Isomerically Pure α_1-Monosubstituted Tungstodiphosphates: Synthesis, Characterization and Stability in Aqueous Solutions

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Isomerically pure samples of α_1-$P_2W_{17}O_{61}M$ were prepared, in which M represents Ca^{II} and mainly the first-row transition metal cations: Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}. The formula is α_1-$P_2W_{17}O_{62}M$ for V^V and Mo^{VI}. The compounds were characterised by elemental analysis, IR, UV/Vis and ^{31}P NMR spectroscopy. The stability of these complexes was monitored by cyclic voltammetry and/or UV/Vis spectroscopy. All the compounds proved to be stable for at least 24 h in a pH = 3 medium, even in the presence of 0.2 M Na^+, except for the precursor lacunary species itself and the Ca^{II}-substituted derivative. In this medium, the transformation of the lacunary heteropolyanion yielded a mixture of α-$[P_2W_{18}O_{62}]^{6-}$ and $[H_2P_2W_{12}]^{12-}$. The same species were obtained, but at a much slower rate, through the decomposition of α_1-$P_2W_{17}O_{61}Ca$. This difference in stability between the lacunary and the Ca^{II}-substituted derivatives might be ascribed to size and charge effects, along with the rigidity of the vacant site. At pH = 5, the final product of the transformation of α_1-$[P_2W_{17}O_{61}]^{10-}$ is α_2-$[P_2W_{17}O_{61}]^{10-}$. The presence of Li^+ appears to be more favourable than Na^+ for the stability of these complexes.

Introduction

It is well established that numerous electrocatalytic processes can be triggered by heteropolyanions (HPA).[1] Specifically, sustained catalytic several-electron reduction processes demand that the necessary number of electrons be accumulated in the framework of the HPA and then delivered to the substrate in potential regions where neither structure change of the HPA nor derivatisation of the electrode might occur.[1d,2] In our continuing efforts to systematically examine the parameters and combinations of parameters that could favour or counteract the merging of the first several waves in the electrochemical study of heteropolyanions, two main parameters were identified. The pH of the solution is one obvious parameter, which can be combined successfully with the second parameter, namely substitution effects, to reveal the rich redox behaviour of HPAs.[3−5] This last parameter is particularly important because it will determine, at least in part, the stability domain of the substituted HPA. Furthermore, the location of the heterometal in the framework and the nature and the number of the substituents are likely to influence the interactions between the electroactive centres in the molecule. In this context, our present efforts are aimed at illustrating such ideas with compounds of the Dawson series. It can be recalled that the Dawson structure is an elongated ellipsoid that consists of six addenda atoms of one kind and twelve of another. The six metal atoms are assembled in two groups of edge-shared M_3O_{13} octahedra that occupy the two "polar" positions of the ellipsoid; the remaining twelve metal atoms form two rings of six alternately edge- and corner-shared MO_6 octahedra in what is usually termed the equatorial position. The metal atoms in the "cap" occupy what is termed α_2-positions and those in the "belt" α_1-positions. With regard to the α_2-series, the synthesis involved first-row transition metal ion substituted complexes[4] derived from $[(1,)2,3\text{-}P_2Mo_2W_{15}O_{61}]^{10-}$. Among other remarkable results, the electrochemistry of this series of compounds shows that the interplay of the pH effect facilitates the build-up of an overall three-electron process on the first wave of the Fe^{III}-substituted complex.[4a,6] Another, possibly complementary direction involves positional isomerism. Perusal of the literature on simple Dawson-type tungstodiphosphates reveals that the α_2-isomer and its substituted derivatives were the preferred,[5] owing presumably to the instability of lacunary α_1-$[P_2W_{17}O_{61}]^{10-}$ which isomerises easily to the α_2-form[7] and reconstitutes the parent $[P_2W_{18}O_{62}]^{6-}$. However, we have succeeded in obtaining previously pure samples of several compounds of the α_1-series.[6]

The aim of the present paper is to describe the synthesis and characterisation of pure samples of the lacunary and

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first-row transition metal ion substituted compounds of the α_1-series. In particular, their transformation in solution as a function of pH and time were monitored by cyclic voltammetry and/or UV/Vis spectroscopy. The interplay of ion-pairing remains a subject of interest,[8] and is obvious in several instances below. In a preceding paper[6c] devoted to the electrochemistry of these compounds and based on the present syntheses, we have demonstrated, by cyclic voltammetry, the successful synthesis of these metal ion substituted derivatives from the α_1-lacunary species. Thus, the conditions under which α_1-$[P_2W_{17}O_{61}]^{10-}$ is fairly stable could be determined. The metal cation substituted derivatives of α_1-$[P_2W_{17}O_{61}]^{10-}$ could then be obtained and studied. Further, in a pH = 3 medium, a characteristic fingerprint for the α_2-series has been found that allows us to distinguish them unequivocally from the corresponding α_1-isomers.[6c] Here, the details of the syntheses are given, with a full characterisation by elemental analysis, ^{31}P NMR, UV/Vis and IR spectroscopy. A further incentive for this work stems from the desire to study the influence of positional isomerism on the redox properties. It has been proposed,[9a][9b] and experimental evidence supports [8c] the fact that α-P_2W_{18} is initially reduced at one of the twelve equivalent tungsten atoms. Substitution in the α_1-position should then markedly influence electron transfer processes relative to the α_2-series.

^{31}P NMR Spectroscopy

In the following, the oxygen atoms and the negative charges are omitted when no confusion is possible.The following species, α-$[P_2W_{18}O_{62}]^{6-}$, α_1-$[P_2W_{17}O_{61}]^{10-}$, and α_2-$[P_2W_{17}O_{61}]^{10-}$, will be abbreviated as α-P_2W_{18}, α_1-P_2W_{17}, and α_2-P_2W_{17}, respectively.

Table 1 presents the ^{31}P NMR spectroscopic features obtained in the present work for α_1- and α_2-derivatives. Jorris et al.[10] have published ^{31}P NMR spectroscopic data on some compounds of the same families. Their results were confirmed, under slightly different experimental conditions, by Finke et al.[5b] on derivatives of the α_2-series. More recently, Francesconi et al.[7a] have published the data pertaining to the lithium salt of α_1-P_2W_{17} and to several other lanthanide complexes of this lacunary species. To the best of our knowledge, Jorris et al.[10] were the first to study the NMR spectroscopic behaviour of paramagnetic element containing HPAs of P_2W_{17} derivatives. Even though their syntheses resulted in mixtures of α_1- and α_2-isomers, their pioneering work constitutes a valuable basis for the interpretation of the present observations. In these complexes, it is convenient to designate the phosphorus atom nearer the substituent (eventually paramagnetic ion) as P(1), and the phosphorus atom further away from this element as P(2). From the ^{31}P NMR spectra of several Dawson structures substituted in the α_2-position, it can be seen that the chemical shift assigned to P(2) is practically unaffected by the nature of the substituent element. The only exception is when Co^{II} is the substituent. Such an observation is confirmed in Table 1. Provisionally, it is worth mentioning that the same observation (with the same exception) was also made for compounds of the $K_8P_2W_{15}Mo_2MO_{61}$ series, where M represents the divalent substituent cation.[4b] Table 1 shows that the same conclusions remain true for the chemical shifts assigned to P(2) in the α_1-P_2W_{17}M derivatives, with the exceptions also extended to cases where M is Ni^{II} and Mn^{II}. As expected, the signal assigned to the P atom closest to the substitution site is shifted downfield considerably in the presence of paramagnetic cations. The shift is larger for α_1-derivatives. The ^{31}P NMR line widths depend on the nature of the particular substituent atom, and especially on its electronic ground state configuration. Usually, as can be seen in Table 1, very narrow or relatively narrow signals are observed for P(2), in contrast to that observed for the P(1) signal, which becomes exceedingly broadened in the case of the Mn^{II} derivative, whose ground state is orbitally nondegenerate. As a whole, it can be considered that satisfactory agreement with the observations of Jorris et al.,[9] and other literature results, [5b][7a] is obtained in the present work, provided the difference in medium composition is taken into account. The same reasoning is also applied to the interpretation of the spectra of the Mg^{II}-, Ca^{II}- and Cu^{II}-substituted derivatives. From the electronic configurations of Mg^{II} and Ca^{II}, no dramatic chemical shifts are expected for either P(2) or P(1) compared with those observed in the diamagnetic Zn^{II} isomorphs. The results in Table 1 validate this reasoning. In contrast, Cu^{II} is a paramagnetic d^9 ion that has a dramatic effect on the observed chemical shift, as expected.

IR Spectroscopy

The characteristic IR peaks were recorded. The assignments were made by taking into account those established in the literature.[11] As in related studies,[6a] introduction of a substituent metal cation in the vacancy basically restores the symmetry of the PO_4 tetrahedron, at least as far as the IR spectra are concerned. Consequently, the IR spectra are very similar from one complex to the next, thus preventing any reliable identification of a given anion. However, it is worth noting that the peak assigned to the P−O$_a$−W vibration, where W is one of the “belt” atoms, is not observed in the Co^{II} and Ni^{II} derivatives.

Stability of α_1-P_2W_{17} and Its Substituted Derivatives: Electrochemistry and UV/Vis Spectroscopy

A constant observation in the transformation of α-P_2W_{18} as a function of pH and time, is that the nature of the resulting species depends strongly on the pH of the solution and on the identity and concentrations of the cations present in the solution.[9] Such a dependence is also expected in the cases of interest here. The evolution of α_1-P_2W_{17} is monitored by cyclic voltammetry at pH = 3 and 5. The

Table 1. ^{31}P NMR shifts (from 85% H_3PO_4) and line widths of α_1- and α_2-monometalloheptadecatungstodiphosphates at 298 K (0.01 M solutions of K^+ salts in LiCl 0.5 M, in 50% D_2O)

Compound	δ(P1) [ppm]	Δν(P1) [Hz]	δ(P2) [ppm]	Δν(P2) [Hz]
$\alpha_1K_9LiP_2W_{17}O_{61}$, 18 H_2O	−8.53 (−9.16)[a]		−12.86 (−13.48)[a]	
$\alpha_1K_8P_2W_{17}CaO_{61}$, 19 H_2O	−9.35	12	−13.04	5
$\alpha_1K_7P_2W_{17}VO_{62}$, 18 H_2O	−11.45	6	−12.52	7
$\alpha_1K_8P_2W_{17}MnO_{61}$, 15 H_2O	not observed	–	−2.55	700
$\alpha_1K_7P_2W_{17}FeO_{61}$, 16 H_2O	not observed	–	−4.6	700
$\alpha_1K_8P_2W_{17}CoO_{61}$, 16 H_2O	1129	150	−34	4
$\alpha_1K_8P_2W_{17}NiO_{61}$, 16 H_2O	895[b]	5700[b]	−16.47	60
$\alpha_1K_8P_2W_{17}CuO_{61}$, 19 H_2O	−1.30	800	−12.00	70
$\alpha_1K_8P_2W_{17}ZnO_{61}$, 16 H_2O	−7.96	2	−12.84	3
$\alpha_1K_6P_2W_{17}MoO_{62}$, 18 H_2O	−11.15	8	−12.08	11
$\alpha_1K_8P_2W_{17}MgO_{61}$, 17 H_2O	−7.44	3	−12.81	4
$\alpha_2K_{10}P_2W_{17}O_{61}$, 18 H_2O	−7.33	3	−13.48	4
$\alpha_2K_8P_2W_{17}CaO_{61}$, 19 H_2O	−7.13	2	−13.66	2
$\alpha_2K_7P_2W_{17}VO_{62}$, 18 H_2O	−10.84		−12.92	
$\alpha_2K_8P_2W_{17}MnO_{61}$, 15 H_2O	600[b]	40000[b]	−12.42	140
$\alpha_2K_7P_2W_{17}FeO_{61}$, 16 H_2O	not observed	–	−12.6	160
$\alpha_2K_8P_2W_{17}CoO_{61}$, 16 H_2O	245	25	−22.71	5
$\alpha_2K_8P_2W_{17}NiO_{61}$, 16 H_2O	226.2	750	−13.46	19
$\alpha_2K_8P_2W_{17}ZnO_{61}$, 16 H_2O	−8.06	15	−13.54	2
$\alpha_2K_8P_2W_{17}MgO_{61}$, 17 H_2O	−7.52	2	−13.53	2
$\alpha_2K_8P_2W_{17}CuO_{61}$, 19 H_2O	−33	1250	−12.58	21

[a] From ref.[7a] [b] From ref.[10]

voltammograms are limited to the first several waves spanning the potential region in which no derivatisation of the electrode surface is encountered.[3n] These waves appear to serve as sufficiently clear fingerprints for the various compounds. The stability of the substituted derivatives was studied by UV/Vis spectroscopy, complemented by cyclic voltammetry when necessary. A sodium medium was selected for a detailed study, since the presence of this cation gives an intermediate rate of transformation, suitable for correct monitoring by cyclic voltammetry.

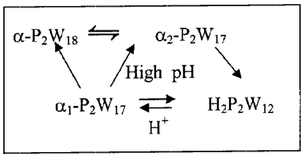
Cyclic Voltammetric Monitoring of α_1-P_2W_{17} at pH = 3 and 5 in an Na^+ Medium

Table 2 summarises the evolution of the main observed cathodic peak potentials as a function of time. The significance of these values is indicated below.

Table 2. Evolution of the reduction peak potentials of the first three waves of $\alpha_1P_2W_{17}$ as a function of pH and time; for the compositions of the electrolytes and other details, see text

		pH = 3	
Duration/h	$-E_{p1}$/mV	$-E_{p2}$/mV	$-E_{p3}$/mV
0	310	580	925
168	30 and 210	635	902
		pH = 5	
0	500	656	1042
72	530	658	922

At pH = 3, the first three waves, run on a freshly prepared solution of α_1-P_2W_{17}, are initially considered. After a period of 2 h, transformation is already significant: the cathodic peak current intensity of the first wave decreases to 75% of its initial value; concomitantly, two new waves appear and begin to grow at a more positive potential than that observed for the former initial first wave. The initial first wave completely disappears after 26 h, after which the cyclic voltammogram remains practically the same and is composed of a four-wave system. The transformation scheme, as a function of pH, established previously for α-P_2W_{18} by Contant and Ciabrini[5k,12] and sketched in Scheme 1, is very helpful for identifying the possible species responsible for the observed voltammogram and for their quantitative determination.



Scheme 1. Decomposition pathways of α_1-P_2W_{17}

The cyclic voltammograms of authentic samples of α-P_2W_{18} and P_2W_{12} are superimposed in Figure 1 (A). Key to the identification of the decomposition products is the observation that the single wave of P_2W_{12} in the explored potential region appears to be very close to the third wave of α-P_2W_{18} in Figure 1 (A). As a result, when a cyclic voltammogram is run on a sample of a mixture of the two species, the third wave is broad and composite, and is clearly different to the third wave observed in the voltammogram of α-P_2W_{18} alone.

Based on the cyclic voltammograms of these authentic samples of α-P_2W_{18} and P_2W_{12}, the decomposition pathways of α_1-P_2W_{17} could be described quantitatively in Figure 1 (B and C), which also shows a representative selection of the cyclic voltammograms of the mixture. It is assumed when calculating the percentages of the various species that

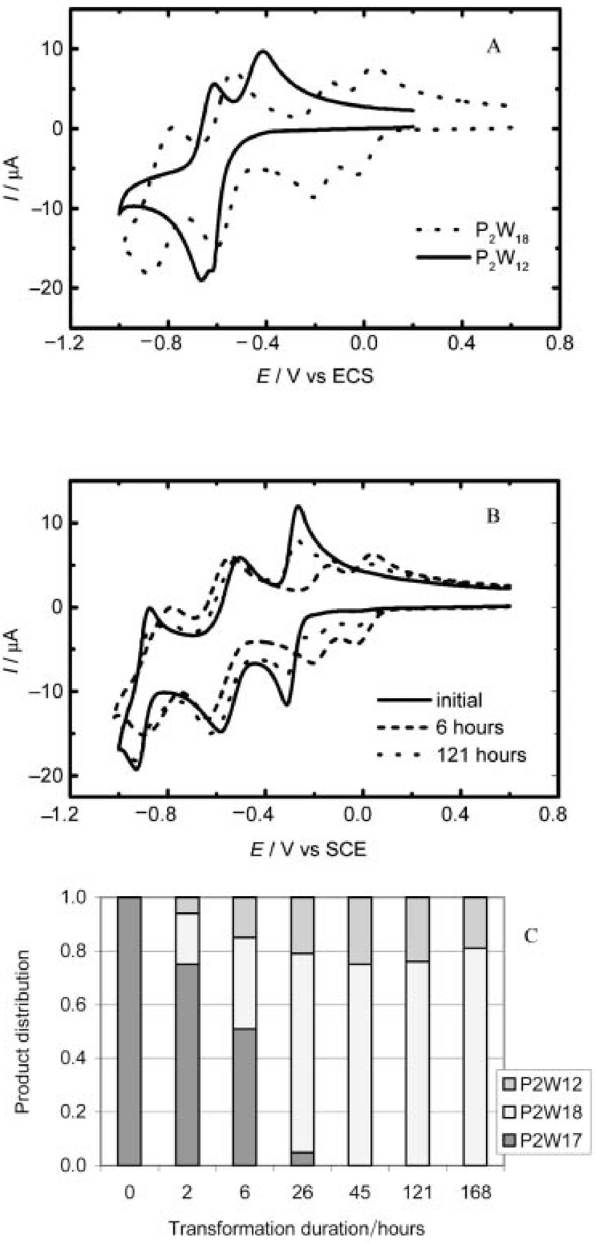


Figure 1. Identification of the decomposition pathway of α_1-P_2W_{17} in a pH = 3 medium (0.2 M Na_2SO_4 + H_2SO_4); (A) Cyclic voltammograms of authentic samples of α-P_2W_{18} and P_2W_{12}; (B) selection of representative cyclic voltammograms of α_1-P_2W_{17}, as a function of time; (C) electroactive products distribution, as a function of transformation duration; for further details, see text

only negligibly small amounts of possible non-electroactive species might exist in the mixture. Finally, the solution obtained after completion of the transformation of α_1-P_2W_{17} at pH = 3 contains α-P_2W_{18} and P_2W_{12}. This is in agreement with previous work.

Parallel experiments were performed at pH = 5 in sodium acetate buffer. The initial cyclic voltammogram is restricted to the three redox peaks observed between +0.6 and −1.1 V; the last two waves are composite. The initial and final reduction peak potential values are presented in Table 2. Cyclic voltammetry reveals that after only a few minutes the formation of the first two waves of α-P_2W_{18} can be seen, while the initial wave system is only slightly different, except for current intensities. However, after standing for 72 h, the waves of α-P_2W_{18} have completely disappeared and a new voltammetric pattern is observed, which can be ascribed to a pure electroactive product. Comparison of the cyclic voltammogram of α_2-P_2W_{17} with that obtained after completion of the transformation of α_1-P_2W_{17} at pH = 5, indicates unambiguously that α_1-P_2W_{17} is initially converted into a mixture of α_2-P_2W_{17} and α-P_2W_{18}, and that the final product at pH = 5 is pure α_2-P_2W_{17}.

The cyclic voltammetric monitoring of the species appearing in solution has allowed for the clarification of the transformation pathways of α_1-P_2W_{17} at pH = 3 and 5, as sketched in Scheme 1. Qualitatively, it is worth noting that the transformations are much slower at pH = 3 than at pH = 5.

Study of the Stability of α_1-$P_2W_{17}M$ Complexes (M = Ca^{II}, V^{V}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Mo^{VI})

A sodium sulfate solution at pH = 3 was selected as the medium for this study. For each complex, the concentration in solution was approximately 2×10^{-5} M, and two spectra were run with the same sample with a time interval of 24 h. All the spectra are relatively featureless, almost identical to each other, and show a shoulder. The characteristic features are presented in Table 3. Not unexpectedly, large magnification of the absorbance scale indicates differences in the onsets of the absorption spectra.

On careful comparison of the spectra, only two complexes are not completely stable after 24 h in the pH = 3 medium: α_1-P_2W_{17} and α_1-P_2W_{17}Ca. The corresponding spectra can be seen in Figures 2 and 3. For the lacunary species, this observation is in agreement with the results of the cyclic voltammetric study. Provisionally, we note the close similarity between the spectra of the two complexes after 24 h at pH = 3, which could suggest similar transformation pathways for them. Therefore, a complementary voltammetric examination of α_1-P_2W_{17}Ca as a function of time was carried out. In the sodium sulfate medium at pH = 3, and as observed for other complexes in the previous section, the relevant cyclic voltammogram consists of

Table 3. Characteristic wavelength and optical density measured for approximately 2×10^{-5} M of the relevant heteropolyanion in a pH = 3 medium

Compound	λ [nm] shoulder	O.D. [a.u.]
$\alpha_1K_9LiP_2W_{17}O_{61}$, 18 H_2O	249	1.15
$\alpha_1K_8P_2W_{17}CaO_{61}$, 19 H_2O	249	1.15
$\alpha_1K_7P_2W_{17}VO_{62}$, 18 H_2O	240	1.46
$\alpha_1K_8P_2W_{17}MnO_{61}$, 15 H_2O	248	1.26
$\alpha_1K_7P_2W_{17}FeO_{61}$, 16 H_2O	245	1.29
$\alpha_1K_8P_2W_{17}CoO_{61}$, 16 H_2O	251	1.15
$\alpha_1K_8P_2W_{17}NiO_{61}$, 16 H_2O	250	1.12
$\alpha_1K_8P_2W_{17}CuO_{61}$, 19 H_2O	253	1.10
$\alpha_1K_8P_2W_{17}ZnO_{61}$, 16 H_2O	260	1.07

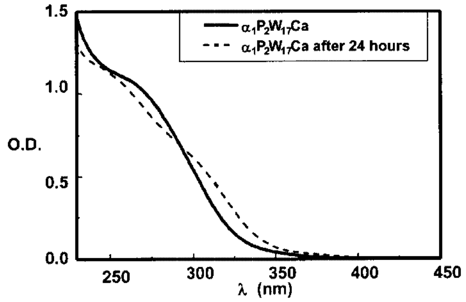


Figure 2. Evolution over 24 h of the UV/Vis spectra of α_1-$P_2W_{17}Ca$

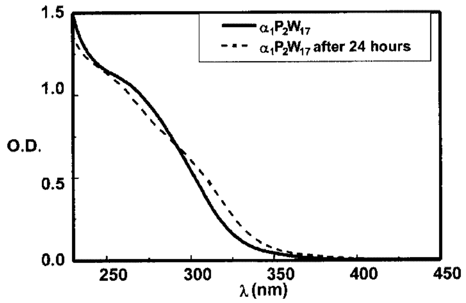


Figure 3. Evolution over 24 h of the UV/Vis spectra of α_1-P_2W_{17}

three chemically reversible waves. Their cathodic peak potentials are at − 0.320, − 0.570 and − 0.916 V. Figure 4 shows the cyclic voltammograms of α_1-$P_2W_{17}Ca$. Comparison of the voltammograms obtained after 15 d with that of α_1-P_2W_{17} after 7 d indicates that α-P_2W_{18} and P_2W_{12} are indeed the transformation products of α_1-$P_2W_{17}Ca$. However, the transformation is distinctly slower in the case of the latter complex; for instance, the transformation of α_1-P_2W_{17} gives 73% α-P_2W_{18} after 26 h, while the percentage obtained from α_1-$P_2W_{17}Ca$ after 15 d is only 67%. These observations agree with the previously discussed trends[4,6b] involving the cyclic voltammograms associated with the tungsten framework in monosubstituted Dawson heteropolyanions. It has been demonstrated that appropriate comparisons among cyclic voltammograms involve those of the monosubstituted species with that of the precursor lacunary complex, except for the cases of substitution by $Mo^{6+/5+}$ and $V^{5+/4+}$. Looking at the present example which is particularly remarkable, it can readily be seen that the reduction peak potentials of the Ca^{II}-substituted complex are very similar to the corresponding ones of the lacunary species. The following rationale, based on the respective charges of Na^+ and Ca^{2+}, can also be used to explain the greater stability of α_1-$P_2W_{17}Ca$ than α_1-P_2W_{17}. On dissolution of α_1-P_2W_{17} (α_1-$LiK_9P_2W_{17}O_{61}$) in 0.2 M Na_2SO_4 + H_2SO_4 (pH = 3), the relatively fast replacement of Li^+ by Na^+ might be favoured by the large concentration of the latter, which is known to be deleterious to the stability of the complex. Owing to the difference in charge, the corresponding replacement of Ca^{2+} by Na^+ is much slower for α_1-$P_2W_{17}Ca$, even though the two cations have approximately the same radius. In other words, the local negative charge of the vacancy is better compensated by Ca^{2+} which is therefore, more difficult to displace than Li^+.

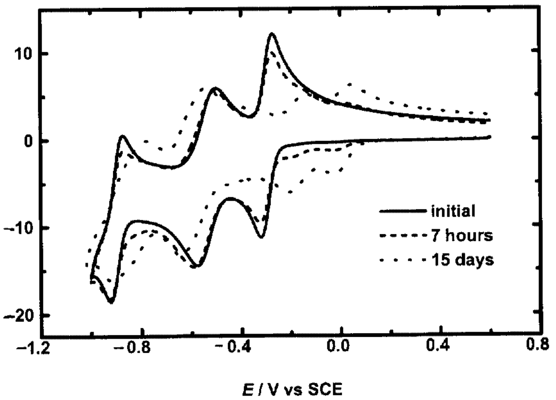


Figure 4. Selection of representative cyclic voltammograms observed during the transformation of α_1-$P_2W_{17}Ca$ in a pH = 3 medium (0.2 M Na_2SO_4 + H_2SO_4); for further details, see text

A study was also carried out to compare the stability of α_1-$P_2W_{17}Ca$ in Li^+ (0.2 M Li_2SO_4/H^+, pH = 3) and Na^+ media. The transformation is slower in the presence of lithium, quantified by a percentage of 43% decomposition in Li^+ medium compared with 63% in Na^+ medium after 2 d. Thus, it appears that the relative stability of α_2-$P_2W_{17}Ca$ and α_1-$P_2W_{17}Ca$ might be explained in terms of steric reasons,[5k,6,13] but in combination with the effect of the charge of the substituent cation. It should be noted that the ideal size for a cation to fit in the vacancy should be very similar to the usually accepted size of W^{6+} ion (0.74 Å). The radii of Ca^{2+} (1.14 Å) and Na^+ (1.16 Å) collected from the literature[14] are similar, but are larger than that of W^{6+} (0.74 Å); hence the relative order of the stabilities of the corresponding species. However, the charge of the substituent cation also plays a part as discussed previously. For a further confirmation of this size hypothesis, Mg^{2+} (0.86 Å), which has the same charge but a smaller radius than Ca^{2+}, was selected for comparison with the latter. In the sodium solution at pH = 3, α_1-$P_2W_{17}Mg$ is remarkably more stable than α_1-$P_2W_{17}Ca$. This observation gives further support to the preceding assumptions. Another aspect of the steric effect must be traced to the location of the vacancy in the α_1- or α_2-position in the tungsten framework.[5k,6,13] The vacancy is distinctly more rigid in the α_1- than in the α_2-position. Therefore, the deformability of the latter vacancy makes it larger and favours the accommodation of a large cation. As a result, it is expected that α_2-$P_2W_{17}Ca$ is more stable than α_1-$P_2W_{17}Ca$. The test in the sodium medium at pH = 3 confirms the hypothesis. The decomposition of α_2-$P_2W_{17}Ca$ begins after 4 d compared with 7 h for α_1-$P_2W_{17}Ca$. After a period of 15 d, the percentage of α-P_2W_{18} formed from α_2-$P_2W_{17}Ca$ is only 20%.

Concluding Remarks

One of the aims of this work is to further investigate the parameters that could influence electron transfer processes involving the first wave of heteropolyanions and, eventually, favour the apparently simultaneous uptake of several electrons. Positional isomerism is likely to be one of these parameters. It has been proposed, and experimental evidence supports the fact that α-P_2W_{18} is initially reduced at one of the twelve equivalent tungsten atoms. With the assumption that this behaviour remains valid in substituted compounds, substitution in the α_1-position should markedly influence electron transfer processes compared with the α_2-series. Conditions were found in which the lacunary ligand α_1-$[P_2W_{17}O_{61}]^{10-}$ is fairly stable. This result was achieved through the use of AcOLi for the dissolution of the complex, or by taking advantage of the favourable kinetics of addition vs. degradation when the solid lacunary HPA was added to a solution of the salt of the substituent cation. Its metal cation-substituted derivatives could then be obtained and studied. To the best of our knowledge, this work constitutes the first systematic synthesis and study of first-row transition metal cation monosubstituted complexes of the α_1-lacunary ligand. ^{31}P NMR spectroscopy and cyclic voltammetry were used to demonstrate the successful synthesis of these species. Their stability was monitored in pH = 3 and 5 media by cyclic voltammetry and UV/Vis spectroscopy. It is worth noting that even the relatively labile α_1-P_2W_{17} and α_1-$P_2W_{17}Ca$ are sufficiently stable to permit NMR spectroscopic and electrochemical characterisations. Relevant comparisons with the same derivatives in the α_2-series were carried out.

Experimental Section

Preparation: The potassium salts of α-$[P_2W_{18}O_{62}]^{6-}$, α_1-$[P_2W_{17}O_{61}]^{10-}$ and α_2-$[P_2W_{17}O_{61}]^{10-}$ were prepared by published methods.[5a] The compounds of the α_2-series have received extensive attention and their syntheses will not be described further.[5] In the α_1-series, the synthesis of Fe^{III}-substituted derivatives was described in detail previously.[6a] The synthesis of Mo- and V-substituted compounds were also described previously by one of the present authors.[5k−5m,7b,8c] The water contents were measured by gravimetric methods. Elemental analyses were performed by the Laboratoire Central d'Analyse of CNRS (Vernaison, France) and checked, except for the metallic cations, by standard methods.[6a] The precision of these analyses is not excellent, as is not unusual in the literature on polyoxometalates.

$\alpha_1K_8P_2W_{17}ZnO_{61}$, 16 H_2O: A sample of $\alpha_1K_9LiP_2W_{17}O_{61}$, 18 H_2O (10 g) was dissolved in 100 mL of acetate buffer at pH = 4.7, 0.5 M in lithium acetate AcOLi. The solution was not perfectly clear. $Zn(NO_3)_2$ (3 mL of a 1 M solution) was added whilst stirring. The solution was filtered through an ashless pleated filter and left to settle. The clear part of the solution (70 mL) was collected and treated with KCl (7 g). The precipitate was filtered, washed with ethanol and diethyl ether and air-dried; recovered: 7.5 g; yield: 75%. $\alpha_1K_8P_2W_{17}ZnO_{61}$, 16 H_2O (4830): calcd. K 6.48, P 1.28, Zn 1.35, W 64.71, H_2O 5.60; found K 6.70, P 1.24, Zn 1.25, W 62.60, H_2O 5.55.

$\alpha_1K_8P_2W_{17}MgO_{61}$, 17 H_2O: $Mg(NO_3)_2$ (5 mL of a 1 M solution) was added to 100 mL of water. $\alpha_1K_9LiP_2W_{17}O_{61}$, 18 H_2O (10 g) was then added whilst stirring, and the solution was filtered if necessary. The clear solution was treated with KCl (10 g) to obtain a white precipitate. The precipitate was filtered, washed with ethanol and diethyl ether and air-dried. Note that the same result could be obtained by starting with $MgCl_2$ instead of the nitrate; recovered: 7.9 g; yield: 80%. $\alpha_1K_8P_2W_{17}MgO_{61}$, 17 H_2O (4807): calcd. K 6.51, P 1.29, Mg 0.51, W 65.02, H_2O 6.00; found K 6.68, P 1.28, Mg 0.48, W 64.20, H_2O 6.02.

$\alpha_1K_8P_2W_{17}CaO_{61}$, 19 H_2O: The synthesis is the same as that of the Mg^{2+} derivative. The magnesium salt is replaced by $Ca(NO_3)_2$; recovered: 8.0 g; yield: 80%. $\alpha_1K_8P_2W_{17}CaO_{61}$, 19 H_2O (4877): calcd. K 6.41, P 1.27, Ca 0.82, W 64.09, H_2O 7.02; found K 6.60, P 1.24, Ca 0.79, W 62.67, H_2O 6.98.

$\alpha_1K_8P_2W_{17}NiO_{61}$, 16 H_2O: Ni^{2+} (2 mL of a 1 M $Ni(NO_3)_2$ solution) was added to LiCl (50 mL of a 0.2 M solution). $\alpha_1K_9LiP_2W_{17}O_{61}$, 18 H_2O (5 g) was then added whilst stirring, and the solution was filtered if necessary. The clear solution was treated with 30 mL of a saturated KCl solution. The precipitate was filtered, washed with ethanol and diethyl ether and air-dried. The same synthesis could be carried out in an acetate buffer containing 0.5 M AcOLi; recovered: 3.7 g; yield: 75%. $\alpha_1K_8P_2W_{17}NiO_{61}$, 16 H_2O (4823): calcd. K 6.49, P 1.28, Ni 1.22, W 64.80, H_2O 5.60; found K 6.74, P 1.25, Ni 1.25, W 62.42, H_2O 5.75.

$\alpha_1K_8P_2W_{17}CoO_{61}$, 16 H_2O: The synthesis is the same as that of the Zn^{2+} derivative; recovered: 7.5 g; yield: 75%. $\alpha_1K_8P_2W_{17}CoO_{61}$, 16 H_2O (4823): calcd. K 6.48, P 1.28, Co 1.22, W 64.80, H_2O 5.60; found K 6.75, P 1.24, Co 1.13, W 63.83, H_2O 5.71.

$\alpha_1K_8P_2W_{17}MnO_{61}$, 15 H_2O: A sample of $\alpha_1K_9LiP_2W_{17}O_{61}$, 18 H_2O (10 g) was dissolved in 100 mL of acetate buffer pH = 4.7, 0.5 M in lithium acetate AcOLi. The solution was not perfectly clear. Mn^{2+} (1.87 mL of a 1.6 M solution) was then added whilst stirring. The solution was filtered through an ashless pleated filter and left to settle. The clear part of the solution was collected and treated with KCl (10 g). The precipitate was filtered, washed with ethanol and diethyl ether and air-dried; recovered: 8.0 g; yield: 85%. $\alpha_1K_8P_2W_{17}MnO_{61}$, 15 H_2O (4819): calcd. K 6.51, P 1.29, Mn 1.14, W 65.09, H_2O 5.25; found K 6.53, P 1.24, Mn 1.13, W 64.01, H_2O 5.44.

$\alpha_1K_8P_2W_{17}CuO_{61}$, 19 H_2O: The synthesis is the same as that of the Zn^{2+} derivative; recovered: 7.5 g; yield: 75%. $\alpha_1K_8P_2W_{17}CuO_{61}$, 19 H_2O (4882): calcd. K 5.41, P 1.27, Cu 1.30, W 64.02, H_2O 6.64; found K 6.50, P 1.21, Cu 1.36, W 61.14, H_2O 6.65.

NMR, IR and UV/Vis Measurements: ^{31}P NMR spectra were recorded using 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 0.5 M LiCl (50% D_2O) solutions, and were referenced to external 85% H_3PO_4 by the substitution method. IR spectra were recorded with a Bio-Rad FTS 165 FTIR spectrophotometer. UV/Vis spectra were recorded with a Perkin−Elmer Lambda 19 spectrophotometer.

Electrochemical Experiments. Chemicals, Equipment and Apparatus: Pure water was used throughout. It was obtained by passing it through a Milli-RO4 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 and Na_2SO_4 were commercial products (Prolabo). The pH = 3 electrolyte was usually made up of 0.2 M Na_2SO_4 + H_2SO_4, and will be abbreviated as Na_2SO_4/H^+ (pH = 3), except for the case where sodium is replaced by lithium, i.e. Li_2SO_4/H^+ (pH = 3). The pH = 5 medium was prepared with 0.4 M CH_3COONa + CH_3COOH and abbreviated CH_3COONa/

H^+ (pH = 5). The solutions were deaerated thoroughly for a 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, Le Carbone Lorraine, France or Tokai, Japan) electrodes have been described.[3p] The glassy carbon samples had a diameter of 3 mm. The electrochemical set-up was an EG & G 273 A driven by a PC with the 270 software. The data were recorded using the computer, and then printed, when necessary to an 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 laboratory temperature.

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