Supporting Information

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General considerations

Reactions and manipulations were carried out under dry, oxygen-free nitrogen or argon using standard Schlenk and dry-box techniques unless stated otherwise.^[1] Reactions were carried out in screw-top Schlenk flasks fitted with PTFE screw valves (Young's valves). Acetonitrile was dried with and distilled from calcium hydride and then stored over 3A molecular sieves. Diethyl ether was dried and distilled from sodium benzophenone ketyl. Dimethyl sulfoxide, dimethylformamide, ethyl acetate and deuterated solvents were all stored over 3A molecular sieves for at least three days prior to use. $(TBA)_2[W_6O_{19}]^{[2]}$, $(TBA)_2WO_4^{[3]}$ and $WO(OMe)_4^{[4]}$ were prepared as described previously. ¹⁷O enriched $(TBA)_2[W_6O_{19}]$ was prepared by hydrolysis of a 5 : 1 mixture of $WO(OMe)_4$ and $(TBA)_2[WO_4]$ respectively with 40% ¹⁷O enriched water (Goss Scientific Instruments) as previously reported.^[5]

NMR – Samples were prepared in 5 mm (¹⁷O) or 10 mm (¹⁸³W) screw top NMR tubes. Spectra were recorded on a Bruker AVANCE III 300 MHz spectrometer operating at 40.69 (¹⁷O) MHz or a Brucker AVANCE III HD 500 MHz operating at 67.80 (¹⁷O) or 20.84 (¹⁸³W) MHz. Chemical shifts are quoted in ppm relative to H₂O (¹⁷O) and saturated aqueous Na₂WO₄ (ca. 2 *M*) external standards. The ¹⁸³W NMR spectrum of degradation reaction (1) below was recorded with and without an internal standard of 2 *M* Na₂WO₄ in D₂O in a 10 mm coaxial insert in order to assess chemical shift variations.

$$5 (TBA)_{2}[W_{6}O_{19}] + 20 TBA(OH) \longrightarrow 6 "(TBA)_{5}[W_{5}O_{18}H]" + 7 H_{2}O$$
(1)

The ¹⁷O NMR spectrum of $(TBA)_2[W_6O_{19}]$ in CD₃CN is shown in Figure S1. The T_1 relaxation time of the peak at -79 ppm was determined using an inverse recovery sequence. A relaxation delay of 600 s was used to allow complete relaxation between pulses and τ_{null} was found to be approx. 38 seconds, corresponding to a T_1 of approx. 55 s, as given by the equation below:

$$\tau_{\text{null}} = T_1 \times \ln 2$$

Single crystal X-ray diffraction - Crystal structure data for (BTMA)₅**1**.2DMSO were collected on a XtaLAB Synergy, HyPix-Arc 100 diffractometer equipped with a fine-focus sealed X-ray tube ($\lambda_{Cu \ K\alpha} = 1.54184$ Å) and for (TBA)₇**1**.[W₆O₁₉] on an Xcalibur, Atlas, Gemini ultra diffractometer using molybdenum radiation ($\lambda_{Mo \ K\alpha} = 0.71073$ Å). All data were collected at 150 K using an Oxford Cryosystems CryostreamPlus open-flow N₂ cooling device. Cell refinement, data collection and data reduction were undertaken *via* software CrysAlisPro. [ref?] Intensities were corrected for absorption analytically using a multifaceted crystal model based on expressions derived by Clark & Reid.^[6] The structure was solved using XT^[7] and refined by XL^[9] using the Olex2 interface.^[8] All non-hydrogen atoms were refined anisotropically and hydrogen atoms were positioned with idealised geometry. The displacement parameters of the hydrogen atoms were constrained using a riding model with U_(H) set to be an appropriate multiple of the U_{eq} value of the parent atom. Details of any disorder and how it was modelled are available in the CIF.

Bond valence sums for the oxygen atoms of $(TBA)_5 \mathbf{1}$ were calculated according to previously reported methods^[10,11] using the equations shown below, where z_j is the oxidation state of the *j*th atom or ion, s_{ij} is the bond valence contribution from the "bond" between the *i*th and

*j*th atom/ion, R_0 is a constant that is dependent on the *ij* pair, r_{ij} is the observed bond length and b is 0.37.

$$z_j = \sum s_{ij}$$
$$s_{ij} = \exp\left[\left(R_o - r_{ij}\right)/b\right]$$

Computational methods - Density functional theory (DFT) calculations were performed using the ADF2019 package.^[12-14] The process for obtaining the ¹⁸³W NMR chemical shifts consists of (i) a geometry optimization step and (ii) a single-point NMR calculation, a procedure expressed throughout the text as FunctionalNMR/BasisNMR//FunctionalOPT/BasisOPT.

The geometries were optimised with Slater- type all-electron basis sets with the GGA-type PBE,^[15] OPBE^[16] and BP86^[17] functionals. For NMR calculations, we used a Slater- type all-electron basis set and PBE, OPBE, BP86 with spin–orbit (SO) corrections The basis sets utilized are all-electron of triple- ζ + polarization (TZP) or triple- ζ + double polarization (TZP) quality for all atoms with scalar relativistic corrections to the electrons via the zeroth-order regular approximation (ZORA).^[18-20] We also tested the performance of a large QZ4P basis set as it was reported to be the best methodology to reproduce ¹⁸³W NMR chemical shifts for polyoxometalates.^[21] Since 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 (ϵ) that induces charge polarization on a surface around the molecule.^[22,23] Taking the optimized geometry, the NMR single-point calculation is carried out for the target and reference (WO4^{2–}) anions introducing spin-orbit (SO) corrections and the GIAO method.^[24-26] The calculated chemical shift is determined as $\delta_{cal} = \sigma_{ref} - \sigma_x$, where σ_x and σ_{ref} are the isotropic average shielding for the nucleus of the target and the reference compounds, respectively.

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

$$MAE = \frac{1}{N} \sum \delta_{cal,i} - \delta_{exp,ii}$$

where $\delta_{cal,i}$ and $\delta_{exp,i}$ are the calculated and experimental chemical shifts, respectively. The coupling constants (J_{WW}) were calculated with the same methodologies stated above.

FTIR Spectra - FTIR spectra were recorded from powders on a Bruker Alpha FTIR spectrometer fitted with an Platinum ATR attachment.

Experimental

Reactions between $^{17}\text{O}\text{-enriched}$ (TBA)_2[W_6O_19] and (TBA)OH

¹⁷O enriched (TBA)₂[W₆O₁₉] (50 mg, 0.03 mmol) was added to a Schlenk flask and suspended in MeCN (1 mL). The appropriate amount of (TBA)OH (0.25 M in MeCN) was added to the flask. The total volume of the reaction mixture was made up to approx. 3 mL. The solution was stirred at room temperature for 3 days. The solvent was removed and the residual oil was dissolved in CD₃CN (0.5 mL). The mixture was transferred to a 5 mm screw top NMR tube for ¹⁷O NMR.

Note: When 0.4 eq of (TBA)OH per $(TBA)_2[W_6O_{19}]$ was used, the solid remaining after stirring the reaction mixture at room temperature for 3 days was dissolved by warming to 60 °C for 2 hours.

^{183}W NMR studies of reactions between (TBA)_2[W_6O_{19}] and (TBA)OH

(TBA)OH (1 *M* in MeOH, 5.3 mL, 5.3 mmol) was added to a Schlenk flask. The solvent was removed and the colourless oil was redissolved in MeCN (5 mL). This process was repeated twice more. The oil was then dissolved in MeCN (10 mL) and $(TBA)_2[W_6O_{19}]$ (2.50 g, 1.3 mmol) was added to give a white suspension that cleared slowly as the solid dissolved over 15-30 minutes. The solution was then stirred at room temperature for three days. The solution was then pumped dry and the residue dissolved in a mixture of MeCN/CD₃CN (1.5 mL/0.5 mL). The solution was then transferred to a 10 mm screw top NMR tube and the ¹⁸³W NMR spectrum recorded.

Preparation of (BTMA)₅[W₇O₂₄H] by treatment of (TBA)₂[W₆O₁₉] with (BTMA)OH.

 $(TBA)_2[W_6O_{19}]$ (1.0 g, 0.5 mmol) was suspended in a mixture of MeCN (20 mL) and MeOH (20 mL). Benzyltrimethylammonium hydroxide (40 wt% in MeOH, 0.95 mL, 2.1 mmol) was added. The slightly cloudy solution was stirred overnight after which a white precipitate formed. The solid was centrifuged, washed with MeOH (10 mL), MeCN (10 mL) and Et₂O (10 mL) with centrifugation at each stage, then dried under vacuum. The crude material (0.8 g) was recrystallized by dissolving in DMSO at 100 °C and dropwise addition of DMF to saturation. The solution was then heated to 160 °C and then cooled slowly on a hot plate. The solution was allowed to stand for two days, after which a mixture of crystalline and amorphous solids had formed (0.29 g, 34%).

Preparation of $(BTMA)_5[W_7O_{24}H]$ by cation exchange.

 $(TBA)_2[W_6O_{19}]$ (2.5 g, 1.3 mmol) was treated with (TBA)OH (5.3 mL, 5.3 mmol) following the procedure described above. After stirring at room temperature for 3 days, the solvent was removed, the residue dissolved in DMSO (3 mL) and a solution of (BTMA)Br (3.0 g, 13.2 mmol) in DMSO (5 mL) was added with vigorous stirring. The white precipitate formed was centrifuged, washed with MeOH (2 x 10 mL), MeCN (2 x 10 mL) and Et₂O (2 x 10 mL) with centrifugation at each stage. The solid product (1.9 g) was dried under vacuum and recrystallized from hot DMSO/DMF as described above (0.82 g, 38%). Crystals for elemental microanalysis were dried *in vacuo* after the unit cell had been determined by XRD. Found: C, 24.6; H, 3.4; N, 2.6 %. Calculated for C₅₀H₈₁N₅O₂₄W₇: C, 24.8; H, 3.4; N, 2.9 %.



Figure S1. ¹⁷O NMR spectrum of the product from treatment of $(TBA)_2[W_6O_{19}]$ with 4 equivalents of (TBA)OH in MeCN.



Figure S2. ¹⁷O NMR spectrum of $(TBA)_2[W_6O_{19}]$ in CD₃CN.



Figure S3. 17 O NMR spectrum of the reaction between (TBA)₂[W₆O₁₉] and 0.4 eq. of (TBA)OH in CD₃CN.



Figure S4. ^{17}O NMR spectrum of the reaction between (TBA)_2[W_6O_{19}] and 1 mole-equivalent of TBA(OH) in CD_3CN.



Figure S5. ¹⁷O NMR spectrum of the reaction between $(TBA)_2[W_6O_{19}]$ with 1.6 mole-equivalents of (TBA)OH in CD_3CN .



Figure S6. ¹⁷O NMR spectrum of the reaction between $(TBA)_2[W_6O_{19}]$ and 2.3 mole-equivalents of TBA(OH) in CD_3CN .



Figure S7. ^{17}O NMR spectrum of the reaction between (TBA)_2[W_6O_{19}] and 3 mole-equivalents of (TBA)OH in CD_3CN.



Figure S8. ¹⁷O NMR spectrum of the reaction between $(TBA)_2[W_6O_{19}]$ and 5.2 mole-equivalents of (TBA)OH in CD_3CN .



Figure S9. ¹⁷O NMR spectrum of the reaction between $(TBA)_2[W_6O_{19}]$ and 10 mole-equivalents of (TBA)OH in CD_3CN .



Figure S10. ¹⁸²W NMR spectrum of the reaction between $(TBA)_2[W_6O_{19}]$ and 4 mole-equivalents of (TBA)OH in CH_3CN/CD_3CN .



Figure S11. ¹⁸³W NMR spectrum of the reaction between $(TBA)_2[W_6O_{19}]$ and 4 mole-equivalents of TBA(OH) in d_6 -DMSO. Peaks marked with an asterisk are due to unknown species.



Figure S12. ¹H NMR spectrum of the product from degradation of $(TBA)_2[W_6O_{19}]$ with 4 mole-equivalents of TBA(OH) after removal of the volatiles and re-dissolution in CD₃CN.

Single Crystal X-ray Diffraction



Figure S13. Single Crystal X-ray diffraction structure of $(TBA)_7 1.[W_6O_{19}]$ with probability ellipsoids at 50% level. Cations shown in wire form for clarity.

| Table S1: Crystal data | and structure refinement for | (TBA) ₇ 1 .[W ₆ O ₁₉]. |
|------------------------|------------------------------|---|
| | | |

| Empirical formula | $C_{118}H_{261}N_{10}O_{43}W_{13}$ |
|---|--|
| Formula weight | 4898.40 |
| Temperature/K | 150.0(2) |
| Crystal system | monoclinic |
| Space group | P21/c |
| a/Å | 32.1867(8) |
| b/Å | 17.5143(4) |
| c/Å | 28.2674(7) |
| α/° | 90 |
| β/° | 90.691(2) |
| γ/° | 90 |
| Volume/Å ³ | 15934.0(7) |
| Z | 4 |
| $\rho_{calc}g/cm^3$ | 2.042 |
| µ/mm⁻¹ | 9.412 |
| F(000) | 9380.0 |
| Crystal size/mm ³ | $0.39 \times 0.14 \times 0.05$ |
| Radiation | Μο Κα (λ = 0.71073) |
| 20 range for data collection/° | 6.682 to 57.86 |
| Index ranges | $-43 \le h \le 43, -21 \le k \le 22, -34 \le l \le 38$ |
| Reflections collected | 139244 |
| Independent reflections | $36504 [R_{int} = 0.0812, R_{sigma} = 0.0967]$ |
| Data/restraints/parameters | 36504/2138/1849 |
| Goodness-of-fit on F ² | 1.069 |
| Final R indexes [I>=2σ (I)] | R ₁ = 0.0514, wR ₂ = 0.0869 |
| Final R indexes [all data] | R ₁ = 0.1213, wR ₂ = 0.1119 |
| Largest diff. peak/hole / e Å ⁻³ | 1.78/-2.61 |



Figure S14. Single Crystal X-ray diffraction structure of (BTMA)₅**1**.2DMSO with probability ellipsoids at 50% level. Cations and solvent shown in wire form for clarity.

| Empirical formula | C54H95.42N5O27.71S2W7 |
|---|--|
| Formula weight | 2605.71 |
| Temperature/K | 150.0(2) |
| Crystal system | monoclinic |
| Space group | P2 ₁ /n |
| a/Å | 23.7639(3) |
| b/Å | 10.4977(2) |
| c/Å | 29.5824(4) |
| α/° | 90 |
| β/° | 99.2090(10) |
| γ/° | 90 |
| Volume/Å ³ | 7284.69(19) |
| Z | 4 |
| $\rho_{calc}g/cm^3$ | 2.376 |
| µ/mm⁻¹ | 21.044 |
| F(000) | 4891.0 |
| Crystal size/mm ³ | $0.07 \times 0.05 \times 0.02$ |
| Radiation | Cu Kα (λ = 1.54184) |
| 20 range for data collection/ | 4.438 to 156.782 |
| Index ranges | $-29 \le h \le 30, -10 \le k \le 12, -37 \le l \le 35$ |
| Reflections collected | 49180 |
| Independent reflections | 14433 [$R_{int} = 0.0434$, $R_{sigma} = 0.0433$] |
| Data/restraints/parameters | 14433/960/922 |
| Goodness-of-fit on F ² | 1.016 |
| Final R indexes [I>=2σ (I)] | $R_1 = 0.0370$, $wR_2 = 0.0889$ |
| Final R indexes [all data] | $R_1 = 0.0492$, $wR_2 = 0.0974$ |
| Largest diff. peak/hole / e Å ⁻³ | 1.15/-2.73 |

Table S2. Crystal data and structure refinement (BMTA)₅1.2DMSO.1.71H₂O

| Atom | W-O bond length (<i>r_{ij}</i>) | S _{ij} | BVS (<i>z_j</i>) |
|------------|---|-----------------|------------------------------|
| 01 | 1.734 | 1.640 | 1.64 |
| 02 | 1.942 | 0.935 | 1 07 |
| | 1.943 | 0.932 | 1.87 |
| 03 | 1.920 | 0.992 | 1 00 |
| | 1.961 | 0.888 | 1.88 |
| | 2.134 | 0.556 | 1 80 |
| 04 | 1.835 | 1.248 | 1.80 |
| 05 | 1.946 | 0.925 | 1 07 |
| 05 | 1.936 | 0.950 | 1.87 |
| O 6 | 1.724 | 1.685 | 1.68 |
| 07 | 1.732 | 1.649 | 1.65 |
| 08 | 1.726 | 1.676 | 1.68 |
| 09 | 1.719 | 1.708 | 1.71 |
| 010 | 1.919 | 0.995 | 1 09 |
| 010 | 1.922 | 0.987 | 1.56 |
| 011 | 1.915 | 1.005 | 1 07 |
| 011 | 1.930 | 0.965 | 1.57 |
| 012 | 1.900 | 1.047 | 1 98 |
| 012 | 1.944 | 0.930 | 1.90 |
| 013 | 1.956 | 0.900 | 1 93 |
| 015 | 1.905 | 1.033 | 1.35 |
| | 2.271 | 0.384 | |
| | 2.286 | 0.369 | |
| 014 | 2.310 | 0.346 | 1.76 |
| | 2.338 | 0.321 | |
| | 2.318 | 0.338 | |
| | 1.844 | 1.218 | |
| 015 | 2.301 | 0.354 | 1.95 |
| | 2.282 | 0.373 | |
| 016 | 1.897 | 1.056 | 2.01 |
| | 1.933 | 0.958 | |
| 017 | 1.748 | 1.579 | 1.58 |
| 018 | 1.903 | 1.039 | 2.01 |
| | 1.929 | 0.968 | 4.65 |
| 019 | 1.732 | 1.649 | 1.65 |
| 020 | 2.114 | 0.587 | 1.18 |
| 034 | 2.111 | 0.592 | 1.00 |
| 021 | 1./38 | 1.622 | 1.62 |
| 022 | 1.740 | 1.013 | 1.61 |
| O23 | 1.950 | 0.912 | 1.85 |
| 024 | 1.942 | 0.935 | 1.65 |
| 024 | 1./31 | 1.003 | T.02 |

Table S3. Bond valence sums for the oxygen atoms of $(TBA)_5 \mathbf{1}$.

DFT Calculations

Optimised structure for anion **1** with PBE/TZ2P methodology

| 0 | 2.026992000 | -1.561976000 | 0.558394000 |
|---|--------------|--------------|--------------|
| 0 | 1.095016000 | 0.102449000 | 2.422638000 |
| 0 | 0.785218000 | -3.899591000 | -0.115066000 |
| 0 | -1.232505000 | -0.302464000 | 3.869409000 |
| 0 | 0.787007000 | -1.598567000 | -1.911462000 |
| 0 | -0.478444000 | -1.958496000 | 1.661875000 |
| 0 | 0.000000000 | 0.000000000 | 0.000000000 |
| 0 | -1.129143000 | 0.248039000 | -2.740587000 |
| 0 | -1.503878000 | -2.551721000 | -0.788809000 |
| 0 | -2.602858000 | -0.171055000 | 1.421698000 |
| 0 | -3.200820000 | -0.581354000 | -1.197412000 |
| 0 | -5.356262000 | -0.236542000 | 0.724185000 |
| 0 | -3.700686000 | 0.245103000 | -3.943135000 |
| W | 2.156664000 | 0.285195000 | 0.790987000 |
| W | 0.142052000 | -2.270435000 | -0.178692000 |
| W | -0.827096000 | -0.142171000 | 2.184635000 |
| 0 | 3.783461000 | 0.541371000 | 1.392527000 |
| 0 | 1.453259000 | 2.105559000 | 0.725787000 |
| 0 | 2.359269000 | 0.462280000 | -1.145730000 |
| 0 | -0.539666000 | 4.103003000 | 0.224778000 |
| 0 | 1.471000000 | 0.468145000 | -3.769605000 |
| 0 | -0.890397000 | 1.770567000 | 1.878284000 |
| 0 | 0.364294000 | 2.126231000 | -1.669616000 |
| 0 | -2.049418000 | 1.807895000 | -0.541693000 |
| 0 | -4.186752000 | 2.187710000 | 1.302044000 |
| 0 | -2.577686000 | 2.651741000 | -3.208525000 |
| 0 | -4.419011000 | 1.465213000 | -1.420975000 |
| W | -0.406681000 | 2.366554000 | 0.096075000 |
| W | 0.727939000 | 0.300105000 | -2.205004000 |
| W | -3.938489000 | 0.730636000 | 0.340845000 |
| W | -2.897753000 | 1.031487000 | -2.590800000 |
| Н | -2.459576000 | -1.218845000 | -0.998855000 |

| Oxygen type | Atom | Chemical Shift |
|-------------|-----------|----------------|
| Central | 014 | 33 |
| Bridging | 015 | 431 |
| | 023 | 368 |
| | O4 | 471 |
| | 012 / 013 | 417 |
| | 016 / 018 | 418 |
| | O20 | 134 |
| | 02 | 438 |
| | 03 / 05 | 435 |
| | 010/011 | 441 |
| Terminal | 08 | 682 |
| | 017 | 627 |
| | 022 / 024 | 653 |
| | 01 | 677 |
| | O6 | 678 |
| | 07 / 09 | 723 |
| | 019 / 021 | 676 |

Table S4. 17 O NMR chemical shifts (in ppm) for anion **1** with OPBE/TZP//PBE/TZ2P. $^{[27]}$

Infrared Spectra



Figure S15. ATR FTIR transmittance spectrum of (BTMA)Br.



Figure S16. ATR FTIR transmittance spectrum of the crude solid isolated from the reaction between $TBA_2[W_6O_{19}]$ and 4 equivalents of (BTMA)OH.



Figure S17. ATR FTIR transmittance spectrum of crystalline (BTMA)₅1.2DMSO.



Figure S18. ATR FTIR transmittance spectrum of the amorphous solid obtained after recrystallisation of the crude product from treatment of $(TBA)_2[W_6O_{19}]$ with 4 equivalents of (BTMA)OH from DMSO/DMF.

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