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Effect of protonation, composition and isomerism on the redox properties and electron (de)localization of classical polyoxometalates

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Abstract:

This publication reviews some relevant features related with the redox activity of two inorganic compounds: $[XM_{12}O_{40}]^{q-}$ (Keggin structure) and $[X_2M_{18}O_{62}]^{q-}$ (Wells-Dawson structure). These are two well-known specimens of the vast Polyoxometalate (POM) family, which has been the subject of extensive experimental and theoretical research owing to their unmatched properties. In particular, their redox activity focus a great deal of attention from scientists due to their prospective related applications. POMs are habitually seen as ‘electron sponges’ since many of them accept several electrons without losing their chemical identity. This makes them excellent models to study mechanisms of electrochemical nature. Their redox properties depend on: (i) the type and number of transition metal atoms in the structure, (ii) the basicity of the first reduced species and, occasionally, of the fully oxidized species; (iii) the size of the molecule, (iv) the overall negative charge of the POM, and (v) the size of the central heteroatom. In the last years, important collaboration between the experimental and theoretical areas has been usual on the development of POM science. In the present chapter three of these synergies are highlighted: the influence of the internal heteroatom upon the redox potentials of Keggin anions; the dependence of the redox waves of Fe-substituted Wells-Dawson compounds with pH; and the role of electron delocalization and pairing in mixed-metal Mo/W Wells-Dawson compounds in their ability to accept electrons. In these three cases, a complete understanding of the problem would not have been possible without the mutual benefit of experimental and computational data.

Keywords: density functional theory, calculations, polyoxometalates, transition metals, electronic structure, redox properties

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1 Introduction

In the area of Inorganic Chemistry, polyoxometalates [1, 2] (POMs) or polyoxoanions – owing to their anionic nature in solution – comprise a growing family of metal oxide molecules. They are primarily made of oxygen and early transition metals such as $M = W, Mo$ and V (called *addenda* or peripheral atoms in the present context), although many other elements can be present as well in the main framework. The smallest members of this family are subnanometric, whereas the largest structures can reach sizes of the nanomaterials domain, close to 4–5 nm [3]. Classical POMs are compact structures that can be classified into isopoly- and heteropolyanions, the latter being characterised by the general formula $[X_aM_bO_c]^{q-}$ (typically $a < b < c$). The internal region of these molecules is occupied by the *heteroatom* (X), typically a p-block or transition metal element but, in principle, there are no restrictions to the type of atoms occupying the cavity. The most common structures of the heteropolyanion class are: $[XM_{12}O_{40}]^{q-}$ or Keggin, $[X_2M_{18}O_{62}]^{q-}$ or Wells-Dawson, $[M'X_5M_{30}O_{110}]^{q-}$ or Preyssler. For the sake of compactness, it is commonplace in the literature to use short-hand formulae, without oxygen or charge, which is used throughout the present text when justified. For instance, XM_{12} and X_2M_{18} are used for the Keggin and Wells-Dawson systems, respectively. In the fully oxidised form of tungstates ($M = W$) and molybdates ($M = Mo$), all the metal centres feature the formal oxidation state VI. Therefore, the total charge, $q-$, is determined by the internal heteroatom, X.

POM structures usually exhibit many (occasionally some at the same time) properties that make them attractive in wide-ranging fields of Chemistry [4–6]. Although the first POM was reported in the early 19th century, the first great surge of this field took place in the 1960s. In 1998, a reviewing work by Baker and Glick [7] boosted

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the study of POMs, which entered an era of systematic investigation which continues in constant academic and technological development. Among the plethora of properties and applications, electronics and magnetism [8–10], electrochemistry [11], catalysis [12], electro- and photochromic systems [13, 14], sensors [15], supramolecular organization [16, 17], (nano)materials science [18–20] and medicine [21] are the most remarkable ones. Among the singular phenomena that have been reported, some were not fully explained just by experiments and needed theoretical support. Since the early 1990s and especially in the 21st. century, the growing use of Computational Chemistry applied to the study of POMs has permitted a better understanding of their properties. Especially, their electronic structure and redox behaviour were soon recognised as essential for many applications. Also, the reactivity, magnetism or the solution behaviour have been tackled theoretically [22].

In the redox area, POMs are often called ‘electron sponges’ for many of them can easily gain several electrons with no appreciable geometrical changes, either at an electrode surface or in the liquid bulk, making them excellent models to study mechanisms of electrochemical nature [20, 23–33]. The following main characteristics govern their redox properties: (i) the type and number of transition metal atoms in the structure, (ii) the basicity of the first reduced species and, occasionally, of the fully oxidised species; (iii) the size of the molecule, (iv) the overall negative charge of the POM, and (v) the size of the central heteroatom. This chapter reviews three examples with strong synergies between the results obtained from experimental and theoretical techniques that came up with plausible explanations on intricate phenomena in the field of POM redox chemistry.

The results herein summarised and discussed are the outcome of a long-lasting collaboration between two research groups: an experimental Electrochemistry group in the Laboratory of Physical Chemistry of the Université de Paris-Sud (Orsay, France) and a theoretical Quantum Chemistry group in the Department of Physical and Inorganic Chemistry of the Universitat Rovira i Virgili (Tarragona, Spain).

2 Background

2.1 Electrochemistry

In electron exchange processes, the redox potential (Φ) and the reaction free energy (ΔG) are formally linked by the number of electrons (n) exchanged in the process and the Faraday constant (F) through the Nernst equation:

$$\Delta G = -nF\Phi$$

In an oxidation-reduction couple, the formal apparent redox potential is defined as $\Phi^\circ = (\Phi_{\text{pa}} + \Phi_{\text{pc}})/2$, where Φ_{pa} and Φ_{pc} are the anodic (oxidation) and cathodic (reduction) peak potentials, respectively.

In this chapter, reduction energies defined as $\text{RE} = E(\text{POM}_{n\text{-red}}) - E(\text{POM}_{\text{ox}})$ are presented for reactions $\text{POM}_{\text{ox}} + ne^- \rightarrow \text{POM}_{n\text{-red}}$. For this purpose, we computed electronic energies for (n -fold) reduced and oxidised forms with the energy of the free electron taken as zero. Assuming that the electronic energy change during the reduction process is practically equal to the Gibbs free energy change (entropic *change* term negligible), $\text{RE} \approx \Delta G$, the computed REs may be seen as theoretical estimates of the experimental reduction potentials:

$$\text{RE} \approx -nF\Phi \quad (1)$$

The last expression shows that a species with a more negative RE than another will consequently have a more positive Φ , and vice versa. The computational results are mostly discussed as *differences* between REs (in eV) or Φ (in V).

2.2 Density functional theory

Herein I present a piece of theoretical work performed within the Kohn-Sham formalism in the framework of density functional theory (DFT) [34]. This is, nowadays, a widespread theoretical approach because of its straightforward use and excellent accuracy/cost ratio [35–41] for most POM chemical phenomena. On the basis of many encouraging results, computational analyses have a general acceptance and remarkable significance among the scientific community. DFT calculations provide molecular geometries and energies, orbital shapes and energies, dipole moments, electron distributions and many other properties that help us understanding the behaviour of molecules. The calculations herein discussed reproduce and explain electrochemical measurements, delivering molecular orbitals and total molecular energies that, combined, give us reaction energies and

other relevant properties. The anion charges of the reduced and oxidised forms differ, and so the RE must be computed in the presence of a solvent model. So, to make the calculations on redox properties reliable, the stabilizing effects of the molecular environment must be included in the model. Otherwise, the energies would be unreliable for comparison, as in the gas phase approximation [42]. It is worth mentioning that the theoretical results are mostly aimed at explaining the trends rather than the experimental absolute redox potentials with high accuracy.

For each particular study presented, slightly different DFT setups were utilised although all of them based on the same principles. The reader is referred to the original papers for the computational details.

3 Influence of the heteroatom size on the redox properties of Keggin anions

Most Keggin $[XW_{12}O_{40}]^{q-}$ anions studied possess electrochemically inactive X heteroatoms. Therefore, their redox behaviour is based on the addenda atoms. During the mid-1960s, Pope and co-workers [24, 26, 27] proved that the one-electron redox potentials of a Keggin anion, in conditions of no protonation, is a linear function of its overall molecular charge, $q-$. Later on, electron addition in Keggin (Figure 1) and other POM anionic species [43, 44] was carefully investigated both from the experimental [6] and the theoretical [22] points of view. However, other physical and/or electronic factors governing the energetics of the first electron transfer process in POMs needed extra explanation, such as the role of the heteroatom size. In a 2010 work, an answer to this question was proposed for one-electron transfer by analysing the electrochemical behaviour of a series of $XW_{12}O_{40}^{q-}$ compounds (with $X = B, Al, Ga, Si, Ge, P, As$) [45]. The goal of these calculations was to find the physical origin for the observed redox potentials. Furthermore, theory might help to identify the better of two parameters, equivalent in principle, to describe this physical origin, in terms of electrical charge or of electrostatic potential.

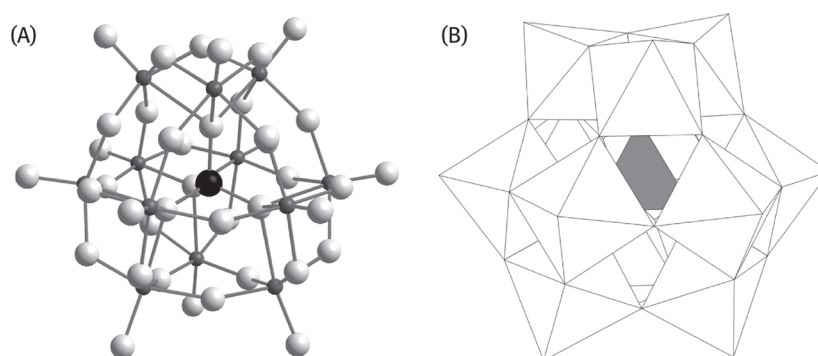


Figure 1: (A) Ball-and-stick and (B) polyhedral views of the Keggin structure, $[XW_{12}O_{40}]^{q-}$. Color code: light grey - oxygen; dark grey - tungsten; black - heteroatom, X. In the fully oxidised state, the internal tetrahedron, XO_4^{q-} , is responsible for the negative charge of the structure whereas the external cage, $W_{12}O_{36}$, is formally neutral. Octahedra in (B) are MO_6 units.

Cyclic voltammetry (CV) and controlled potential coulometry were used to analyse the electrochemical behaviour of each compound in aqueous solution at controlled pH 5 medium to guarantee stability (0.4 M $CH_3COONa + CH_3COOH$). The first CV wave for each compound features a one-electron reversible process, the electron transfer not being perturbed by protonation. Therefore, the corresponding apparent potential values, Φ° , could be used to assess the influence of the central heteroatom size on the reducibility of the POM. This section compares the variations in the redox potentials of Keggin anions in the mentioned conditions upon changes in X of the same group (III: B, Al, Ga; IV: Si, Ge and V: P-As). Table 1 gathers the apparent formal potentials Φ° for the first one-electron redox process of selected Keggin compounds. The molecular charge per volume unit (volumic charge densities) issued from the DFT calculations are added and will be commented later. A general trend emerges from the Φ° quoted in this table. The reader may notice that apparent Φ° values get more negative (more difficult to reduce clusters) as the size of the central heteroatom decreases within a given family of Keggin compounds with the same overall negative charge. Within each group, heteroatoms with smaller atomic numbers are smaller in size. Figure 2 illustrates the CVs for the series of Keggin anions with $X = B, Al, Ga$, where the B derivative is the most difficult to reduce of its group, about 100 mV more than the Ga-derivative. What is the subjacent reason explaining these observations?

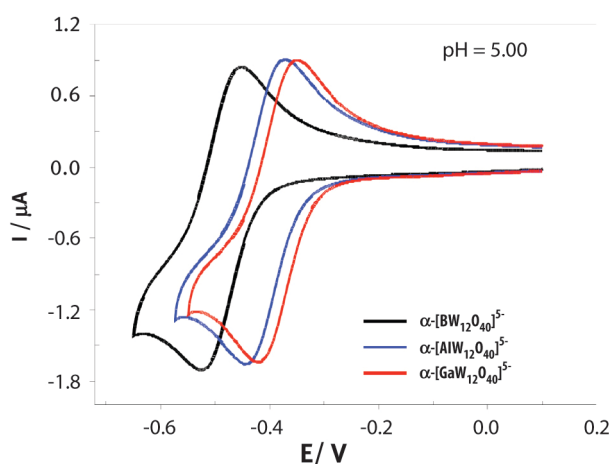


Figure 2: Cyclic voltammograms of α -[BW₁₂O₄₀]⁵⁻ (black line), α -[AlW₁₂O₄₀]⁵⁻ (blue line) and α -[GaW₁₂O₄₀]⁵⁻ (red line) at pH 5 (0.4M CH₃COO + CH₃COOH). Polyoxometalate concentration: 0.5 mM; scan rate: 10 mV.s⁻¹; working electrode: glassy carbon; reference electrode: SCE.

Table 1: Apparent potentials, $\Phi^{\circ} = (\Phi_{pa} + \Phi_{pc})/2$, for the first one-electron redox process of selected Keggin compounds at pH 5 (0.4 M CH₃COONa + CH₃COOH),^a and volumic charge density for each compound.

Family	Compound	Volumic charge density ^b [10 ²² C.Å ⁻³]	Φ° [V vs SCE]
Keggin-I	[H ₂ W ₁₂ O ₄₀] ⁶⁻		-0.608
Keggin-III	[BW ₁₂ O ₄₀] ⁵⁻	1.882	-0.491
	[AlW ₁₂ O ₄₀] ⁵⁻	1.868	-0.410
	[GaW ₁₂ O ₄₀] ⁵⁻	1.866	-0.387
Keggin-IV	[SiW ₁₂ O ₄₀] ⁴⁻	1.506	-0.227
	[GeW ₁₂ O ₄₀] ⁴⁻	1.503	-0.190
Keggin-V	[PW ₁₂ O ₄₀] ³⁻	1.138	+0.064
	[AsW ₁₂ O ₄₀] ³⁻	1.133	–

^aScan rate: 10 mV.s⁻¹; working electrode: glassy carbon. ^bValues issued from DFT calculations.

As has been previously proposed [46–49] and applied [50–53], many close-packed POMs may be seen as an internal anionic fragment encapsulated by a neutral metal oxide cage. For Keggin tungstates it is customary to write [XO₄]^{q-}@W₁₂O₃₆ to denote this concept. This assumption can simplify the interpretation of some chemical properties [53]. In the present case, it was taken for granted that the internal XO₄^{q-} unit is the responsible of the observed variations, ruling out the geometrical differences between W₁₂O₃₆ cages as a determinant factor. Actually, X-ray characterization revealed that W₁₂O₃₆ cages of compounds in a group are nearly equal. In the same line, DFT calculations show that the volume of Keggin molecules fluctuates by 0.4 to 0.9% within a group, showing that the overall size of the Keggin anion can be considered constant.

To compare theoretical and experimental first reduction processes, we computed the REs shown in Table 2, for Keggin-III, IV and V compounds, for the process [XW₁₂O₄₀]^{q-} + e → [XW₁₂O₄₀ 1e]^{(q+1)-}.

Table 2: Computed reduction energies (RE), RE differences (Δ RE), measured apparent potential differences ($\Delta\Phi^{\circ}$) and computed LUMO energies for XW₁₂O₄₀^{q-} compounds in solution.

Family	X	Charge	RE [meV]	Δ RE ^a [meV]	$\Delta\Phi^{\circ}$ ^a [meV]	LUMO ^b [eV]
Keggin-III	B	-5	458			-3.83
	Al		373	-85	-81	-3.87
	Ga		337	-121	-104	-3.89
Keggin-IV	Si	-4	191	-72	-37	-4.13
	Ge		119			-4.15
Keggin-V	P	-3	0	-45	-30	-4.38
	As		-45			-4.41

^a ΔRE and $\Delta\Phi^0$ are relative to the first element of the same group. ^bLowest Unoccupied Molecular Orbital.

As we are interested in redox potential differences between species, the $RE = -4.10$ eV for PW_{12} is taken as the computational reference for the other values. Three sets of REs with the correct trend are obtained, the lowest ones corresponding to the strongest oxidants (XW_{12} , $X = P$ and As) and lowest anion charge (-3). Intermediate and more positive REs are computed for $X = Si$ and Ge (191 and 119 meV more positive, respectively), with an anion charge of -4 and, finally, the most positive ones (and least oxidizing species) correspond to $X = B$, Al and Ga (458, 373 and 337 meV above the reference, respectively) since they carry a charge of -5 . This trend is simply attributed to the anion charge. The differences encountered within each group are, however, smaller in general, and must be assigned to other factors.

The REs in Table 2 can be compared with the experimental half-wave potentials (Φ^0) shown in Table 1, taking into account equation 1. The ΔRE computed by DFT are, in absolute terms, very similar to those of $\Delta\Phi^0$, so DFT calculations nicely reproduce the experimental trends. The LUMOs [54] in these fully oxidised compounds have d(W)-like character and are the ones accepting the first electrons upon reduction. In a simplistic fashion, more stable LUMOs give more negative REs and a greater tendency to gain electrons, although this statement is not conclusive. In the present case, the LUMO energies in compounds of the same group are not the only reason for the differences encountered. It can be accepted to be the case for the P/As couple (the energy difference is 30 meV). However, for Si/Ge , their LUMO energies differ by 20 meV only, a much smaller value compared to their mutual $\Delta RE = 72$ meV. Especially for group III compounds ($X = B$, Al and Ga), where the energy differences of d(W)-like orbitals between the compound are as small as 20–30 meV, we discard this fact as the reason for the large variations in the redox potentials.

One hypothesis is based on the different electrostatic potentials created by the internal XO_4^{q-} units on their surroundings, as the W position, where an incoming electron goes. As previously, we keep to the view that the Keggin tungstates under consideration can be expressed as $[XO_4]^{q-}@W_{12}O_{36}$ and focus on the properties of the XO_4^{q-} units in order to explain the observations made on the redox potentials of the studied POMs.

The negative charge that we tentatively assign to each XO_4^{q-} fragment, despite being formally -3 , -4 and -5 for different X , can be considered to be somewhat smaller. Actually, a fraction of the electron density is transferred from the internal XO_4 to the $W_{12}O_{36}$ cage [52]. If XO_4^{q-} remained more charged in some cases, we could have an explanation for the different redox potentials measured. However, the computed fragment charges do not fully correlate with the REs. An alternative magnitude that can be computed and mapped is the electrostatic potential, being in addition much more realistic than atomic or fragment charges. A graphical representation of the molecular electrostatic potential (MEP) of XO_4^{q-} shows appreciable differences in Keggin anions of the same group (MEPs for $X = P$, As and Si , Ge are shown in Figure 3). These representations allow us to estimate the electrostatic potential that the W atoms feel in the real Keggin structures since they are mapped over an electron density isosurface coincident with the W positions (*blue* denotes more positive and *red* more negative potentials). Thus, electrons get less destabilised around the more positive potential regions (in blue). In the Keggin-IV and V groups, the differences are small between X , in agreement with the similar redox potentials measured. Larger differences are observed within the Keggin-III group (see Figure 4), where the redox potentials are more different, especially between boron and the other two heteroatoms (Al and Ga). This may be attributed to the larger electronic differences between B (2nd period) and the atoms from the 3rd and 4th periods. In fact, a deeper analysis of the electronic structure of BO_4^{5-} reveals that its highest occupied orbitals are higher than those of XO_4^{5-} of the same group, affecting its environment in the Keggin structure. As a matter of fact, the highest occupied molecular orbital (HOMO) in $[BO_4]^{5-}@W_{12}O_{36}$ belongs to the internal anion, a very uncommon feature when dealing with X of the p-block. **Figure 5** represents this situation.

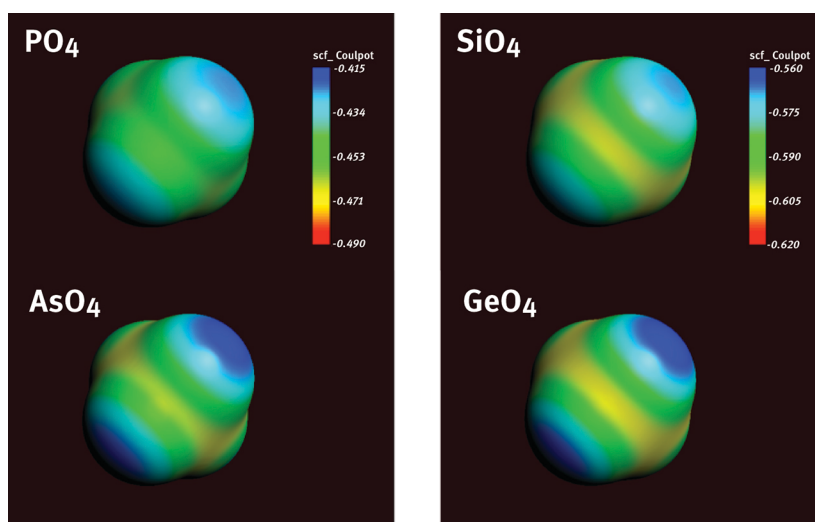


Figure 3: Molecular electrostatic potentials for XO_4^{q-} units ($\text{X} = \text{P}, \text{As}$ and Si, Ge) represented over a surface placed exactly at the X-W distance. The apparent differences in the shape and extension of the surface come from the slight geometrical variations from one XO_4 to another. The potential range in each case is shown to the right in atomic units, and it changes from P-As to Si-Ge (red for more negative and blue to less negative potentials). The species displaying more intense blue regions will be reduced at less negative potentials.

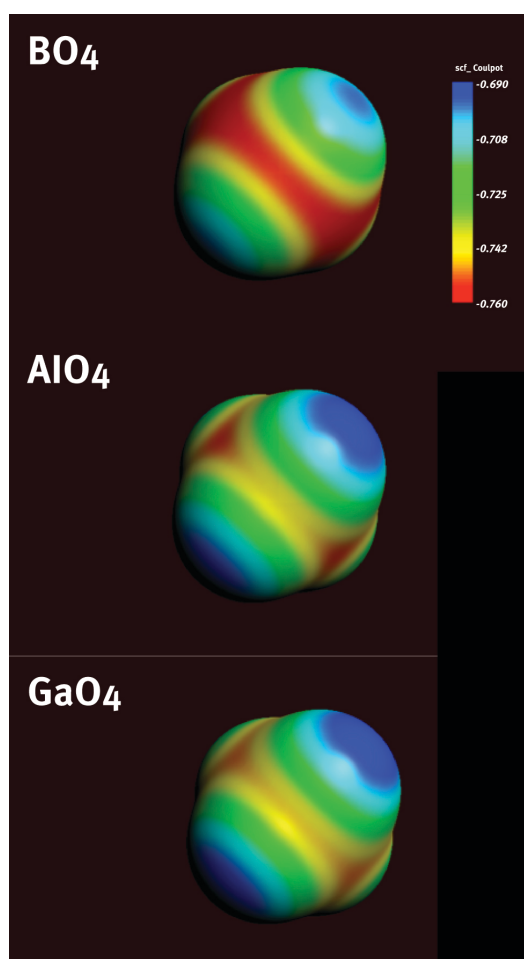


Figure 4: Molecular electrostatic potentials for XO_4^{q-} units ($\text{X} = \text{B}, \text{Al}$ and Ga) represented over a surface placed exactly at the X-W distance. The potential range is shown to the right in atomic units.

This high orbital energy is linked to the small size of the BO_4^{5-} unit, the smallest of the whole series (DFT computed equilibrium $d(\text{X}-\text{O}_{\text{tetra}}) = 1.545 \text{ \AA}$) and its high anionic charge. Similarly, in Keggin IV group, SiO_4^{4-} is more compressed than GeO_4^{4-} , featuring $d(\text{X}-\text{O}_{\text{tetra}}) = 1.653 \text{ \AA}$ and $1.757 \text{ \AA}$, respectively. The MEP obtained for SiO_4^{4-} also shows a slight shift towards more negative potentials compared to GeO_4^{4-} , in agreement with

the redox potentials obtained by CV. Also in the latter case, the SiO_4^{4-} orbitals are higher in energy than those of GeO_4^{4-} , although not to the point of being higher than the $\text{W}_{12}\text{O}_{36}$ oxo-like orbital set.

For $X = \text{B}$ at least, for which the electrostatic potential is so much different compared to the other two heteroatoms of the group, we have computed the purely electrostatic repulsion that an incoming electron feels in the LUMO (with $d(\text{W})$ character) without any orbital relaxation. In general, the differences are small, of the order of 70–75 meV for group IV and V heteroatoms. On the other hand, for group III we found that the repulsion of an extra electron in BW_{12} is 240 meV larger than that of AlW_{12} or GaW_{12} . Even if this difference gets reduced to ca. 100 meV after orbital relaxation, it remains large and this could explain the negative shift in the redox wave of $X = \text{B}$ vs. the other two heteroatoms of the same group.

In summary, internal XO_4 units carrying the same charge can affect differently the tungstate oxide cage. Within each group of the periodic table, X atoms with lower atomic numbers are also smaller in size, producing a more negative electrostatic potential in the surroundings, and thus a smaller ability of the cage to be electron reduced. The case of BW_{12} is paradigmatic, with the smallest heteroatom of the Keggin-III series, and a very negative reduction potential with respect to the other elements of the same group. Even if the differences in the electrostatic potentials from a qualitative level are modest, they correlate well with the also tiny differences in experimental redox potentials.

4 pH-dependent electrochemical behaviour of α_1/α_2 - $[\text{Fe}(\text{H}_2\text{O})\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-}$ isomers

In the second study presented, protonation plays a crucial role. As most POMs, the Wells-Dawson structure can be functionalised or varied by degradation, substitution or complexation [55–57]. The resulting compound has a different behaviour owing to its new structure or composition, and understanding the origin of such changes, as well as finding general trends, are the main goals of experimental and theoretical investigations. An analysis of two isomers of the Wells-Dawson structure, in which one W position has been replaced by Fe , is carried out with electrochemical and computational methods. The α_1 and α_2 isomers of $[\text{Fe}(\text{OH}_2)\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-}$ (Figure 6) differ in the location of the Fe atom, either in the equatorial region (or *belt*) or in one polar region (or *cap*).

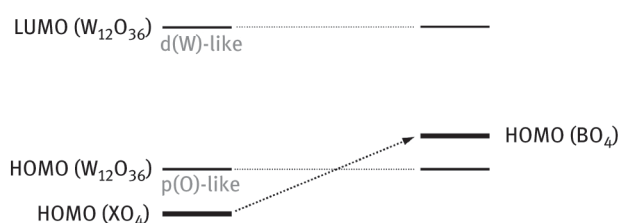


Figure 5: Destabilization of the BO_4 -like HOMO in BW_{12} with respect to other X heteroatoms, attributed to the combination of high charge and small size of the fragment. Indicated is the character of the main orbitals depicted.

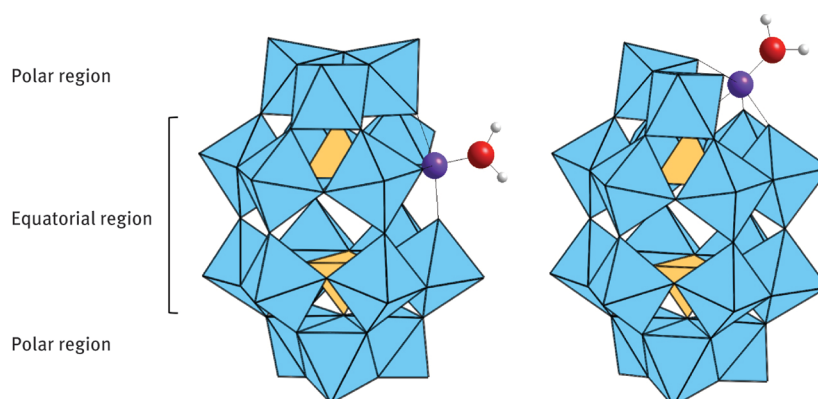


Figure 6: Polyhedral view of the Fe-monosubstituted Wells-Dawson derivatives α_1 - $[\text{Fe}(\text{H}_2\text{O})\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-}$ (left) and α_2 - $[\text{Fe}(\text{H}_2\text{O})\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-}$. The $\text{Fe}(\text{H}_2\text{O})$ group, depicted in ball-and-stick, is placed either at the *equatorial* region (α_1 isomer) or at the *polar* region (α_2 isomer).

The acidity of a solution containing $\text{Fe}(\text{OH}_2)\text{P}_2\text{W}_{17}$ was varied and its effects on the redox properties tracked. The most thoroughly studied properties of Wells-Dawson derivatives are related to their redox behaviour. As regards of the Fe-monosubstituted $[\text{Fe}^{\text{III}}(\text{OH}_2)\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-}$ system at neutral pH, the α_1 isomer is reduced before the α_2 form, as expected. However, the α_2 form turns to be more oxidizing as we acidify the solution, reversing

the original situation. Electrochemical and DFT inspection can explain that the different coordination of Fe at different pH (-OH or -OH₂ terminal groups) changes the Fe-like orbital that will accept the incoming electron [58]. CVs of α_1 (**1**) and α_2 (**2**) isomers were recorded in several aqueous media (with pH varying from nearly 0 to 8) and in CH₃CN + 0.1 M LiClO₄. Below pH 6, (Fe³⁺)₂ is easier to reduce than (Fe³⁺)₁ i.e. $\Phi_{pc}(\text{Fe}^{3+})_2 > \Phi_{pc}(\text{Fe}^{3+})_1$. This is an unexpected behaviour since all theoretical and experimental studies performed on this family of compounds (plenary Wells-Dawson structures, X₂W₁₈O₆₂⁶⁻ X = As or P, and monosubstituted complexes, α_1 - and α_2 -[X₂MW₁₇O₆₂]^{q-} M = Mo, Tc, V, Re) pointed out that the first electronic exchange preferentially takes place on one of the 12 W atoms located on the equatorial region of the molecule i.e. α_1 position [26, 35, 37, 42, 59–63]. In other words, the α_1 isomer should be always easier to reduce than the corresponding α_2 isomer. However, this accepted and demonstrated rule, in the case of α_1 - and α_2 -P₂W₁₇Fe forms, was put up-to-default. Indeed, we report here that the influence of the protonation makes a difference in the electrochemical behaviour of both isomers making the reduction of the Fe centre in α_2 position easier than in the case of the α_1 isomer. In contrast, when the protonation effect becomes negligible (for pH $\geq$ 6 or in organic medium) the normal trend is recovered, i.e. the Fe centre in α_1 position (**1**) is easier to reduce than in the α_2 position (**2**). Figure 7 illustrates these facts. Complementing the electrochemical study, DFT calculations help explaining the relative stability and redox potentials of compounds **1** and **2**, and their dependence with protonation. The acidity of the solution revealed determinant in the evolution of the redox properties of both isomers.

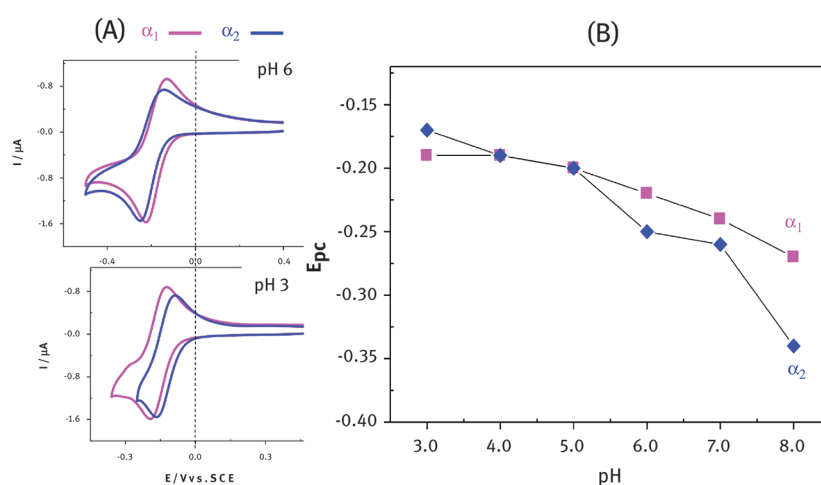


Figure 7: pH-dependent redox properties of **1** (magenta) and **2** (blue). (A) Cyclic voltammograms recorded for **1** and **2** on a glassy carbon working electrode at pH 6 and 3. (B) Evolution of the peak reduction potentials, $\Phi_{pc}(\text{Fe}^{3+/2+})$, of **1** and **2** between pH 3 and 8. Values in V vs SCE.

Since we are not capable of explicitly imposing a given pH value to our standard DFT calculations, we have generated a number of differently protonated model structures derived from the parent [P₂W₁₇Fe^{III}O₆₂]⁹⁻ one that are assumed to be dominant at different pH values. Namely, at neutral pH, the deprotonated [Fe^{III}OP₂W₁₇O₆₁]⁹⁻ structure could be predominant. However, this is not expected regarding the experimental evidences that rule out the stability of these molecules [64]. Another likely structure at neutral pH is the mono-protonated one, [Fe^{III}(OH)P₂W₁₇O₆₁]⁸⁻. The next protonation step will occur when acidity increases to pH 5, obtaining [Fe^{III}(OH₂)P₂W₁₇O₆₁]⁷⁻. Finally, at even lower pH, two other structures could be formed: one without terminal atom on the Fe site, [Fe^{III}P₂W₁₇O₆₁]⁷⁻, and one with a water molecule linked to Fe and a protonated bridging oxygen, [HFe^{III}(OH₂)P₂W₁₇O₆₁]⁶⁻.

Fully optimised structures were obtained for this set of systems either with Fe^{II} or Fe^{III}, and evaluated the reduction free energy [65], ΔG_1 and ΔG_2 , for the two isomers. We have also extracted the reduction free energy differences ($-\Delta\Delta G_{2-1} = -\Delta G_2 + \Delta G_1$) to compare them with the experimental data ($\Delta\Phi$) (see Table 3). If the Fe^{III}(OH) species are considered, reduction of **1** is easier than **2** by 17 meV, in good agreement with the experimental half-wave potentials ($\Delta\Phi = +30$ mV). The tendency is reversed by adding the second proton to the iron-substituted species (simulated moderately acidic pH), when $-\Delta\Delta G_{2-1} = 47$ meV. Under conditions of further protonation (pH 1), this phenomenon is more notable and $-\Delta\Delta G_{2-1} = 68$ or 90 meV, depending on the model, in favour of **2**. Calculations reproduce the experimental trends.

Table 3: Computed reduction energies for differently protonated forms of isomers **1** and **2** (ΔG_i , in eV), reduction energy differences ($-\Delta\Delta G_{2-1}$), and experimental data ($\Delta\Phi$, in V).

ΔG_1	ΔG_2	$-\Delta\Delta G_{2-1}$	$\Delta\Phi$
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$[\text{Fe}(\text{OH})\text{P}_2\text{W}_{17}\text{O}_{61}]^{8-}$	-4.017	-4.000	-0.017	-0.030
$[\text{Fe}(\text{OH}_2)\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-}$	-4.592	-4.639	+0.047	+0.080
$[\text{FeP}_2\text{W}_{17}\text{O}_{61}]^{7-}$	-4.746	-4.814	+0.068	-
$[\text{HFe}(\text{OH}_2)\text{P}_2\text{W}_{17}\text{O}_{61}]^{6-}$	-4.853	-4.943	+0.090	

It is worth pointing out that three different species, $[\text{Fe}(\text{OH}_2)\text{P}_2\text{W}_{17}\text{O}_{61}]$, $[\text{FeP}_2\text{W}_{17}\text{O}_{61}]$ and $[\text{HFe}(\text{OH}_2)\text{P}_2\text{W}_{17}\text{O}_{61}]$, are proposed to exist in increasingly acidic solutions. No experimental or theoretical evidence suggest which the predominant species is, or if a mixture of them coexist in solution. Nevertheless, all of them feature the same redox behaviour in good agreement with electrochemical measurements (Table 3).

The uncommon feature that isomers **1** and **2** reverse the ordering of their first reduction potentials at pH 6 deserves further insight. From experiments, the first 1e-reduction is assumed to take place at the Fe centre (irrespective of the isomer and the pH), in detriment of the formation of the blue species with one electron delocalised over the W framework ($\text{P}_2\text{W}_{17}\text{Fe}^{3+} + \text{e}^- \rightarrow [\text{P}_2\text{W}_{17}\text{Fe}^{3+} 1\text{e}]$). Since the latter process needs more energy and is not favoured, the delocalised d_{xy} -like molecular orbital of W character appearing at higher energies, also of nonbonding nature, can be ruled out of the competition towards the first incoming electron. The orbitals of the oxidised forms of **1** and **2** ready to accept an extra electron are, in principle, the formally nonbonding $d_{xy}(\text{Fe})$ (perpendicular to the terminal oxygen) and the antibonding $\pi^*(\text{Fe}-\text{O})$, which is oriented towards the terminal oxygen. The energy of the latter orbital is strongly pH-dependent because of its orientation. The Fe-O(terminal) distance can change with protonation following pH variations, and so the $\pi^*(\text{Fe}-\text{O})$ energy. In both Fe^{2+} isomers, the d_{xy} orbital is more stable than the π^* orbital under conditions of poor protonation ($\text{FeOP}_2\text{W}_{17}$ and $\text{Fe}(\text{OH})\text{P}_2\text{W}_{17}$ structures) while the inversion occurs for $\text{FeP}_2\text{W}_{17}$ and $\text{Fe}(\text{OH}_2)\text{P}_2\text{W}_{17}$ molecules, assumed to be the predominant species at low pH. This is not so evident for both isomers of the Fe^{3+} form, where the orbital reversal occurs for the α_2 isomer only. This particular behaviour depending on pH is not observed in other metal-substituted Dawson-type tungstodiphosphates, such as $\text{P}_2\text{W}_{17}\text{M}$ with $\text{M} = \text{V}$ or Mo [59–63].

The protonation state of the system governs the inversion of the order in reduction potentials observed around pH 5 for **1** and **2**. As expected, the computed Fe-O(terminal) distance increases with the number of protons attached to the terminal oxygen. In conditions of no protonation at Fe-O, the computed distance is $d(\text{Fe}-\text{O}) \sim 1.66\text{--}1.76 \text{ \AA}$ depending on the isomeric form, with the $\pi^*(\text{Fe}-\text{O})$ orbital lying at high energies with respect to the $d_{xy}(\text{Fe})$ one due to its marked antibonding nature. The general evolution of the $\pi^*(\text{Fe}-\text{O})$ orbital from neutral (left) to acidic (right) pH is depicted in Figure 8, showing the differences in the molecular orbital sequence for the mono- and diprotonated forms of **1** and **2**. For the monoprotonated species, $\text{Fe}^{\text{III}}(\text{OH})$, the Fe-O distance increases to $\sim 1.87 \text{ \AA}$ and the $\pi^*(\text{Fe}-\text{O})$ is stabilised due to the lower participation of the $2p\text{-O}(\text{terminal})$ orbital, but still remains located above the $d_{xy}\text{-Fe}$ orbital. Finally, when the apical group is doubly protonated, $\text{Fe}^{\text{III}}(\text{OH}_2)$, the Fe-O distance becomes very long ($2.08 \text{ \AA}$) and the $\pi^*(\text{Fe}-\text{O})$ orbital turns into a pure $d_{xz}(\text{Fe})$ orbital, more stable than the formally nonbonding $d_{xy}(\text{Fe})$ orbital when an extra electron is added.

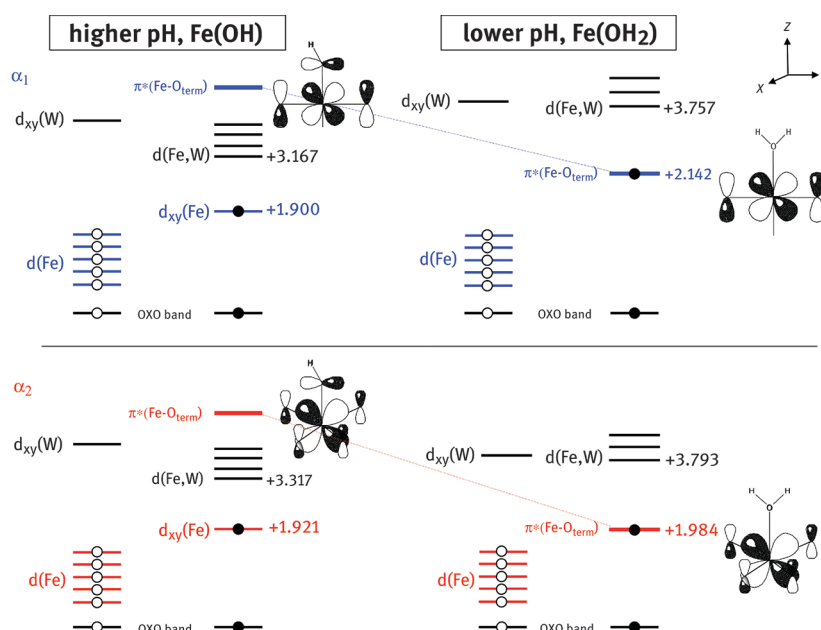


Figure 8: Computed frontier orbitals for higher pH, dominating species $\text{Fe}^{\text{II}}(\text{OH})$, and lower pH conditions, dominating species $\text{Fe}^{\text{II}}(\text{OH}_2)$ of α_1 (**1**, top) and α_2 (**2**, bottom). The character (blue for α_1 and red for α_2 Fe-like orbitals) and relative energies are shown for selected molecular orbitals (in eV vs. the highest orbital of the oxo band). Spin-up and spin-down electrons (empty and filled circles, respectively) are separated in two columns for each compound.

The more favourable reduction of **2** at $\text{pH} \leq 5$ compared to **1** can be explained by (i) the dominant role of the $\pi^*(\text{Fe}-\text{OH}_2)$ orbital in the reduction process, and (ii) the different orientation of this orbital in either isomeric form with respect to the bridging oxygen atoms surrounding the iron centre. The right hand part of Figure 8 shows that the orientation of the π^* orbital in **1** coincides with the direction of two Fe-O(bridging) bonds, therefore conferring it a stronger antibonding character than the homologous orbital in **2**. In the latter case, the π^* orbital bisects the Fe-O(bridging) bonds, making the 3d(Fe)-2p(O) interaction weaker. Thus, electron reduction takes place in a higher π^* orbital in **1** isomer than in **2**, and makes the reduction of the latter compound more favourable at sufficiently acidic pH.

Inspection of the computed atomic spin populations confirms the above statements. The computed change in spin density localised on O(terminal) when going from Fe-OH to Fe-OH₂ is remarkable: 0.36 to 0.06 for both α_1 and α_2 forms of $\text{P}_2\text{W}_{17}\text{Fe}^{\text{III}}$. This indicates the decreasing participation of the terminal oxygen in the $\pi^*(\text{Fe}-\text{O})$ orbital. For the reduced $\text{P}_2\text{W}_{17}\text{Fe}^{\text{II}}$ compounds, the homologous spin density changes from 0.16 to 0.02 on average for both isomers. The smaller spin densities in the case of reduced forms arise from the longer Fe-O(terminal) distances produced by the population of the $\pi^*(\text{Fe}-\text{O})$ orbital.

In summary, DFT calculations allowed to interpret the experimental results according to the different molecular orbital energies. It has been shown that protonation on the terminal Fe-O site gradually stabilises the π^* orbital with respect to the d_{xy} one, leading to an inversion of the d_{xy} and π^* (d_{xz} -Fe) orbital energies when the apical group of iron is water (see Figure 9). In both isomers, the d_{xy} orbital is more stable than the π^* orbital for $[\text{Fe}(\text{OH})\text{P}_2\text{W}_{17}\text{O}_{61}]^{8-}$, assumed to be dominant at neutral pH, while the inversion occurs for $[\text{Fe}(\text{OH}_2)\text{P}_2\text{W}_{17}\text{O}_{61}]^{7-}$ and $[\text{FeP}_2\text{W}_{17}\text{O}_{61}]^{7-}$, the principal species at low pH.

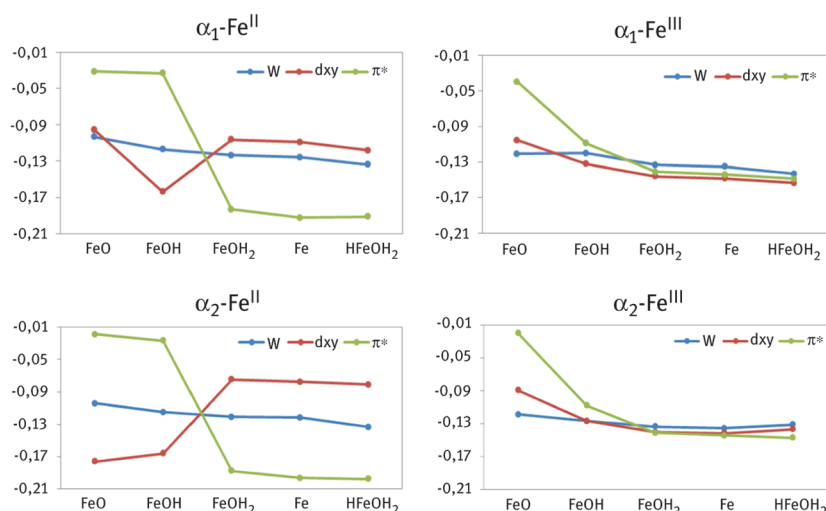


Figure 9: Energies (in eV) of d(W) orbital, Fe-like d_{xy} and π^* orbitals for $\text{FeOP}_2\text{W}_{17}$ (FeO), $\text{Fe}(\text{OH})\text{P}_2\text{W}_{17}$ (FeOH), $\text{Fe}(\text{OH}_2)\text{P}_2\text{W}_{17}$ (FeOH₂), $\text{FeP}_2\text{W}_{17}$ (Fe) and $\text{HFe}(\text{OH}_2)\text{P}_2\text{W}_{17}$ (HFeOH₂) molecules respectively of α_1 and α_2 isomers.

5 Effect of electron (de)localisation and pairing in the redox properties of Wells-Dawson molybdotungstophosphates

From the Wells-Dawson polyoxotungstate, $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, controlled stereo-selective, multi-step syntheses allow replacement of one up to six W^{VI} centres by Mo^{VI} or V^{V} [62, 66–68]. Molybdenum-containing Wells-Dawson systems, $[\text{P}_2\text{Mo}_x\text{W}_{18-x}\text{O}_{62}]^{6-}$ and in particular the behaviour of electrons transferred to them, is an attractive field. One focus of study is to determine, in a first step, if extra electrons gained by these structures are preferentially transferred into a definite atom or region of the molecule and, in a second step, to check whether the added electrons remain located in a single site or if they delocalise over neighbouring sites or the whole molecule in ordinary conditions, as is the case in the highly symmetrical Keggin compounds.

In this section, the mechanisms governing electron transfer and electron distribution in mixed-metal (W, Mo) Wells-Dawson-type POMs are discussed. The structures selected for the present study are shown in Figure 10: α_1 - and α_2 - $[\text{P}_2\text{MoW}_{17}\text{O}_{62}]^{6-}$, α - $[\text{P}_2\text{Mo}_3\text{W}_{15}\text{O}_{62}]^{6-}$ and α - $[\text{P}_2\text{Mo}_6\text{W}_{12}\text{O}_{62}]^{6-}$. They contain one Mo^{VI} centre, three equivalent Mo^{VI} centres and six Mo^{VI} centres, equivalent in a 2(cap):4(belt) fashion, respectively.

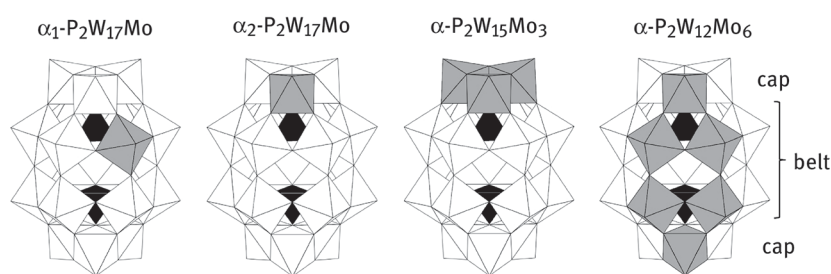


Figure 10: Idealised structure of α_1 - $P_2W_{17}Mo$, α_2 - $P_2W_{17}Mo$, α - $P_2W_{15}Mo_3$ and α - $P_2W_{12}Mo_6$ derivatives. In the fully oxidised form all carry a charge of -6 . White and grey octahedra contain W and Mo atoms in the centre, respectively. The two different types of regions are indicated as *cap* (three metal centres each) and *belt* (12 metal centres – two connected six-membered rings). See above for more details.

Figure 11(A) shows the CVs of the two isomers, α_1 and α_2 - $[P_2W_{17}Mo^{VI}O_{62}]^{6-}$, obtained at pH 3.0. As expected, Mo^{VI} is easier to reduce in equatorial (α_1) than in cap (α_2) position. From DFT calculations it can be deduced that the 1st electron captured by the α_1 isomer partially delocalises over the belt region of the molecule, while it is trapped in one of the caps in the α_2 isomer. In a subsequent electron transfer, expected to be the 1st reduction at the W centres, the α_1 isomer is still easier to reduce than the α_2 isomer (Table 4). Interestingly, for this electron transfer, the quantum mechanical calculations for the α_1 and α_2 isomers show that the electron preferentially goes into the metal centres situated in a belt position of the Wells-Dawson structure [35, 42]. After this 2nd redox process, and if we concentrate on the belt region of these molecules, which is strongly implicated in electron transfer, we realise that the electron density is higher in the case of the α_1 isomer than in the case of the α_2 isomer. As a consequence, the 3rd reduction wave is found at a more negative potential for isomer α_1 since the belt region is more electron populated (two belt electrons) than in the α_2 isomer (one belt electron) at this stage. Indeed, an inversion in the precedence of the waves occurs, that is, the 3rd wave appears now at a more negative potential for α_1 than for α_2 (Figure 11). This observation reinforces the fact that the belt region will preferentially accept the first extra electrons in Wells-Dawson-type structures.

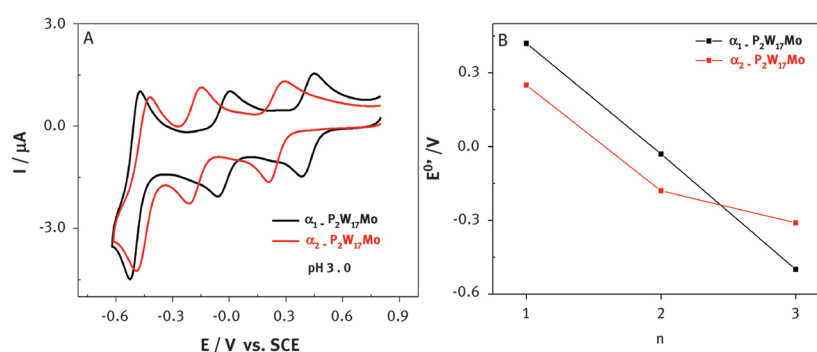


Figure 11: (A) CVs of α_1 - $[P_2W_{17}Mo^{VI}O_{62}]^{6-}$ (black line) and α_2 - $[P_2W_{17}Mo^{VI}O_{62}]^{6-}$ (red line) in 0.5 M $Na_2SO_4 + H_2SO_4$, pH 3. Polyoxometalate concentration: 0.5 mM; scan rate: 10 $mV.s^{-1}$; working electrode: glassy carbon; reference electrode: SCE. (B) Evolution of the midpoint redox potentials for the 1st three one-electron redox processes (Φ_1^0 , Φ_2^0 and Φ_3^0) for α_1 - $P_2W_{17}Mo^{VI}$ (black line) and α_2 - $P_2W_{17}Mo^{VI}$ (red line).

Table 4: Experimental midpoint redox potentials¹ for the 1st three redox processes of α_1 - and α_2 - $[P_2W_{17}Mo^{VI}O_{62}]^{6-}$. In parentheses, the number of electrons exchanged in each wave.

V vs. SCE	Φ_1^0	Φ_2^0	Φ_3^0
	Mo (1e)	W (1e)	W (2e)
α_1 - $[P_2W_{17}Mo^{VI}O_{62}]^{6-}$	0.42	-0.03	-0.50
α_2 - $[P_2W_{17}Mo^{VI}O_{62}]^{6-}$	0.25	-0.18	-0.31
$\Delta\Phi(\alpha_1-\alpha_2)$	0.17	0.15	-0.19

¹ Values in V.

The REs listed in Table 5 constitute the main computational results, which will be referenced to P_2W_{18} (RE = -4.234 eV) along the following discussion. Most REs are more negative than -4.234 eV, indicating the presence of stronger oxidant species than P_2W_{18} , in line with the reduction potentials discussed above. In the present

section, a theoretical analysis of the distribution of the extra electrons among the metal centres and how this is related with electrochemical measurements is made, making a special emphasis in the different oxidant power of the α_1/α_2 isomers of P_2MoW_{17} .

Table 5: Computed REs and E relative to P_2W_{18} (in parentheses) for the Wells-Dawson compounds discussed in this section. Values in eV.

	P_2W_{18}	$\alpha_2-P_2W_{17}$	$\alpha_2-P_2MoW_{17}$	$\alpha_1-P_2MoW_{17}$	$P_2Mo_3W_{15}$	$P_2Mo_6W_{12}$
1 st reduction	-4.234 (0.0)	-2.590 (-1.644)	-4.426 (+0.192)	-4.594 (+0.360)	-4.495 (+0.261)	-4.610 (2e) ^a (+0.376)
2 nd reduction			-3.586 (-0.648)	-3.767 (-0.467)		
1 st reduction			$\alpha_2-P_2VW_{17}$ -4.576 (+0.342)	$\alpha_1-P_2VW_{17}$ -4.673 (+0.439)		
2 nd reduction			-3.255 (-0.979)	-3.298 (-0.936)		

^aTwo-electron process.

5.1 Calculations on $\alpha-P_2W_{18}$, $\alpha_2-P_2W_{17}$, $\alpha_2-P_2Mo_3W_{15}$ and $P_2Mo_6W_{12}$

The plenary $\alpha-P_2W_{18}$ system is an oxidant species as strong as, for instance, the Keggin anion $[PW_{12}O_{40}]^{3-}$, despite carrying a higher negative charge, owing to the fact that the charge -6 is distributed over a larger structure composed of 18 metal centres [69]. For $\alpha-P_2W_{18}$, the first electron(s) occupy the belt region, which is more electron attracting than the cap regions [35, 42, 59, 60]. Compared to it, the lacunary $\alpha_2-P_2W_{17}$ system is more difficult to reduce, with a RE 1.6 eV less favourable (in non-protonated form) than for $\alpha-P_2W_{18}$, a fact arising from the large negative charge of -10. However, the electrochemical measurement gives a smaller difference between the reduction waves of these two compounds. In the conditions of measurement $\alpha_2-P_2W_{17}$ is protonated, its total absolute charge being less negative than -10, explaining the theoretically predicted value for $\alpha_2-P_2W_{17}$. Inspection of the molecular orbital occupied by the first incoming electron shows that it is also delocalised over the equatorial (*belt*) region.

As shown in Table 5, $\alpha-P_2Mo_3W_{15}$ and the mono-substituted $\alpha_2-P_2MoW_{17}$ compounds have similar REs, the former being 70 meV more negative. The presence of the Mo_3 unit in one of the caps allows for some degree of electron delocalisation after reduction and, consequently, a more favourable process than the extra electron being more localised in a single Mo^V site. The CV measurements give a difference of 35 mV at pH 3 between the mentioned compounds. The theoretical data show that each Mo in the cap retains the same amount of the extra electron, with some participation of the nearest W neighbours.

In $\alpha-P_2W_{12}Mo_6$, the ellipsoidal Mo_6 framework can favour delocalisation of extra electron(s) even more than in the above-mentioned $\alpha-P_2W_{15}Mo_3$ system. For the DFT calculations we have taken into consideration the experimental fact that the first reduction wave is a 2e process. To obtain computationally a RE (or E) comparable with the position of the first reduction CV wave, a 2e-wave, we computed the 2e-reduced and the oxidised forms and therefore obtained -4.610 eV as the value to be compared with the first midpoint potential of 0.465 V vs SCE. The theoretical value is in good agreement with the measurements since it is the most negative RE of the series, slightly more negative than the RE obtained for the 1e-reduction of $\alpha_1-P_2W_{17}Mo$. The more advantageous reduction in the hexamolybdate derivative is a consequence of electron delocalisation observed in the calculations. DFT results also suggest that the 1st electrochemically injected electrons are confined to the four belt-Mo atoms with the participation of some neighbouring belt-W centres. We also computed the hypothetical 1e-reduction process ($\alpha-P_2W_{15}Mo_6^{6-} + e^- \rightarrow \alpha-P_2W_{15}Mo_6^{7-}$), obtaining atomic spin populations of 0.25 electrons per Mo, and therefore reinforcing the idea that the 1st electron(s) is (are) delocalised over the belt positions only, leaving the two cap Mo centres fully oxidised. These data reveal the importance of delocalisation in the electrochemical properties of POMs.

5.2 Calculations on α_1 - and $\alpha_2-P_2W_{17}Mo$

First reduction process. The molybdenum mono-substituted Wells-Dawson anions deserve a detailed analysis since they lead to interesting conclusions. Besides the well-known fact that Wells-Dawson compounds con-

taining Mo are more oxidant than the parent species α -P₂W₁₈, the position of Mo within the structure plays a crucial role in the overall oxidising power, not only with respect to the first reduction process but also in the second and third ones. In the cap-substituted α_2 isomer there is some sort of competition for the first incoming electron between the Mo^{VI} atom, in a polar position, and the belt W atoms. Such competition derives from two opposing facts: (i) the empty orbitals of Mo^{VI} have lower energy compared to the W^{VI} ones, and (ii) the empty belt orbitals are lower in energy than the empty cap orbitals. In the end, DFT results show that the cap-Mo^{VI/V} process is 440 mV more favourable than the belt-W reduction for α_2 -P₂MoW₁₇. Thus, the 1st extra electron is localised in the cap. The other positional isomer, α_1 -P₂MoW₁₇, behaves similarly although a larger degree of electron delocalisation can be observed in the 1e-reduced form based on atomic population analysis. When Mo is in the cap position it retains about 82% of the extra electron, whereas it decreases to 77% when Mo is in the belt site. Since electron delocalisation usually gives extra stabilisation to reduced forms in POMs, the computed 1e-reduction process ($P_2W_{17}Mo^{6-} + e^- \rightarrow P_2W_{17}Mo^{7-}$) is energetically more favourable by ~170 meV for the α_1 form, in excellent agreement with the experimental difference of 170 mV (see Table 4). Thus, thermodynamically, the first 1e-reduction process is more favourable for the belt-substituted compound, where the chemical and structural effects add up to favour reduction.

The oxidising power of α_1/α_2 -P₂W₁₇Mo must also be compared with that of α -P₂W₁₅Mo₃. DFT calculations, in agreement with CV measurements, show that α_1 -P₂W₁₇Mo is stronger oxidant than α -P₂W₁₅Mo₃ by about 100 mV (see Table 5). The advantageous delocalisation in the Mo₃ polar group experienced by the metal electron in the 1e-reduced α -P₂W₁₅Mo₃ system cannot be on a par with the extra stabilisation produced in the Mo belt position of α_1 -P₂W₁₇Mo. The fact that α_2 -P₂W₁₇Mo is slightly less oxidising than α -P₂W₁₅Mo₃, both being cap-substituted compounds, is easily explained by the enhanced electron delocalisation occurring in the latter compound.

To end up with the discussion on the first reduction processes, we add a comment on the mono-substituted vanadate, P₂W₁₇V since it helps to rationalise the previously discussed facts. The relative shift between the first 1e-wave for α_1 - and α_2 -P₂W₁₇V is $\Delta RE = 97$ meV (measured $\Delta E = 89$ mV). This small difference compared with P₂MoW₁₇ is attributed to the more localised nature of the extra electron in reduced V-containing systems. In other words, V preserves its nature more than Mo when placed in the Wells-Dawson structure and, therefore, its position (cap or belt) is electrochemically less relevant. The computed atomic spin populations for the 1e-reduced α_1 and α_2 tungstovanadates are ~1.0 on the V centre, a value to be compared with 0.82 and 0.77 per Mo atom in the homologous molybdate compounds.

The above discussion allows us to establish a difference of about 90 meV as the energy change of belt vs. cap metal position, which we estimate from the one-electron RE difference for α_1/α_2 -P₂W₁₇V. Extra RE difference between both isomers, like in Mo-substituted anions, comes from the more delocalised nature of the involved orbitals (which is more pronounced in the belt region). In other words, the ability of an electron to hop from one centre to another, larger in Mo than in V, stabilises the molecular orbital containing that electron and favours reduction. This explains that the RE difference for α_1 - and α_2 -P₂W₁₇V be smaller than that for α_1 - and α_2 -P₂W₁₇Mo. Therefore, we infer that the extra stabilisation of a belt-localised electron compared to the cap-localised case is intimately related with the different degree of electron delocalisation in the belt region.

We carried out complementary calculations to evaluate further the effect of electron delocalisation upon the reduction potential. We compare two systems: α_1 -P₂W₁₇Mo and the hypothetical α -P₂W₁₂Mo₆ structure with six neighbouring Mo atoms in a single belt ring (W₃:Mo₆:W₆:W₃). Both molecules are equally charged and contain Mo atoms in the equatorial positions, the difference being the number of Mo atoms. If we consider the 1st reduction as a 1e-process we find a reduction potential difference of 290 mV in favour of α -P₂W₁₂Mo₆. Such a difference can only be attributed to the effect of electron delocalisation. A very similar value of ~265 mV was recently computed for the Keggin structure [40]. As a matter of fact, the energies of the LUMOs of the oxidised form for each compound are progressively deeper in energy as the number of implicated Mo atoms increases, namely, the LUMO for α -P₂W₁₂Mo₆ is 120 meV below that of α_1 -P₂W₁₇Mo. If we look at the atomic spin populations of the 1e-reduced forms, we find that in α_1 -P₂W₁₇Mo the extra electron is delocalised among the Mo atom and two or three vicinal W atoms. In the case of α -P₂W₁₂Mo₆, 80% of the extra electron is delocalised over the Mo₆ ring, and the other 20% among the other W₆ in the belt. The larger the number of metal centres accepting a fraction of the incoming electron, the more favourable the reduction process is. This phenomenon is applicable when comparing α_2 -P₂W₁₇Mo and α -P₂W₁₅Mo₃, for instance, or α_1 -P₂W₁₇Mo and α -P₂W₁₂Mo₆.

Second and third reduction processes. At this point, let us discuss the computational results for the 2nd 1e-reduction process in α_1/α_2 -P₂W₁₇Mo to complement the CV data. We are especially interested in unravelling the complete CV (1st three reduction waves) of α_1/α_2 -P₂W₁₇Mo, notably the tricky (at least at first sight) relative positions of the 2nd and 3rd waves. Experimental data cannot reveal if the 2nd metal electron, going to the belt region, is mostly localised (Mo^{IV} character) or partially delocalised (Mo^VW₁₇1e⁻ character). If we assumed that the 1st 1e-reduction produces Mo^V in either isomer, the 2nd electron must go to the fully oxidised belt-

W^{VI} positions, but at a more negative potential due to the molecular charge increment that the 1st reduction entails. But what causes the mutual shift of 100 mV of the 2nd wave for each isomer? The reduction potentials computed for the $POM(1e) + e^- \rightarrow POM(2e)$ process for both isomers predict that shift to be around 150 mV and, thus, we may inspect what is the origin of this phenomenon. We computed the possible solutions for the 2e-reduced systems, namely, the unpaired and the paired electron cases represented in Figure 12.

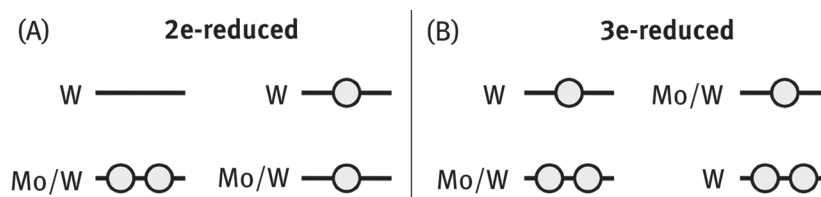


Figure 12: Schematic view of the most plausible electron distributions for (A) the 2e-reduced, and (B) the 3e-reduced forms of $P_2W_{17}Mo$. Horizontal lines represent molecular orbitals. When two electrons (circles) occupy the molecular orbital designated Mo/W, some Mo^{IV} character is present, whereas only one electron in the Mo/W-like orbital implies Mo^V .

Interestingly, at the level of calculation applied, each of these solutions is the most stable for one of the isomers when $M = Mo$. In α_2 - $P_2W_{17}Mo$, the unpaired situation is the most stable by 70 meV, indicating that the 2nd electron prefers to delocalise over the W atoms thus avoiding any Mo^{IV} character. On the other hand, the electron-paired solution is 173 meV more stable than the unpaired one in α_1 - $P_2W_{17}Mo$. In the two cases (α_1 and α_2), the 2nd electron goes to the belt region but in a different manner and, consequently, with a different energy. The pairing process occurring in α_1 appears as a favourable one, with some Mo^{IV} character as depicted in the scheme, with respect to the non-paired situation in α_2 . In α_1 , the presence of one electron in the belt Mo^V does not hinder the 2nd one from occupying the same region, but it actually favours it by e–e pairing. In α_2 , provided that the 2nd electron is forced to go to the belt region, the 2nd reduction is just favoured by the lower e–e electrostatic repulsion that, from the present data, appears to be a weaker advantage than e–e pairing. The electron pairing argument is reinforced by the well-known and proved fact that the 2e-reduced α - P_2W_{18} species is strongly diamagnetic [45, 70]. The character of an electron can be measured by inspection of the molecular orbital it occupies, and also by atomic populations. Both of them coincide in the more delocalised nature of the belt electrons with or without Mo.

Present calculations show that, after the 2nd 1e-reduction, the α_2 - $P_2W_{17}Mo^V 1e^-$ situation is the most stable by an energy difference of 70 meV. However, things are different in the α_1 isomer, for which an important Mo^{IV} character is acknowledged. As shown in Table 3, the RE difference between the 2nd 1e-processes ($\alpha_1 - \alpha_2$) agrees with the experimental results and justify them by the different character of the second electron in either isomer in favour of α_1 . Thus, the mentioned facts suggest a possible competition between two factors, namely (a) the unfavourable e–e electrostatic repulsion, and (b) the favourable electron pairing. Each isomer is characterised by a dominating factor. In α_1 , the 1st electron already occupies a part of the belt region (Mo^V and some W^V character of the vicinal atoms). Although the second electron experiences the repulsive presence of the 1st one, they can pair and thus stabilise the couple (see Figure 13, left diagram). On the other hand, the α_2 isomer has the 1st electron trapped in the cap region, the belt region being free of extra electron density prior to the second reduction. This being an electrostatic advantage with respect to the α_1 isomer, electron pairing will not be possible. We may deduce that, as long as the region is sufficiently large for delocalisation, the 1st two electrons will be paired and stabilised. This explanation is schematically depicted in Figure 13.

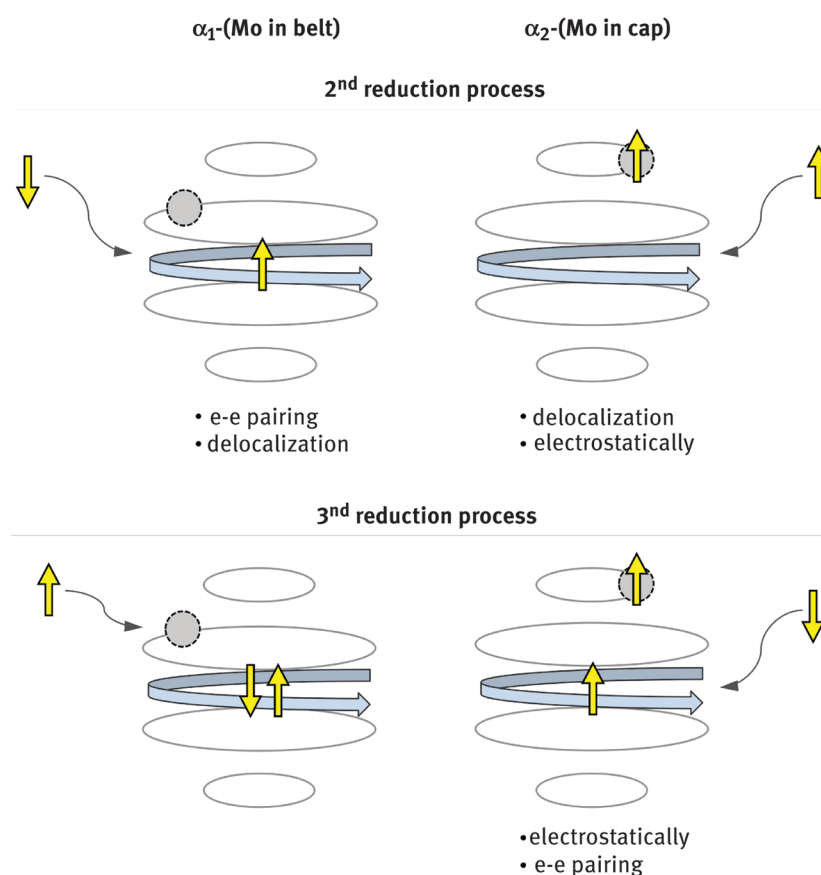


Figure 13: Representation of the 2nd and 3rd reduction processes taking place in the α_1 and α_2 isomers of $P_2W_{17}Mo$ (Mo atoms represented by grey circles), and the factors favouring them in each case. The four 3:6:6:3 loops of metal atoms are sketched as thin grey lines. Yellow arrows are electrochemically added electrons, and grey-blue curved arrows represent the delocalised nature of the belt electrons.

It must be pointed out that the present discussion stands for $P_2W_{17}V$ but giving a different result. Since the 1st 1e-reduction in this vanadotungstate produces a highly localised V^{IV} electron, the 2nd one has hardly a chance of pairing with it (see Table 5). Thus, the electrostatic repulsion will be similar irrespective of the position of the initial electron (cap- V^{IV} or belt- V^{IV}). This results in two 2nd reduction waves close to each other. The computed values differ by 33 mV only.

The 3rd reduction wave, although it is pH dependent, may be justified using the above arguments. At this stage (2e-reduced anions), the situation favours reduction of α_2 at a more positive potential since this isomer contains two unpaired electrons, one in the cap (Mo^V) and one in the belt (W^V character). The 3rd electron can pair with one of these, the one in the belt being the most favourable one. Concerning α_1 , no advantages towards electron-gain with respect to α_2 are envisaged since the belt region is highly electron-populated by two paired electrons at this point. Since the 3rd electron is forced to go to the belt, no electron pairing is possible and a notable electrostatic repulsion will force this process to be less exothermic than that for the α_2 form. The schematic view of the molecular orbital occupations for 3e-reduced anions is shown in Figure 12), where the left-hand situation implies some Mo^{IV} character, whereas the right-hand one corresponds to Mo^V .

6 Summary

Polyoxometalates, a vast family of inorganic compounds, are the subject of both experimental and theoretical studies among chemists, physicists or engineers. Particularly their redox properties, which best define their importance as technological compounds, have been the focus of extensive research during decades. In this chapter, some synergies between experiments and calculations have been shown, putting the stress in how they mutually benefit to solve difficult problems or intricate interpretations. Three cases have been chosen: the influence of the internal heteroatom upon the redox potentials of Keggin anions, the dependence of the redox waves of Fe-substituted Wells-Dawson compounds with pH, and the role of electron delocalization and pairing in mixed-metal Mo/W Wells-Dawson compounds in their ability to accept electrons. In the three cases analysed, considerable merit should be put on the theoretical calculations, which played a crucial role to explain the data

collected in the laboratory. DFT demonstrates again its preponderant role over other computational techniques in this class of chemical problems. In the author's opinion, as long as computational power keeps on growing in the near future, the relevance of Computational Chemistry in leading research will become even greater.

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