Ab Initio Study of the Relative Basicity of the External Oxygen Sites in M₂W₄O₁₉⁴⁻ (M = Nb and V)

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Geometry optimizations were carried out for the cis and trans forms of Nb₂W₄O₁₉⁵⁻. The energy difference between the two conformations was found to be 2.3 kcal mol⁻¹, the structure in which the two Nb atoms are in the cis formation being the most stable. Several isomers of the Nb₂W₄O₁₉H₃⁻ anion were also studied for the cis form, suggesting that the oxygen bonded to two Nb atoms is the most basic center. The energetic determination of the oxygen basicities in hexametalates was compared with the indirect and less computationally demanding methodology based upon molecular electrostatic potential (ESP) distributions. The ESP distribution in HNb₂W₄O₁₉⁻ suggests that a second proton should fix onto an OW₂ oxygen site and that the ONb terminal O’s remain the most basic terminal centers. In V₂W₄O₁₉⁵⁻, the unique OV₂ was identified as the most basic center. Although at variance with the niobotungstate anion, the most basic center does not support the highest net negative charge. The terminal OV oxygen sites were found to be the least basic terminal O’s.

Introduction

Most of the current interest in polyoxometalates derives from the fact that they are relevant to catalysis, analytical chemistry, biology, medicine, and material science.¹⁻⁴ Their properties are related to their high charges and the strong basicity of the oxygen surfaces. Four isopolyanions are known to have a hexametate structure, M₆O₁₉⁻⁵.¹⁻⁶ These distributions had been obtained from an ω⁻¹ ESP and determining the charge concentrations near the oxygen sites. These distributions had been obtained from an ω⁻¹ ESP and determining the charge concentrations near the oxygen sites.

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ab initio SCF wave function. The investigations on the decavanadate anion showed that the basicity of the oxygen atoms in polyoxometallates is directly related to the oxygen type. The relative oxygen basicity order was found to be \( \text{OV}_3 \) (triple-bridging) oxygen > \( \text{OV}_2 \) (double-bridging) oxygen > \( \text{OV} \) (terminal) oxygen. However, the basicity difference between two oxygen atoms connected to the same number of metal centers is quite small, and therefore, their classification is more difficult. The main goal of the present study is to directly determine a basicity scale for double-bridging oxygens in \( \text{M}_2\text{W}_4\text{O}_{19}\text{H}_3^+ \) for \( \text{M} = \text{Nb} \) (I) and V(2) by calculating the relative energy of the corresponding protonated anion. The relatively small \( \text{M}_2\text{O}_{19} \) framework allows the geometries for \( \text{M}_2\text{W}_4\text{O}_{19}\text{H}_3^+ \) and \( \text{M}_2\text{W}_4\text{O}_{19}\text{H}^+ \) to be computed. The electrostatic potentials and the Laplacian of the charge density distributions are also derived for anions 1 and 2 and analyzed in connection with the relative energies of the protonated anions.

### Computational Details

The geometries and energies were determined at the Hartree–Fock level, using the TURBOMOLE program. Since the metal atoms are formally \( \sigma \), correlation effects are not of the utmost importance, and the HF approach should be appropriate. The basis sets used for geometry optimizations (basis set I) are defined as follows: V, Nb, and W, a Hay and Wadt effective core potential\(^\text{17} \) models the potential of the inner electrons. The 13 valence electrons of V and Nb are described by a \( (8s, 5p, 5d) \) and \( (8s, 6p, 4d) \) basis set, respectively, contracted into \( [3s/3p/2d] \).\(^\text{17} \)

Electrostatic potentials were computed for planar grids of points defined in planes containing several oxygen sites. Minima in the ESP distribution were located by gradient procedures. The topological properties of the charge density were determined using the AIMPACK package of programs.\(^\text{20} \) Finally, the integrations of the charge density were carried out with ATOMIC—VECSURF,\(^\text{21} \) a modified version of the original PROAIM program.\(^\text{20} \)

To check if the geometries were well reproduced at the proposed level, we optimized the \( \text{W}_6\text{O}_{19}\text{H}_3^+ \) anion structure in \( \text{O}_h \) symmetry with basis set I. From the bond distances given in Table 1, we can see that \( \text{W} = \text{O}_h \) (O\(_h\) terminal oxygen) and \( \text{W} = \text{O}_h \) (O\(_h\) bridging oxygen) computed bond distances are in good agreement with the X-ray parameters. The discrepancies are less than 0.02 Å. For the weaker interaction between the tungsten atoms and the central oxygen, the calculated distance is 2.403 Å, 0.07 Å longer than the averaged \( \text{W} = \text{O} \) distances (O\(_c\) central oxygen). An interpretation of the structure of the inclusion complexes \( \text{R} = \text{CN} \subset (\text{V}_3\text{O}_3)^4^- \) from electrostatic potentials has also been carried out at the HF level by Benard and co-workers.\(^\text{22} \)

Polyoxometalate anions most often are highly charged species, which are only observed in solution or in solid phase. The presence of counterions in the vicinity of the anion raises the potential and stabilizes the cluster. Recently, a procedure has been developed by Benard and co-workers in order to model the crystal field in studies of polyoxometalates.\(^\text{21} \) The procedure reproduces the electrostatic potential generated by the crystal by means of an isotropic field created by a charged sphere located at a large distance from the cluster. That model was used in the study of the interaction energy between the anionic host \( \text{H}_2\text{O}_2\text{O}_9\text{H}^+ \) and the \( \text{Cl}^- \) guest anion and in the analysis of the redox properties of the highly reduced Keggin anion \( \text{PMo}_{12}\text{O}_{40}(\text{VO})_2\text{H}^+ \).\(^\text{21} \)

In both cases, the calculations showed that the inclusion of the crystal field dramatically decreases the energy of the frontier orbitals but does not alter the electronic structure of the free anion. Such a procedure, however, requires a good X-ray description of the crystal structure including an unambiguous characterization of the counterions. This prerequisite was not fulfilled in the present case because of disorder problems in the crystal structure. The authors think, however, that the inclusion of the counterion effects would not modify the main conclusions in the present work since they rely on the relative properties of the distinct oxygen sites in an anion.

### Results and Discussion

**Structure of \( \text{Nb}_2\text{W}_4\text{O}_{19}\text{H}^+ \).** The optimal structures and their relative energies for cis and trans configurations of \( \text{Nb}_2\text{W}_4\text{O}_{19}\text{H}^+ \) were computed. The optimized trans structure with \( D_{4h} \) symmetry was found to be 1 kcal mol\(^{-1} \) less stable than the cis isomer with \( C_{2v} \) symmetry. Single point calculations carried out with basis set II increased the energy gap in favor of the cis form to 2.3 kcal mol\(^{-1} \). The main difference between the \( D_{4h} \) and \( C_{2v} \) structures is the presence of a permanent dipole moment in the isomer where the Nb atoms are cis. These relative energetic values are in agreement with IR and RAMAN studies, which suggest that the symmetry of \( \text{Nb}_2\text{W}_4\text{O}_{19}\text{H}^+ \) is \( C_{2v} \).\(^\text{24} \) The \( C_{2v} \) geometry was also found to be the most stable form for the isoelectronic tungstovanadate anion 2. The energy difference between the cis and trans forms is 3 kcal mol\(^{-1} \) with basis set I.\(^\text{25} \)

Bond distances for 1 are collected in Table 2. No direct structural information is available for mixed isopolyanions such as 1 since X-ray characterization of these kinds of compounds is plagued with disorder problems.\(^\text{10} \) However, good approximations to the \( \text{Nb} = \text{O} \) bond lengths may be found from the related structures of \( \text{Mn}(\text{Nb}_2\text{O}_{19})_2\text{H}^+ \) or \( \text{Nb}_{10}\text{O}_{26}^2- \). The expected distances should be \( \text{Nb} = \text{O} \) (terminal) \(~1.73\)–\(~1.76\), \( \text{Nb} = \text{O} \) (bridging) \(~1.95\)–\(2.10\), and \( \text{Nb} = \text{O} \) (central) \(~2.4\) Å.\(^\text{26} \)

From the values in Table 2 we can see that the computed \( \text{Nb} = \text{O} \) bond lengths are in the right range and that they do not differ significantly from the \( \text{W} = \text{O} \) bond distances.

**Electrostatic Potential Distributions and Relative Protonation Energies.** In Figure 2 the ESP distribution is displayed in the plane containing oxygens 1–5. Constant contour intervals (0.01 au) were selected for the plane diagram, the lowest value

### Table 1. Bond Lengths for \( \text{W}_6\text{O}_{19}\text{H}_3^+ \) Anion\(^a\)

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\(^a\) Values are in Å. O\(_t\), terminal oxygens; O\(_b\), bridging OM\(_3\) oxygens; O\(_c\), central, OM\(_2\) oxygen. \(^b\) Values averaged to O\(_h\) symmetry, ref 8.
Table 2. Bond Distances (in Å) Computed for Nb₂W₄O₁₉⁴⁻ and V₂W₄O₁₉⁴⁻.²,³

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See Figure 1 for oxygen atom numeration. ² Determined from density integration of the atomic basin (Bader’s method). ³ The absolute value is −0.5381 au. ⁴ The absolute value is −0.5144 au. ⁵ Basis set I.

Figure 2. Section of the electrostatic potential (ESP) for Nb₂W₄O₁₉⁴⁻: Nb₂W₂ plane containing one O₁, one O₂, two O₃, two O₄, and two O₅ oxygen sites; highest contour, −0.424 au; lowest contour, −0.538 au; contour interval, −0.011 au. The black dots denote the positions of the distinct ESC minima in this plane. The deepest minimum is located in the vicinity of the ONb₂ oxygen.

starting at −0.538 au. In the vicinity of each oxygen site, a minimum in the ESP distribution was detected. The deepest minimum appears facing O₁, the unique ONb₂ oxygen. The minima associated with O₂ (an OW₂ oxygen site) and O₃ (an ONbW oxygen site) are only 5.3 and 6.4 kcal mol⁻¹ higher, respectively, than that of the potential well connected with O₁. The minima associated with the terminal oxygen sites 4 and 5 are higher than that of O₁ by 16 and 27 kcal mol⁻¹, respectively. This behavior is widespread in polyoxoanions: minima connected with terminal oxygens are markedly higher than those associated with bridging oxygens. This tendency is also followed by the potential wells detected near O₆, O₇, and O₈. All the ESP minima found for the distinct oxygen sites are summarized in Table 3.

Using basis set I, we analyzed six HNb₂W₄O₁₀⁻² isomers, ³, corresponding to the protonation sites of the distinct external oxygen atoms on the Nb₂W₂ plane and the protonation at O₈. One of the constraints was that all geometries computed for ³ had to retain a symmetry plane; therefore, for the additions at the O₅, O₆, and O₇ oxygen sites, the hydrogen atom was not allowed to bend out of the Nb₂W₂ plane. The two other possible conformations without symmetry elements were not calculated since the study of structures with C₁ symmetry (protonations at O₆ and O₇) demands an enormous computational effort. Moreover, it can be estimated that the basicities of O₆ and O₇ must be only marginally different from those of O₁ and O₂, respectively.

According to the experimental evidence the proton fixation occurs predominantly at the unique bridging ONb₂ oxygen. Consequently, the structure in which the hydrogen atom is bonded to O₁ is found to be the most stable isomer. This conformation was optimized with a C₁ symmetry but also under the constraints of the C₂ᵥ point group. The relative energy of the C₁ geometry with respect to the relative energy of the C₂ᵥ form is close to 0.5 kcal mol⁻¹, which means that the hydrogen-bonding energy is almost negligible. Some bond distances for ³ are given in Figure 3. The values in parentheses in Figure 3 represent the changes in the bond separation from the unprotonated precursor. The formation of the H−O bond leads to a considerable lengthening of the bond between the niobium atoms and the protonated oxygen (0.187 Å). The weakening of these bonds increases the interaction between the Nb atoms and all other bonded oxygens, shortening the bonding distances. Even though some W−O bond lengths in the Nb₂W₂ plane are altered by protonation, the overall distortion in the rest of the molecule is noticeably lower.

The relative energies of the H−O₂ and H−O₃ isomers (the hydrogen is bonded to O₂ and O₃, respectively) were computed to be 3.1 and 3.8 kcal mol⁻¹, respectively. In these two isomers the conformation lowest in energy has the hydrogen atom out of the Nb₂W₂ symmetry plane. The structures corresponding to the protonation of the terminal oxygen atoms 4 and 5 were also optimized. Their relative energies with respect to the most stable conformation (H−O₁) were computed to be 8.9 and 25.4 kcal mol⁻¹, respectively. Thus, the calculated relative energies, which are given in Table 3, fully confirm the estimations made by Klemperer, who proposed that the bridging oxygens are more basic than the terminal oxygens, the ONb₂ site being the most basic center. Moreover, our relative energetic data strongly suggest that in Nb₂W₄O₁₉⁴⁻, the ONb oxygen bas have basicities significantly greater than those of the terminal OW oxygens.

Table 3. Atomic Net Charges (Q), Relative Values of ESP Minima (in kcal mol⁻¹), and Relative Protonation Energies (Eₚ in kcal mol⁻¹) computed for Nb₂W₄O₁₉⁴⁻ Using Basis Set I and II

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metal

¹ See Figure 1 for oxygen atom numeration. ² Determined from density integration of the atomic basin (Bader’s method). ³ The absolute value is −0.5381 au. ⁴ The absolute value is −0.5144 au. ⁵ Basis set I.
The hexametalate framework with an \( \text{O}_2^{2-} \) anion proposed by Bader et al.\(^{27}\) consists of defining the atomic charge density around the protonated oxygen site and with the atomic charge density integration on such domains for all atoms of anion \(-\). The net charge obtained is \( +1.59 \) e for the oxygen atom located inside the cage and connected to six metal atoms. As a matter of fact, the Bader population analysis assigns net charges of \( +1.59 \) e for the oxygen atom located inside the cage and connected to six metal atoms. The hexametalate clusters \( \text{M}_6\text{O}_{18}^{2-} \) have been described as an \( \text{M}_6\text{O}_{18}^{2-} \) framework with an \( \text{O}^{2-} \) species inside the cage.\(^{28}\) The high electronic population of \( \text{O}_8 \) indicates that this description is quite appropriate. All the bridging oxygens exhibit considerable net charges (Table 3), the largest value being computed for the oxygen atom located inside the cage and connected to six metal atoms. The ESP minima associated with \( \text{O}_1 \), \( \text{O}_5 \), and \( \text{O}_3 \) are now placed above and below the oxygen core (Table 3). Therefore, the \( \text{ESP minimum} \) and to the Bader charge of the terminal oxygen site appears to be strongly correlated to the relative orbital energies of Nb and W atoms.\(^{17}\) The net charge obtained is \( +1.59 \) e for the oxygen atom located inside the cage and connected to six metal atoms. As a matter of fact, the Bader population analysis assigns net charges of \( +3.12 \) and \( +3.46 \) e to Nb and W atoms, respectively. This means that, whereas niobium atoms transferred 62% of their valence electrons to oxygens, tungsten atoms transferred 57%. These charge-transfer values confirm the high ionic character of the metal–oxygen interaction in cluster 1. Actually, the depth of the potential well facing an oxygen site increases with the negative net charge of the oxygen core (Table 3). Therefore, the relative protonation energy of an oxygen site appears to be strongly correlated to the corresponding ESP minimum and to the Bader charge of the protonated oxygen atom. This relationship indicates that the proton fixation in \( \text{NB}_2\text{W}_6\text{O}_{19}^{4+} \) is mainly driven by electrostatic forces.

The use of basis set II slightly increases the charge transfer from the metal atoms to the oxygen cores but does not modify the basicity scale of the distinct oxygen sites in anion 1. The inclusion of diffuse orbitals and polarization functions in all oxygen centers, however, diminishes the basicity difference of the oxygens. With basis set II, the electron population difference between the most and least populated external oxygen atoms (\( \text{O}_1 \) and \( \text{O}_5 \), respectively) is \(-0.13 \) e, whereas the corresponding value with basis set I is \(-0.21 \) e. The effect of polarization functions appears to be quite important in the ESP distribution around the oxygen sites. With the smaller basis set, the ESP distribution exhibits a minimum per oxygen. All these ESP minima become saddle points which connect two new minima when the extended basis set II is used. The ESP minima associated with \( \text{O}_1 \), \( \text{O}_2 \), and \( \text{O}_3 \) are now placed above and below the \( \text{NB}_2\text{W}_2 \) plane. The ones associated with oxygens 6 and 7 are also out of the pseudo-\( \text{NB}_2\text{W}_3 \) planes. Drawing 5 displays the XOX angles (\( \text{X} = \text{ESP}_{\text{min}} \)) and the relative energy values of the ESP saddle points with respect to the ESP local minima for the most basic oxygens (\( \text{O}_1 \) and \( \text{O}_2 \)).

In the case of the ONb oxygen, the XOX angle is \( 130^\circ \), and the energy difference between the minima and the saddle point is only \( 1.7 \) kcal mol\(^{-1} \). These values suggest that if the reoptimization of the most stable isomer of \( \text{HNb}_2\text{W}_7\text{O}_{19}^{3-} \) (the hydrogen atom is bonded to \( \text{O}_1 \)) with basis set II were carried out, the most stable conformation for this isomer should belong to the \( \text{C}_5 \) plane of symmetry point group rather than to the \( \text{C}_2 \) minimum found with basis set I. Presently, this kind of calculation is still formidable and has not been carried out. In any case, we think that the energy difference between the \( \text{C}_5 \) and \( \text{C}_2 \) conformations would not be very high. The values of the ESP stationary points found near \( \text{O}_2 \) (5) indicate that this oxygen presents a less spherical distribution of its charge density, the relative energy of the saddle point with respect to the local minima being \( +6.6 \) kcal mol\(^{-1} \). Therefore, any protonation of this oxygen should take place out of the \( \text{NB}_2\text{W}_2 \) plane. At variance with the minima corresponding to bridging oxygens, the two ESP minima connected with \( \text{O}_4 \) and \( \text{O}_5 \) remain on the \( \text{NB}_2\text{W}_2 \) plane when calculations are carried out with basis set II. The minima associated with \( \text{O}_4 \) are located on the symmetry plane that contains this terminal oxygen. The energy difference between the ESP saddle point and the corresponding minima is about \( 5 \) kcal mol\(^{-1} \) for all terminal oxygens.
Basicity of the External Oxygen Sites in M₂W₄O₁₉⁴⁻

Figure 4. Section of the electrostatic potential (ESP) for HNb₂W₄O₁₉³⁻: Nb₂W₂ plane containing one O₁, one O₂, two O₃, two O₄, and two O₅ oxygen sites; highest contour, −0.182 au; lowest contour, −0.405 au; contour interval, −0.016 au. The black dots denote the positions of the distinct ESP minima in this plane.

ESP Distribution in HNb₂W₄O₁₉³⁻. The distribution of the electrostatic potential on the plane containing the hydrogen atom and sites O₁ and O₂ is shown in Figure 4. The comparison between Figures 2 and 4 shows that the proton fixation modifies the ESP distribution near the protonated oxygen site quite considerably, but modifies the ESP distribution very little in the proximity of the other oxygens. The absolute values, however, are lower than those of the unprotonated partner since the depth of the potential wells correlates with the anion charge. In less charged anions, the protonation effect is quite different. For instance, in the case of the divalent Mo₆O₁₉²⁻, the fixation of a proton induces an important modification of the ESP distribution of the terminal and bridged oxygen sites nearest the bridged protonated oxygen.²⁹ In the niobotungstate anion, upon protonation, the minima associated with the unprotonated bridging oxygen sites exhibit similar depth, the energy difference being lower than 0.2 kcal mol⁻¹. Another interesting feature of Figure 4 is the presence of a quite deep minimum close to the oxygen site which is nearest to the protonated center. According to the ESP distribution, the terminal ONb site is still the most basic terminal oxygen after protonation. This minimum is less stable than the one associated with O₂ by 8.4 kcal mol⁻¹ (Table 5).

The integrated net charges confirm that protonation induces a low electronic perturbation on the cluster. According to Bader’s method, the population of the hydrogen atom is as high as 0.42 e. The corresponding depopulation of the M6 O₁₉⁻ anion is 0.85 e and 0.89 e to the bridging OV₂ oxygen, whereas the corresponding value for O₂, a bridging OW₂ oxygen, is −1.31 e. The net charges obtained for the terminal oxygens O₁ and O₂ are −0.89 e and −1.13 e, respectively. Thus, oxygens bonded to vanadium atoms support an electronic charge density lower than that for oxygens connected to tungsten atoms. The oxygen charge density in polyoxoanions depends heavily on the oxygen type and, to a lesser extent, on the specific molecule. The O₁ and O₂ net charges for instance, are identical in anions 1 and 2. Another interesting example is that of the terminal OV oxygen sites. The computed value for O₁ in V₂W₄O₁₉⁴⁻ (−0.89 e) is similar to the values reported for the decavanadate anion,¹⁵ in which net charges of −0.85 e and −0.89 e were found for the two distinct terminal oxygen sites, respectively. As in the niobotungsten anion, the inclusion of diffuse functions and d polarization orbitals in all oxygen atoms increases somewhat the charge transfer from metals to oxygens, the highest increment taking place in the terminal oxygens.

The next section will be devoted to the analysis of the ESP distribution around the external oxygen sites located on the V₂W₂ plane. The number and space distribution of the potential minima computed using basis set I is not significantly different from those obtained for anion 1. Figure 5 displays the section of the electrostatic potential for V₂W₄O₁₉³⁻ containing sites 1−5. According to the atomic charges, the deepest minimum of the ESP distribution is found in the vicinity of the O₁ site. The minima associated with the bridging OV₂ oxygen site is 4.1 kcal mol⁻¹.

Table 4. Atomic Net Charges (Q), Relative Values of ESP Minima (in kcal mol⁻¹), and Relative Protonation Energies (Eₚ) Computed for V₂W₄O₁₉³⁻ Using Basis Set I and II

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* See Figure 1 for oxygen atom numeration. † Determined from density integration of the atomic basin (Bader’s method). ‡ The absolute value is −0.5397 au. § The absolute value is −0.5829 au. ¶ Basis set I.

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<td>1.22</td>
<td>3.1</td>
</tr>
<tr>
<td>O₄</td>
<td>OM</td>
<td>−1.12</td>
<td>8.4</td>
<td>−0.84</td>
<td>36.6</td>
</tr>
<tr>
<td>O₅</td>
<td>OW</td>
<td>−1.05</td>
<td>15.1</td>
<td>−1.06</td>
<td>15.5</td>
</tr>
<tr>
<td>hydrogen</td>
<td></td>
<td>+0.58</td>
<td>+0.55</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The absolute value is −0.4093 au. † The absolute value is −0.4185 au. ‡ The hydrogen atom is bonded to O₁.

The Tungstovanadate Anion V₂W₄O₁₉⁴⁻. From NMR studies, Klemperer and Shum¹⁴ have identified the unique OV₂ oxygen in V₂W₄O₁₉³⁻, an isoelectronic anion of the niobotungstate anion 1, as the protonation site. We carried out HF calculations and geometry optimizations on V₂W₄O₁₉³⁻, 2, and on five isomers of the protonated ion using basis set I. Selected

(29) Benard, M.; Rohmer, M.-M., unpublished work.
located near the OW2 oxygen. With the largest basis set II, the ESP
the distinct ESP minima. The deepest minimum with basis set I is
remains upon protonation, its energy being 37 kcal mol

Figure 5. Section of the electrostatic potential (ESP) for V$_2$W$_4$O$_{19}^{4-}$: V$_2$W$_4$ plane containing one O$_1$, one O$_2$, two O$_3$, two O$_4$, and two O$_5$ oxygen sites; highest contour, $-0.424$ au; lowest contour, $-0.583$ au; contour interval, $-0.011$ au. The black dots denote the positions of the distinct ESP minima. The deepest minimum with basis set I is located near the OW$_2$ oxygen. With the largest basis set II, the ESP minimum near the OV$_2$ oxygen is the deepest (see text).

Figure 6. Section of the electrostatic potential (ESP) for HV$_2$W$_4$O$_{19}^{3-}$: V$_2$W$_4$ plane containing one O$_1$, one O$_2$, two O$_3$, two O$_4$, and two O$_5$ oxygen sites; highest contour, $-0.182$ au; lowest contour, $-0.405$ au; contour interval, $-0.016$ au. Dots indicate the positions of the distinct ESP minima.

protonation ($\sim$3 kcal mol$^{-1}$). The relative depth between the
stationary points associated with the OV and the OW O’s increases by 4 kcal mol$^{-1}$ due to proton fixation. According
to the present calculations, OV oxygen sites remain the least
basic terminal centers of the polyoxoanion. The most interesting
result for the HV$_2$W$_4$O$_{19}^{3-}$ anion (4) is, however, the presence
of a minimum connected to the protonated OV$_2$ oxygen site
which is 4.1 kcal mol$^{-1}$ lower than the minimum found near
O$_2$. Anion 4 was optimized in $C_{2v}$ and $C_{6v}$ symmetries. In
contrast to anion HNb$_2$W$_4$O$_{19}^{3-}$, the geometry with symmetry
$C_{2v}$, is computed to be higher in energy than the geometry in
which the hydrogen atom is allowed to bend out of the V$_2$W$_2$
plane. As a matter of fact, the minimum in the ESP
distribution found in the vicinity of protonated site O$_1$ appears
in the nonbonding region opposite the tripod formed by one
hydrogen atom and two vanadium atoms. The comparison of
the atomic net charges computed for anion 4 (Table 5) and the
charges of its precursor (Table 4) leads us to conclude that
proton fixation increases the atomic charge density of the
protonated oxygen. The net charge of the hydrogen atom is
$+0.55$ e; therefore oxygen O$_1$ is connected to three positively
charged atoms. This could explain the most basic character
predicted for O$_1$ from the ESP distribution since oxygen O$_1$
in 4 has a certain triple bridging nature. It should be pointed out
that ESP studies on HV$_2$W$_4$O$_{19}^{3-}$ were only carried out with the
smallest basis set and that the use of larger basis sets may
slightly modify the present conclusions.

The isomers corresponding to the O$_1$ and O$_2$ protonations
were optimized with basis set I. The optimization process
yielded the lowest energy for the conformation in which the
hydrogen atom is bonded to the OV$_2$ oxygen site. The energy
difference between the two isomers was found to be 5.2 kcal
mol$^{-1}$. This shows that relative protonation energies can be
computed with a relatively small basis set. At variance from
anion 1, protonation considerably modifies the ESP distribution
in the protonated hemisphere. Figure 6 shows the contour map
of electrostatic potential for the V$_2$W$_2$ plane. It can be seen
that, near the OV oxygen, only the minimum closest to O$_3$
remains upon protonation, its energy being 37 kcal mol$^{-1}$ with
respect to the energy of the minimum connected with O$_2$, the
deepest potential well on the V$_2$W$_2$ plane. The second deepest
minimum is facing the OVW oxygen site. Its relative energy,
with respect to the minimum near O$_2$, is not modified by

The final section analyses the distribution of the Laplacian
of charge density ($\nabla^2\rho$) around bridging oxygens O$_1$ and O$_2$
for anions 2 and 4. The map of Figure 7 shows that the
distribution of $\nabla^2\rho$ around the oxygen atoms exhibits a very low
polarization. The Laplacian of charge density remains close to
In Bader’s formalism, an atom is a region of real space that contains factors in determining the position and magnitude of the ESP.

The spherical symmetry for all oxygen sites, which is consistent with their high negative charge. In ionic bonds, the negatively charged atom exhibits small charge concentrations in the nonbonding region. In the case of oxygen $O_2$ which bridges between two $W$ atoms, the laplacian of $\rho$ presents two symmetric maxima in the nonbonding region above and below the $V_3W_2$ plane. These maxima of charge concentrations have a value of $-5.09 \text{ au}$ for $\nabla^2 \rho$. In the nonbonding region of the $OV_2$ site, two maxima were also found. Despite the lower negative charge of $O_1$, the corresponding value for the Laplacian of $\rho$ maxima is $-5.15 \text{ au}$. This demonstrates the role of local factors in determining the position and magnitude of the ESP.

The critical points in the charge density distribution, points where $\nabla \rho = 0$, play a prominent role in the boundary definition of an atom. In the interatomic surface of a diatomic molecule, all the gradient paths originate at the bond critical point which links the atoms of the molecule. In polyoxoanions, an example of this kind of elementary interatomic surface is found in the terminal oxygen atoms, which are bonded to only one metal center. The other atoms, however, exhibit very complicated interatomic surfaces. For example, the zero-flux surface which defines the volume of the central oxygen atom in the $M_6O_{19}$ framework contains 30 critical points (7 bond critical points, 15 ring critical points, and 8 cage points). In contrast to a previous study on $V_3O_8^{5-}$, in which the zero-flux surface for several atoms could not be established, the charge density integration was carried out for all $Nb_2W_4O_{19}^{4-}$ atoms. This was viable since an optimal geometry was used in the topological analysis of charge density.

Conclusions

In the present work we have reported the first ab initio calculations on hexametalate anions. These calculations have reproduced the geometries very well and determined the basicity of the external oxygens. Even though geometry optimizations of polyoxoanions at the ab initio–$HF$ level still require considerable computational effort, ab initio calculations can help to characterize hexametalate structures since in these kinds of compounds, the X-ray determinations often present disorder problems.

In the $Nb_2W_4O_{19}^{4-}$ anion, the deepest minimum in the ESP distribution appears near the unique ONb$_2$ oxygen site. Accordingly, and in full agreement with experimental protonation data, the conformation of lowest energy for HNb$_2W_4O_{19}^{3-}$ corresponds to the structure in which the hydrogen atom is bonded to the ONb$_2$ oxygen, the most basic nature of which may be explained by the highest net charge supported by this oxygen. In the isoelectronic tungstovanadate anion, $V_2W_4O_{19}^{4-}$, the situation is slightly different. The relative protonation energies and the ESP distribution identify the least populated bridging $OV_2$ oxygen as the most basic center. The terminal OV O’s are by far the least basic oxygen sites. The ESP distribution in HNb$_2W_4O_{19}^{3-}$ suggests that a second proton should fix onto an OW$_2$ oxygen site and that the ONb terminal O’s are still the most basic terminal centers. ESP distribution for the HV$_2W_4O_{19}^{3-}$ anion suggests that the protonated OW$_2$ oxygen has a considerable basic nature.

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Supporting Information Available: A listing of HF Cartesian coordinates for anions 1 to 4 (7 pages). Ordering information is given on any current masthead page.

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