Toward a qualitative understanding of the initial electron transfer site in Dawson-type heteropolyanions

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EPR, NMR, optical spectra and electrochemistry experiments on an extended series of one-electron reduced Dawson-type heteropolyanions converge to support the conclusion that the equatorial (α_1) tungsten atoms are first reduced in $[P_2W_{18}O_{62}]^{6-}$. This conclusion is reinforced, for instance, by the interpretation of the electrochemical behaviours of a series of $[P_2W_{18-x}Mo_xO_{62}]^{6-}$ derivatives. In search for a rationale, the study of the electronic structure of such Dawson-type heteropolyanions by means of extended Hückel calculations provides a qualitative understanding of this reduction process. It is found that the lowest unoccupied molecular orbital (LUMO), which is likely to be involved in the initial electron transfer, is essentially "belt"-centred in $[P_2W_{18}O_{62}]^{6-}$. Also, the change of the reduction site ($\alpha_1 \rightarrow \alpha_2$) upon substitution in the "cap" region (α_2 site) by a more electronegative metal centre (Mo for instance) is consistent with the localization of the LUMO on the substituted centre(s).

Introduction

Catalysis by heteropolyanions (HPAs) remains at a high level of interest in laboratories and in industry.[1–3] Most such processes combine strong acid–base catalytic influences with remarkable oxidation abilities. More recently reviewed,[4] electrocatalysis by reduced heteropolyanions (HPBs: heteropolyblues), extensively studied by this group and others, is becoming more and more popular among the essential facets shown by these chemicals. Specifically, electrochemistry investigations continue to establish unambiguously[1,5–16] the existence of catalytic properties for heteropolyanions towards numerous chemicals in solution. In this context, electron transfer processes of both Keggin-type and Dawson-type HPAs deserve special attention: as a matter of fact, it can be anticipated that the "blue" electrons distribution within these molecules might influence the electrocatalysis pathways. This challenging problem was primarily considered from experimental points of view: EPR and NMR spectra and redox potential measurements in electrochemistry were performed on extended series of HPAs and HPBs.[1–3] Very elegant and convincing conclusions, to be described in the following, were drawn concerning the distribution of added electrons in the skeletons of these molecules. However, the proofs remain indirect. Therefore, we wondered whether it were possible to rationalize these observations, even by a qualitative theoretical approach. The work described here is performed on Dawson-type tungstodiphosphates, which are the favourites in most of our electrochemistry investigations. With two caps and a belt region, even unsubstituted Dawson structures are interesting in their own right. Also their ability to generate lacunary species and then metal cation substituted derivatives, arouses extensive attention.[1–16] The impetus was triggered by the pioneering remark by Baker[17] that monosubstituted heteropolyanions can be considered as analogues of metallated porphyrins, and used in catalytic processes with the advantage, over their organic counterparts, of thermal stability, robustness and inertness toward oxidizing environments. With regard to their electrochemistry and, correspondingly, their use in electrocatalysis, we are currently studying the parameters, which eventually in conjunction with pH effects, could induce the merging of the first waves of heteropolyanions (HPAs). The incentive behind this search is to trigger by reduced HPAs, those energetically favourable cathodic processes that require several electrons for effectiveness.[6,8–11] Among several possibilities, the guideline constituted by the substitution effects is considered with attention: the location of the metal in the framework; the nature and number of substituents are expected to influence more or less the interactions between the electroactive centres within the HPA molecule.

In this paper, the electronic structure of a variety of Dawson-type heteropolyanions is studied by means of extended Hückel calculations.[18] The properties of the lowest unoccupied molecular orbital (LUMO), which is likely to be involved in the initial electron transfer, will be used to afford a qualitative understanding of this reduction process.

Key prior knowledge

EPR, NMR and optical spectra

Several techniques comprising optical spectra, EPR, NMR spectra and electrochemistry were used, mostly in conjunction, to study the properties of heteropolyanions and elucidate their structures. In this section, stress will be put on the conclusions, with an indication only of the technique(s) which can be considered as the best support(s) of these conclusions.

Keggin-type heteropolyanions are not the subject of the present work. However, the main results concerning the structures of their oxidized and reduced forms do provide a framework with which to compare and contrast corresponding structures of Dawson derivatives. Complete structural equivalence of the twelve tungsten atoms of α-Keggin anions has been

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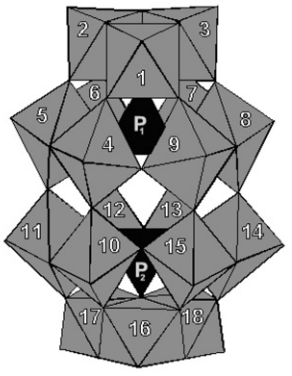

Fig. 1 Idealized structure of α-$[P_2W_{18}O_{62}]^{6-}$ and its substituted derivatives. The numbering of atoms follows the IUPAC recommendations.

demonstrated.[19] In agreement with this result, EPR experiments show that the "blue" electron is delocalized over all twelve tungsten atoms, for instance in α-$[PW_{12}O_{40}]^{4-}$, as obvious from the pioneering work by Pope and co-workers.[20] Then, ample confirmation by EPR and also NMR followed in the literature for this compound and several others and even two-electron reduced Keggin derivatives.[21–25] Substitution of one or several W atom(s) by Mo or V atom(s) in the Keggin framework was then useful in revealing that the added electrons can be trapped, according to various time scales, over certain atoms in the case of monosubstitution and/or regions for multisubstituted derivatives.[22,23,25–28] In short, complete delocalization of the added electrons over all the addenda atoms appears as a rule for unsubstituted α-Keggin anions; introduction of a dissymmetry through substitution of one or several of these addenda atoms results in a variation in the degrees of valence trapping.

Conclusions concerning Dawson-type derivatives should be still more complicated. Unlike the overall symmetry of the α-Keggin structure, the Dawson structure[29,30] is an elongated ellipsoid shown in Fig. 1. It is constituted of six addenda atoms of one type and twelve of another. The six metal atoms are assembled in two groups of edge-shared M_3O_{13} octahedra that occupy the two "polar" positions of the ellipsoid; the remaining twelve metal atoms form two rings of six alternately edge- and corner-shared MO_6 octahedra in what is usually termed an equatorial position. In Fig. 1, the tungsten atoms in α-$[P_2W_{18}O_{62}]^{6-}$ (abbreviated as a-P_2W_{18} in the following; more generally, oxygen atoms will be omitted in abbreviated formulas) are numbered according to the IUPAC recommendations.[31] The two P atoms are numbered (1) and (2), respectively, for the upper and the lower halves of the molecule. Considering the upper half of the molecule and taking into account the numbering, the metal atoms in the "cap" occupy what will be termed α_2 positions and those in the "belt" α_1 positions. In the lacunary species, the vacancies (missing W atoms) are numbered in the same way. Any heterometal filling the vacancy will keep the same index.

The non-equivalence of the "cap" and "equatorial" atoms raises the problem of the initial site of electron transfer in Dawson anions. In the aforementioned pioneering work,[20] a striking similarity of magnetic and EPR properties in $[WOX_5]^{2-}$ complexes and Keggin and Dawson one-electron blues was pointed out. Comparisons of the widths of the spectra and, especially, observation of the distinctly longer relaxation times in reduced 2:18 anions than in the other anions guided Pope to the following statement: "This may mean that it is the "equatorial" (non-Keggin-like) tungsten atoms which are reduced first in 2:18 anions".[20] A subsequent paper from Prados and Pope[27] reinforced this tentative conclusion through a closer examination of the structural properties which rationalize the differences in the EPR spectra of 1:12 and 2:18 derivatives. Since then, various lines of experimental evidence, culled from the results of different techniques, have converged to support the fact that the added electrons should first be introduced into the equatorial atoms.[21–28,32–35] For direct electron distribution studies, EPR, NMR and optical spectra, alone or in combination, must be retained, while electrochemistry, alone or associated to the aforementioned techniques, may be considered as offering more indirect proofs. Several experiments among those of the first series of techniques, are worth emphasizing briefly. For instance, ^{17}O NMR spectroscopy suggested, in the case of the two-electron reduced species $[P_2Mo_{18}O_{62}]^{8-}$ that the two paired electrons should be localized on two adjacent Mo atoms in both half-units; this conclusion was also extended to the corresponding W derivative.[33] In a more recent paper, the one-electron reduced species $[P_2Mo_{18}O_{62}]^{7-}$ was detected and its EPR and ^{31}P NMR studies converged to suggest that the added electron is "delocalized (or is rapidly hopping) between a mirror-plane-related pair of equatorial Mo atoms of the Dawson structure, and, presumably, undergoes much slower hopping to other equatorial molybdenums".[35] Substitution within the framework of heteropolyanions by V or Mo atoms was also helpful in several issues, comprising the degrees of valence trapping.[22,23,26] For instance, the procedure was applied to α-$[P_2Mo_3W_{15}O_{62}]^{6-}$: its first reduction steps are restricted to the Mo centres and the delocalization of the added electron over the three cap Mo atoms is reflected in the electron exchange rate between the oxidized anion and its one-electron reduction product;[23] and intracomplex exchange rates were calculated for α-$[P_2W_{18}O_{62}]^{7-}$ and α-$[P_2Mo_3W_{15}O_{62}]^{7-}$; also ^{183}W NMR has allowed the direct determination of the location of the two added electrons in the EPR-silent heteropolyblue $\alpha[P_2Mo_3W_{15}O_{62}]^{8-}$.[22]

Electrochemistry

Tables 1–4 gather the reduction half-wave potentials or peak potentials of selected heteropolyanions. These values are culled from the current literature, comprising our own work.[10,32,36–41] In the formulae of these anions, oxygen atoms and charges are omitted. Extensive series of Dawson tungstates substituted in the α_1 or α_2 position mainly by first row transition metal cations were studied. However, most of these cations are not reduced in the same potential domain as the tungsten framework. Therefore, it is useful to distinguish these two groups of derivatives and the conclusions to which they guide. In any case, the interpretations are based on the comparisons of the reduction potentials of the same element within α_1- and α_2-substituted Dawson anions on one hand and with those of the corresponding unsubstituted derivatives on the other. In the group of cations reducible in the same potential domain as the tungsten framework, can be gathered the reduction potentials of Mo^{6+}, V^{5+}; Fe^{3+} and Cu^{2+} within Dawson derivatives. The aim is to select conditions where reduced anions are not protonated, in order to discuss pure redox processes. However, in the Tables, only the first two cations are retained because they correspond straightforwardly to the desired conditions; the other two cations will be considered briefly in the following. Experimental evidence proved that the first wave observed for Mo^{6+} and V^{5+}- substituted derivatives and gathered in Tables 1–4 are restricted to the reduction of these cations. Specifically, it appears that α_1-P_2MoW_{17}, which contains the Mo atom in an equatorial position, is more reducible than P_2Mo_{18}.[36,41] In contrast, α_2-P_2MoW_{17} in which the Mo atom is in one cap is less reducible than P_2Mo_{18}. This observation is in agreement with the proposal that P_2W_{18} is initially reduced at one of the twelve equatorial tungsten atoms. This assumption can be extended to P_2Mo_{18} itself, as strongly suggested by the results in Tables 1–4. As a matter of fact, all the

Table 1 Half-wave potential for the various complexes at pH = 4.7. The values in this table are essentially those from ref. 36, but the same measurements were also carried out in ref. 40 and 41, with small numerical variations which have no consequence on the interpretations. The numbering of the substituents(s) follows the IUPAC recommendations

Compound	$E_{1/2}$/V *vs.* SCE (number of electrons)	Ref.
P_2W_{18}[a]	+0.04 (1)	36, 40, 41
(4)-P_2MoW_{17} (α_1)[a]	+0.39 (1)	36, 40, 41
(1)-P_2MoW_{17} (α_2)[a]	+0.23 (1)	36, 40, 41
(1,2,3)-$P_2Mo_3W_{15}$[a]	+0.26 (1)	36, 40, 41
(4,9,10,15)-$P_2MO_4W_{14}$[a]	+0.48 (2)	36
(1,4,9,10,16)-$P_2W_{13}Mo_5$	+0.46 (1)	36
(1,4,9,10,15)-$P_2W_{13}Mo_5$	+0.47 (2)	36
(1,4,9,10,15,16)-$P_2W_{12}Mo_6$	+0.45 (2)	36
P_2Mo_{18}[a]	+0.32 (2)	36, 41

[a] Indicated compounds are those directly considered in the calculations.

$P_2Mo_nW_{18-n}$ compounds that contain molybdenum atoms in the α_1 position are more reducible than P_2Mo_{18} while $P_2Mo_3W_{15}$ in which molybdenum atoms form a Mo_3O_{13} cap is less reducible than P_2Mo_{18}.[36,41] Exactly the same conclusions appear from the examination of $As_2Mo_nW_{18-n}$ derivatives,[37] several $P_2V_nW_{18-n}$ compounds[32,38,39] and also several α-(1,2,3)-[$P_2MM'_2W_{15}$] compounds (with M, M′ = Mo, V, W).[40] Summing up, it appears that these substituent cations are more easily reduced and stabilized in the α_1 position, which would indicate that 2:18 compounds are initially reduced at one of their equatorial atoms.

Examination, in appropriate pH conditions, of the reduction potentials of Fe^{3+}-substituted Dawson derivatives leads to the same conclusion.[11] It is worth noting, however, that the reduction of Fe^{3+} is easily engulfed in that of the anion framework as the pH of the supporting electrolyte is decreased.[11] The case of Cu^{2+}-substituted compounds is complicated by the deposition of the metal during reduction processes.[14–16]

The reduction potential of the first wave of the framework itself can also be considered, tentatively, when the substituent cation is not reduced in the vicinity of the skeleton itself.[10] On average, the cathodic peak potential is more negative in the α_1 than in the α_2 series. This situation is indeed observed throughout. This observation was argued[2,41,42] to support the idea that the initial electron addition of the W framework occurs in one of the equatorial atoms. It can therefore be seen that electrochemistry experiments, like those with other techniques, also support the proposal that 2:18 unsubstituted compounds are initially reduced at one of the twelve equatorial atoms.

Table 2 Half-wave potential for the various complexes. The values in this table are taken from ref. 37. The numbering of the substituent(s) follows the IUPAC recommendations

Compound	pH	$E_{1/2}$/V *vs.* SCE (number of electrons)
α-As_2W_{18}	1	+0.08 (1)
(4)-As_2W_{17} (α_1)	4.6	−0.47 (2)
(1)-As_2W_{17} (α_2)	4.6	−0.44 (2)
(1,2)-$As_2W_{15}Mo_2$	4.6	−0.42 (2)
(1)-$As_2W_{17}Mo$ (α_2)	1	+0.28 (1)
(4)-$As_2W_{17}Mo$ (α_1)	1	+0.45 (1)
(1,2)-$As_2W_{16}Mo_2$	1	+0.29 (1)
(1,2,3)-$As_2W_{15}Mo_3$	1	+0.31 (1)
(1)-$As_2W_{17}V$ (α_2)	1	+0.46 (1)
(1,2)-$As_2W_{16}V_2$	1	+0.42 (2)
(1,2,3)-$As_2W_{15}V_3$	1	+0.32 (3)

Table 3 Half-wave potential for various V-substituted complexes. The numbering of the substituent(s) follows the IUPAC recommendations

Compound	pH[a]	$E_{1/2}$/V *vs.* SCE (number of electrons)	Ref.
(4)-$P_2W_{17}V$ (α_1)	5.5 (Li^+)	+0.48 (1)	38
(1)-$P_2W_{17}V$ (α_2)	5.5 (Li^+)	+0.39 (1)	38
(1,2)-$P_2W_{16}V_2$	5.5 (Li^+)	+0.27 (1)	38
(1,2,3)-$P_2W_{15}V_3$	5.5 (Li^+)	+0.23 (1)	38
(1,2,3)-$P_2W_{15}V_3$	7.0 (Li^+)	+0.11 (1)	38
(4)-$P_2W_{17}V$ (α_1)	4.7 (Na^+)	+0.51 (1)	32, 38
(1)-$P_2W_{17}V$ (α_2)	4.7 (Na^+)	+0.41 (1)	32, 38
(4)-$P_2W_{17}V(\alpha_1)$	7	+0.48 (1)	39
(1)-$P_2W_{17}V(\alpha_2)$	7	+0.39 (1)	39
(1,2)-$P_2W_{16}V_2$	7	+0.28 (2)	39

[a] In the explored pH domains, the reduction potentials depend on the nature of the cation (Li^+ or Na^+) other than H^+ in the supporting electrolyte.

Theoretical approaches

As a consequence of the high number of heavy atoms in such molecules in addition of the complexity of the problems of interest, attempts at direct theoretical rationalization of these observations and/or prediction of behaviours are rather limited. A remarkable characteristic, however, is that different issues have been tackled as directly as possible, whatever the available theoretical tools at hand at the time. Even the earliest theoretical works on polyoxometalates using the simple semi-empirical extended Hückel approach are devoted to problems as complicated as the comparison of the catalytic and structural properties of heteropolycompounds,[43] or the behaviours of polyoxometalates as models of oxide catalysts.[44] Other achievements include the molecular orbital theory treatment of the photodimerization of cyclohexene and methane by decatungstate anions[45] or the oxidative dehydrogenation of methanol by metal oxide surfaces.[46] Progressively, more sophisticated *ab initio* or DFT methods are being introduced.[47–60] Their ability of tackle problems as diverse as the acidity and basicity of polyoxometalates,[54,55] the localization or delocalization of metal electrons in reduced species[52,53,56,59,60] is receiving increasing attention. Among these papers, those devoted to the electronic structures of dodecamolybdo-heteropolyanions and to their reduction and catalytic behaviours deserve particular emphasis[47,48] as the points under scrutiny are close to those examined in the present work.

Theoretical details

In the following, a qualitative rationalization of some of the experimentals recalled above for the Dawson-type heteropolyanions is proposed on the basis of the molecular orbital

Table 4 Half-wave potential for variously substituted complexes at pH = 1. The values are taken from ref. 40. The numbering of the substituent(s) follows the IUPAC recommendations

Compound	$E_{1/2}$/V *vs.* SCE (number of electrons)
P_2W_{18}	+0.04 (1)
(1,2)-$P_2W_{16}Mo_2$	+0.27 (1)
(1,2,3)-$P_2W_{15}Mo_2V$	+0.46 (1) (V^V/V^{IV})
(1,2,3)-$P_2W_{15}MoV_2$	+0.37 (2) (V^V/V^{IV})
(1,2,3)-$P_2W_{15}V_3$	+0.42 (1) (V^V/V^{IV})
(1,2)-$P_2W_{16}V_2$	+0.36 (2)
(4)-$P_2W_{17}V(\alpha_1)$	+0.49 (1)
(1)-$P_2W_{17}V(\alpha_2)$	+0.41 (1)

properties derived from extended Hückel calculations.[18,61] The calculations were performed with the EHT method[18] using weighted H_{ij} formula.[61] The atomic parameters for the calculations were taken from classical relevant references[62] (ref. 62(*a*) for O, P and Mo and ref. 62(*b*) for W).

Results and discussion

Calculations were first performed on the unsubstituted Dawson structure with D_{3h} geometry derived from the crystallographic data.[29,30] In this $P_2W_{18}O_{62}^{6-}$ heteropolyanion, the metal centres, either in the α_1 (belt) or the α_2 (cap) positions, are in a distorted octahedral environment with a d^0 electronic configuration. Since the d block is vacant, the lowest unoccupied MOs on each metal unit are the three metal d orbitals derived from the t_{2g} block of an ideal octahedron, destabilized by antibonding interactions with the oxygen p orbitals (lone pairs) of matching symmetry. By contrast, the highest occupied MOs are mainly developed on the oxygen lone pairs, slightly stabilized by bonding interactions with the metal d orbitals. With the oxygen p orbitals being much lower in energy than the tungsten d orbitals (−14.80 and −10.37 eV, respectively, according to the EH parameters), there is a large energy gap, of about 5 eV, between the highest occupied (HOMO, *oxygen centred*) and the lowest unoccupied (LUMO, *metal centred*) molecular orbitals on each metal unit. The symmetry-adapted MOs of the $P_2W_{18}O_{62}^{6-}$ heteropolyanion result from the interactions of the metal units' orbitals and the main features described above are preserved: the lowest vacant orbitals are mainly developed on the metal centres and the highest occupied MOs on the oxygen atoms, the computed energy gap between the LUMO (−9.57 eV) and the HOMO (−14.48 eV) being equal to 4.91 eV. Due to the size of the anion, there is a large number of MOs within a small energy range. For instance, the $18 \times 3 = 54$ lowest vacant MOs are lie between −9.57 and −8.42 eV.

The non-equivalence of the "cap" (α_2 positions) and the "belt" (α_1 positions) metal atoms in $P_2W_{18}O_{62}^{6-}$ is reflected by the composition of metal-centred vacant orbitals (Fig. 2). It is worth noting that the LUMO (a''_1) is almost entirely developed on the α_1 positions (96%), with equal weights on each of the twelve metal atoms. With the reasonable assumption that the initial electron transfer involves the LUMO of the starting species, the shape of this molecular orbital nicely rationalizes the experimental evidence that the added electrons should first be introduced into the equatorial atoms. Interestingly, the composition of the vacant orbitals located above the LUMO is very different. For instance, in the first set of degenerate MOs, of e″ symmetry, the orbitals are spread out over both the α_1 (61%) and the α_2 (33%) positions in such a way that almost equal weights are found for the eighteen metal centres (twelve and six in the α_1 and the α_2 positions, respectively). In the second set of degenerate MOs (e′), the orbitals are mainly located on the α_2 positions (81% instead of only 12% for the twelve α_1 positions). Finally, the sixth low-lying vacant orbital (a''_2) is developed on both the α_1 (44%) and the α_2 (46%) positions.

The shape and the energies of the metal-centred vacant molecular orbitals are sensitive to the substitution of W atom(s) by more electronegative metal atom(s) (Mo for instance). Assuming the geometry of the substituted $P_2W_{18-x}Mo_xO_{62}^{6-}$ heteropolyanions is identical to that of the unsubstituted species, the electronegativity perturbation can be accounted for, in the first approximation, by the lowering of the atomic orbital energies on the substituted metal centre(s).[63] Consequently, the vacant metal-centred MOs, with non-zero coefficients on the substituted centre(s), are stabilized and the lowest energy ones become more concentrated on the more electronegative centre(s). On the other hand, the shape and the energy of the MOs which were not developed on that centre(s) in the parent unsubstituted species remain unchanged. These include all the oxygen-centred occupied MOs and the metal-centred vacant MOs which were not developed on the substituted centre(s).

Let us now analyse how the localization of the LUMO, which was entirely developed on the twelve α_1 ("belt") position(s) leads to a LUMO of lower energy, still developed on the α_1-Mo centre(s). For instance, with a single α_1-Mo atom, the LUMO is lowered by 0.08 eV and remains located on the "belt" (93%). However, instead of an equal weight of about 8% on each metal atom, 45% of the LUMO is now concentrated on the single α_1-Mo centre. Note that such a localization of the LUMO upon substitution has been recently reported by Poblet and co-workers for α-Keggin anions (DFT orbitals).[60] The same conclusions apply for compounds with several α_1 substituted centres. For instance, in the edge-substituted (4,9,10,15)-$P_2Mo_4W_{14}$ complex, 82% of the LUMO is located on the four α_1-Mo centres and only 10% on the eight remaining α_1-W centres. By contrast, substitution at the α_2 position(s) leaves this α_1-centred vacant orbital unchanged but stabilizes the MOs developed on the α_2 sites. Therefore, a dramatic change in the localization of the LUMO can occur with respect to the unsubstituted compound, as is illustrated in Fig. 3 for the (1,2,3)-$P_2Mo_3W_{15}O_{62}^{6-}$ complex with three Mo centres is one cap. In this compound, a set of two degenerate LUMOs of e symmetry (C_{3v}), centred on the three α_2-Mo positions (86%), is now located 0.10 eV below the α_1-centred (94%) vacant orbital which has been left unchanged by the

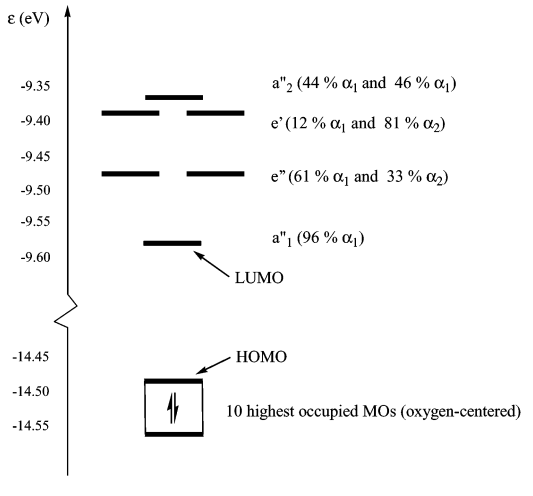

Fig. 2 Selected frontier orbitals of the $P_2W_{18}O_{62}^{6-}$ heteropolyanion (EH calculations). The symmetry and the contributions of the α_1 and α_2 positions to the six lowest vacant MOs are given.

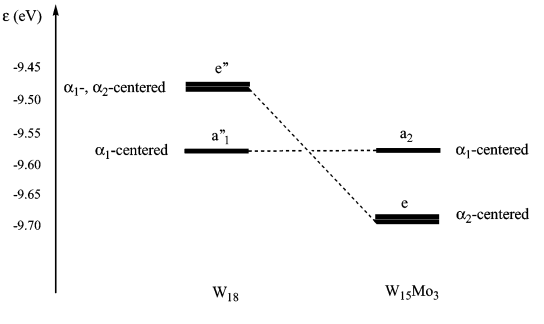

Fig. 3 Inversion of the energy levels of the three lowest unoccupied MOs in the $P_2W_8O_{62}^{6-}$ heteropolyanion upon substitution by three molybdenum centres in a "cap" (α_2 positions) (EH calculations).

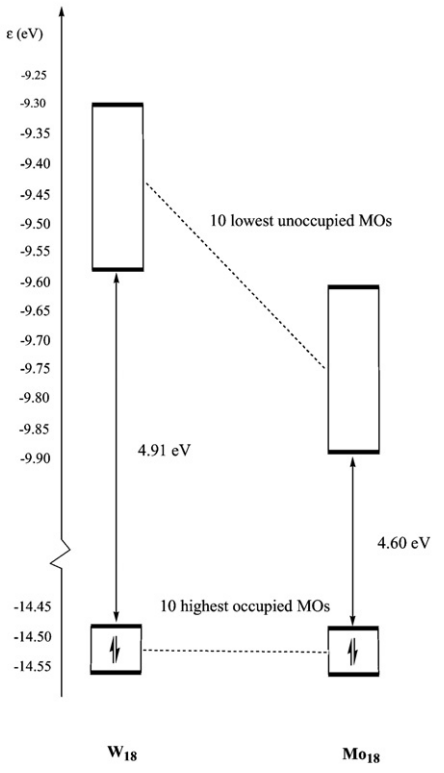

Fig. 4 Energy change of the ten highest occupied (oxygen-centred) and the ten lowest unoccupied (metal-centred) MOs in going from the $P_2W_{18}O_{62}^{6-}$ heteropolyanion to its molybdenum analog $P_2Mo_{18}O_{62}^{6-}$ (EH calculations).

substitution. Even for a single substitution, the LUMO is located at 80% on the α_2-Mo centre and its energy is 0.06 eV below that of the belt-centred vacant orbital. In the "mixed" face-substituted complex, with four α_1-Mo and two α_2-Mo centres, the LUMO remains located on the four substituted α_1 positions (82%) while the vacant MO just above is mainly developed on the two substituted α_2 positions (77%). Finally, in the fully substituted Mo_{18} compound, the situation is identical to that found in the starting W_{18} species, with a LUMO entirely developed on the twelve α_1 centres. A nice correlation is thus found between the localization of the LUMO (either α_1- or α_2-centred) and the nature of the first reduction site in the substituted $P_2W_{18-x}Mo_xO_{62}^{6-}$ heteropolyanions deduced from the experimental evidences recalled above.

Finally, the HOMO–LUMO energy gap depends on the substitution pattern since the HOMO level (oxygen-centred) remains unchanged while the LUMO level (metal-centred) is lowered when more electronegative metal centres are introduced. This is illustrated in Fig. 4 for the $P_2W_{18}O_{62}^{6-}$ heteropolyanion and its fully substituted analog $P_2Mo_{18}O_{62}^{6-}$. The HOMO energy level is −14.48 eV in both complexes but the LUMO energy level is lower by 0.31 eV in the Mo_{18} species (−9.88 instead of −9.57 eV in the tungsten analog). Such a lowering of the LUMO level upon substitution can be correlated with the easier reduction of the Mo substituted species (Table 1).

Concluding remarks

In conclusion, it has been shown that the experimental evidence for an initial electron transfer site in an equatorial position (α_1) of the unsubstituted Dawson-type $P_2W_{18}O_{62}^{6-}$ heteropolyanion can be rationalized by the "belt"-centred character of the lowest unoccupied molecular orbital (LUMO). The change of the reduction site ($\alpha_1 \rightarrow \alpha_2$) upon substitution in the "cap" region (α_2 site) by a more electronegative metal centre (Mo for instance) is also consistent with the localization of the LUMO on the substituted centre(s). Finally, the easier reduction process observed in the substituted species can be correlated to an energy lowering of the LUMO. Despite the large number of vacant orbitals in a rather small energy range, it thus appears that the LUMO properties (shape and energy) derived from simple EH calculations might afford a powerful tool for a qualitative understanding of the experimental trends recalled in the first part of this paper for Dawson-type heteropolyanions.[64] It is clear however that problems such as the localized or delocalized nature of the electronic state(s), the sites for further electron transfers and the magnetic properties of these reduced species are beyond the scope of such qualitative calculations.

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64 After the present paper was submitted for publication, Professor Poblet *et al.* communicated to us, before publication, the manuscript of their independent study using DFT calculations on selected mixed-addenda Keggin and Wells–Dawson anions. The results confirm the trends obtained here concerning the energy variations. A complementary point of interest in this study is the demonstration that the presence of a solvent shifts the MOs, but retains their relative positions; in other words, "the study of the isolated anions is enough to understand many redox properties of the POMs".