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**17**O NMR Chemical Shifts in Oxometalates: From the Simplest Monometallic Species to Mixed-Metal Polyoxometalates

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We report a theoretical analysis on **17**O NMR chemical shifts for a family of prototypical polyoxometalate anions. The huge diversity of structures and compositions in this family of oxometalates provides a unique resource for evaluating the influence of the metal type and connectivity over the resonance of **17**O nuclei. For a set of 75 signals, we show that DFT calculations performed with the GGA-type PBE functional, including spin-orbit and scaling corrections, provide a mean absolute error <30 ppm, a small value considering that the range of δ(17O) values in these systems is ~1200 ppm. For terminal M=O oxygens, the chemical shifts primarily depend on the energy gap between π*MO and σMO orbitals. When M is in its highest oxidation state, the energy of π*MO increases as we replace M going to the left and down in the periodic table. Consequently, we must expect large energy gaps and uphill shifts for O atoms linked to more electropositive ions. Although there is not a direct relationship between δ(17O) and the negative charge of the oxygen, it is not entirely wrong to correlate atomic charge and chemical shift because the ionicity of the M–O bond, the orbital energy gap and the charge density of oxygen are related. The **17**O NMR chemical shifts move uphill with an increasing number of bound metal ions because of the larger energy gain in the involved orbitals. Finally, we explored the effect of protonation on δ(17O) in oxometalates and demonstrated that **17**O NMR can be a powerful tool to identify the site(s) of protonation at low pH.

1. Introduction

Polyoxometalates (or POMs) are discrete early transition metal oxides assembled from corner-, edge- and face-sharing [MOₙ] units, with x = 4–7 and typically M = W⁶⁺, Mo⁶⁺, V⁵⁺, Nb⁵⁺ or Ta⁷⁺.⁷ Several polyanions made of U⁶⁺, Sb⁵⁺,⁸ and Mn¹¹⁺,¹⁰ as well as late transition metals such as Pd⁴⁺, Pt⁷⁺ and Au₃³⁺,¹¹,¹² are also known. The versatility of POMs is extraordinary; they conform a family of inorganic compounds with unmatched tunable physical and inorganic properties. From the pioneering studies on the magnetic properties of atomic nuclei, it was quickly understood that the nuclear resonance frequencies depend on the chemical and electronic environment of the nuclei.¹⁷,¹⁹ This property has been used for many years and, thus, nuclear magnetic resonance (NMR) has become probably the most popular spectroscopic technique for compound characterization. Despite the fact that oxygen is one of the most important elements chemically and biologically, other nuclei such as ¹H, ¹⁷C, ³¹P, or even ¹⁸W have been prevalent in NMR studies of polynuclear systems. The reasons are manifold, although the main shortcoming is the low natural abundance (0.037%) of the active ¹ = 5/2 nucleus. Thus, enrichment of the sample with **17**O is needed. In addition, δ(17O) NMR signals are problematic to determine accurately compared with ¹H or ¹³C because the nuclear quadrupolar interaction for **17**O is very often much larger than the magnetic shielding interaction, thus causing significant line broadening in NMR spectra. However, recent advances in instrumentation, the extremely large chemical shift (δ) range — up to 2000 ppm — and the availability of **17**O-enriched compounds have allowed an increasing use of **17**O NMR spectroscopy.²⁰,²¹ In 1965, **17**O NMR was applied to the Cr₂O₂⁻ anion.²² Soon after, the **17**O NMR spectra of a range of other oxometalates were obtained.²³ In a systematic study of **17**O NMR parameters of POM structures, Klemperer and co-workers clearly established the relationship between chemical shift and metal-oxygen bond lengths.²⁷ Modern quantum chemistry methods have always encountered more difficulties in describing systems containing transition metal atoms than simpler organic molecules, where approximate methods such as the density functional theory (DFT) have had great success from the beginning. However, the last two decades have seen the success of computational chemistry in tackling practically any physicochemical property related to POMs.²⁴ Quantum chemistry calculations of NMR properties in POMs have s…
possible $\delta^{17}\text{O}$ values for mixed-metal polyoxoanions in solution. We first made an extensive exploration of density functional and basis sets to establish a good strategy to determine accurate values. In addition, the diversity of POMs studied provides a unique opportunity to compare $\delta$ values of nuclei bonded to different transition metals, allowing us to clearly identify and understand factors contributing to these values. In the present work we focused on two main goals. First, we applied several computational methodologies based on the DFT to predict $\delta^{17}\text{O}$ with the best accuracy possible. Secondly, we sought to understand the dependence of $\delta^{17}\text{O}$ in POMs on the position, connectivity, vicinal metal atoms and degree of protonation of the relevant O atoms.

2. Computational details and theoretical background

Density functional theory (DFT) calculations were performed using the ADF2010 package. In the present work we apply a family of functionals, either GGA-type or hybrid. The latter include some % of exact Hartree-Fock exchange, which makes them more computationally demanding. The process for obtaining the $^{17}\text{O}$ NMR chemical shifts consists of (i) a geometry optimization step and (ii) a single-point NMR calculation, a procedure expressed throughout the text as Functional$\rightarrow$Basis$\rightarrow$Functional$\rightarrow$Basis$\rightarrow$. The basis sets utilized are all-electron of triple $\zeta$ polarization (TZP) or triple-$\zeta$ double polarization (TZ2P) quality for all atoms with scalar relativistic corrections to the electrons via the zeroth-order regular approximation (ZORA). We also tested the results for the large QZ4P basis set. Geometry optimizations were carried out under the constraints of the maximal point group symmetry of each molecule (reported in Figure 1) and with high numerical integration accuracy (parameter set to 6 in ADF). Since we were dealing with anionic species in solution, we applied the effects of solvent and counterions as a continuum via the conductor-like screening model (COSMO), with a given dielectric constant that induces charge polarization on a surface around the molecule. Taking the optimized geometry, the NMR single-point calculation is done for the target and reference (H$_2\text{O}$) compounds introducing spin-orbit (SO) corrections and the GIAO method. The calculated chemical shift is determined as $\delta_{\text{cal}} = \delta_{\text{ref}} - \delta_{\text{x}},$ where $\delta_{\text{x}}$ and $\delta_{\text{ref}}$ are the isotropic average shielding for the nucleus of the target and the reference compounds, respectively.

It is known that the fundamental quantity underlying the phenomenon of chemical shift of a nucleus is its magnetic shielding tensor, $\sigma$. The shielding tensor of nucleus $A$, $\sigma_A$, is obtained as the second derivative of the total quantum mechanical energy $E$ of the system with respect to the external magnetic field $B_0$ and the magnetic moment $\mu_A$ of the nucleus.\(^{55}\)

$$\sigma_A = \frac{\partial^2 E}{\partial \mu \partial B_0} \bigg|_{B_0=0} \tag{1}$$

In general, $\sigma$ can be written as the sum of the paramagnetic and the diamagnetic contributions,\(^{56}\) although if the relativistic theory is taken into account, the SO contribution is further included:

$$\sigma = \sigma^d + \sigma^P + \sigma^{SO} \tag{2}$$

The diamagnetic part depends on the ground state only, while the paramagnetic shielding depends also on the excited states of the unperturbed system, expressed in terms of the virtual (unoccupied) molecular orbitals (MOs). The diamagnetic contribution for a given nucleus remains fairly constant irrespective of its chemical environment so that chemical shifts are usually dominated by the paramagnetic part. The leading contribution to $\sigma_{\text{p}}$ is given by the coupling between occupied and virtual MOs due to the external field $B_0$.

$$\sigma_{\text{p}} = \sum_i n_i \sum_{\alpha} \langle \psi \left| \frac{\partial^2}{\partial \mu \partial B_0} \right| \psi \rangle \tag{3}$$

and describe virtual and occupied MOs (with occupation number $n_i$), respectively, is the electronic position operator and $\vec{p}$ is the electronic momentum operator. The magnitude of the coupling is given by $u_{\text{eff}}$ which is proportional to:

$$u_{\text{eff}} \propto \frac{\langle \psi | \vec{M} | \psi \rangle}{2(\epsilon_0^e - \epsilon_0^o)} \tag{4}$$

where $\epsilon_0^e$ and $\epsilon_0^o$ are the orbital energies of the occupied and unoccupied MOs and the integral in the numerator is the first-order magnetic coupling between them. The action of the magnetic operator $\vec{M}_u$ on $\psi_i$ is simply to work with $\vec{L}_u$ on each atomic orbital. Here $\vec{L}_u$ is the $\mu$-component of the angular momentum operator with its origin at the center $\vec{R}_\mu$ on which $\chi_\mu$ is situated. The electron orbital angular momentum operator ($L_x$, $L_y$, $L_z$) acts on atomic wave functions. For example,

$$L_x | \psi_i \rangle = i\hbar | \psi_i \rangle \tag{5}$$

A significant magnetic coupling occurs when an occupied orbital localized around the atomic nucleus of interest can have considerable overlap with an empty orbital after 90° rotation about the direction of the external magnetic field.\(^{34, 37, 38}\) Some recent studies that put emphasis in these concepts can be found in refs 60-62.

The quality of a given calculation is referred to the mean absolute error (MAEs) either per site or as an average of them. The reported MAE values have been obtained as:

$$\text{MAE} = \frac{1}{N} \sum | \delta_{\text{cal},i} - \delta_{\text{exp},i} | \tag{6}$$

where $\delta_{\text{cal},i}$ and $\delta_{\text{exp},i}$ are the calculated and experimental chemical shifts, respectively. Figure S1 explains how the chemical shifts for oxygens of the same type (equivalent or not) are obtained from computations.

3. Results and discussion

3.1. Calculation of accurate $\delta^{17}\text{O}$ for mixed-metal polyoxometalates

The family of POM structures represented in Figure 1 has been computed and analyzed at the DFT level to provide a large set of $\delta^{17}\text{O}$ values. The compounds can be organized into two main groups:
Figure 1. Main structures analyzed, with oxygens as white spheres: (a) \([\text{M}_6\text{O}_{19}]^n\), (b) \([\text{M}_6\text{W}_{n}\text{O}_{19}]^n\), (c) \([\text{M}_2\text{W}_4\text{O}_{19}]^n\), (d) \([\text{MeO}\text{M}_6\text{W}_{18}\text{O}_{19}]^n\), (e) \([\text{[µ-O]}\text{TiW}_{5}\text{O}_{18}]^2\), (f) \([\text{[µ-}\text{HO})\text{ZrW}_{5}\text{O}_{18}]^2\). Blue atoms are W, orange are M ≠ W. Point group symmetries are also shown.

(i) Single- and mixed-metal hexametallate compounds based on the Lindqvist framework, \([\text{M}_6\text{O}_{19}]^n\) and \([\text{M}_x\text{W}_x\text{O}_{19}]^n\). Single-metal compounds, \([\text{M}_6\text{O}_{19}]^2\) (Figure 1a), feature terminal (M=O), bridging (M₂O) and central (M₆O) oxygen types. The latter, internal site is weakly connected to the six M atoms. The mixed-metal derivatives \([\text{M}_x\text{W}_x\text{O}_{19}]^n\) with M = V, Ta or Nb (Figure 1b-d), present the same three types of structural oxygen types but they can be bonded to more than one metal type, introducing additional variability to the \(^{17}\text{O}\) NMR values.

(ii) Larger structures: dimers of the Lindqvist anion, \([\text{[µ-O]}\text{TiW}_{5}\text{O}_{18}]^2\) and \([\text{[µ-}\text{HO})\text{ZrW}_{5}\text{O}_{18}]^2\) (Figure 1e-f). The Keggin, \([\text{XW}_{12}\text{O}_{40}]^n\) (X = P, Si), and Wells-Dawson \([\text{P}_2\text{W}_{18}\text{O}_{62}]^6\)-anions also feature terminal (M=O) and bridging (M₂O) oxygens, plus the internal (XOM₃) sites. Figure 2 shows the M-O connectivity modes of the POM structures presented.

Many variables affect the quality of the chemical shifts from computational techniques. A comprehensive analysis of the various sources of improvement in DFT calculations were studied for \(^{17}\text{O}\) in \([\text{Ru(CO)}_3\text{I}]^+\). The accurate determination is affected principally, besides the inclusion of the spin-orbit and solvent effects, by the density functional and the basis set size. In the first part of this work we discuss the influence of the latter two on the quality of the computed \(^{17}\text{O}\) NMR chemical shifts.

Selection of the density functional. We first focus on the effect of the density functional on the calculation of \(^{17}\text{O}\) NMR chemical shifts. Table 1 shows a family of \(\delta(^{17}\text{O})\) values computed for the simple \([\text{W}_{6}\text{O}_{19}]^2\) structure. We carried out single-point calculations with various GGA and hybrid functionals after having optimized the geometry with the B3LYP functional and a TZP basis set. A comparison of the calculated values with the experimental ones shows that three distinct oxygen types of \([\text{W}_{6}\text{O}_{19}]^2\) (terminal, bridging and central) can be clearly resolved with any functional. However, there is an evident overestimation of the computed \(\delta(^{17}\text{O})\), that is, they are too
positive with only a few exceptions. Recent theoretical studies on $^{17}$O NMR of terminal transition-metal oxo compounds based on DFT using ZORA show that, in general, DFT calculations reproduce the experimental chemical shifts reasonably well but the results are not within the experimental error. In the present case, the accuracy achieved is modest, as shown in the rightmost column of Table 1, with averaged MAEs ranging 40–58 ppm. The errors obtained with GGA functionals were found to be around 40–48 ppm, whereas the MAEs with hybrid functionals are ~10 ppm larger than GGA ones. GGA functionals perform very well for the tungsten-terminal oxygen ($W=O$) whereas the error is larger for the bridging one ($W=O$). Conversely, the central $\mu_4$-O oxygen is better reproduced with hybrid functionals, probably because these are able to reproduce their special electronic properties, namely its more ionic nature, weakly bound and highly charged oxygen atom. We have observed that the GGA-type PBE and OPBE functionals perform better than the more time-consuming hybrid functionals (PBE0 and B3LYP). Previous studies testing a variety of density functional methods for small molecules also found that the OPBE performs remarkably well.\(^{66,67}\)

### Table 1. Site-specific and Average MAEs\(^ a\) for the $\delta(^{17}$O) of [W$_6$O$_{19}$]$_2^-$ Compounds (M = Ta, Nb, V) Computed with Different Methodologies\(^ b\)

<table>
<thead>
<tr>
<th>NMR/OPT</th>
<th>M$_2$O</th>
<th>W$_5$O</th>
<th>W$_6$O</th>
<th>Avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-B3LYP/TZP//B3LYP/TZ2P</td>
<td>24</td>
<td>77</td>
<td>75</td>
<td>92</td>
</tr>
<tr>
<td>2-PBE/TZ2P//PBE/TZ2P</td>
<td>58</td>
<td>54</td>
<td>54</td>
<td>41</td>
</tr>
<tr>
<td>3-BP86/TZP//B3LYP/TZ2P</td>
<td>59</td>
<td>74</td>
<td>60</td>
<td>42</td>
</tr>
<tr>
<td>4-PBE/TZP//B3LYP/TZ2P</td>
<td>61</td>
<td>70</td>
<td>60</td>
<td>38</td>
</tr>
<tr>
<td>5-PBE/TZP//PBE/TZ2P</td>
<td>31</td>
<td>58</td>
<td>55</td>
<td>37</td>
</tr>
<tr>
<td>6-PBE/TZP//PBE/QZ4P</td>
<td>33</td>
<td>68</td>
<td>55</td>
<td>34</td>
</tr>
<tr>
<td>7-OPBE/TZP//OPBE/TZ2P</td>
<td>31</td>
<td>48</td>
<td>22</td>
<td>46</td>
</tr>
<tr>
<td>8-KT2/TZP//PBE/TZ2P</td>
<td>34</td>
<td>36</td>
<td>50</td>
<td>38</td>
</tr>
<tr>
<td>9-OPBE/TZP//PBE/TZ2P</td>
<td>27</td>
<td>40</td>
<td>41</td>
<td>41</td>
</tr>
</tbody>
</table>

\(^a\)Values in ppm. Methods are sorted by descending average MAE. The experimental data can be found in parentheses in Table 3. \(^b\)See Tables S1–S9 for the full list of computed chemical shifts.

First of all, we can confirm that the trends observed in Table 1 for [W$_6$O$_{19}$]$_2^-$ are also followed in the mixed-metal compounds, namely, after using the B3LYP functional for the geometry optimization step, the single-point NMR calculation gives better results with GGA functionals than with B3LYP (entries 1, 3 and 4). In general, the NMR step gives better results with GGA functionals (PBE, OPBE). We also checked the relevance of the geometry optimization step with other functionals. Comparing entries 4 and 5 we can see what is the effect upon the total MAE of changing the geometry optimization step without changing the NMR calculation step (fixed to PBE/TZP). The MAEs do not significantly differ between B3LYP/TZ2P and PBE/TZ2P optimizations, confirming that the choice of the functional is more determinant in the NMR step than in the geometry optimization (as long as the latter is performed at least with a GGA functional and a TZP or TZ2P basis set). In addition, the difference in the average quality of the results when optimizations are performed with PBE or OPBE only differ by ~1 ppm, a fact showing how similar these two functionals are with respect to the geometry optimization step. Finally, the effect of the basis set in the geometry optimization step (entries 5 and 6) is residual when going from TZ2P to QZ4P. Therefore, structures optimized with a TZ2P basis set combined with the appropriate functional are good enough for NMR calculations.

To summarize, performing a test over a variety of methodologies (Table 2) shows that the best accuracy in $^{17}$O NMR chemical shifts is achieved when GGA functionals are used. Except for the poor results obtained with the B3LYP/TZP//B3LYP/TZ2P procedure with an average MAE = 70 ppm, the rest of entries give much lower average MAEs, ranging 48–39 ppm. Notably, the last three methodologies in Table 2, characterized by GGA functionals, have very similar
From the results listed in Table 2, we can choose any of the last three procedures to carry on our study. However, the OPBE/TZP/PBE/TZ2P procedure (last row of Table 2 and Table S9) gives more constant deviations per site, whereas the KT2 functional has more fluctuating error values. In the following, all the values computed are referred to the OPBE/TZP/PBE/TZ2P computational procedure although one could consider using the KT2/TZP/PBE/TZ2P procedure with a comparable success.

For the chosen procedure, then, the average MAE = 39 ppm is still moderate despite the wide range of $\delta^{17}$O ~1200 ppm in POMs. At this point we consider a general approach to overcome this issue. Empirical scaling is the application of corrections to the computed data derived from linear regression procedures using experimental data. In this case, computed isotope shieldings ($\sigma$) with the OPBE/TZP/PBE/TZ2P procedure and experimental chemical shifts ($\delta$) are related via an equation of the form $\delta = b \sigma + a$. The major benefit of this analysis is that the slope (b) is a scaling factor to robustly account for the systematic errors in computed chemical shifts. This procedure is able to reduce errors from sources such as solvation effects, rovibratory effects and other methodological limitations. Figure 3 shows the linear equation $\delta = -1.079\sigma + 313.0$ fitting the computed $^{17}$O shielding to the experimental $^{17}$O chemical shifts for the set of compounds listed in Table 3. So, using that equation we can therefore, they are presumed of similar quality. For these methodologies, some positions are more accurately reproduced than others, such as W=O sites (MAE between 15 and 24 ppm with this set of molecules). On the other hand, the systematic error associated with terminal M=O positions is much larger (71 to 96 ppm), markedly influenced by the vanadium atom (i.e. 1015 ppm computed vs. 1217 ppm measured for V=O in $[V_2W_6O_{19}]^{6-}$). Excluding the values for V=O, the M=O MAE dramatically reduces. The deviations for bridging W=O, WMO and M=O positions are, on average, around 40 ppm. For the less chemically relevant central oxygen (M=O), the accuracy of calculations is intermediate.

The knowledge gained from present calculations suggests that further improvement in $^{17}$O NMR chemical shifts is not expected upon changes in the density functional or the basis set in the computational procedure. Also, the computed $\delta^{17}$O values are systematically too positive.

### 3.2. Linear scaling to reduce the mean absolute errors in $\delta^{17}$O

From the results listed in Table 2, we can choose any of the last three procedures to carry on our study. However, the OPBE/TZP/PBE/TZ2P procedure (last row of Table 2 and Table S9) gives more constant deviations per site, whereas the KT2 functional has more fluctuating error values. In the following, all the values computed are referred to the OPBE/TZP/PBE/TZ2P computational procedure although one could consider using the KT2/TZP/PBE/TZ2P procedure with a comparable success.

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The values of δ(17O) shown in Table 3 have been obtained with the mentioned linear equations. Notice that we have enlarged the number of compounds to which we applied the linear scaling to systems classified as (i) and (ii) in Section 3.1. The fitted values are more accurate in general than the non-fitted ones. The two of them coincide, though, in that the most systematic errors in Δ(17O) are those of terminal W=O oxygens. The empirical fitting also provides a quantitative accuracy for oxygens of the Keggin compound such as the internal XOM$_2$ position (MAE = 10 ppm). However, it does not perform so well for M$_2$O oxygens, maybe because the fitting includes a majority of values for W$_2$O oxygens. The improvement is therefore more evident for oxygens linked to W, although better results are also observed with the other metals, M. Table 4 summarizes the % improvement experienced when computed Δ(17O) are fitted using the linear equation in Figure 3. The systematic errors in Δ(17O) are notably reduced applying the linear fitting technique to the values computed with the OPBE/TZP/PBE/TZ2P procedure. The oxygens bonded to W atoms feature small MAEs between 7 and 17 ppm. On the other hand, the terminal V=O site is a special case since the computed chemical shift is still large after applying such fitting correction.

Table 4. MAEs for Calculated and Fitted δ(17O) for Hexametallate Compounds.

<table>
<thead>
<tr>
<th>Site</th>
<th>Calculated$^a$</th>
<th>Fitted</th>
<th>improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO</td>
<td>38</td>
<td>17</td>
<td>55%</td>
</tr>
<tr>
<td>W$_2$O</td>
<td>60</td>
<td>13</td>
<td>78%</td>
</tr>
<tr>
<td>WMO</td>
<td>44</td>
<td>14</td>
<td>68%</td>
</tr>
<tr>
<td>M$_2$O</td>
<td>59</td>
<td>48</td>
<td>19%</td>
</tr>
<tr>
<td>W=O</td>
<td>7</td>
<td>6</td>
<td>14%</td>
</tr>
<tr>
<td>M–O$^c$</td>
<td>69 (11)</td>
<td>60 (15)</td>
<td>13%</td>
</tr>
<tr>
<td>average$^d$</td>
<td>46 (36)</td>
<td>26 (19)</td>
<td>44% (47%)</td>
</tr>
</tbody>
</table>

$^a$Values in ppm. $^b$Data in Table S1. $^c$In parentheses, MAEs obtained excluding δ(17O) of terminal V=O sites.

### 3.3. Influence of the metal on the chemical shift

To help us explain the 17O NMR of complex POM systems, we first analyze its behavior in the simpler and well characterized MO$_x$ family, with M of groups 5, 6, 7 and 8 of the periodic table. These compounds were previously studied as models for the performance of theoretically methods in 17O NMR properties. Calculated and experimental δ(17O) values are shown in Table 5. As stated above, the chemical shifts are governed by the paramagnetic term, $\delta^p$, in which the MO$_x$ anions is dominated by a np(0) → $\pi^*$ (M-O) electronic transition.

Scheme 1

where np(0) is the occupied symmetry-adapted lone pair of the oxygen atoms (l.h.s. of Scheme 1). Recalling equation 4, the term $\alpha^p$, responsible for $\delta^p$, depends on the reciprocal of the energy gap between these two orbitals, ΔE$,\pi^*$, but also on the overlap (considering rotation due to the external magnetic field) between the oxygen atomic contributions in both orbitals. Figure 4 shows that the energies of np(O) and π* orbitals, defining ΔE$,\pi^*$, decrease as we go right and up in the periodic table. Interestingly, the π* orbital does more dramatically. This is linked to the varying M-O bond polarization towards a larger oxygen character in the same sense. However, the occupied lone pair orbital remains constant at ≈95% p(O) character, its energy change being attributed to the different negative charges in the MO$_x$ family.

Table 5. Calculated and Experimental 17O NMR Shifts for MO$_x$.

<table>
<thead>
<tr>
<th></th>
<th>V$_4$O$_2$</th>
<th>Cr$_2$O$_3$</th>
<th>MnO$_2$</th>
<th>Nb$_2$O$_5$</th>
<th>MoO$_2$</th>
<th>TcO$_2$</th>
<th>RuO$_3$</th>
<th>Ta$_2$O$_5$</th>
<th>W$_2$O$_5$</th>
<th>ReO$_2$</th>
<th>OsO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δ(17O)</td>
<td>758 (871)</td>
<td>548 (568)</td>
<td>1030 (1255)</td>
<td>419 (-)</td>
<td>578 (576)</td>
<td>783 (786)</td>
<td>1071 (1142)</td>
<td>332 (-)</td>
<td>452 (456)</td>
<td>597 (605)</td>
<td>800 (832)</td>
</tr>
</tbody>
</table>

$^a$Data in parentheses from refs. 77, 78 except for RuO$_3$ (ref. 79). $^b$Values in ppm.

Within this series the correlation of 17O chemical shifts with the orbital gaps is highly linear, as shown in Figure 4. When we move left and down in the periodic table, the ionicity of the metal-oxygen bond increases. After having analyzed the computational results we can conclude that the numerator of the $\alpha^p$ term is quite irrelevant (constant) vs. the chemical shift, the energy gap being entirely responsible for the trend in $\delta(17O)$. Hence, for example, the contribution of p(O) to $\pi^*$ (M-O) is only 35% in WO$_2$ whereas it reaches up to 60% in RuO$_3$. This might affect the numerator of $\alpha^p$, but it does so only slightly and the varying % p(O) contributions have little effect, apart from the indirect effect on the energy of the $\pi^*$ orbital. Thus, the observed $\delta(17O)$ resonance in WO$_2$ appears at 456 ppm, whereas that for...
RuO$_4$ is shifted 700 ppm downfield to 1142 ppm. The computed values are rather close to the observed ones, 452 and 1071 ppm, respectively. The mentioned downfield shift can be attributed in simple terms to the increase of covalency in the M-O bond and to the higher electron affinity of the metal. Both effects are present in the orbital gap mentioned. Likely, many chemists would prefer an interpretation based on atomic populations. It is true that the atomic charge of oxygens in WO$_6^{2-}$ is larger than in RuO$_4$ (−1.00e vs. −0.46e, respectively, with multipole-derived atomic charges) but the reader should take into account that δ(17O) correlates much better with the reciprocal of orbital energy gaps, $\Delta E^{-1}$, than with atomic populations (see Figure S2). Both factors—orbital energy gap and, secondarily, orbital polarization—make the $n \rightarrow \pi^*$ electron transfer less accessible in the tungstate species. A deeper analysis of the MO$_4^{-}$ model set shows that the behavior of δ(17O) can be rationalized mainly in terms of the orbital energy gap, the % contribution of p(O) in the implicated orbitals being indirect, affecting their relative energies.

![Figure 4](image)

**Figure 4.** Dependence of 17O chemical shifts on the energy gaps associated with the leading occupied → virtual electronic transitions in the $d^6$ component for the MO$_4^{-}$ series. Top: computed $n \rightarrow \pi^*(M-O)$ energy gaps (in eV). More covalent M-O bonds are associated with smaller gaps (thicker arrows) and more deshielded nuclei. Bottom: linear correlation of the calculated δ(17O) vs. the reciprocal of the energy gap ($\Delta E^{-1}$).

The computed δ(17O) values fitted by the expressions shown in Figure 3 for bridging MOW and MOM oxygens in hexametalate anions are listed in Table 6 along with experimental values. If we consider MOW sites, the variations in the chemical shift are within the range 400–600 ppm, smaller than in MO$_4^{-}$. The changes are larger if we look at the MOM sites. Notably, an increase in the covalency of M-O bonds, going up in a group, produce larger chemical shifts. In a period, though, they remain fairly constant (fitted and experimental values). Viewed as a whole, the δ(17O) values for hexametalate POM compounds follow the same trends as the MO$_4^{-}$ set. Therefore their behaviors can be assigned to the same origin.

**Table 6.** Fitted and Experimental $\delta$(17O) Values for MOW and M$_2$O$_4$ Positions in Mixed-metal Hexametalates.

<table>
<thead>
<tr>
<th></th>
<th>MOW</th>
<th></th>
<th>MOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>570 (562)</td>
<td>814 (848)</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>475 (456)</td>
<td>505 (485)</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>440 (426)</td>
<td>394 (413)</td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>440 (426)</td>
<td>394 (413)</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>440 (426)</td>
<td>394 (413)</td>
<td></td>
</tr>
</tbody>
</table>

*In parentheses. *Values in ppm.

3.4. Relevance of the bonding mode

In addition to the metal atom bonded to the oxygen site, the nature of this interaction, related to the number of vicinal metal atoms, notably affects the chemical shift. For a family of polyoxotungstates computed (Figure 5a) it is relevant that the negative atomic charge assigned to the oxygen atom increases as W < W$_2$O < W$_3$O, i.e. when more vicinal metal atoms and larger W-O distances are present. Thus, the W-O bonds become less covalent and the occupied and virtual orbitals split apart, lowering the δ(17O) due to a decrease in the paramagnetic contribution to σ. Within any one type of oxygen (W$_2$O, for example), though, one cannot find any correlation between atomic charges and the associated chemical shifts.

![Figure 5](image)

**Figure 5.** Correlation of the calculated 17O chemical shifts with (a) oxygen charges in substituted hexametalate anions, and with (b) V-O distances in the [V$_{10}$O$_{28}$]$^{4-}$ anion.
Regarding the M-O bond distance, it provides an indication of the nature of the bond, which is important in determining the variations in δ(\(^{17}\)O). For MO\(_2\)\(^+\), we studied the main electronic transitions, but herein we focus on the relationship between V-O bond distances and δ(\(^{17}\)O) in [V\(_{10}\)O\(_{28}\)]\(^{6}\) due to the increase in the number of paramagnetic transitions, which makes the analysis of orbital couplings much more intricate (Figure 5b). We chose the decavanadate system (Figure 7) to illustrate this trend because it contains four different V-O oxygen types (\(x = 1, 2, 3\) and 6). The relationship between energy gaps and bond distances is used to explain the trends in the δ(\(^{17}\)O) in this oxovanadate. As can be seen in Figure 5b, as the V-O bond distance increases, the nature of the interaction becomes more ionic and the chemical shift decreases.

The paramagnetic contribution is the most important source of the shielding. Therefore, we further examined the main orbital transitions dominating this contribution in M=O and M\(_2\)O oxygen sites since they are the most common in POMs. In the models represented in Figure 6, there is one dominant contribution, namely the \(\sigma \rightarrow \pi^*\) magnetic coupling, in terminal M=O sites, which accounts for about 40–70\% of the total depending on the metal. On the other hand, the largest contribution to M\(_2\)O shifts comes from the np(O) → \(\pi^*\) coupling, which accounts for about 30\% of all transitions. Figure 6 schematically shows how if one rotates a \(\sigma\) or \(n\) orbital by 90° as indicated by the arrows, it overlaps with the empty \(\pi^*\) orbital, particularly in the region around the oxygen. As the number of metal atoms bonded to the oxygen increases, there is no single dominant transition any more, but many of them contribute to the paramagnetic term.

**Figure 6.** Main contributions to the paramagnetic shielding for M=O (top) and M\(_2\)O (bottom) oxygen types obtained with simplified models. The symbolic representation of the \(\sigma\) and \(\pi\) occupied orbitals qualitatively illustrates how the action of the magnetic field rotates the atomic orbitals by 90°.

3.5. Effects of localised and mobile protons on the chemical shift

POMs are anionic species that can be protonated at neutral to acidic pH conditions, depending on their composition and charge. The identification of basic oxygens has significant implications regarding chemical reactivity and, more specifically, catalytic activity of metal oxides in general. However, the protonation sites in POMs are an elusive subject (i) naturally, since protons are itinerant in structures with chemically similar oxygen sites, and (ii) technically, due to the difficulties associated with the structural determination of H atom positions. Even so, in some cases, protonation sites have been determined experimentally using the empirical relationship between ‘bond length’ and ‘bond strength’ \(\delta\). In other cases, positions can be proposed based on \(^{17}\)O NMR spectra.\(^{25}\)–\(^{84}\) Computationally, this subject has been tackled by many authors. To analyze the effect of protonation on \(^{17}\)O NMR of POMs, we focus on the well characterized decavanadate [V\(_{10}\)O\(_{28}\)]\(^{6}\) anion, represented in Figure 7, since it features seven structural oxygen sites, six of which are external and could potentially be protonated. In a series of experimental studies,\(^{70}\)–\(^{82}\) the location of protons in this compound and their effect on \(^{17}\)O NMR was analyzed. First, it must be stressed that seven signals (labeled A-G) appear in the spectrum at any pH, proving that the effective C\(_{3a}\) symmetry is preserved irrespective of the protonation state of the species due to fast proton exchange at the NMR timescale.

Second, as the solution is acidified, two NMR signals, assigned to the bridging oxygens B (OV\(_{3}\)) and C (OV\(_{2}\)), experience an upfield shift (\(\Delta\delta < 0\)), whereas the other oxygen signals shift downfield (\(\Delta\delta > 0\)) by small amounts. Terminal positions F and G (V=O) are not basic. A general sequence of increasing negative charge has been proposed as O\(_x\) \(\approx\) O\(_{8}\) < O\(_{7}\) < O\(_{6}\) < O\(_{5}\) < O\(_{4}\) < O\(_{3}\) that can be related to their basicity.\(^{85}\) Because O\(_{8}\) is inaccessible to protons, O\(_{8}\) and O\(_{7}\) are effectively the most basic oxygens, with O\(_{8}\) slightly more basic than O\(_{7}\).

![Figure 7. The [V\(_{10}\)O\(_{28}\)]\(^{6}\) anion with labeling of one member of each set of symmetry-equivalent oxygens: A: V\(_{1}\)O; B: V\(_{2}\)O; C-E: V\(_{4}\)O; F-G: VO.](image)

The main goal of our calculations was to reproduce and explain these experimental trends and to extract some general conclusions related to protonation in POMs. In general, calculations predict a huge and apparently unrealistic decrease of δ(\(^{17}\)O) when a single oxygen is protonated. For V\(_{10}\)O\(_{28}\)\(^{6}\), the computed change in δ(\(^{17}\)O) for the bridging OV\(_{2}\) is \(\Delta\delta(\(^{17}\)O) \approx -580\) ppm when protonation occurs considering the short timescale (a static protonated structure with a non-itinerant proton). In the...
same way, the bridging oxygens of the Lindqvist structure listed in Table 7 feature large $\Delta \delta^{(17)O}$ changes. However, basic oxygens (VOV) change their $\Delta \delta^{(17)O}$ more than non-basic ones, for which $\Delta \delta^{(17)O}$ ranges from $-300$ to $-400$ ppm for $M = W, Nb$.

Hence, the change in chemical shift associated to protonation depends on the metal atoms linked to the oxygen.

Table 7. Calculated $\Delta \delta^{(17)O}$ for Non-Protonated and Protonated Metal Substituted Lindqvist Structures, and Their Difference $\Delta \delta$. The Structural Change, $\Delta \delta$(M-O), is Shown.

<table>
<thead>
<tr>
<th></th>
<th>WOW</th>
<th>WONb</th>
<th>NbONb</th>
<th>WOV</th>
<th>VOV</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-prot.</td>
<td>445</td>
<td>516</td>
<td>563</td>
<td>563</td>
<td>808</td>
</tr>
<tr>
<td>protonated</td>
<td>152</td>
<td>150</td>
<td>171</td>
<td>149</td>
<td>237</td>
</tr>
<tr>
<td>$\Delta \delta^{(17)O}$</td>
<td>$-293$</td>
<td>$-366$</td>
<td>$-392$</td>
<td>$-414$</td>
<td>$-571$</td>
</tr>
<tr>
<td>$\Delta \delta$(M-O)</td>
<td>$+0.149$</td>
<td>$+0.159$</td>
<td>$+0.166$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Values in ppm. $^b$M-O change upon protonation, in Å.

The geometrical effects of protonation might help us find an explanation for the variations in $\delta$. The last row in Table 7 shows the change in some M-O distances if we attach a proton to a single oxygen site. It can be seen that the structural change is large, ranging from $+0.149$ Å for OW to $+0.166$ Å for OV at the present level of computation. Consequently, the protonated oxygens gain some ionic character and the protonated form, the equivalent sites. If symmetry must be preserved in the protonated species, belongs to the point group, with four $O_8$ and eight $O_C$ equivalent sites. If symmetry must be preserved in the protonated form, the $^{17}O$ chemical shift of the protonated oxygen ($\Delta \delta < 0$) and its non-protonated partner sites ($\Delta \delta > 0$) will be duly averaged to take into account proton exchange between these N equivalent sites, in such a way that a unique signal is obtained for this set of sites.

(3) Coexistence of two protonated species. During the NMR measurements, more than one protonated species can be present in solution at sufficiently low pH, namely, $[V_{10}O_{28}]^{6-}$ can be protonated in oxygens B or C.

Table 8. Evolution of the Experimental and Calculated $\delta^{(17)O}$ of External Oxygens upon Protonation.

<table>
<thead>
<tr>
<th>$[V_{10}O_{28}]^{6-}$</th>
<th>HO$_6$</th>
<th>HO$_{10}$</th>
<th>HO$_{14}$,40$_b$</th>
<th>$\Delta \delta_{\text{cal}}$</th>
<th>$\Delta \delta_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_6$</td>
<td>498</td>
<td>433</td>
<td>520</td>
<td>468</td>
<td>$-30$</td>
</tr>
<tr>
<td>O$_C$</td>
<td>785</td>
<td>803</td>
<td>734</td>
<td>776</td>
<td>$-9$</td>
</tr>
<tr>
<td>O$_{19}$</td>
<td>791</td>
<td>814</td>
<td>818</td>
<td>816</td>
<td>25</td>
</tr>
<tr>
<td>O$_{28}$</td>
<td>826</td>
<td>830</td>
<td>837</td>
<td>833</td>
<td>7</td>
</tr>
<tr>
<td>O$_{101}$</td>
<td>1000</td>
<td>1020</td>
<td>1025</td>
<td>1022</td>
<td>22</td>
</tr>
</tbody>
</table>

$^a\Delta \delta_{\text{cal}} = \delta^{(17)O}(60_b,40_b) - \delta^{(17)O}(V_{10}O_{28}^{6-})$. See text for details. $^b\Delta \delta_{\text{exp}} = \delta^{(17)O}(pH 4.5) - \delta^{(17)O}(pH 6)$. Data taken from ref. 80.

Table 8 lists the computed $\Delta \delta^{(17)O}$ for the non-protonated, and the two protonated species derived from the decavanadate anion in the long timescale, along with the experimental changes in $\delta^{(17)O}$. The complete list of non-averaged chemical shifts for every individual oxygen position in the two protonated species can be found in Table S3. For each particular protonated species (columns ‘HO$_6$’ or ‘HO$_{10}$’), one $\delta^{(17)O}$ decreases and the others increase compared to the non-protonated species. This behavior reveals that protonation does not only occur at the most basic site B but rather at both B and C sites, as their negative $\Delta \delta_{\text{exp}}$ values reveal. Column ‘60$_b,40_b’ shows the results if the two previous columns are combined as if $HV_{10}O_{28}^{6-}$ was 60% protonated in B and 40% protonated in C. We found that this balanced combination of the $^{17}O$ shields calculated for HO$_6$ and HO$_{10}$ reproduce the experimental data in the rightmost column, not only for protonated sites B and C, but also for non-protonated sites that shift downfield. Other ratios different from 60$_b,40_b$ provided poorer estimations when comparing with experimental shifts (Table S12). The present procedure applied to DFT calculations prove that the observed $\delta^{(17)O}$ signals are a weighted mixture of those resonances assigned to equivalent oxygen types because they undergo mutual proton exchange in the timescale of $^{17}O$ NMR measurements. It has also been proven that oxygen B is more basic than C since the weighted combination that matches the experiments contains a higher % of $[HV_{10}O_{28}^{6-}]$ protonated at B. Therefore, the calculated values are only comparable with experimental ones if the effects discussed above are duly combined.

Finally, the case of $V_2W_4O_{19}^{4-}/HV_2W_4O_{19}^{3-}$, that was experimentally analyzed, revealed a change in the OV$_2$ site of $-238$ ppm upon protonation. Dramatic changes in $\delta^{(17)O}$ shifts were also detected and computed for various amide types. Although it is much larger than $\Delta \delta = -7$ ppm obtained for the chemically similar $O_C$ in the decavanadate anion, it is still much smaller than our predicted value of $\Delta \delta = -571$ ppm (Table 7). As described in this section, a small change in $\delta^{(17)O}$ when protonation occurs can be explained by proton delocalization over other equivalent or non-equivalent oxygen sites. In the case of $[V_2W_4O_{19}^{4-}]$, the absence of other similarly basic (equivalent or non-equivalent) sites discards the possibility of dissipation of $\Delta \delta$ by proton delocalization. As a matter of fact, there is a lone OV$_2$ position, and WOW sites are not expected to be protonated because of their relatively low basicity. We speculate that the protonated form $[HV_2W_4O_{19}^{3-}]$ represents only 30% of the total species present under the conditions specified by the authors. On
the NMR timescale, the protonated and non-protonated forms would rapidly interconvert giving a single resonance.

4. Conclusions

We have established a DFT-based strategy to accurately compute and rationalize $^{17}$O NMR chemical shifts of polyoxoanions. The lowest deviations between experimental and theoretical values were obtained at OPBE/TZP/PBE/TZ2P (NMR/optimization) level incorporating also solvent and relativistic effects. With this approach and using linear fitting we predict $\delta$ values with mean absolute error $\sim 26$ ppm for a set of 75 signals.

The paramagnetic contribution of the shielding ($\sigma^P$) dominates the $^{17}$O chemical shift. It arises from the occupied $\pi$* orbital transitions with oxygen contribution promoted by the external magnetic field acting in NMR. The $\sigma^P$ correlates in general with M-O bond distances. For terminal M=O oxygens, the $\sigma \rightarrow \pi^*$ transition governs the shielding, which also has a linear dependence with the reciprocal of the energy gap. We used the simple MO$_4^{17-}$ anion to clarify the dependence of $\delta$ vs. M.

Electronegative ions such as V$^{17-}$, Cr$^{17VI}$ or Ru$^{18VII}$, with rather deep $\pi^*(M-O)$ orbitals, lead to very positive $\delta(^{17}$O). The less electronegative Nb$^{V}$ or W$^{VI}$ ions have the opposite behaviour. The number of metal ions linked to the oxygen atom also affect $\delta(^{17}$O).

The effect of protonation on POMs has been analysed in detail for hexametalates and $[\text{V}_6\text{O}_2\text{O}_{28}]^{16-}$. When proton-exchange occurs between chemically similar or equivalent, $\delta(^{17}$O) signals of protonated oxygens move upfield ($\Delta \delta < 0$), whereas the non-protonated ones slightly move downfield ($\Delta \delta > 0$). When a molecule has many similar/equivalent oxygen sites that can accept an itinerant proton, the net effect of protonation is largely dissipated and the changes in $\delta(^{17}$O) signals could become tiny or even undetectable by NMR as, for instance, the protonated Keggin $[\text{H}_2\text{O}_{2}\text{O}_{5}]^{15-}$ anion. On the other hand, when a distinctively basic oxygen is present, as the bridging V$^2$O in $[\text{V}_2\text{W}_2\text{O}_{19}]^{9+}$, the proton gets trapped in one location and a large change (hundreds of ppm) in one $^{17}$O NMR signal is observed upon protonation.

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Supporting Information

Figures: Equivalence and classification of oxygen sites in hexametallate compounds; Plot of calculated $^{17}$O chemical shifts vs. oxygen charges. Tables: computed and experimental $^{17}$O NMR chemical shifts for Lindqvist anions; computed chemical shifts for hexametallate anions with different computational methodologies; computed $^{17}$O chemical shifts of every oxygen position for the non-protonated, $[\text{V}_6\text{O}_2\text{O}_{28}]^{16-}$, and two monoprotontated, $[\text{H}_6\text{V}_6\text{O}_{28}]^{17-}$, forms of the decavanadate anion along with oxygen labeling.

Notes and references

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