



Article Electrochemical, Electrocatalytic, and Magnetic Properties of Vanadium-Containing Polyoxometalates

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Abstract: Mono-substituted vanadium-containing Dawson-type polyoxometalates having the general formula α_1 -[V^{IV}W₁₇X₂O₆₂]⁸⁻ and α_2 -[V^{IV}W₁₇X₂O₆₂]⁸⁻, with X = As or P, were synthesised and subject to a comprehensive electrochemical study comprising the pH dependency. These POMs exhibit an electrocatalytic behaviour towards the oxidation of thiols (namely cysteine), rendering them interesting species for mimicking oxidative stress situations, at physiological pH values. The efficiency of the electro-oxidation was assessed with thiols of different nature, and the substrate that responded best was used to compare the electrocatalytic capabilities of the POM series. The magnetic behaviour of these POMs was also evaluated and compared to their analogues, α_1 - and α_2 -[V^VW₁₇X₂O₆₂]⁷⁻ (X = As or P), at low temperatures and showed, as expected, a paramagnetic behaviour of V^{IV} based compounds.

Keywords: polyoxometalates; vanadium; magnetism; electrochemistry; electroctalysis

1. Introduction

The polycondensation of oxoanions in aqueous or nonaqueous solution leads to the formation of large molecular structures referred to as polyoxometalates (POMs) [1,2]. A classic POM contains several oxygen atoms, and often hydrogen atoms and at least two other different elements in positive oxidation states. Its structure resembles a fit of discrete oxide fragments of defined sizes and shapes. Its formula is $[X_xM_mO_y]^{q-}$, where M is generally tungsten, molybdenum, or vanadium, or other elements such as niobium, zinc, or tantalum. M can also be a mixture of these elements, which are then in their highest oxidation states. The element X, when it exists, is referred to as a hetero-element, and is usually an atom of phosphorus, arsenic, silicon, or any other transition or nonmetallic element [3].

POMs are characterised by the ratio M/X, which is the number of atoms of the condensed element, M, to the number of atoms of the hetero-element, X. Many compounds are obtained either by varying the M/X ratio (12, 11, 9, 18, 17...) or by changing X (Si^{IV}, Ge^{IV}, P^V, As^V...) or M (W^{VI}, Mo^{VI}, V^V...) [2]. Different models have been proposed to describe the arrangement of M atoms condensed around X hetero-atoms. These models all have in common the basic unit MO₆, which is an octahedron whose apexes are each occupied by an oxygen atom, and the centre by the metal atom M. In this study, we were interested in the M/X = 18/2 model, known as the Dawson structure [4].

In the Dawson structure, the octahedra associate in two different ways: (1) three MO_6 octahedra can join together at their vertices to form a trimetallic aggregate M_3O_{13} ; (2) two



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). MO₆ octahedra will join together by sharing an edge to form a dimetallic unit M₂O₁₀. Using X-ray diffraction, Dawson showed that three M₂O₁₀ dimetallic units and one M₃O₁₃ trimetallic cluster join around a hetero-atom X to form the fragment $[XM_9O_{34}]^{m-}$. The assembly of two such fragments leads to the structure α - $[X_2M_{18}O_{62}]^{n-}$, as demonstrated by Lefort in 1882 [5], who indicated the value 9 for the M/X ratio. The molecule thus has a σ plane of symmetry separating its two identical halves, leading to the general formula $[X_2M_{18}O_{62}]^{n-}$. In 1947, Souchay showed that these compounds are in fact dimers and should be described as belonging to the 18/2 model [6]. It was not until 1953 that Dawson used single-crystal X-ray diffraction to describe the structure of this molecule [4]. The structure shows that the metal atoms M are divided into two groups: 6 atoms (2 × 3) in the apical position ("hat"), with the sites they occupy said to be of type α -₂; and 12 atoms (2 × 6) in the equatorial position ("crown"), with the sites they occupy said to be of type α -₁ (Figure 1) [3,7].



Figure 1. Polyhedral representations of the α_{-1} (**A**) and α_{-2} (**B**) isomers of the Dawson structure $\alpha_{-}[X_2M_{18}O_{62}]^{n-}$.

In solution, the action of suitably chosen bases allows a Dawson-type POM to be partially and selectively hydrolysed, leading to the departure of one or more MO₆ groups. This results in a Dawson-type structure with one or more vacant sites, some examples being α_1 -[X₂M₁₇O₆₁]ⁿ⁻, α_2 -[X₂M₁₇O₆₁]ⁿ⁻, [X₂M₁₅O₅₆]ⁿ⁻, and [X₂M₁₂O₄₈]ⁿ⁻. From these lacunar compounds, mixed species can be prepared by inserting metal cations into the vacant sites. All these transformations allow the creation of a multitude of substituted POMs (for example: α_1 - or α_2 -[M(H₂O)X₂W₁₇O₆₁]ⁿ⁻) [8–10], mixed POMs (for example: α_1 - or α_2 -[X₂Mo_xV_yW_{18-(x+y)}O₆₂]ⁿ⁻) [11–18], sandwich-type POMs [19–35] (for example: [M₄(H₂O)₂(X₂W₁₅O₅₆)₂]¹⁶⁻), or even more diverse structures [36–40].

In the unreduced state, the two compounds $[X_2W_{18}O_{62}]^{6-}$ (where X = As or P), which have all their tungsten atoms in the +VI oxidation state, are diamagnetic. It appears interesting to see how their electronic properties will evolve as a function of the nature, oxidation state, and position of substituents on the tungstic skeleton of these compounds.

In this study, we were interested in α_1 -K₈[X₂W₁₇V⁴⁺O₆₂] 18H₂O and α_2 -K₈[X₂W₁₇V⁴⁺O₆₂] 18H₂O substituted mixed compounds (with X = As or P) [41]. These compounds were synthesised from the two POMs α -K₆[X₂W₁₈O₆₂].14H₂O (where X = As or P) [42,43], then characterised in solution by electrochemistry. The description of the syntheses of the different compounds used in this study is given in the ESI. Cyclic voltammetry allowed us to show the influence of pH on the redox properties of the four compounds. Magnetic studies carried out on the four compounds containing V⁴⁺ centres, as well as on the homologues containing V⁵⁺ centres, confirmed that the former were paramagnetic and the latter diamagnetic.

2. Materials and Methods

All the compounds used in this study and their precursors were synthesised according to published methods, and their purity attested by electrochemistry [41–44]. Indeed, cyclic voltammetry and controlled potential coulometry are two electrochemical techniques that allow the unambiguous characterisation of POMs and the certification of their purity [45–47].

2.1. Magnetic Properties

Magnetic measurements were carried out with a MPMS-5 Quantum Design SQUID magnetometer with applied fields of 1 T for the M vs. T measurements and from 0 to 5 T for the M vs. H measurements at 6, 4, and 2 K. Sample powders were pressed in pellets and held in a straw with sewing cotton to avoid sample holder corrections and the orientation of the crystallites along the magnetic field. The susceptibility data were corrected from diamagnetic contribution by using Pascal's tables.

2.2. Electrochemistry

Pure water was obtained with a Milli-Q Integral 5 purification set. All reagents were of high-purity grade and were used as purchased without further purification: CH_3CO_2H (Glacial, Fisher Scientific, Loughborough, UK), H_2SO_4 (Sigma Aldrich, Steinheim, Germany), H_3PO_4 (Prolabo, Briare le Canal, France), Na_2SO_4 (Sigma Aldrich, St. Louis, MO, USA, NaCH₃CO₂ 3H₂O (Sigma Aldrich, St. Louis, MO, USA), H_3BO_3 (Sigma Aldrich, St. Louis, MO, USA), M_3CO_2 3H₂O (Sigma Aldrich, St. Louis, MO, USA), H_3BO_3 (Sigma Aldrich, St. Louis, MO, USA), and NaH_2PO_4 H₂O (Merck, Darmstadt, Germany. The compositions of the various media were as follows: for pH 0.5, 1.0, 2.0, and 3.0: 0.2 M Na_2SO_4 + H_2SO_4 ; for pH 4.0 and 5.0: 0.4 M CH_3COONa + CH_3COOH ; for pH 6.0 and 7.0: 0.4 M NaH_2PO_4 + NaOH; for experiments covering a pH range of 1.0 to 8.0: Britton-Robinson buffer (see ESI, S3).

Electrochemical data were obtained using an EG & G 273 A potentiostat driven by a PC with the M270 software. A divided cell with a standard three-electrode configuration was used for cyclic voltammetry experiments. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode a platinum gauze of large surface area; both electrodes were separated from the bulk electrolyte solution via fritted compartments filled with the same electrolyte. The working electrode was a 3 mm outer diameter glassy carbon (GC) from Mersen, France. The pretreatment of the electrode before each experiment is adapted from a method described elsewhere [48]. Prior to each experiment, solutions were thoroughly deaerated for at least 30 min with pure argon. A positive pressure of this gas was maintained during subsequent work. The potentials are quoted against SCE unless otherwise stated, and all experiments were performed in solution at room temperature. Results were very reproducible from one experiment to the other, and slight variations observed over successive runs were rather attributed to the uncertainty associated with the detection limit of our equipment (potentiostat, hardware, and software) and not to the working electrode pretreatment, nor to possible fluctuations in temperature (polyanion concentrations: 0.5 mM).

3. Results and Discussion

3.1. Cyclic Voltammetry Characterisation at pH 3

The four compounds, α_1 -K₈[As₂W₁₇V⁴⁺O₆₂].18H₂O (α_1 -As), α_2 -K₈[As₂W₁₇V⁴⁺O₆₂] 18H₂O (α_2 -As), α_1 -K₈[P₂W₁₇V⁴⁺O₆₂] 18H₂O (α_1 -P), and α_2 -K₈[P₂W₁₇V⁴⁺O₆₂] 18H₂O (α_2 -P), were first characterised in the 0.2 M Na₂SO₄ + H₂SO₄/pH3 medium, used as a reference pH. These first results were in line with our expectations and the results of the scientific literature [41,49,50]. Indeed, in the cyclic voltammograms (CVs) in Figure 2a below and Figure S1a in the SI, we observed that the CVs of the phosphorus-containing species were slightly shifted to the left (towards the negative potentials) compared to the CVs of the arsenic-containing species. The W(VI) centres of the α_1 -As and α_2 -As species were more easily reduced than those of their phosphorus-containing counterparts (α_1 -P and α_2 -P). This difference in the reduction peak potential, ΔE_c , between the different tungsten waves

varied between 38 and 64 mV for the α_1 -As and between 34 and 72 mV for the α_2 -As (see Table 1). Indeed, previous studies have shown that Dawson-type POMs containing As as a hetero-element were easier to reduce than their P-containing counterparts [46,47]. This outcome, which has also been observed and studied in the case of Keggin-type POMs, was the consequence of differences in the atomic radius of the heteroatoms and in their electronegativities [51,52].



Figure 2. CVs of (a) α_1 -As (black) and α_1 -P (red); (b) α_1 -As (black) and α_2 -As (red) in 0.2 M Na₂SO₄ + H₂SO₄/pH3. Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 10 mV s⁻¹.

Table 1. Oxidation peak potentials (E_a) and reduction peak potentials (E_c) measured from CVs recorded in 0.2 M Na₂SO₄ + H₂SO₄/pH 3 (see above for the conditions).

	V	W_1	W2	W3	W_4	
Ea	0.610	-0.314	-0.552	-0.836	-	
E _c	0.514	-0.386	-0.596	-0.884	-	α_1 -As
$E^{0'} = (E_a + E_c)/2$	0.562	-0.350	-0.574	-0.860	-	
# electrons	1	2	2	2	-	
	V	W_1	W2	W3	W_4	
Ea	0.512	-0.304	-0.504	-0.664	-0.776	
Ec	0.366	-0.350	-0.550	-0.728	-0.826	α_2 -As
$E^{0'} = (E_a + E_c)/2$	0.439	-0.327	-0.527	-0.696	-0.801	
# electrons	1	2	2	1	1	
	V	W_1	W2	W3	W4	
Ea	0.532	-0.366	-0.616	-0.874	-	
E _c	0.446	-0.436	-0.656	-0.922	-	α ₁ -Ρ
$E^{0^\prime} = (E_a + E_c)/2$	0.489	-0.401	-0.636	-0.898	-	
# electrons	1	2	2	2	-	
	V	W1	W2	W3	W_4	
Ea	0.450	-0.338	-0.550	-0.736	-0.840	
E _c	0.346	-0.386	-0.586	-0.774	-0.876	α ₂ -Ρ
$E^{0'} = (E_a + E_c)/2$	0.398	-0.362	-0.568	-0.755	-0.858	
# electrons	1	2	2	1	1	

On the other hand, and as a logical consequence, the V^{IV} centre of the arseniccontaining species was more difficult to oxidise than that of the phosphorus-containing ones. For isomers α_1 , there was a potential difference of 78 in favour of α_1 -P, and this difference was lower for isomers α_2 , with a value of 62 mV in favour of α_2 -P. The comparison of the CVs of the two isomers was also in line with the results of previous studies, and allowed us to distinguish them very clearly, especially at the level of their third reduction wave. Indeed, the third reduction step appeared as a two-electron wave with a single reduction peak located at -0.882 V and -0.922 V vs. SCE for α_1 -As and α_1 -P, respectively; whereas in the case of the α_2 isomers, this ultimate reduction occurred in two separate one-electron steps, each with reduction peaks located at -0.728 V and -0.826 V vs. SCE for α_2 -As and at -0.774 V and -0.876 V vs. SCE for α_2 -P, respectively (Figure 2b and Figure S1b; Table 1).

3.2. Influence of the pH

It is known that, in general, in an aqueous medium, the exchange of electrons involving POMs on the interface between the solution and the surface of the working electrode is accompanied by an exchange of protons. It is therefore interesting to study the variation of the redox properties of these compounds as a function of the pH, in a buffered medium. The four compounds were characterised in two other media, 0.4 M $CH_3CO_2Na + CH_3CO_2H/pH 5.0$ and 0.2 M $Na_2HPO_4 + H_3PO_4/pH 7.0$.

When we went from pH 3.0 to pH 5.0 and then pH 7.0, the redox potentials attributed to the tungstic centres became increasingly negative, whereas those of the vanadic centres remained invariant (Tables S1 and S2). It should be noted that in certain cases, this shifting of the redox waves towards more negative redox potentials was accompanied by a more or less marked evolution of their shapes (Figure 3). At pH 3.0, the first reduction step of the four compounds was bielectronic, and a well-defined wave with a single reduction peak was observed on the CVs. At pH 5.0, on the CVs of the α_1 isomers, we observed a slight splitting of this wave with the appearance of a second distinct peak in the case of compound α_1 -P, whereas in the case of compound α_1 -As, it was just a shoulder. At pH 7.0, the separation was clear regardless of the CV of the compound considered. This observation showed that the capture of two electrons during the first reduction step was facilitated by the relatively high proton concentration of the pH 3.0 medium. Indeed, the ratio of proton to POM concentration, [H+]/[POM], was 2 at pH 3.0. When we moved to pH 5.0 and pH 7.0, it was divided by 100 and by 10,000, respectively, which made electron transfer more difficult.



Figure 3. CVs of (a) α_1 -As; (b) α_1 -P; (c) α_2 -As and (d) α_2 -P in 0.2 M Na₂SO₄ + H₂SO₄/pH3 (black), 0.4 M CH₃CO₂Na + CH₃CO₂H/pH 5.0 (red) and 0.2 M Na₂HPO₄ + H₃PO₄/pH 7.0 (blue). Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 10 mV s⁻¹.

A closer comparison of the CVs of the α_1 isomers and those of the α_2 isomers led us to make an observation that may have escaped us at first sight: as early as pH 3.0, the first reduction step of α_1 -X (X = As or P) was already more or less composite (Figure S2). Indeed, this first reduction wave presented a flattened cone shape compared to the pointed cone shape of the α_2 isomer. The other observation worth noting was that only this first reduction step split into two monoelectronic steps when the pH of the medium increased. The other reduction steps were just shifted to negative potentials, without splitting. Moreover, the third reduction step of the α_2 isomer merged with the fourth reduction step into a single, bielectronic step, as from pH 5.0 (Figure S3).

In order to be able to study all these phenomena, which seemed to be the consequence of the variation of the concentration of protons in the medium, and to eliminate any disturbance that would come from the nature of the electrolyte, we then chose to work with an electrolyte solution that had a buffering capacity in a wide pH window, the Britton-Robinson buffer (S3). For this study, only the phosphorus-based compounds, α_1 -P and α_2 -P, were analysed in a pH range of 1.0 to 8.0, a range in which these vanadic POMs have been shown to be stable [44]. A comparative study between the As- and the P-containing compounds did not appear to be of any interest, as the only difference observed between the two families of compounds was the potential shift mentioned above.

When looking at the redox behaviour of the vanadic centre, it can be seen that for both isomers α_1 and α_2 , the value of the apparent potential, $E^{0'} = (E_a + E_c)/2$, of the V^{V/IV} couple remained invariant in this interval (Figure 4). We concluded that the oxidation of the V^{IV} centre was not accompanied by an exchange of protons, but was just an exchange of electrons, as shown in the chemical equation (1) below:

$$V^{\rm IV} = V^{\rm V} + e^- \tag{1}$$



Figure 4. $E^{0'}$ of V^{V/IV} as a function of the pH of the electrolyte (Britton–Robinson): α_1 -P (black squares); α_2 -P (red circles). Values were taken from CVs recorded as follows: working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 100 mV s⁻¹.

In the case of the redox processes attributed to the tungstic backbone, the redox behaviours of the two isomers were not similar, as was the case for the vanadic centre. In the case of the α_1 -P isomer, for example, one would have expected to see the first reduction wave lose its composite character completely when the pH of the electrolyte became well below 3. On the contrary, at pH 1.0, the composite character of this first reduction wave was strengthened, and the CV recorded in this medium had a shoulder at -0.22 V vs. SCE which stood out very clearly from the main peak located at -0.32 V vs. SCE. The shape of the other two reduction waves that followed, although bielectronic, corresponded to a single reduction peak located at -0.49 V and -0.77 V vs. SCE, respectively (Figure 5a). Taking the pH 1.0 solution as a starting point, and increasing the pH very slowly, we observed the progressive disappeared, and we had a slightly broad wave with a single reduction peak at -0.39 V vs. SCE (Figure 5a). The CV of α_1 -P then consisted of three two-electron waves that shifted, all three towards negative potential values, as the pH of



the solution increased. This pattern of three two-electron waves having a single reduction peak each would remain the same until pH values around 3.5.

Figure 5. CVs of α_1 -P in Britton–Robinson buffer at several pH values: (**a**) pH 1.0 (black) and pH 2.3 (red); (**b**) pH 4.7 (black) and pH 5.5 (red); (**c**) pH 6.3 (black) and pH 7.5 (red). Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 100 mV s⁻¹.

From pH 3.8 onwards, the progressive separation of the first reduction wave into two more or less distinct steps was again observed. At pH 4.7, there were two distinct reduction peaks at -0.42 V and at -0.49 V vs. SCE. These two peaks would gradually disappear to give way to a wave with a single reduction peak, as shown on the CV recorded at pH 5.5 (Figure 5b). However, there would still be a final separation of this first reduction step, as from pH 6.3.

Of the three reduction steps observable in this wide pH range, only the first wave exhibited this behaviour. As for the next two, the only observation made was the very expected decrease in the values of the reduction peak potentials when the pH of the electrolyte increased. However, it should be noted that, for the second reduction wave, a plateau was reached at pH values between 3.64 and 5.38. This behaviour already was noted in one of our previous studies, in which an inversion of the slope of the evolution of the reduction peak potential values was observed between pH 4 and 5 [48].

The redox behaviour of the α_2 -P isomer as a function of the pH was more classical. No wave splitting was observed for pH values below 5.4 (Figure 6a). All three bielectronic waves shifted towards the negative potential values, with all three keeping their starting shapes almost unchanged. When we compared the first reduction of the α_2 -P isomer with that of the α_1 -P isomer, we realised that their behaviours, which seemed to diverge between pH 1.0 and pH 5.4, began to converge, as from pH 6.3 (Figure S4). At pH 7.5, two almost superimposable monoelectronic waves were obtained (Figure 6b).



Figure 6. (a) CVs of α_2 -P in Britton–Robinson buffer at pH 1.0 (black) and pH 5.4 (red); (b) CVs of α_1 -P (black) and α_2 -P (red) in Britton–Robinson buffer at pH 7.5. Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 100 mV s⁻¹.

Let us now turn to the last reduction step of the α_2 -P isomer. Indeed, in the pH range between 2 and 4, this wave split to give two very distinct reduction peaks. Outside these two limits, as shown on the CVs in Figure S5, there was a single-peak reduction wave. This singular behaviour was only observed in the case of this isomer. Indeed, beyond the first reduction step, no wave splitting was observed in the case of the α_2 isomer.

In summary, when the pH of the electrolyte was varied, the redox behaviour of the two isomers could be distinguished, as from the first reduction wave. The latter, which was globally bielectronic, could split into two monoelectronic steps or merge into a single step, depending on the pH. The pH ranges in which the wave separation or fusion were observed were not identical for the two isomers (see Scheme 1). In fact, for the α_2 -isomer, the reduction took place in a single bielectronic step up to pH 5.5, and above this pH value, a process with two very distinct monoelectronic steps was observed. In the case of the α_1 -isomer, we observed an alternation of bielectronic and monoelectronic processes. Up to pH 1.9, two single-electron steps were observed more or less distinctly, which merged from this pH value onwards into a single double-electron wave. A new separation was observed at pH 3.7, from which two new monoelectronic steps would coexist until pH 5, at which point they merged again. A final splitting took place, as from pH 6.2.



Scheme 1. Behaviour of the first reduction wave of the α_1 -P and the α_2 -P isomers as a function of the pH of the Britton–Robinson buffer solution.

The redox behaviour of the α_1 -P isomer was also singular at the second reduction wave (Figure 7a below). While the evolution of the reduction peak potentials as a function of the pH was continuous and uniform for the α_2 -P isomer (for pH < 6.3), a plateau was observed between pH 3.6 and 4.6 for the α_1 -P isomer. On the other hand, the two isomers showed an almost identical behaviour as far as the third reduction wave was concerned. The evolution of the values of the reduction peak potentials as a function of the pH of the electrolyte followed a similar linear trend for both isomers (see SI). This corresponded broadly to the involvement of two protons concomitant with the exchange of two electrons.



Figure 7. E_{pc} ' of the tungstic centres as a function of the pH of the electrolyte (Britton–Robinson buffer) for α_1 -P (black) and α_2 -P (red): (**a**) second reduction wave; (**b**) third reduction wave. Values were taken from CVs recorded as follows: working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 100 mV s⁻¹.

3.3. Electrocatalytic Properties

The 0.2 M Na₂HPO₄ + H₃PO₄/pH 7.0 medium was selected to evaluate and compare the efficiency of the four compounds with respect to the electro-oxidation of a thiol (3mercaptopropanol). For this purpose, we will focus on the V^{V/IV} redox couple. We observed for each of the compounds a reversible and monoelectronic oxidation wave when they were the sole electroactive species in solution, as shown in Figures S6b and S7a. In the presence of the thiol, we noticed the exponential increase of the oxidation current, as well as the loss of reversibility of the said waves. These two phenomena clearly indicated the existence of an electrocatalytic process at the level of the V^{V/IV} wave (Figure 8a, Figures S6a and S7b). Two parameters allowed us to quantify and compare the efficiency of these four compounds with respect to the electrocatalytic oxidation of the thiol: (1) the catalytic efficiency, CAT, which was calculated using the formula $CAT = [(I_{cat} - I_0)/I_0] \times 100$; and (2) the onset potential of the catalytic reaction, ONSET.



Figure 8. (a) CVs of α_1 -P alone (black) and in presence of the thiol (red); (b) CVs in presence of the thiol for α_1 -P (black) and α_2 -P (red). Electrolyte, 0.2 M Na₂HPO₄ + H₃PO₄/pH 7.0. Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 2 mV s⁻¹. Concentrations: [POM] = 0.2 mM, [Thiol] = 5.0 mM.

As expected, the electrocatalytic process began earlier in the case of the α_2 -isomers, for which the oxidation of the vanadium centre took place at more favourable potentials. However, when comparing the CAT values calculated at the same potential (E = 0.75 V vs. SCE), it became clear that the α_1 -isomers showed the highest catalytic efficiency (Table 2). This was in agreement with previous experimental and theoretical studies, which showed that the electron density was higher at the equatorial region of the Dawson structure (position α_1 -) than at its apical region (position α_2 -) [53,54].

Table 2. Oxidation peak currents in the absence (I_0) and in the presence (I_{CAT}) of thiol. *CAT* and *ONSET* data were calculated or measured from values taken from CVs recorded in 0.2 M Na₂HPO₄ + H₃PO₄/pH 7.0 (see above for the conditions).

	α_1 -As	α_2 -As	α ₁ -Ρ	α ₂ -Ρ
$I_0 (\mu A)$	0.17	0.16	0.15	0.15
I_{cat} (μA)	1.86	1.34	1.83	0.85
CAT (%)	994	738	1120	467
ONSET (V vs. SCE)	0.42	0.35	0.42	0.37

4. Magnetic Properties

The magnetic behaviours of the four V⁴⁺ compounds (α_1 -As V⁴⁺, α_2 -As V⁴⁺, α_1 -P V⁴⁺, and α_2 -P V⁴⁺) and two V⁵⁺ compounds (α_2 -As V⁵⁺ and α_2 -PV⁵⁺) were investigated.

 V^{5+} compounds were assumed to be diamagnetic, but their characterisation could allow us to evaluate the diamagnetic correction that should be applied for the calculation of the magnetization of V^{4+} compounds. Indeed, this evaluation by Pascal's tables is always delicate in the case of POMs, as is the case for V^{4+} POMs, for which we had only a spin 1/2 for a molar mass of the order of 4900 g.mol⁻¹ and an important number of water molecules.

M vs. B at 2 K plots are shown in Figure 9, and $\chi_m T$ vs. *T* curves (where χ_m is the molar susceptibility) in the range of 250 to 2 K (B = 1 T) in Figure 10. Both compounds presented a weak paramagnetic behaviour that may have been due to V⁴⁺ impurities. The amount of impurities could be deduced from the M vs. B curves at 2 K. For an ion S = 1/2 with g = 2, the value of the magnetization expected at 5 T was 0.93 µB (black curve in Figure 9). Here, for α_2 -AsV⁵⁺ the magnetization was 0.0115 µB and 0.0313 for α_2 -PV⁵⁺, representing about 1.2% and 3.3% of impurities, respectively.



Figure 9. M vs. B measurements for α_2 -AsV⁵⁺ (•) and α_2 -PV⁵⁺ (•) at 2 K compared to the theoretical curve for S=1/2.



Figure 10. χT vs. *T* curves for α_2 -AsV⁵⁺ (•) and α_2 -PV⁵⁺ (•) under a magnetic field of 1 T.

For α_2 -AsV⁵⁺ and α_2 -PV⁵⁺, the $\chi_m T$ decreased linearly from 0.035 cm³.mol⁻¹ K (0.03 cm³.mol⁻¹.K, respectively) at 250 K to about 0.009 cm³mol⁻¹ K (0.015) at 20 K. If it is expected that the impurity obeys Curie's law, the slope of this straight line can be due to the presence of temperature-independent paramagnetism (TIP) relative to the POM. Curie's law can be written: $\chi_M T = x_i C + \chi_{TIP}.T$, where C stands for the Curie constant, x_i the fraction of impurity, and χ_{TIP} the TIP. The value obtained for the TIP was 115×10^{-6} cm³.mol⁻¹ for α_2 -AsV⁵⁺ and 16×10^{-6} cm³ mol⁻¹ for α_2 -PV⁵⁺. TIP with similar values could be expected for the V⁴⁺ compounds.

Regarding to the V⁴⁺ compounds, the results are shown in Figure 11 in the form of $\chi_m T$ vs. *T* plots.



Figure 11. Susceptibility measurements under an applied field of 1 T in the form of $\chi_m T$ vs. *T* plots for α_1 -AsV⁴⁺ (•), α_2 -As V⁴⁺ (•), α_1 -PV⁴⁺ (•) and α_2 -PV⁴⁺ (•).

At 250 K, the $\chi_m T$ values for α_1 -AsV⁴⁺ and for α_2 -AsV⁴⁺ were 0.366 and 0.368 cm³.mol⁻¹.K, respectively, and close to 0.375 cm³.mol⁻¹.K, as expected for a S=1/2 ion with g = 2. However, for α_1 -PV⁴⁺ and α_2 -PV⁴⁺, the values were weaker than expected (0.278 and 0.317 cm³.mol⁻¹ K, respectively).

For the As compounds, $\chi_m T$ decreased linearly when lowering the temperature from 250 K to 20 K. As seen previously, this may have been due to presence of TIP, which could be estimated at 60×10^{-6} and 29×10^{-6} cm³.mol⁻¹ for α_1 -AsV⁴⁺ and α_2 -AsV⁴⁺, respectively. The Curie constants and the corrections deducted from these measurements are summarised in Table 3. Below 20 K, the decrease of χT was faster to reach 0.332 and 0.338 cm³.mol⁻¹ K. This decrease was expected at low temperatures under a magnetic field of 1 T (see Figure S8).

		S = 1/2 (S.O.)	α_1 -AsV ⁴⁺	α_2 -AsV ⁴⁺	α_1 -PV ⁴⁺	α_2 -PV ⁴⁺
	C (cm ³ .mol ⁻¹)	0.375	0.352	0.362	0.307	0.325
χT vs. T	$\chi_{\rm TIP}$ (cm ³ .mol ⁻¹)		$60 imes 10^{-6}$	$29 imes 10^{-6}$		
	$\chi_{ m dia}$ (cm ³ .mol ⁻¹)				$-112 imes 10^{-6}$	$-25 imes 10^{-6}$
M vs. B	g	2.0	1.91	1.93	1.75	1.82

Table 3. Curie constants and corrections of the susceptibilities deducted from the χ T vs. T measurements and g values calculated from the Brillouin function for the AsV⁴⁺ and the PV⁴⁺ compounds.

For the P compounds, the $\chi_m T$ increased linearly when lowering the temperature. This may have indicated that the diamagnetism was not correctly taken into account. An additional correction (χ_{dia}) of -112×10^{-6} and -25×10^{-6} cm³.mol⁻¹ for α_1 -PV⁴⁺ and α_2 -PV⁴⁺, respectively, was added so that Curie's law was verified ($\chi_m T = C + \chi_{dia} T$).

Nevertheless, to exclude other possibilities of such behaviour (antiferromagnetic coupling for the As-containing POMs or ferromagnetic coupling for the P-containing POMs), magnetization M vs. field B measurements were carried out at low temperatures (6, 4, and 2 K). The results are depicted in Figure 12. These curves, in the form of M vs. B/T plots, could be simulated with a Brillouin function [55] for a S = 1/2 ion, thus showing that the V⁴⁺ ions were isolated, and that the decrease or the increase observed in $\chi_m T$ in the range 20–250 K was not the result of a magnetic coupling.



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Figure 12. M vs. B/T measurements for α_1 -As (**a**), α_2 -As (**b**), α_1 -P (**c**), α_2 -P (**d**): experimental data at 6 K (**•**), 4 K (**•**), and 2 K (**•**); Brillouin function (-) for a S = 1/2 ion. The g values are given in Table 3.

For the AsV⁴⁺ compound, the *g* values obtained, even if weak, were in agreement with the values found in the literature [56,57], but those obtained for the PV^{4+} compound were very weak, confirming the possible underestimation of the molar mass for these compounds (Table 3).

Despite the experimental difficulties related to the weak magnetization of these POMs (a spin of 1/2 in a large diamagnetic matrix), it was confirmed that the V⁴⁺-containing compounds behaved as isolated S = 1/2 monomers, while the V⁵⁺-containing ones were globally diamagnetic.

5. Conclusions

The redox behaviour of four POMs from the Dawson family was studied in detail using cyclic voltammetry. New observations were made regarding the influence of the pH of the electrolyte on the nature of electron transfer and the evolution of the associated redox potentials. The position of the V substituent within the POM structure, α_1 or α_2 , had a very marked influence on the behaviour of the redox waves associated with the tungstic skeleton. The low-temperature magnetic behaviour of these four compounds containing a V^{IV} centre was compared to that of their counterparts containing a V^V centre, which confirmed a paramagnetic behaviour for the former and a diamagnetic behaviour for the latter.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/ 10.3390/magnetochemistry7120157/s1. S1. Cyclic voltammetry characterisation at pH 3.0 (0.2 M Na₂SO₄ + H₂SO₄). Working electrode: GC; counter electrode: Pt; reference electrode: SCE. Scan rate: 10 mV s⁻¹. Figure S1. CVs of (a) α_2 -As (black) and α_2 -P (red); (b) α_1 -P (black) and α_2 -P (red). Figure S2. CVs of (a) α_1 -As (black) and α_2 -As (red); (b) α_1 -P (black) and α_2 -P (red). S2. Cyclic voltammetry characterisation in three different media: 0.2M Na₂SO₄ + H₂SO₄/pH 3.0 (black), 0.4M CH₃CO₂Na + CH₃CO₂H/pH 5.0 (red) and 0.2 M Na₂HPO₄ + H₃PO₄/pH 7.0. Figure S3. CVs of (a) α_1 -As; (b) α_1 -P; (c) α_2 -As and (d) α_2 -P. Table S1. Oxidation peak potentials (*E_a*) and reduction peak potentials (E_c) measured from CVs recorded in 0.4 M CH₃CO₂Na + CH₃CO₂H/pH 5.0. Table S2. Oxidation peak potentials (E_a) and reduction peak potentials (E_c) measured from CVs recorded in 0.2 M Na₂HPO₄ + H₃PO₄/pH 7.0. Table S3. Preparation of the Britton-Robinson buffer solution. Figure S4. CVs of α_1 -P (black) and α_2 -P (red) in Britton-Robinson buffer. (a) pH 1.0; (b) pH 2.3; (c) pH 3.8; (d) pH 4.7; (e) pH 6.3. Figure S5. CVs of α_2 -P in Britton-Robinson buffer at (a) pH 1.0 (black) and pH 2.5 (red); (b) pH 3.5 (black) and pH 5.0 (red). S4. Electro-catalytic properties. Figure S6 (a) CVs of α_2 -P alone (black) and in the presence of thiol (red); (b) CVs of α_1 -P (black) and α_2 -P (red), both alone. Figure S7. CVs of α_1 -As (black) and α_2 -As (red): (a) alone and (b) in presence of thiol. S5. Magnetic properties. Figure S8: Theoretical susceptibility under an applied field of 1T in the form of a χ_m T vs. T plot for a S = 1/2 ion. S.6. Syntheses of different POMs.

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