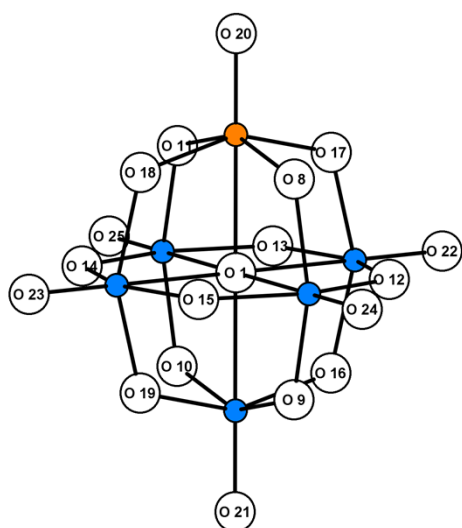


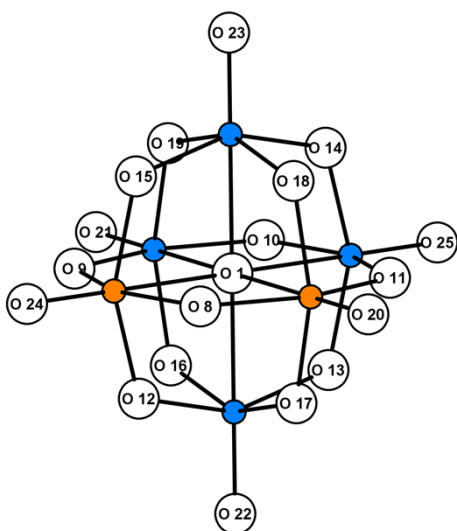
^{17}O NMR Chemical Shifts in Oxometalates: From the Simplest Monometallic Species to Mixed-metal Polyoxometalates

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Supporting Information



C_{4v}				
Oxygen label	Nr. Of symmetry equivalent positions	Type	Compd. value	Tabulated value
1	x1	M_6O	δ_1	δ_1
20	x1	$M=O$	δ_2	δ_2
8,11,17,18	x4	MOW	δ_3	δ_3
22-25	x4	$W=O$	δ_4	$\left. \begin{array}{l} \\ \end{array} \right\} (4 \cdot \delta_4 + \delta_5)/5$
21	x1	$W=O$	δ_5	
12-15	x4	W_2O	δ_6	$\left. \begin{array}{l} \\ \end{array} \right\} (\delta_6 + \delta_7)/2$
9,10,16,19	x4	W_2O	δ_7	



C_{2v}				
Oxygen label	Nr. Of symmetry equivalent positions	Type	Compd. value	Tabulated value
1	x1	M_6O	δ_1	δ_1
20,24	x2	$M=O$	δ_2	δ_2
8	x1	M_2O	δ_3	δ_3
12,15,17,18	x4	MOW	δ_4	$\left. \begin{array}{l} \\ \end{array} \right\} (4 \cdot \delta_4 + \square \cdot \delta_5)/6$
9,10	x2	MOW	δ_5	
21,25	x2	$W=O$	δ_6	$\left. \begin{array}{l} \\ \end{array} \right\} (\delta_6 + \delta_7)/2$
22,23	x2	$W=O$	δ_7	
10	x1	W_2O	δ_8	$\left. \begin{array}{l} \\ \end{array} \right\} (\delta_8 + \square \cdot \delta_9)/5$
13,14,16,19	x4	W_2O	δ_9	

Figure S1. Two examples illustrating how the ^{17}O chemical shifts for compounds featuring several non-equivalent oxygens *of the same type* are tabulated from computations. Oxygen labels for MW_5O_{19} and $M_2W_4O_{19}$ hexametalate compounds are displayed showing their point group symmetries. The molecular orientations are chosen to facilitate seeing the equivalence of sites. To the right, we specify how the different oxygen positions are grouped into types. In the article, the tabulated values refer to *oxygen types* and are listed as averaged values of the signals computed as indicated.

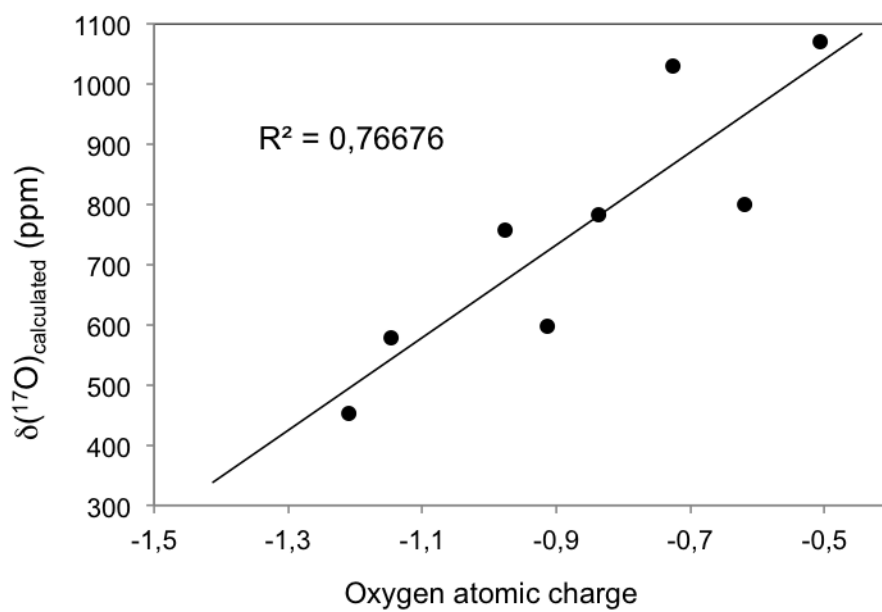


Figure S2. Correlation between the computed oxygen atomic charges and the ^{17}O chemical shifts for MO_4^{n-} compounds.

Tables. All the data are in ppm. There were obtained 17 signals with each methodology. The MAE values are referred to the experimental values listed in parentheses in Table 3 of the main text (see references in the rightmost column). The missing values (×) were not calculated assuming that they hardly affect the MAEs of that site and, consequently, the average ones. This assumption arises from the values in Table S6, for which the complete study was carried out. The errors obtained are so similar that we decided to compute only one of these W₂O sites, that of Nb₂W₄.

Table S1. Computed ¹⁷O Chemical Shifts with the B3LYP/TZP//B3LYP/TZ2P methodology.

Anion	M ₆ O	W ₂ O	MWO	M ₂ O	W=O	M=O
[W ₆ O ₁₉] ²⁻	−57	499	—	—	842	—
[Ta ₂ W ₄ O ₁₉] ⁴⁻	−41	×	477	464	×	633
[Nb ₂ W ₄ O ₁₉] ⁴⁻	−41	449	507	572	757	805
[V ₂ W ₄ O ₁₉] ⁴⁻	−20	×	608	1034	×	1348
MAE	24	77	75	92	67	119

Table S2. Computed ¹⁷O Chemical Shifts with the PBE/TZ2P//PBE/TZ2P methodology.

Anion	M ₆ O	W ₂ O	MWO	M ₂ O	W=O	M=O
[W ₆ O ₁₉] ²⁻	−23	459	—	—	749	—
[Ta ₂ W ₄ O ₁₉] ⁴⁻	−1	×	467	459	×	631
[Nb ₂ W ₄ O ₁₉] ⁴⁻	11	444	502	571	712	759
[V ₂ W ₄ O ₁₉] ⁴⁻	−9	×	571	824	×	1046
MAE	58	54	54	41	24	61

Table S3. Computed ¹⁷O Chemical Shifts with the BP86/TZP//B3LYP/TZ2P methodology.

Anion	M ₆ O	W ₂ O	MWO	M ₂ O	W=O	M=O
[W ₆ O ₁₉] ²⁻	−30	497	—	—	790	—
[Ta ₂ W ₄ O ₁₉] ⁴⁻	−18	×	469	466	×	642
[Nb ₂ W ₄ O ₁₉] ⁴⁻	−13	445	501	572	713	572
[V ₂ W ₄ O ₁₉] ⁴⁻	52	×	583	884	×	1140
MAE	59	74	60	42	19	14

Table S4. Computed ^{17}O Chemical Shifts with the PBE/TZP//B3LYP/TZ2P methodology.

Anion	M_6O	W_2O	MWO	M_2O	$\text{W}=\text{O}$	$\text{M}=\text{O}$
$[\text{W}_6\text{O}_{19}]^{2-}$	−32	490	–	–	784	–
$[\text{Ta}_2\text{W}_4\text{O}_{19}]^{4-}$	−18	×	468	465	×	640
$[\text{Nb}_2\text{W}_4\text{O}_{19}]^{4-}$	−13	445	501	555	711	759
$[\text{V}_2\text{W}_4\text{O}_{19}]^{4-}$	53	×	584	888	×	1139
MAE	61	70	60	38	15	15

Table S5. Computed ^{17}O Chemical Shifts with the PBE/TZP//PBE/QZ4P methodology.

Anion	M_6O	W_2O	MWO	M_2O	$\text{W}=\text{O}$	$\text{M}=\text{O}$
$[\text{W}_6\text{O}_{19}]^{2-}$	−41	488	–	–	790	–
$[\text{Ta}_2\text{W}_4\text{O}_{19}]^{4-}$	−26	×	466	460	×	636
$[\text{Nb}_2\text{W}_4\text{O}_{19}]^{4-}$	−20	443	500	572	717	764
$[\text{V}_2\text{W}_4\text{O}_{19}]^{4-}$	−34	×	575	830	×	1048
MAE	33	68	55	34	21	63

Table S6. Computed ^{17}O Chemical Shifts with the PBE/TZP//PBE/TZ2P methodology.

Anion	M_6O	W_2O	MWO	M_2O	$\text{W}=\text{O}$	$\text{M}=\text{O}$
$[\text{W}_6\text{O}_{19}]^{2-}$	−48	459	–	–	757	–
$[\text{Ta}_2\text{W}_4\text{O}_{19}]^{4-}$	−26	445	460	466	700	637
$[\text{Nb}_2\text{W}_4\text{O}_{19}]^{4-}$	−20	443	501	575	719	767
$[\text{V}_2\text{W}_4\text{O}_{19}]^{4-}$	−34	444	574	831	726	1049
MAE	31	58	55	37	28	52

Table S7. Computed ^{17}O Chemical Shifts with the OPBE/TZP//OPBE/TZ2P methodology.

Anion	M_6O	M_2O	$\text{M}'\text{MO}^c$	$\text{M}'_2\text{O}$	$\text{M}=\text{O}$	$\text{M}'=\text{O}$
$[\text{W}_6\text{O}_{19}]^{2-}$	−46	457	–	–	748	–
$[\text{Ta}_2\text{W}_4\text{O}_{19}]^{4-}$	−31	×	437	434	×	601
$[\text{Nb}_2\text{W}_4\text{O}_{19}]^{4-}$	−24	414	472	548	679	731
$[\text{V}_2\text{W}_4\text{O}_{19}]^{4-}$	−40	×	536	784	×	993
MAE	31	48	22	46	20	96

Table S8. Computed ^{17}O Chemical Shifts with the KT2/TZP//PBE/TZ2P methodology.

Anion	M ₆ O	W ₂ O	MWO	M ₂ O	W=O	M=O
[W ₆ O ₁₉] ²⁻	-46	448	–	–	784	–
[Ta ₂ W ₄ O ₁₉] ⁴⁻	-23	×	456	450	×	637
[Nb ₂ W ₄ O ₁₉] ⁴⁻	-17	419	493	572	712	770
[V ₂ W ₄ O ₁₉] ⁴⁻	-32	×	571	817	×	1038
MAE	34	36	50	38	15	71

Table S9. Computed ^{17}O NMR Chemical Shifts with the OPBE/TZP//PBE/TZ2P methodology.

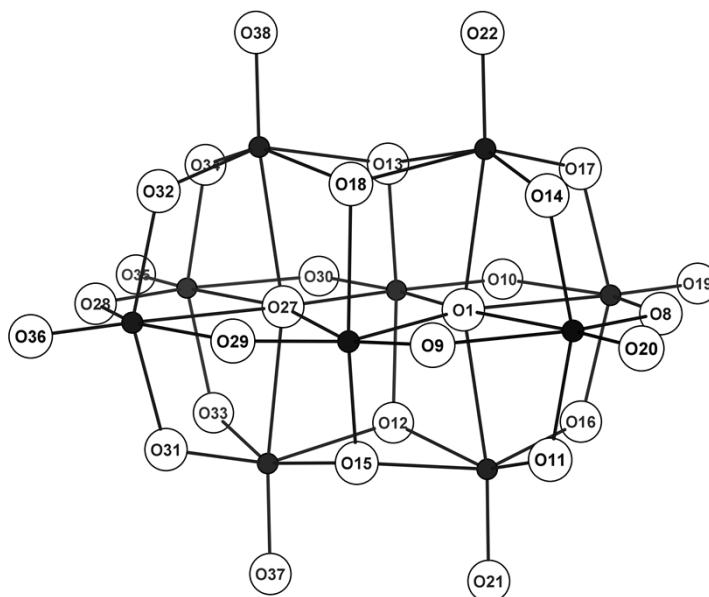
Anion	M ₆ O	W ₂ O	MWO	M ₂ O	W=O	M=O
[W ₆ O ₁₉] ²⁻	-52	445	–	–	732	–
[Ta ₂ W ₄ O ₁₉] ⁴⁻	-30	432	452	443	700	612
[Nb ₂ W ₄ O ₁₉] ⁴⁻	-23	430	491	563	696	749
[V ₂ W ₄ O ₁₉] ⁴⁻	-39	430	563	808	702	1015
Partial MAE	27	40	41	41	24	76

Table S10. Computed (OPBE/TZP//PBE/TZ2P) and Experimental ^{17}O NMR Chemical Shifts for Compounds in Table 3

Anion	M ₆ O	W ₂ O	WMO	M ₂ O	W=O	M=O
[W ₆ O ₁₉] ²⁻	-52 (-80)	445 (413)	-	-	732 (772)	-
[Mo ₆ O ₁₉] ²⁻	-33 (-32)	611 (563)	-	-	930 (933)	-
[TaW ₅ O ₁₉] ³⁻	-38 (-71)	452 (394)	485 (426)	-	732 (732)	648 (666)
[NbW ₅ O ₁₉] ³⁻	-30 (-67)	450 (393)	516 (456)	-	730 (731)	810 (799)
[VW ₅ O ₁₉] ³⁻	-43 (-75)	451 (392)	597 (562)	-	734 (731)	1053 (1217)
[Ta ₂ W ₄ O ₁₉] ³⁻	-30 (-40)	432	452	443 (454)	700	612
[Nb ₂ W ₄ O ₁₉] ³⁻	-23 (-67)	430 (379)	491 (435)	563 (493)	696 (691)	749 (753)
[V ₂ W ₄ O ₁₉] ³⁻	-39 (-65)	430 (378)	563 (530)	808 (848)	702 (687)	1015 (1162)
[(MeO)SnW ₅ O ₁₈] ³⁻	71 (17)	443,455 (363,383)	428 (395)		713,670 (720,684)	
[(MeO)ZrW ₅ O ₁₈] ³⁻	-12 (-58)	438,441 (385,377)	517 (484)		715,703 (711,691)	
[(MeO)TiW ₅ O ₁₈] ³⁻	-17 (-58)	438,444 (380,390)	566 (525)		718,723 (721,713)	
[(μ-O)(TiW ₅ O ₁₈) ₂] ⁶⁻	-26 (-63)	441,448 (381,390)	576 (534)	759 (697)	721,717 (722,714)	
[{(μ-HO)ZrW ₅ O ₁₈ } ₂] ⁶⁻	-23 (-58)	435,444 (378,387)	530 (479)		711,700 (712,692)	
MAE	38	60	44	59	7	69

Table S11. Computed ^{17}O Chemical Shifts^a for the Non-protonated ($\text{V}_{10}\text{O}_{28}^{6-}$) and Two Monoprotonated ($\text{HV}_{10}\text{O}_{28}^{5-}$) Forms of the Decavanadate anion. The 28 Oxygen Positions are Labeled in the Figure. The Chemical Shifts of the Protonated Oxygens in Each Case (two rightmost columns) are Highlighted in Bold.

O label	$\text{V}_{10}\text{O}_{28}^{6-}$	$\text{HV}_{10}\text{O}_{28}^{5-}$	
		O_C	O_B
1	108	113	166
8	790	827	814
9	826	826	833
10	826	832	827
11	785	828	803
12	498	509	526
13	498	533	556
14	785	199	816
15	499	516	572
16	784	832	788
17	784	807	805
18	499	521	77
19	994	1027	1010
20	995	1028	1019
21	1005	1032	1023
22	1005	1038	1031
27	108	158	166
28	791	810	814
29	827	837	834
30	826	851	827
31	785	801	804
32	785	799	816
33	785	806	789
34	784	804	805
35	994	1014	1009
36	994	1010	1018
37	1005	1026	1023
38	1005	1023	1031



^aValues in ppm.

Table S12. Changes in the Experimental and Calculated $\delta(^{17}\text{O})$ of External Oxygens upon Protonation, $\Delta\delta_{\text{cal}} = \delta(^{17}\text{O}, \text{X}_\text{B}:100\text{-X}_\text{C}) - \delta(^{17}\text{O}, \text{V}_{10}\text{O}_{28}^{6-})$, for Different $\text{HO}_\text{B}:\text{HO}_\text{C}$ Ratios.

	90 _B :10 _C	70 _B :30 _C	60_B:40_C	50 _B :50 _C	$\Delta\delta_{\text{exp}}^{\text{a}}$
O _B	−57	−39	−30	−22	−28
O _C	12	−2	−9	−16	−7
O _D	24	24	25	25	23
O _E	5	6	7	7	11
O _{F, G}	21	22	22	23	17

^a $\Delta\delta_{\text{exp}} = \delta(^{17}\text{O}, \text{pH } 4.5) - \delta(^{17}\text{O}, \text{pH } 6)$. Data taken from ref. 80.

The calculated value $\Delta\delta_{\text{cal}}$ for each mixture is simply, for example, $\Delta\delta_{\text{cal}}(60_\text{B}:40_\text{C}) = \delta_{\text{cal}}(60_\text{B}:40_\text{C}) - \delta_{\text{cal}}(\text{V}_{10}\text{O}_{28}^{6-})$, where $\delta_{\text{cal}}(60_\text{B}:40_\text{C}) = 0.6 \cdot \delta_{\text{cal}}(\text{HO}_\text{B}) + 0.4 \cdot \delta_{\text{cal}}(\text{HO}_\text{C})$, see Table 8. The ratio that best fits the experimental shifts $\Delta\delta_{\text{exp}}$ is **60_B:40_C**.