_2W_{17}Ni$	406	86
α_2-$As_2W_{17}Cu$	288	−10
α_2-$P_2W_{17}Cu$	306 (composite W/Cu wave)	−14
α_2-$As_2W_{17}Zn$	360	62
α_2-$P_2W_{17}Zn$	386	66

[a] $\Delta E_p = E_{p,lacunary} - E_{p,substituted}$.

At pH = 3, the first W wave for α-As_2W_{18} and α-P_2W_{18} features a one-electron process, as confirmed by controlled potential coulometry. Otherwise, throughout Table 1, the first redox process associated with the W centres involves two electrons. Examination of the values in this table underscores the previously demonstrated fact[9,10,16] that the appropriate comparison among the present compounds must be made between the precursor lacunary species and their metal ion substituted derivatives. In this series of "unsaturated" species, it can be seen that the first W wave is shifted in the positive potential direction in all the As compounds relative to the P derivatives. This trend appears even in the lacunary species and can be ascribed to the larger basicity of the reduced forms of the As derivatives. However, it is worth noting that these W peak potentials in the substituted As derivatives are rather close from one compound to the next, except in the case of the Cu-substituted species. This observation would indicate, even in the case of the Fe derivative in which the reduction of the iron centre occurs prior to the W centres, that a roughly constant change in basicity exists between the precursor lacunary species and its metal ion complexes.

Several complementary results characteristic of the diarsenates are worth noting and are presented in Table 2. The influence of pH is obvious, except for the $Co^{2+/3+}$ redox couple. The pH dependence of the $Mn^{2+/3+}$ redox couple in α_2-$As_2W_{17}Mn$ is very apparent. The significance of this observation will be studied in conjunction with the electrocatalytic properties of this system. In the α_2 series it is found that the reduction peaks for the substituent cations, that are reduced in a potential domain close to that of the W centres, are observed at more positive potentials in the As than in the P derivatives; in the As compounds, the reduction peak potentials are located at −66 mV vs. SCE for Fe^{3+} and −212 mV vs. SCE for Cu^{2+}, compared with −130 mV and −306 mV, respectively for the P derivatives.

Table 2. Oxidation or reduction peak potentials for the electroactive substituent cations within the α_2-$As_2W_{17}M$ species (M represents the substituent metal cation) at pH = 3 and 5; scan rate 10 mV$\cdot$s^{-1}

	$Mn^{2+/3+}$	$Mn^{3+/4+}$	$Fe^{3+/2+}$	$Co^{2+/3+}$	$Cu^{2+/0}$
E_p [mV] (pH = 3)	1040	1186	−66	1130	−212
E_p [mV] (pH = 5)	624	950	−134	1124	−270

A short comparison is made in Table 3, between some compounds of the α_1 series. The corresponding results of the α_2 series are added to facilitate further comments. The location of the vacant site has no influence (for As), or only a small influence (for P), on the reduction peak potential of the lacunary species, irrespective of the identity of the central atom. Even so, a small positive shift is observed for the diarsenates relative to the diphosphates. Substantially larger shifts in the same direction are seen for the first reduction process of W centres in the iron-substituted species. The same trend can be seen for the reduction of the Fe^{3+} centre within the heteropolyanions with regard to the comparison between the diarsenates and the diphosphates. It must be noted that the influence of the pH on the $Fe^{3+/2+}$ redox couple in the α_1 derivatives is rather small. In contrast, the maximum shift in the negative potential direction for the α_2 species is 68 mV for the As derivative and 46 mV for the P compound. It is also worth noting that the iron centre is less easily reduced in the α_1 than in the α_2 derivatives. Such an observation should be related to a more general problem; it has been proposed[20,21] that α-P_2W_{18} is first reduced at one of the twelve equivalent tungsten atoms in the "belt". Experimental evidence supports this fact.[22] This behaviour still holds for the α_1-substituted species, the first observed wave depends on the relative reducibility of the substituent cation and W. It is then conceivable that the reduction potential of this hetero-cation is influenced by the neighbouring W atoms.[6] This point is being elaborated and will be published in a forthcoming paper.[23]

Tables 1−3 are complemented by Figure 2, which displays cyclic voltammograms of selected representative heteropolyanions that show more specific descriptions of their behaviour. Figure 2A compares the cyclic voltammograms of the α_1- and α_2-$As_2W_{17}Fe$ derivatives at pH = 3, and Figure 2B compares those of the corresponding P derivatives. Provisionally, it must be pointed out that the characteristic fingerprint for the α_2-type derivatives is present, as expected. Although the assignment of the observed first wave might appear straightforward, the novelty of the compounds prompted us to carry out several complementary coulometric determinations. Controlled potential coulometric experiments at pH = 3, and at the relevant peak potential or just negative of this value, suggest that one electron per molecule of α_1- or α_2-$As_2W_{17}Fe$ is involved. The characteristic blue colour of the reduced W centres was not observed, thus confirming that only the Fe^{3+} centre was reduced. Complete reoxidation to the Fe^{3+} state was achieved, and this indicated the stability of the $Fe^{3+/2+}$ system within the heteropolyanions, at least on the coulometric

Table 3. Reduction peak potential vs. SCE for $Fe^{3+/2+}$ redox couple and first tungsten wave in complexes of the α_1 and α_2 series; electrolytes: pH = 3 and 5; scan rate 10 mV$\cdot$s^{-1}; for further details, see text

Compound	pH	$-E_p$ [mV] (Fe^{3+}/Fe^{2+})wave	$-E_p$ [mV] (1st W wave)
α_1-$As_2W_{17}\square$	3	–	298
α_2-$As_2W_{17}\square$	3	–	298
α_1-$P_2W_{17}\square$	3	–	306
α_2-$P_2W_{17}\square$	3	–	320
α_1-$As_2W_{17}Fe$	3	114	350,[a] 468, 544
	5	128	498,[a] 558, 666
α_2-$As_2W_{17}Fe$	3	66	360
	5	134	510
α_1-$P_2W_{17}Fe$	3	198	500
	5	192	602
α_2-$P_2W_{17}Fe$	3	130	(340) 402[b]
	5	176	548

[a] The combined 1st and 2nd W waves are split into three components, the peaks of which are located at the potentials indicated in the table (see Figure 2A). [b] The number in parentheses corresponds to the first part of a composite wave.

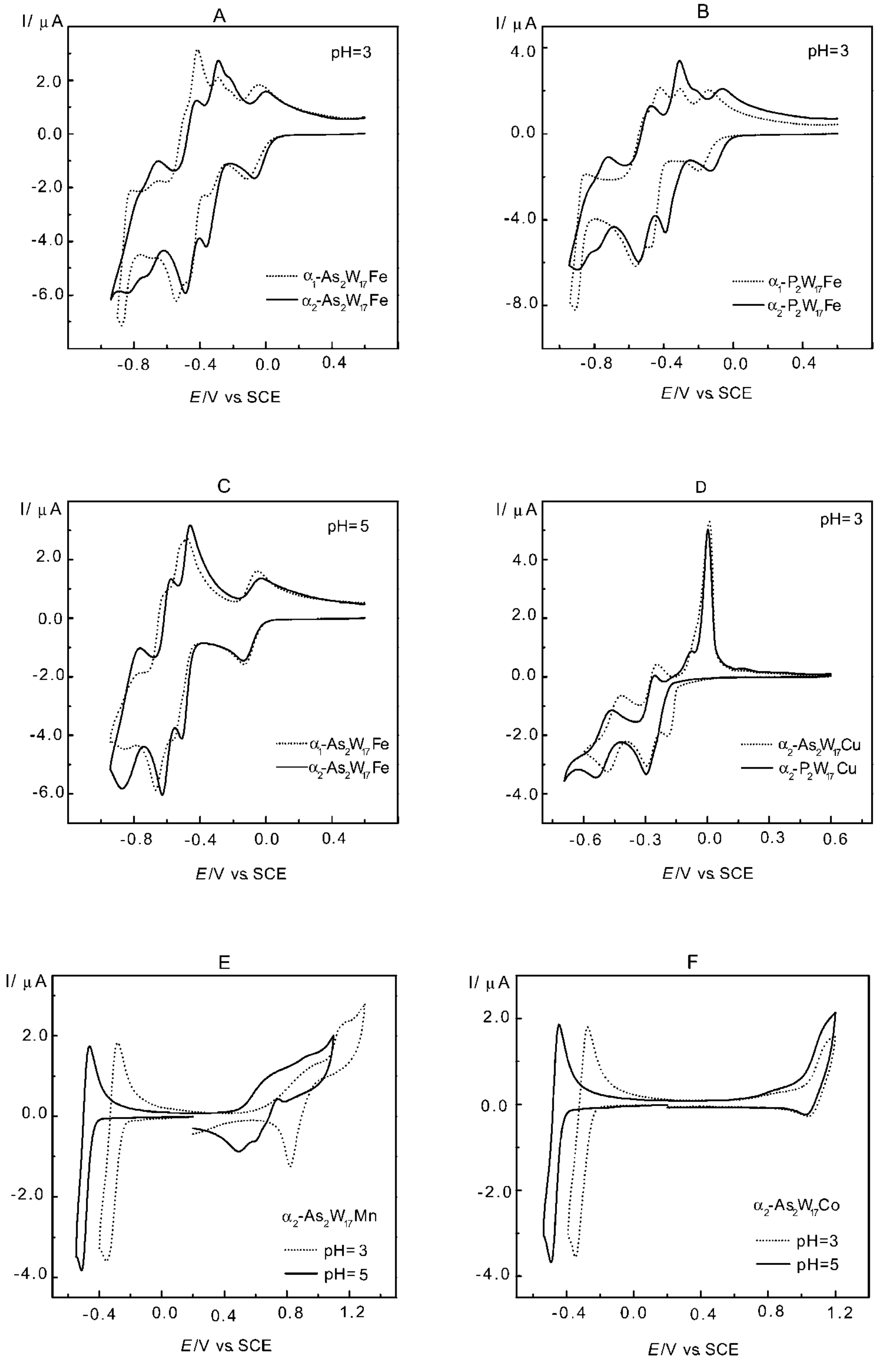

Figure 2. Cyclic voltammograms of a 5 × 10^{-4} M solution of the relevant heteropolyanion; working electrode glassy carbon; scan rate 10 mV·s^{-1}, unless otherwise stated: A and B: 0.2 M Na_2SO_4 + H_2SO_4 (pH = 3); C: 0.4 M CH_3COONa + CH_3COOH (pH = 5); D: 0.2 M Na_2SO_4 + H_2SO_4 (pH = 3); scan rate 2 mV·s^{-1}: E and F: 0.2 M Na_2SO_4 + H_2SO_4 (pH = 3) and 0.4 M CH_3COONa + CH_3COOH (pH = 5)

timescale. Under the same experimental conditions, a parallel behaviour was obtained for α_1- and α_2-$P_2W_{17}Fe$.[10,16] In Figure 2A, the Fe^{3+} reduction wave for α_2-$As_2W_{17}Fe$ is followed by two two-electron W waves. The same observation is seen for α_2-$P_2W_{17}Fe$ in Figure 2B, with a slight splitting of the first W wave in the P derivative. In contrast, for the α_1-$As_2W_{17}Fe$ derivative in Figure 2A, the expected two two-electron tungsten waves are separated into three components, with a remarkable reduction in the current of the first W wave and an enhancement of the intermediate part. A different behaviour is displayed by α_1-$P_2W_{17}Fe$ in Figure 2B. An important negative shift of the first W wave, and a large enhancement of the first wave relative to the second wave is seen. Comparison of these two Figures indicates a sharp difference in the acid-base behaviour between the α_1 and α_2 derivatives in each series, and also between the α_1 derivatives of the two series. Such a difference between α_1-$As_2W_{17}Fe$ and α_2-$As_2W_{17}Fe$ is less striking at pH = 5, as can be seen in Figure 2C. The last example selected for comparison can be seen in Figure 2D, and involves α_2-$As_2W_{17}Cu$ and α_2-$P_2W_{17}Cu$. The cyclic voltammograms were run at pH = 3, and clearly show the good separation between the Cu^{2+}- and W^{6+}-centred processes in α_2-$As_2W_{17}Cu$, in contrast to the almost complete merging of the corresponding processes in α_2-$P_2W_{17}Cu$. Coulometry at the peak potential of the Cu^{2+} reduction wave in α_2-$As_2W_{17}Cu$ clearly showed the involvement of two electrons per molecule of heteropolyanion. No blue colour was observed, which would have indicated the concomitant reduction of the W centres. Using the same experimental conditions, it was necessary to use spectroelectrochemistry to appreciate the degree of separation of these two processes in α_2-$P_2W_{17}Cu$.[24] Finally, Figure 2E,F illustrates the behaviour of the Mn^{2+} and Co^{2+} diarsenate derivatives at the two pH values studied. Two oxidation-reduction steps are easily observed for Mn^{2+} and one for Co^{2+}.

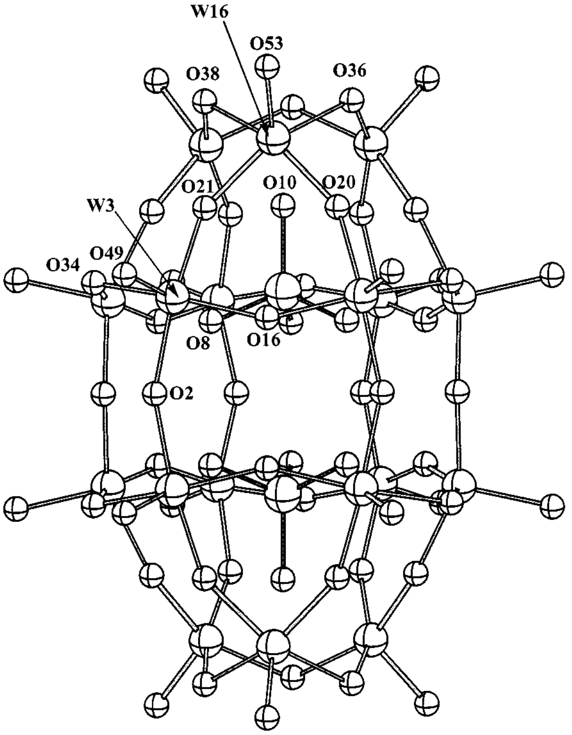

Figure 3. Numbering of atoms in the idealised structure of α-$[P_2W_{18}O_{62}]^{6-}$, used in the working out of crystallographic distances in Table 4

Table 4. Mean W−O distances in Å in an idealised structure of $[P_2W_{18}O_{62}]^{6-}$

W3−O2	1.9220	W16−O10 (W−O−P)	2.3010
W3−O8 (W−O−P)	2.3196	W16−O20	1.9235
W3−O49	1.8986	W16−O21	1.9235
W3−O21	1.9401	W16−O36	1.9917
W3−O16	1.9575	W16−O38	1.9917
W3−O34 (W−O$_t$)	1.9147	W16−O53 (W−O$_t$)	1.8230

3. Discussion

We attempted to rationalise the experimental results by considering the interplay between several influences that ultimately determine the physical properties of the vacant site and hence, the behaviour of the substituted species. A crude evaluation of the size of the vacant site can be obtained by measuring the W−O distances around a selected W atom in the Dawson-type structure, with special attention being paid to the W−O terminal bond, which disappears when the vacancy is created. It is assumed during this process that the bond lengths or bond angles do not change on creating the vacant site. In this context, the numbering of atoms in the idealised structure in Figure 3 is based directly on the crystallographic results of D'Amour[25] and are used for the evaluation of the energies of molecular orbitals,[23] and more specifically here, for the determination of bond lengths. Table 4 shows the bond lengths recalculated from this idealised structure of P_2W_{18}. This evaluation of the sizes of vacant sites is primarily useful when comparing the behaviours of the derivatives of α_1- and α_2-P_2W_{18}.

The two possible nonequivalent locations for a monovacant site are outlined by the W3−O and the W16−O distances; extraction of a W−O$_t$ moiety from the appropriate position will create a vacant site in the so-called α_1 position for W3−O, or α_2 position for W16−O. Examination of the bond lengths would then suggest that the vacant site in the α_2 position is slightly larger than that in the α_1 position. However, this evaluation does not take into account the influence of the bond angles, which could minimise the difference in size between the two sites, whether the volume or the entrance surface is considered. In any case, a direct study of the size of the vacant site is severely plagued by the lack of precise crystallographic data on the lacunary species. As a matter of fact, it was pointed out that the vacancy in such species is statistically distributed over several or all of the equivalent positions.[26,27] Therefore, although the same kind of derivation as above could have been carried out using the crystallographic determinations on As_2W_{18} by Neubert and Fuchs,[28] we found that the following complementary qualitative observations might prove more useful. From a general point of view in the Dawson-type tungstodiphosphates and tungstodiarsenates, the physical behaviour of a vacancy depends on its location in the polyoxometalate frame. The greater rigidity of the α_1 sites compared with the relative fluidity of the α_2 sites might be explained as follows: a WO_6 octahedron in an α_1 position is once edge-shared and three times corner-shared, while in an α_2 position it is twice corner-shared and twice edge-shared. Such an explanation clearly predicts the influence of the degree of matching between the size of the vacant site and the radius of the substituent cation on the stability constants of the complexes. Incidentally, it is worth noting that such a reasoning suggests a parallel behaviour for monolacunary Keggin species and α_2 Dawson-type lacunary compounds that possess the same kind of vacancy. Thus, the variations in the stability constants of the metal(II) and alkaline ion complexes of lacunary heteropolytungstates can be explained.[12,15] In contrast, it also justifies that the stability constants for the divalent metal ion complexes of α_1-$P_2W_{17}\square$ and α_1-$As_2W_{17}\square$ are not really affected by the nature of the central heteroatom.[12] Such an observation is important to propose a tentative explanation for some of the results in Table 3. The following suggestion can be made: the first W wave is driven in the positive potential direction in α_1-$As_2W_{17}Fe$ relative to the corresponding wave in α_1-$P_2W_{17}Fe$, due to the electronic effects of the central heteroatom, which ultimately is reflected in the relative basicity of the reduced species. The same influence holds for the compounds substituted in the α_2 position. Turning then to the general comparison between Dawson-type tungstodiphosphates and diarsenates, it can be assumed that, all things being equal, the size of the central atoms becomes the main relevant parameter. Considering the ionic radii of As^{5+} (0.46 Å) and P^{5+} (0.35 Å)[29] the larger space-filling ability of As should decrease the size of vacancies in the tungstodiarsenates relative to the -diphosphates. On this basis it is expected that the substituent cations would be attached less tightly in As than in the P derivatives. Stability constant values confirm this reasoning.[12] The only two examples of complexes in the present series in which the substituent cations are reduced in the vicinity of the W centres are the Fe^{III}- and Cu^{II}-substituted derivatives. The reduction potentials of these heterometal centres are substantially less negative in the As than in the P species, thus corroborating the expectations from the aforementioned reasoning.

4. Concluding Remarks

In the present work, Dawson-type tungstodiarsenates were synthesised, as well as their mono-lacunary species and several corresponding metal ion substituted derivatives. Attention was focused mainly on α_2-type derivatives, however, the Fe^{3+} derivatives of the α_1-, as well as the α_2-lacunary precursors were used. Systematic comparisons of the cyclic voltammograms of these compounds with those of tungstodiphosphates reveal that the first several voltammetric waves are driven in the positive potential direction by the presence of As as the central atom in the heteropolyanions. Precise crystallographic data are lacking for such compounds, in the diarsenate or in the diphosphate series. In spite of this situation, the present electrochemical results agree with the rough geometrical considerations, and with the knowledge of the stability constants of the metal ion substituted compounds indirectly reveal a coherent picture of the behaviour of the vacant sites in diarsenates and diphosphates. In particular, the influence of the central heteroatom on the redox and/or acid-base properties could be assessed and compared. Steric effects, expected on geometrical grounds, and already reflected in the values of the stability constants of the metal ion substituted compounds, also influence the cyclic voltammogram.

In conclusion, the identity of the central heteroatom substantially influences the redox behaviour of heteropolyanions, and must therefore be taken into account in our study of the parameters, which could modify electrocatalytic properties of this class of chemicals. It is rewarding to note that indirect methods can be used when evaluating the influence of changing the central atom in heteropolyanions. The study of multi-substitutions in the diarsenates and diphosphates is currently in progress.

5. Experimental Section

Pure water from a Milli-RO_4 unit, followed by a Millipore Q purification set was used throughout. All the chemicals were of high-purity grade and were used as received. H_2SO_4, Li_2SO_4, Na_2SO_4, CH_3COOH, CH_3COONa (Prolabo Normapur) were commercial products. In the present study, the medium of pH = 3 was made up with 0.2 M Na_2SO_4 + H_2SO_4 and that of pH = 5 with 0.4 M CH_3COONa + CH_3COOH. The heteropolyanions used in this work have been cited previously, along with appropriate abbreviations and preparations. Their stability was checked in a 0.2 M Na_2SO_4 + H_2SO_4 medium (pH = 3) using UV/Vis spectroscopy over a period of at least 24 h. The solutions were deaerated thoroughly for at least 30 min with pure argon and kept under argon during the electrochemical experiments. The source, mounting and polishing of the glassy carbon electrode (GC, Le Carbone Lorraine, France, 3 mm diameter) have been described.[5,6] The electrochemical setup was an EG & G 273 A driven by a PC with the 270 software. Potentials are quoted against the saturated calomel electrode (SCE), in a compartment separated from the test solution by a fine porosity glass frit. The counter electrode was platinum gauze with a large surface area in a separated compartment with a medium porosity glass frit. The UV/Vis spectra were recorded with a Perkin−Elmer Lambda 19 spectrophotometer. Experiments were performed at 23 ± 1 °C.

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