Electronic Properties of Polyoxometalates: Electron and Proton Affinity of Mixed-Addenda Keggin and Wells–Dawson Anions

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Received March 20, 2002

Abstract: A series of systematic DFT calculations were conducted on Keggin \([SiW_9M_3O_{40}]^{n−}\), \(M = Mo, V, and Nb\); and Wells–Dawson anions \([P_2M_{15}M_3O_{62}]^{n−}\), \(n = 1\) or \(2\). The electronic configuration of the metal is usually \(d^0\) or \(d^1\) and related to their redox properties.3 POMs are structures that contain arrays of corner- and edge-sharing pseudo-octahedrally substituted derivatives are a large group of transformable anionic architectures, Keggin anions4 \([XM_{12}O_{40}]^{−}\), \(X = W, Mo, and V\) to analyze the redox properties and the basicity of the external oxygen sites in polyoxometalates with nonequivalent addenda metals. The energy and composition of the lowest unoccupied orbitals, formally delocalized over the addenda atoms, determine the redox properties of a polyoxometalate. When a \(Mo^{VI}\) substitutes one \(W^{VI}\) in the 1:12 tungstate, the energy of the LUMO decreases and the cluster is more easily reduced. The tungstoniobates behave differently because the niobium orbitals insert into the tungsten band and the reduction of \([SiW_9Nb_2O_{40}]^{−}\) yields the blue species \(SiW_6Nb_2\) 1e and not the cluster \(SiW_9Nb_2\) \(V^V\). In Wells–Dawson structures, the polar and equatorial sites have different electron affinities and the reduction preferentially occurs in the equatorial sites. Inserting ions with larger electron affinities into the polar sites can modify this traditional conduct. Hence, the trisubstituted \([P_2W_{15}V_3O_{62}]^{9−}\) anion is reduced in the vanadium polar sites. By means of molecular electrostatic potential maps and the relative energy of the various protonated forms of \([SiW_9V_3O_{40}]^{7−}\) and \([SiW_9Mo_3O_{40}]^{−}\), we established the basicity scale: \(OV_2 > OM_2 > OW_2 > OV > OW > OM\). Finally, a continuum model for the solvent enabled us to compare anions with different total charges.

Introduction

Polyoxometalates1,2 (POMs) and their transition-metal-substituted derivatives are a large group of transformable anionic clusters that have multiple applications, many of which are related to their redox properties.3 POMs are structures that contain arrays of corner- and edge-sharing pseudo-octahedrally coordinated \(MO_6\) units, packed to form an ionic core, where the electronic configuration of the metal is usually \(d^0\) or \(d^1\) and is commonly called addenda or peripheral element. The most typical addenda elements that form molecular (discrete) metal oxides are \(W^{VI}\), \(Mo^{VI}\), and \(V^V\) because their ionic radii and charge are suitable for combining with \(O^{2−}\). Nonetheless, many POMs have been synthesized by incorporating (substituting or adding) other metallic centers. Among many other heteropoly architectures, Keggin anions5 \([XM_{12}O_{40}]^{−}\) and Wells–Dawson (W–D) anions5 \([X_2M_{10}O_{62}]^{−}\), as well as their derived aggregates, form a basic set of clusters that have given rise to a vast literature. In the formulation of heteropolyanions (HPAs), \(X\) is the internal element.1

The composition of the metal and the shape of the framework define the properties of a POM. For example, the improvement in the catalytic activity of polyanions is closely related to addenda substitution.6 At the end of the 1960s, the work of C. Tourné and G. Tourné2 created interest in how addenda substitution affected POMs, and this interest grew rapidly in the subsequent decades. Most research on the Lindqvist iso-family was carried out by Klemperer and co-workers7,8 with the aim of obtaining suitable polyoxometalate-supported organometallic derivatives. Mixed-addenda HPA research is even more extensive since Keggin- and Dawson-type derivatives can give rise to a greater number of stoichiometries, shapes, and aggregations. The addenda \(W^{VI}\), \(Mo^{VI}\), \(V^V\), and \(Nb^{V}\) and the main group heteroatoms P and Si are the most usual metal ions in Keggin and W–D HPAs, but other fourth (Ti,6,10 Zr11), fifth (Ta),12 and sixth (Cr)13 row transition-metal elements have been incorporated into the POM framework. Lanthanides, actinides,14


and non-transition-metal derivatives have also been reported.\(^{12,15}\)

A considerable number of traditionally paramagnetic atoms have been included in the framework of Keggin and W–D anions, as well as in the sandwich-type molecules\(^{16}\) derived from them. This is a growing area in which rational methods for systematically modifying POM structures have still to be fully developed.\(^{17}\)

In two previous papers, we showed that quantum chemistry calculations also correctly described the redox properties in anions with transition-metal heteroatoms such as Co(II), Co(III), or Fe(III)\(^{18,19}\) and their magnetic features.\(^{20}\) In the present paper, we report a detailed DFT study on the series of anions A-x-[SiW\(_6\)Mo\(_5\)O\(_{49}\)]\(^{6-}\), M = V(V), Nb(V), or Mo(VI); A-x-[P\(_2\)M\(_{17}\)O\(_{62}\)]\(^{6-}\), M = W(VI) or Mo(VI); and [P\(_2\)M\(_{15}\)V\(_{8}\)O\(_{62}\)]\(^{6-}\), M = W(VI) or Mo(VI) to analyze the redox properties and the basicity of the external oxygen sites in clusters with nonequivocal addenda. Only clusters preserving a three-fold axis were considered since three-substituted clusters are very frequent and usually the substitution takes place in three neighboring octahedra. Moreover, C\(_5\) systems require less computational demands. Throughout the paper, we will generally use the shorthand notation without either oxygen atoms or charge. Thus, for example, P\(_2\)W\(_9\) denotes the fully oxidized [P\(_2\)M\(_{18}\)O\(_{62}\)]\(^{6-}\) Wells–Dawson anion. P\(_2\)W\(_{18}\) means that the cluster is single-reduced. These kinds of systems are also known as blue species.\(^{1}\) Despite the enormous effort made in the last thirty years to synthesize and study the chemical properties in these molecular systems,\(^{2,22}\) we believe that their basic electronic properties still need to be systematically analyzed.

The Keggin structure may be viewed as the assembly of four M\(_{2}O_{12}\) edge-sharing triads (B-triads) or as the packing of four

\[ \text{A} \quad \text{B} \quad \text{C} \quad \text{D} \]
M$_{15}$O$_{15}$ corner-sharing triads (A-triads). Figure 1 shows, in polyhedral representation, the pattern of three neighboring octahedra that are removed from the Keggin framework to give the lacunary A-form. Of the lacunary XM$_3$ units, the anions that contain A-fragments are the most frequent, although many aggregates of the B-XM$_9$ precursor are also known. All the structures reported in the present work are formal derivatives of the Keggin anion: the A-[SiW$_3$Mo$_3$O$_{40}$]‘⁻ species maintain their shape after the substitution, and the W-D structures are an assembly of two A-XM$_{14}$ units.

Theoretical Details

The calculations were carried out using the DFT methodology with the ADF2000 program. The local density approximation (LDA) characterized by the electron-gas exchange together with the Vosko–Wilk–Nusair (VWN) parametrization for correlation were used. Gradients were corrected by means of the Becke-Alder–Perdew exchange and correlation energy, respectively. Triple-$\zeta$ plus polarization Slater basis sets were used to describe the valence electrons of main group atoms, (Si, P) whereas for transition-metal atoms a frozen core composed of 1s to 2p shells for vanadium, 1s to 3spd shells for niobium and molybdenum, as well as 1s to 4spd shells for the sixth period element, tungsten, were described by means of single Slater functions. $ns$ and $np$ electrons were described by double-$\zeta$ Slater functions, $nd$ and $(n+1)s$ by triple-$\zeta$ functions, and $(n+1)p$ by a single orbital.

Addenda-Substituted Keggin Anions. The electronic structure of the fully oxidized XM$_3$ anions is quite simple and can be described in terms of the energy levels and shape of the molecular orbitals (MOs). Two sets of orbitals are easily identifiable in Keggin clusters without paramagnetic ions: a set of doubly occupied MOs, delocalized over the oxo ligands, and a set of unoccupied d-like addenda orbitals that conform the metallic band. In this band, the lowest orbitals are symmetry-adapted combinations of d$_{x^2}$-like orbitals with some antibonding participation of oxygen orbitals. The d$_{x^2}$- and d$_{y^2}$-type orbitals are higher in energy since the shorter terminal bonds destabilize them. For the tungsto-derivatives A-α-[SiW$_3$M$_3$] with M = Mo, Nb, V, and Nb, full geometry optimizations were carried out under C$_3v$ symmetry constraints. In general, present DFT calculations reproduce very well the geometry of the heteropolyanions with the exception of the metal-terminal oxygen bond lengths that are computed systematically longer than the experimental ones. The deviations are on average 0.04 Å and seem to depend on the net charge in the internal tetrahedron. The empty set of d-tungsten orbitals appears, after the metallic substitution, as a mixture of W and M orbitals. The order and composition of the molecular orbitals depend heavily on M. There is no doubt that the redox properties of the substituted cluster will depend on the nature and energy of the lowest unoccupied orbitals. In the dodecatungstates, the HOMO–LUMO (H–L) gap was computed to be ~2.8 eV (Figure 2). This energy decreases to ~2 eV for molybdates. The lower H–L gap in molybdates means that they are, in general, more easily reduced. Hence, for instance, SiMo$_{12}$ and GeMo$_{12}$ are more powerful oxidizing agents than the corresponding tungstates by ~0.5 V. The other fundamental variable that plays an essential role in the oxidant power is the total negative charge of the anion. Pope and Varga corrected core potentials was used to make quasirelativistic corrections for the core electrons. The quasirelativistic frozen core shells were generated using the auxiliary program DIRAC. Open shell electronic configurations were computed with the unrestricted methodology. The solvent effects were included by means of the COSMO software, included in the ADF2000 package. The geometries of the Keggin and Wells–Dawson anions were fully optimized for each state.

Results and Discussion

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rationalized the first cathodic potential dependence with the negative charge for Keggin anions.\(^{32}\) The substitution of three tungsten ions by three molybdenum ions modifies the relative energy of the LUMO from 2.5 eV in the dodecatungstate to 2.5 eV in A-α-SiW\(_9\)Mo\(_3\). In the tungstomolybdate, the LUMO is a degenerate orbital of \(e\) symmetry with a larger participation of \(d\)-molybdenum orbitals. Since the total charge of the anion does not change, the simple substitution of tungsten by molybdenum increases the oxidizing power of the anion. In particular, present DFT calculations indicate that the mono-reduction of SiW\(_9\)Mo\(_3\) is \(\sim 0.4\) eV more favorable than that of SiW\(_9\), a value comparable to the previously reported 0.54 V obtained experimentally.\(^{33}\)

The group 5 derivative, A-α-SiW\(_9\)V\(_3\), has an H–L gap of 2.21 eV, an even lower energy than that computed for A-α-SiW\(_9\)Mo\(_3\). The LUMO in the vanadium derivative, which is a degenerate orbital of \(e\) symmetry, and the LUMO+1, which appears \(\sim 2.9\) eV from the HOMO, are \(d_e\)-orbitals essentially localized on the vanadium centers. This means that the vanadotungstate will preferentially be reduced in the vanadium centers, as electrochemical studies by Hervé and co-workers have demonstrated.\(^{34,35}\) On the other hand, the analogous niobium derivative has an H–L gap of 2.92 eV, somewhat larger than the single addenda dodecatungstate. This behavior combined with the higher negative charge in the substituted derivative means that the substitution of \(W\) by \(Nb\) always decreases the oxidizing power of the anion.

The relative energy and composition of the LUMO correlate quite well with the electron affinity of each isolated \(M^{n+}\) ion that is in the order Mo\(_{6}^{5+}\) > V\(_{5}^{5+}\) > W\(_{6}^{6+}\) > Nb\(_{5}^{5+}\). Although the first ionization potential of \(W\) is greater than that of Mo, there is an inversion in the subsequent ionization energies and the 6th ionization potential is higher for Mo. +68.10 eV (Mo) and +63.95 eV (W) are the 6th ionization potentials computed at the present level of theory. In contrast, Nb systematically shows a greater predisposition than \(W\) to lose its electrons. In agreement with these ionization energies, present DFT calculations gave the following LUMO compositions: for the tungsten-niobate, only 7\% of Nb and 59\% of W contribution. When \(M = Mo\), the sharing of the LUMO is 46/20% for Mo/W and, finally, the LUMO has the largest heteroatom participation, 65\%, for SiW\(_9\)V\(_3\). The tungsten contribution is 10\%. This mixed cluster has the lowest H–L gap. Unrestricted calculations of single-reduced Keggin anions were performed to check predictions made by orbital analysis. Jahn–Teller effects might take place in monoreduced species since a degenerate \(e\) orbital is populated with one electron. Nevertheless, previous calculations on single addenda Keggin anions\(^{19}\) showed that the stabilization due to the Jahn–Teller effect is very small, and it has not been considered here. Spin polarizations given in Table 1 reinforce the qualitative predictions based on the molecular orbitals of the oxidized species, which suggest that the additional electron in the monoreduced species A-α-SiW\(_9\)V\(_3\) is delocalized among the three vanadium centers (0.35 spin alpha electrons per V). Some extra polarization in the molecule yields a population of 0.012 spin alpha electrons per \(W\). In the analogous molybdate, 70\% of the additional electron is distributed among the three Mo centers. Finally, when the substituting addenda is a Nb\(^{5+}\), the orbitals of the heteroatom do not participate in the LUMO and the spin density is localized in the \(W\) centers in 87\%. Although the ionization energies of isolated metal ions would suggest that the reduction of mixed molybdovanadates would take place at the molybdenum centers, the extra electron mostly goes to a vanadium atom.\(^{18,34}\) In Figure 2, the \(V\) orbital is the lowest of the four LUMO. The particular behavior of the Mo\(^{6+}\) and V\(^{5+}\) pair arises from the different electronic population of \(d\) orbitals in fully oxidized clusters, which is larger for \(Mo\) atoms.

### Electronic Structure of Wells–Dawson Anions

Electronic studies of Wells–Dawson Anions. ESR and electrochemical studies\(^{36}\) have shown that \(W–D\) anions are chemically different from Keggin species because of their structural differences. Hence, whereas all metals are equivalent in the α-Keggin anion, a clear distinction can be made between polar (cap regions) and equatorial octahedrons (belts) in the \(W–D\) framework. The equatorial M\(_{12}\) array is formed via alternative corner- and edge-sharing of the \(MO_6\) units, as can be deduced from Figure 1. They are also linked to polar octahedra by a single corner per \(MO_6\) group. This makes \(W–D\) molecules different from the Keggin anions, in which every octahedron shares two edges with neighboring \(MO_6\) units. Special attention should be paid to the \(M–O–M\) angle of the corner-sharing octahedra in the equatorial zone, which was computed to be 163° in both \(P_2\)W\(_{18}\) and \(P_2\)Mo\(_{15}\); the experimentally measured value is 162°.\(^{37}\) The corresponding \(M–O–M\) angle in the \(cap\) is close to 125°. The presence of almost linear \(M–O–M\) angles linking the two halves of the anion implies these two adjacent metals to be separated by 3.7–3.8 Å, while in a \(PM_6\) moiety the distance between two neighboring metals is \(\sim 3.4\) Å. We will show that this structural characteristic determines the electronic properties and, therefore, the redox chemistry of \(W–D\) molecules.\(^{38}\) The other structural parameters are much less important: all the \(M=O\) (terminal) bond lengths were computed to be \(\sim 1.74\) Å, a value that is very similar to the \(M=O\) distance found for \(XM_{12}\) structures\(^{18,19}\) and is 0.05 Å longer than the experimental distance.\(^{5,37}\) The \(M–O\) (bridge) distances are also similar to those found in Keggin anions. They are about 1.90–1.94 Å in the tungstate. The deviations in the

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**Table 1. Spin Polarizations (α–β) Electrons for Several Single-Reduced A-α-[SiW\(_9\)Mo\(_3\)O\(_{40}\)]\(^{2−}\) Anions**

<table>
<thead>
<tr>
<th>anion</th>
<th>spin polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-[SiW(_9)Mo(<em>3)O(</em>{40})](^{2−})</td>
<td>0.20</td>
</tr>
<tr>
<td>A-[SiW(_9)V(<em>3)O(</em>{40})](^{2−})</td>
<td>0.15</td>
</tr>
<tr>
<td>A-[SiW(_9)Nb(<em>5)O(</em>{40})](^{2−})</td>
<td>0.87</td>
</tr>
</tbody>
</table>

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\(^{36}\) See ref 38b for the first assignment proposed for cathodic waves in the reduction of 2:18 anions.

Figure 3. Molecular orbitals scheme for the α-PW12 anion and the single-addenda Wells–Dawson heteropolyanions with M = W and Mo. In the latter case, we show the orbitals associated to the $D_{3h}$ and $D_3$ structures. The orbitals in frames are those localized on the polar triads of the corresponding Wells–Dawson anions.

Table 2. Percentile Contributions of Belt and Cap Metal Centers to the LUMO, LUMO+, and LUMO+2 for Several Wells–Dawson Anions

<table>
<thead>
<tr>
<th>anion</th>
<th>sym</th>
<th>belt</th>
<th>cap</th>
<th>belt</th>
<th>cap</th>
<th>belt</th>
<th>cap</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_2W_{18}$</td>
<td>$D_{3h}$</td>
<td>70</td>
<td>53</td>
<td>20</td>
<td>48</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_2Mo_{18}$</td>
<td>$D_{3h}$</td>
<td>62</td>
<td>1</td>
<td>9</td>
<td>22</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>$P_2W_{18}V_1$</td>
<td>$C_{3v}$</td>
<td>13</td>
<td>60</td>
<td>0</td>
<td>55</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>$P_2Mo_{18}V_3$</td>
<td>$C_{3v}$</td>
<td>36</td>
<td>33</td>
<td>0</td>
<td>39</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>$P_2W_{18}(Mo_3)$</td>
<td>$C_{3v}$</td>
<td>70</td>
<td>2</td>
<td>55</td>
<td>15</td>
<td>49</td>
<td>19</td>
</tr>
</tbody>
</table>

terminal bonds should not alter the reduction properties discussed in the present work since they essentially would affect the $d_{xy}$- and $d_{xz}$-type orbitals that are not the lowest ones.

$W$–$D$ anions present the typical MO arrangement of HPAs, where the oxo band and the empty set of $d_{xy}$ metal orbitals are perfectly separated. The redox properties of a POM are closely related to the relative energy and composition of the lowest unoccupied orbitals. In an $\alpha$-Keggin anion, the twelve metals are equivalent and, therefore, they all have the same probability of trapping the additional electron after the cluster has been reduced. In an $\alpha$-Keggin, the formal substitution of three octahedrons by another PM$_9$ unit breaks the equivalence of all metals and a direct consequence is that the metallic orbitals in the $W$–$D$ and Keggin anions are slightly different. Figure 3 contains an energy diagram for the lowest unoccupied orbitals of 1:12 and 2:18 tungstates and molybdates and Table 2 gives percentile metal contributions to the LUMO, LUMO+, and LUMO+2 for all the $W$–$D$ anions studied. All these unoccupied orbitals, like in the Keggin anions, are formally symmetry-adapted $d_{xy}$-tungsten orbitals with some antibonding participation of the oxygen orbitals. Under the constraints of the $D_{3h}$ point group, their symmetries are $a_1''$, $e''$, and $e'$, respectively. The contribution of cap and belt metals to these orbitals is unequal; the $d_{xy}$-orbitals centered on the belt metals are the major contributors to the LUMO and LUMO+. When the energy of the orbital increases, the participation of the cap-centered atomic orbitals also increases (from $\sim$1% in the LUMO to $\sim$48% in the LUMO+2 in the tungstate and to $\sim$40% in the molybate).

A 3D representation of the $a_1''$ orbital (Figure 4) shows that the LUMO is only localized over the belt tungsten. This orbital appears at 2.25 eV above the occupied oxo band and 0.55 eV lower than the degenerate LUMO of $e'$ symmetry in the PW$_{12}$ anion of $T_d$ symmetry. The metallic orbitals in PW$_{12}$ and P$_2W_{18}$ have an antibonding character between the metal and oxygen orbitals but also between two adjacent metals. The $M$–$M$ antibonding interaction is lower when the two adjacent metals belong to different PW$_6$ moieties (the metal–metal distances are longer), and therefore, the $d_{xy}$-type orbitals delocalized among the equatorial tungstens have lower energies than the corresponding orbitals in the Keggin structure. Exactly the same behavior occurs in the molybdate. 1.47 eV is the relative energy of the LUMO in the $D_{3h}$ $P_2Mo_{18}$ anion, an energy that represents a decrease of 0.56 eV with respect to the $H$–$L$ gap in PMo$_{12}$. The $\alpha$-PMo$_{18}$ anion is very interesting since it has been characterized as a chiral structure of $D_3$ symmetry, which is accompanied by a considerable stabilization of 0.32 eV (\textgreek{gamma}7 kcal mol$^{-1}$) and an enlargement of the $H$–$L$ gap to 1.89 eV, a value that is quite close to the energy gap of 2.03 eV found for PMo$_{12}$. In general, the transformation of a PM$_{12}$ into a P$_2M_{18}$ decreases the $H$–$L$ gap more in tungstates than in molybdates (Figure 3).

The redox properties of heteropolyanions are closely related to the energy and composition of the LUMO. According to the orbital diagram in Figure 3, the first reduction in the $W$–$D$ anions should take place in the belt region. Calculations conducted on the reduced structures confirmed this hypothesis and the ground state for the single-reduced $P_2W_{18}$ is a $2\Delta_{1''}$ with 98% of the spin density localized over the belt metals (Table 3). The first excited state ($2E''$) has the spin density essentially localized over the belt metal centers (87%) and lies at 0.30 eV above the ground state. The reduction in the cap sites involves the addition of one electron to the LUMO+2 ($e'$) and the associated state $3E'$ is 0.84 eV higher in energy than the ground state. The spin polarization for $E'$ is 0.69 alpha.

of the VV ion \( \text{P}_2 \text{W}_{18} \), there is an inversion in the order of belt/cap d
\( \tilde{\text{A}}_1 \) among the twelve belt centers. For the analogous molybdate
\( \text{P}_2 \text{Mo}_{15} \), show that the metallic electron is effectively trapped by
the vanadium centers. In the analogous vanadomolybdate heteropolyanion, there is
considerable competition between vanadium and molybdenum orbitals. As Table 2 shows, the LUMO of e
symmetry in \( \text{P}_2 \text{Mo}_{13} \text{V}_3 \) is not localized on one of the regions of the molecule
and the participation of belt Mo (36%) and cap V (33%) orbitals is similar. The next metallic orbital of a2 symmetry is only
separated from the LUMO by 0.19 eV and is basically a belt orbital (59%). This competition between Mo and V orbitals
yields a spin density distribution in the reduced complex of 0.55 e for cap V atoms and 0.44 e for belt Mo atoms. The energy
difference between the two states \( ^2 \text{E} \) and \( ^2 \text{A}_2 \) was computed to be
only 0.18 eV. This competition is still more important in
\( \text{P}_2 \text{W}_{18} \text{V} \) since those two states associated to the first reduction in cap
(\( ^2 \text{E} \)) and belt (\( ^2 \text{A}_2 \)) sites were found degenerate, a result
that does not fully match with the fact that the first reductions in \( \text{P}_2 \text{W}_{18} \text{Mo}_3 \) are restricted to the Mo centers.42,43 Although
the origin of this discrepancy is unclear, we believe that present
electron delocalized among the six cap tungsten atoms and 0.26 e among the twelve belt centers. For the analogous molybdate
structure, the energy associated to the belt (\( ^2 \text{A}_1 \)) and cap (\( ^2 \text{E} \))
reductions differs by 0.69 eV for the \( \text{D}_{3h} \) isomer (exactly the energy gap between the LUMO and the LUMO+2). In the D1
form, the separation between these MOs is the same, which suggests that the energy difference between both site reductions
should be very close to the value obtained for the \( \text{D}_{3h} \) form. All these results fully agree with the experimental data of
Pope40b and Contant23 who demonstrated that equatorial sites
are more easily reduced than polar sites.

Effect of the Chemical Substitution on the Redox Properties of the Wells–Dawson Anions. If we wish to invert the
traditional belt/site reduction order, a more electronegative ion must be inserted in the polar region. \( \text{P}_2 \text{W}_{15} \text{V}_3 \) and \( \text{P}_2 \text{Mo}_{15} \text{V}_3 \) are suitable anions for illustrating this phenomenon. In these
two clusters, the three vanadium atoms occupy the three cap sites of one \( \text{P}_6 \text{M}_6 \) moiety. Calculations were carried out using
the restrictions of the \( \text{C}_{3v} \) symmetry group. Now, two factors—
the most favorable belt position and the higher electronegativity
of the VV ion—strongly compete to capture the additional electron. When three vanadins replace three cap tungstens in
\( \text{P}_2 \text{W}_{15} \), there is an inversion in the order of belt/cap \( \text{d}_{xy} \)-like orbitals. The degenerate orbital of e symmetry (e in
the unsubstituted species), mainly centered on the cap region, turns out to be the LUMO in the substituted molecule and appears
well separated (0.50 eV) from the next two orbitals of a2 and e
symmetries, which are basically d–W (belt) orbitals (Figure 5). According to this orbital ordering, the first reduction occurs
in vanadium cap orbitals and the energy difference between the
two site reductions (\( ^2 \text{E} \) – \( ^2 \text{A}_2 \)) was 0.33 eV. The spin
polarization for the \( ^2 \text{E} \) ground state of \( \text{P}_2 \text{W}_{15} \text{V}_3 \) Ie confirms
that the additional electron is essentially located on the vanadium centers (Table 3). We did not study the substitution in the

<table>
<thead>
<tr>
<th>( \text{sym} )</th>
<th>( \text{belt} )</th>
<th>( \text{cap} )</th>
<th>( \text{belt} )</th>
<th>( \text{cap} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{P}<em>2 \text{W}</em>{15} )</td>
<td>( \text{D}_{3h} )</td>
<td>0.98</td>
<td>-0.03</td>
<td>0.00</td>
</tr>
<tr>
<td>( \text{P}<em>2 \text{Mo}</em>{15} )</td>
<td>( \text{D}_{3h} )</td>
<td>0.89</td>
<td>-0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>( \text{P}<em>2 \text{W}</em>{15} \text{V}_3 )</td>
<td>( \text{C}_{3v} )</td>
<td>0.18</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>( \text{P}<em>2 \text{Mo}</em>{15} \text{V}_3 )</td>
<td>( \text{C}_{3v} )</td>
<td>0.44</td>
<td>0.55</td>
<td>0.00</td>
</tr>
<tr>
<td>( \text{P}<em>2 \text{W}</em>{15} \text{Mo}_3 )</td>
<td>( \text{C}_{3v} )</td>
<td>0.34</td>
<td>0.61</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Figure 5. Molecular orbital diagram for the cap trisubstituted \( \text{P}_2 \text{W}_{15} \text{V}_3 \)
and \( \text{P}_2 \text{Mo}_{15} \text{V}_3 \) heteropolyanions.

Table 3. Spin Densities on Belt and Cap Metal Centers (\( \alpha-\beta \)) and Relative
 E (in eV) for the First Three Lowest States in Several Single-Reduced Wells–Dawson Anions

anion \([\text{V}_{10}\text{O}_{28}]^{6-}\) showed that the oxygen bonded to three vanadiums is more basic than bridging oxygens and the terminal oxygens are the least basic sites. From the theoretical point of view, the topology of the molecular electrostatic potentials (MEP) proved to be very useful for detecting the most electrophilic regions of a POM. Electrophilic species will tend to minimize its potential energy by approaching as much as possible a minimum of the MEP distribution.

Figure 6 shows three views of the MEP distribution on a 3D surface for the mixed anions SiW\(_9\)M\(_3\) (M = Mo and V). The color of the electronic density isosurface (\(\rho = 0.017\) e/\(\text{ua}\)) is a function of the MEP value. In the figure, red identifies regions in which the electrostatic potential is negative (nucleophilic regions) and blue denotes positive or less negative electrostatic potential regions (electrophilic sites). When tungstens are substituted by molybdenums in SiW\(_{12}\), the electronic reorganization is quite small and the basicity of the substituted anion is not very different from that of the single-addenda anion. Clearly, bridging oxygens are generally more basic than terminal oxygens in the MEP of SiW\(_9\)Mo\(_3\) since the regions close to the bridging oxygens. In Figure 6, the red color is darker in the domains of OV\(_2\) oxygens is not a good position for protonation. Calculating the basicity scale in SiW\(_9\)V\(_3\): OV\(_2\) > OW\(_2\) > OV\(_2\) > OW\(_2\) > OW, the difference in the proton affinity between the most and least basic sites being ~30 kcal \(\text{mol}^{-1}\). This is ~10 kcal \(\text{mol}^{-1}\) greater than in tungstomolybdate anion.

A proton residing in a bridging oxygen OM\(_2\) with M’ = W, Mo, or V and on a terminal OM’ has energy differences, according to present DFT calculations, that range between 9 and 20 kcal \(\text{mol}^{-1}\), a considerable amount of energy but significantly lower than the 71 kcal \(\text{mol}^{-1}\) suggested by Davis et al. through model clusters. These authors, however, used calculations of triprotonated H\(_3\)PM\(_{12}\) clusters to determine a reliable proton affinity difference between the bridging oxygens in PM\(_{12}\) and PW\(_{12}\) of 9 kcal \(\text{mol}^{-1}\), a value that is similar to the ~6 kcal \(\text{mol}^{-1}\) computed in the present work for the mixed tungstomolybdate cluster. When the proton attaches to a bridging oxygen, there is an additional stabilization via a hydrogen bond with the nearest bridging oxygen. In H–OM\(_2\), the H is bonded to OM\(_2\) with a bond length of 0.99 Å and the distance to OW\(_2\) is 2.03 Å. The conformation with the H oriented away from the molecular framework is notably higher in energy, more than 10 kcal \(\text{mol}^{-1}\). This additional stabilization is similar in H–OM\(_2\) and H–OW\(_2\) and, therefore, does not modify their relative stability, but it is an important factor in the difference of affinity between a proton residing on a terminal and in a bridging oxygen.

### Solvent Effects

In the discussions above, we have implicitly assumed that the anions were in the gas phase with neither

### Table 4. Relative Protonation Energies (in kcal \(\text{mol}^{-1}\)) for All the Distinct External Oxygens of A-\(\alpha\)-(SiW\(_9\)Mo\(_3\)O\(_{28}\))\(^{6-}\), with M = Mo and V

<table>
<thead>
<tr>
<th>M</th>
<th>site</th>
<th>relative energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>OM(_2)</td>
<td>–4.9</td>
</tr>
<tr>
<td></td>
<td>OM(_2)W</td>
<td>–1.2</td>
</tr>
<tr>
<td></td>
<td>OW(_2)</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>OW</td>
<td>+11.0</td>
</tr>
<tr>
<td></td>
<td>OM(_2)</td>
<td>+15.0</td>
</tr>
<tr>
<td>V</td>
<td>OV(_2)</td>
<td>–12.4</td>
</tr>
<tr>
<td></td>
<td>OW(_2)</td>
<td>–1.4</td>
</tr>
<tr>
<td></td>
<td>OW(_2)</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>OV</td>
<td>+5.6</td>
</tr>
<tr>
<td></td>
<td>OW</td>
<td>+19.2</td>
</tr>
</tbody>
</table>


For a better comparison between the two clusters, the zero-energy protonation site was arbitrarily chosen to be OW\(_2\).

energies of H–OM\(_2\) and H–OW\(_2\) isomers were computed to be 19.8 and 15.9 kcal \(\text{mol}^{-1}\) above the energy of H–OM\(_2\), respectively. These results are consistent with the acidity order of HPAs, for which tungstates are slightly more acidic than molybdates.
counterions nor solvent molecules. It is well known that highly charged title anions do not exist in the gas phase and that the external field generated by the counterions and the solvent is crucial to stabilize the POMs. In solution, many of the properties of the POMs depend on the concentration, the ionic strength, the pH of the solution, and so forth. At present, it is still not possible to take all these factors into account in a quantum chemistry study. However, a first-order approximation for dilute solutions is to model the solvent effect by a polarizable continuum.

Let us take, for example, the Keggin anion \([\text{PW}_{12}\text{O}_{40}]^{3-}\). In the gas phase, the molecular orbitals are very high in energy because of the large negative charge of the anion. In general, POMs may be viewed as neutral cages encapsulating an anion in its interior;\(^1,8\) this is the so-called clathrate model that allows \([\text{PW}_{12}\text{O}_{40}]^{3-}\) and \([\text{PW}_{18}\text{O}_{62}]^{6-}\) to be reformulated as \([\text{PO}_4]^{3-}\text{@}\text{W}_{12}\text{O}_{36}\) and \([\text{PO}_4]^{6-}\text{@}\text{W}_{18}\text{O}_{54}\), respectively. The unoccupied metallic band of the neutral \(\text{W}_{12}\text{O}_{36}\) and \(\text{W}_{18}\text{O}_{54}\) cages appears very low in energy. The LUMO lies near \(-6.5\) eV in both frameworks. The encapsulation of the phosphate anions in the interior of the neutral cages shifts all the molecular orbitals of the POM toward higher energies. Hence, the absolute energies of the frontier orbitals in the 1:12 tungstate are \(+0.06\) eV and \(+2.85\) eV, respectively. If \(\text{W}_{12}\text{O}_{36}\) encapsulates a silicate, with a charge of \(-4\), the shift is even more considerable but the \(\text{H}–\text{L}\) gap is still independent of the total charge of the encapsulated anion. We kept in mind that POMs are easily reducible chemical species and, therefore, the energy of the lowest unoccupied orbitals must be low enough to accept the incoming electron. The crystal field in the solid state\(^50\) and the solvent molecules in dilute solutions stabilize the anion, placing the molecular orbitals at the appropriate level. Chart 1 gives the energy of some frontier orbitals for several clusters in water solution and gas phase (in parentheses). There is a considerable decrease in MO energies after the solvation and the magnitude of this decrease parallels the charge of the anion. In Chart 1, the lowest metallic orbitals and particularly the LUMO appear at quite negative energies (about \(-4\) eV). This is a necessary condition for an easy reduction.

It is well known that although \(\text{P}_2\text{W}_{18}\) has a larger charge it is more oxidant than \(\text{PW}_{12}\). In the gas phase, the process

\[
[\text{PW}_{12}\text{Ie}]^{4-} \rightarrow [\text{PW}_{18}\text{Ie}]^{6-} \rightarrow [\text{PW}_{12}\text{Ie}]^{3-} + [\text{PW}_{18}\text{Ie}]^{1-}
\]

is highly endothermic (\(\Delta E = +5.07\) eV) because, in absolute value, the LUMO in the \(\text{W}–\text{D}\) anion has much greater energy. Consequently, in the absence of external fields, the extra electron simply prefers to go to the least charged Keggin anion. Otherwise, in solution, the frontier orbitals have similar energies (Chart 1) and the process becomes slightly exothermic (\(\Delta E = -0.11\) eV). We checked whether the inner reduction properties of \(\text{W}–\text{D}\) anions are affected by the solvent. The difference in the stability of \(\text{P}_2\text{W}_{18}\text{Ie}\) reduced at a polar site and \(\text{P}_2\text{W}_{18}^-\text{Ie}\) reduced at an equatorial site is not altered by the presence of the solvent. We also did not observe any difference in the relative stability of the reduced anions of the mixed cluster \(\text{P}_2\text{W}_{18}\text{Ie}\text{V}_4\). These results are consistent with the almost isotropic field generated by the continuum model that modifies the absolute MO energies but does not change their relative values.

Therefore, in the absence of short intermolecular contacts, the study of isolated anions is enough to understand many redox properties of POMs. Often, the properties of a POM may simply be described by the electronic properties of the corresponding neutral cage; for example, the difference in the reduction energy between the polar and equatorial sites in the neutral cage \(\text{W}_{18}\text{O}_{54}\) was computed to be \(0.71\) eV, a value that is very similar to the energy difference computed for the complete cluster \([\text{PO}_4]^{6-}\text{@}\text{W}_{18}\text{O}_{54}\), \(0.84\) eV.

Finally, we shall briefly discuss the effect of protonation on the redox properties of a POM. In particular, we reanalyzed the reduction of the tungstovanadate \(\text{SiW}_9\text{V}_3\) after protonation of one of the bridging \(\text{O}_2\text{V}\) oxygens. In the unprotonated species, the reduction involves the addition of one electron to a degenerate orbital delocalized over the three vanadium centers. Because of the \(C_{3v}\) molecular symmetry, the three vanadiums are equivalent and so the metallic electron is equally shared with a spin population of \(0.35\) e per vanadium. The protonated form retains only one symmetry plane, and so the doubly degenerate LUMO in the unprotonated form splits into two orbitals of symmetry \(\alpha'\) and \(\alpha''\). Orbital \(\alpha'\) is \(0.83\) eV lower in energy than \(\alpha''\) and has a larger participation of the \(V_2\) \(d\)-orbitals (Chart 2). As a result, the reduction yields an asymmetric distribution of the spin density between the three vanadiums, \(0.28\) e (\(V_2\)) and \(0.51\) e (\(V_1\)). In summary, the protonation process changes the chemical nature of the \(V\)-substituted part of the molecule, making the vanadium atoms different from one other.

Conclusions and Summary

DFT calculations were carried out on a series of mixed Keggin and Wells–Dawson (\(\text{W}–\text{D}\)) anions so that their redox and basicity properties could be analyzed. The unoccupied metallic orbitals of POMs without paramagnetic ions, in general, and these anions, in particular, are well separated in energy from the band of occupied oxo orbitals. Two factors govern the redox properties of a POM: the energy and composition of the lowest unoccupied \(\alpha\)-type orbitals

\([\text{PO}_4]^{6-}\text{@}\text{W}_{18}\text{O}_{54}\), \(0.84\) eV.

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easily reduced, the additional electron going to a Mo orbital. The same phenomenon takes place when a V$^5^+$ replaces a W$^{6+}$: the extra electron goes to the vanadium center. Mixed tungstoniobiates behave differently since niobium orbitals are inserted into the tungsten band and the reduction of SiW$_9$Nb$_3^-$, for example, yields the blue species SiW$_9$Nb$_3^-\text{Ie}$ and not the cluster SiW$_9$Nb$_{12}\text{Vi}^2\text{NbVI}$.

W$^-$D P$_2$M$^{18}$ structures formally consist of two PM$_9$ halves linked by almost linear M$-$O$-$M bonds ($\approx$162$^\circ$). In the most compact Keggin anion, all M$-$O$-$M angles range between 125 and 150$^\circ$. This structural difference determines the electronic and redox properties of the W$^-$D anions. The LUMO in P$_2$W$_{18}$ is an orbital that is formally delocalized over the belt addenda atoms. Consequently, the reduction preferentially occurs in the belt sites. The alternative reduction on the cap sites requires 0.84 eV more. For the analogous 2:18 molybdate, the reduction 0.69 eV. When three V’s replace the three polar W’s in one and the reduction occurs in the vanadium center located at the cap site. If molybdenums occupy the cap sites, the competition between those two factors is heavier.

The bridging oxygens are the most basic sites in single-addenda and mixed Keggin anions. The calculations carried out on protonated forms of the mixed clusters SiW$_9$V$_3$ and SiW$_9$Mo$_3$ suggest the following basicity scale for the various terminal and bridging oxygen types: OV$_2^- > OMo_2^- > OW_2^- > OV > OW > OMo$. The difference in the proton affinity between the terminal and bridging oxygens ranges between 6 and 32 kcal mol$^{-1}$.

Many POMs can be considered as supramolecular species since the host cage and the encapsulated guest are clearly identifiable. Lindqvist, Keggin, and W$^-$D structures have also been formulated as clathrate structures like O$_2^{-}$@[M$_6$O$_{18}$]$^{(m-2)}^-$, [XO$_4$]$^{n-}$$\text{Ie}$@[M$_{12}$O$_{36}$]$^{(m-n)}^-$, and [XO$_4$]$^{n-}$@[M$_{18}$O$_{54}$]$^{(m-2a)}^-$. The incorporation of the solvent in the calculations by means of a continuum model represents a first step in the analysis of the stabilizing effects produced by the external field on the anion. Studies are underway to include the water molecules explicitly in the calculations by means of molecular dynamics in combination with the DFT methodology. We hope that in the near future the better knowledge of the role that the solvent molecules and the counterions play in the polyoxometalate chemistry will allow computing absolute redox potentials as well as absolute protonation energies.

Acknowledgment. All the calculations have been carried out on workstations purchased with funds provided by the DGICYT of the Government of Spain and by the CIRIT of Generalitat of Catalunya (Grants n˚ PB98-0916-C02-02 and SGR01-0315). We thank Y. Jean and L. Nadjo for sharing the information of their unpublished work. We also thank the referees for their comments and suggestions.

Supporting Information Available: The computed xyz coordinates for several structures. This material is available free of charge via the Internet at http://pubs.acs.org.

JA020407Z