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A thirty-year old mystery solved: identification of a new heptatungstate from non-aqueous solutions†

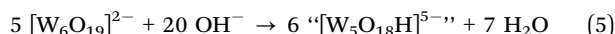
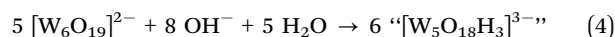
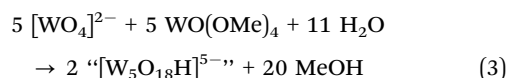
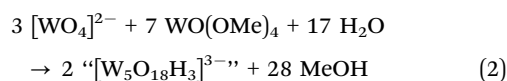
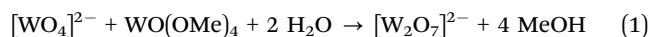
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A new isopolyoxotungstate has been characterised, thirty years since the first spectroscopic evidence of its existence. The heptatungstate [W₇O₂₄H]^{5−}, containing a {W₅} lacunary Lindqvist unit fused to a ditungstate fragment, has significant stability and is only the third isopolytungstate structure to be obtained from non-aqueous systems.

The formation of isopolyoxotungstates [W_xO_yH_z]^{n−} by acidification of aqueous [WO₄]^{2−} solutions is well established.¹ Anions with different *n/x* values may be isolated from such solutions and characterised by single crystal X-ray diffraction, but these do not necessarily provide a true indication of the structures present in solution and, in this regard, the detailed ¹⁸³W and ¹⁷O NMR studies of Maksimovskaya and Howarth were pivotal in developing an understanding of the pH-dependent speciation in aqueous isopolytungstate solutions.^{2,3} Recently, Falaise and co-workers have demonstrated that supramolecular interactions in the presence of γ -cyclodextrin can have a profound effect on the tungstate species present in such solutions.⁴ Details of isopolytungstate formation in non-aqueous media have been far less investigated and, importantly, the influence of water on the formation and solution stability of isopolytungstate structures in organic media is poorly understood. Although organic-soluble tetraalkylammonium salts of isopolytungstates have been characterised by liquid state ¹⁸³W and ¹⁷O NMR spectroscopy, these are generally prepared from aqueous solutions by cation exchange,¹ so these studies provide limited insight into the effects on the assembly process of moving from aqueous to organic solvents. An exception is the seminal work of Jahr and co-workers, who prepared polyoxometalates (POMs)

by basic hydrolysis of metal alkoxides in organic solvents, including the synthesis of [W₆O₁₉]^{2−} from the oxoalkoxides WO(OR)₄ (R = Me, Et).⁵

In 1993, we reported ¹⁸³W NMR studies of non-aqueous attempts to prepare the unknown molecular ditungstate [W₂O₇]^{2−} as its ⁿBu₄N⁺ (TBA) salt, including the hydrolytic approach shown in eqn (1).⁶ These revealed an intriguing and apparently new isopolytungstate, but its high solubility has frustrated all subsequent attempts at crystallographic characterisation. Our non-aqueous studies of heterometal-containing {MW₅} Lindqvist-type POMs have involved syntheses from putative lacunary precursors [W₅O₁₈H₂]^{(6−z)−}, targeted either by the controlled hydrolysis of WO(OMe)₄ in the presence of [WO₄]^{2−} as in eqn (2) and (3) or, more recently, by base-degradation of [W₆O₁₉]^{2−} as in eqn (4) and (5). Both approaches facilitate ¹⁷O enrichment of the POM framework, either by addition of ¹⁷O enriched water or by degradation of ¹⁷O-enriched [W₆O₁₉]^{2−}. Direct treatment of these dynamic reaction mixtures with heterometal precursors M(OR)₄ (z = 3) or MX₂ (z = 1) provides versatile access to a series of reactive Lindqvist polyoxometalates [(RO)MW₅O₁₈]^{3−} or [(MW₅O₁₈H)₂]^{6−} respectively.^{7–11}



In attempts to identify the species generated in non-aqueous reactions targeting “virtual” lacunary [W₅O₁₈H₂]^{(6−z)−} precursors, we have examined the solutions by ¹⁸³W and ¹⁷O NMR spectroscopy. Degradation of [W₆O₁₉]^{2−} with the stoichiometry in eqn (5), *i.e.* where *z* = 1 and *n/x* = 1.0, followed by removal of the volatiles gave a product with the ¹⁷O NMR spectrum shown in Fig. S1

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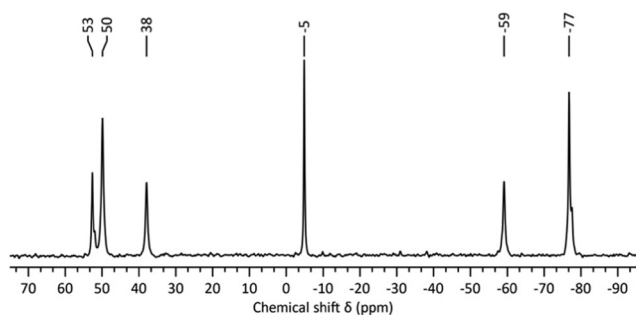


Fig. 1 ^{183}W NMR spectrum of the product from treatment of $(\text{TBA})_2[\text{W}_6\text{O}_{19}]$ with 4 equivalents of $(\text{TBA})\text{OH}$ in MeCN.

(ESI †), where the two sets of broad peaks 721–642 ppm and 395–328 ppm are characteristic of terminal $\text{W}=\text{O}$ and bridging WOW respectively. The peaks at 437 and -1.6 ppm are assigned to $[\text{WO}_4]^{2-}$ and H_2O respectively. The ^{183}W NMR spectrum of this solution shown in Fig. 1 contains a peak at -5 ppm due to $[\text{WO}_4]^{2-}$ and five peaks at 53, 50, 38, -59 and -77 , ppm in the ratio 1:2:1:1:2 respectively, which is indicative of an isopolytungstate containing $7n$ tungsten atoms in five unique environments. These spectra are remarkably similar to those obtained during our attempts to prepare $[\text{W}_2\text{O}_7]^{2-}$ by reaction (1),⁶ although peaks in previous ^{183}W NMR spectra were ~ 9 ppm upfield of those in the current studies. This further indicated that the 5-line ^{183}W NMR spectrum with 1:2:1:1:2 peak intensities is associated with a fundamental polytungstate structure in non-aqueous solutions of $[\text{W}_x\text{O}_y\text{H}_z]^{n-}$ with $n/x = 1.0$.

Details of our extensive investigations into non-aqueous tungstate speciation will be reported elsewhere, but ^{17}O and ^{183}W NMR spectra from the degradation of $(\text{TBA})_2[\text{W}_6\text{O}_{19}]$ with varying amounts of $\text{TBA}(\text{OH})$ are shown in Fig. S2–S11 (ESI †). Note that the spectrum of $(\text{TBA})_2[\text{W}_6\text{O}_{19}]$ (Fig. S2, ESI †) was recorded with a significantly longer delay time between pulses (600 seconds) to enable observation of the central oxygen at -79 ppm. This oxygen has an extremely long T_1 relaxation time of $\sim 55(\pm 1)$ s due to the absence of an electric field gradient and associated relaxation mechanism for the quadrupolar ^{17}O in the centre of the highly symmetrical $[\text{W}_6\text{O}_{19}]^{2-}$ anion. After addition of 0.4 mole-equivalent of $\text{TBA}(\text{OH})$ to $(\text{TBA})_2[\text{W}_6\text{O}_{19}]$ a complex ^{17}O NMR spectrum was observed with several broad peaks in both terminal $\text{W}=\text{O}$ and bridging $\text{W}-\text{O}-\text{W}$ regions. The more intense, narrow peaks at 416 ppm and 776 ppm are characteristic of $[\text{W}_6\text{O}_{19}]^{2-}$, indicating incomplete degradation of the hexatungstate. With increasing amounts of base, the spectra simplified somewhat as the residual $[\text{W}_6\text{O}_{19}]^{2-}$ was consumed, while the peak assigned to $[\text{WO}_4]^{2-}$ at 437–439 ppm steadily increased in intensity with a concomitant decrease in the intensity of the broad $\text{W}=\text{O}$ and $\text{W}-\text{O}-\text{W}$ features. The complexity of ^{17}O NMR spectra prevented definitive peak assignments for the species responsible for the ^{183}W NMR spectrum shown in Fig. 1.

Vapour diffusion of diethyl ether into the NMR solution for the reaction between $(\text{TBA})_2[\text{W}_6\text{O}_{19}]$ and 1 mole-equivalent of $\text{TBA}(\text{OH})$ to give $n/x = 0.5$ produced colourless crystals over several weeks. Single-crystal X-ray crystallographic analysis showed these

to be a 1:1 co-crystalline mixture of $[\text{W}_6\text{O}_{19}]^{2-}$ and the new isopolytungstate $[\text{W}_7\text{O}_{24}\text{H}]^{5-}$ **1** shown in Fig. 3. The average n/x value in the crystal is 0.53 and the full structure is shown in Fig. S13 (ESI †). The protonated formula for **1** is supported by the number of TBA cations in the crystal structure of $(\text{TBA})_7\cdot[\text{W}_6\text{O}_{19}]\cdot 3\text{MeCN}$, the hydrogen-bonded O17–O20 distance and the observation of a peak at 8.51 ppm in the ^1H NMR spectrum (Fig. S12, ESI †). The structure of **1** is markedly different from that of the heptatungstate $[\text{W}_7\text{O}_{24}]^{6-}$ obtained from aqueous solutions, and can be regarded as a fusion of lacunary $\{\text{W}_5\text{O}_{18}\}$ and ditungstic $\{\text{W}_2\text{O}_5\text{OH}\}$ fragments, a feature similar to that observed in (W_2) -capped lacunary $\{\text{BW}_{11}\text{O}_{39}\}$ units isolated from aqueous borotungstate solutions.¹² Using Pope's classification, **1** can be described as a type III POM containing addenda atoms with both one or two terminal $\text{M}=\text{O}$ bonds.¹³ The longer terminal $\text{W}=\text{O}$ bond lengths in the W_5 unit of **1** ($\text{W1}-\text{W4}$, average *ca.* 1.73 Å) compared with those for the $[\text{W}_6\text{O}_{19}]^{2-}$ anion in the co-crystal (average *ca.* 1.69 Å) can be ascribed to the higher charge associated with **1**. The bridging $\text{W}-\text{O}$ bond lengths in **1** show significant distortions compared with those in $[\text{W}_6\text{O}_{19}]^{2-}$ (average bridging $\text{W}-\text{O}$ of *ca.* 1.92 Å). The asymmetric links between the $\{\text{W}_5\}$ and $\{\text{W}_2\}$ units in **1** have WOW angles of 146.8° and 146.1° , with shorter $\text{W}-\text{O}$ bonds to the $\{\text{W}_5\}$ unit ($\text{W2}-\text{O15}$, $\text{W3}-\text{O16}$ and $\text{W5}-\text{O18}$, average *ca.* 1.88 Å), while the lengthening of $\text{W2}-\text{O2}$, $\text{W3}-\text{O3}$, $\text{W4}-\text{O4}$ and $\text{W5}-\text{O5}$ bonds within the $\{\text{W}_5\}$ unit (average *ca.* 1.99 Å) is consistent with a *trans* effect from more strongly π -bonding oxygens. Bridging $\text{W}-\text{O}$ bonds in the $\{\text{W}_5\}$ equatorial plane and those to W1 are similar to those observed in $[\text{W}_6\text{O}_{19}]^{2-}$, with an average of *ca.* 1.92 Å. Bond valence sum analysis (Table S3, ESI †) indicates localisation of the proton on O20 rather than on O17 ($V_{\text{O20}} = 1.18$ vs. $V_{\text{O17}} = 1.58$). Together with the short $\text{W4}-\text{O17}$ bond length of 1.750(7) Å, indicating significant $\text{W}=\text{O}$ π -bonding, this implies that this linkage is best described as $\text{W}=\text{O} \cdots \text{HOW}_2$ rather than $\text{WOH} \cdots \text{OW}_2$ involving terminal $\text{W}-\text{OH}$. The capping $\{\text{W}_2\}$ unit contains two *cis*- WO_2 fragments with average terminal $\text{W}=\text{O}$ bond lengths of *ca.* 1.74 Å, which is similar to the others in the structure. For the three oxygens bridging W6 and W7 , the shortest $\text{W}-\text{O}$ bonds (1.940(7) and 1.949(7) Å) are to O23, which is $\mu_2\text{-O}$, while those to O20 ($\mu_2\text{-OH}$) and O15 ($\mu_3\text{-O}$) average *ca.* 2.20 Å. The effective C_s symmetry of **1** gives a ratio of 1:2:1:1 for the five tungsten atoms in the $\{\text{W}_5\}$ unit, with equivalent W atoms in the $\{\text{W}_2\}$ capping unit. This is consistent with the 5-line pattern of the ^{183}W NMR spectrum in Fig. 1, and also with the $^2J_{\text{WW}}$ coupling previously observed for the two most intense peaks, as $^2J_{\text{WW}}$ values of ~ 20 Hz are associated with larger WOW angles.¹⁴ The numbers of $\text{W}=\text{O}$ and WOW peaks observed in ^{17}O NMR spectra of products from reactions (1) and (5) are also consistent with the structure in Fig. 3.

Density functional theory was used to optimise the structure of $[\text{W}_7\text{O}_{24}\text{H}]^{5-}$ and calculate ^{183}W NMR parameters, including $^2J_{\text{WW}}$ between $\text{W3}/\text{W5}$ and $\text{W6}/\text{W7}$ (ESI †). The computed ^{183}W chemical shifts obtained from different computational procedures are shown in Table 1 and deviations from the experimental values obtained in this study are given as mean absolute errors (MAEs). The best methodology for reproducing the experimental ^{183}W NMR spectrum of **1** is OPBE/TZP//PBE/



Table 1 Computed and observed ^{183}W NMR chemical shifts and $^2J_{\text{WW}}$ (W3O7/W5O6) using different methodologies for **1** as shown in Fig. 3

Procedure (NMR/OPT)	Chemical shift/ppm						$^2J_{\text{WW}}/\text{Hz}$
	W1	W4	W5/3	W2	W6/7	MAE	
PBE/TZP//PBE86/TZ2P	-44	138	152	118	-38	64	22.6
OPBE/TZP//PBE/TZ2P	-98	93	105	70	-80	34	22.8
PBE/TZP//OPBE/TZ2P	-66	94	126	87	-60	38	22.8
BP86/TZP//BP86/QZ4P	-51	135	146	112	-46	58	23.0
Observed	-59	53	50	38	-77	—	22.6 ^a

^a Value taken from ref. 6.

TZ2P, with a MAE of 34 ppm compared to the values shown in Fig. 1. Calculated values for $^2J_{\text{WW}}$ coupling between W3/W5 and W6/W7 are in excellent agreement with our previous experimental values,⁶ regardless of the methodology used. ^{17}O NMR chemical shifts for **1** were also computed (Table S4, ESI[†]) in order to rationalise the series of peaks observed in the terminal W=O and bridging W–O–W regions of the ^{17}O NMR spectrum and results were consistent with the overlapping pattern of peaks shown in Fig. S1 (ESI[†]).

Despite the minor variations in ^{183}W chemical shifts for different samples, this led us to believe that anion **1** was indeed responsible for the 5-line ^{183}W and complex ^{17}O NMR spectra observed for reactions (1) and (5). To shed light on the chemical shift variations, eliminate ambiguity from spectral assignments and confirm the presence of $[\text{WO}_4]^{2-}$, ^{183}W NMR studies of the degradation mixture from (5) after removal of the volatiles were repeated with a capillary insert containing 2 M $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in D_2O (Fig. 2a), which provided a consistent reference peak at 0.5 ppm. The upfield peak for **1** at ~ -75 ppm showed the greatest chemical shift variation of *ca.* 4 ppm but most striking

was the *ca.* 20 ppm variation in the $[\text{WO}_4]^{2-}$ chemical shift (Fig. 2a). The effects of concentration and the presence of water on the chemical shift of $[\text{WO}_4]^{2-}$ were therefore investigated. ^{183}W NMR spectra of 2 M and 1 M solutions of $(\text{TBA})_2[\text{WO}_4]$ in MeCN (Fig. 2b and c) showed an upfield shift of 2 ppm for the 1 M solution but, as the reaction mixtures used for the ^{183}W NMR spectra shown in Fig. 1b and 2a contained similar relative amounts of $[\text{WO}_4]^{2-}$, concentration did not appear to be the cause of the large chemical shift difference. More significantly, the addition of one equivalent of water to the 1 M solution of $(\text{TBA})_2[\text{WO}_4]$ in MeCN (Fig. 2d) produced an upfield shift of >9 ppm. Given that water is an expected product from base-degradation of $[\text{W}_6\text{O}_{19}]^{2-}$, it is likely that this is the cause of the variation in the $[\text{WO}_4]^{2-}$ peak position, which is not surprising in view of the high basicity of the $[\text{WO}_4]^{2-}$ anion as exemplified by the hydrogen-bonded water in the crystal structure of $(\text{BTMA})_2[\text{WO}_4] \cdot \text{H}_2\text{O}$ (BTMA = $\text{PhCH}_2\text{Me}_3\text{N}^+$).¹⁵ The presence of H_2O or MeOH might similarly be expected to affect chemical shifts of W atoms bonded to basic oxygens in **1**.

It was also evident that the linewidth of the $[\text{WO}_4]^{2-}$ peak is significantly broader in reaction mixtures produced by base-degradation of $(\text{TBA})_2[\text{W}_6\text{O}_{19}]$ than in spectra of $(\text{TBA})_2[\text{WO}_4]$ alone. The FWHM increases from *ca.* 2.5 Hz in Fig. 2b–d to *ca.* 10.5 Hz in spectra of solutions that also contain **1**. This was confirmed by combining the reaction mixture responsible for the ^{183}W spectrum in Fig. 2a with the 1 M $(\text{TBA})_2[\text{WO}_4]$ solution containing one equivalent of water. In the ^{183}W NMR spectrum of the resulting mixture (Fig. 2e), the chemical shift of $[\text{WO}_4]^{2-}$ is approximately the mean of the corresponding shifts in the original solutions, which may be explained by the lowered $\text{H}_2\text{O}:[\text{WO}_4]^{2-}$ ratio in the mixture. The broadened $[\text{WO}_4]^{2-}$ peak in Fig. 1 and 2a compared with that for the 1 M solution of $(\text{TBA})_2[\text{WO}_4]$ with 1 eq. of water also suggests exchange between $[\text{WO}_4]^{2-}$ and **1**. Peaks in the ^{183}W NMR spectra of **1** from our previous studies were notably narrower than those from these current studies, and a $^2J_{\text{WW}}$ coupling of 22.6 Hz was resolved from satellites associated with the larger peaks now assigned to W(3/5) and W(6/7). The absence of resolved coupling in Fig. 1

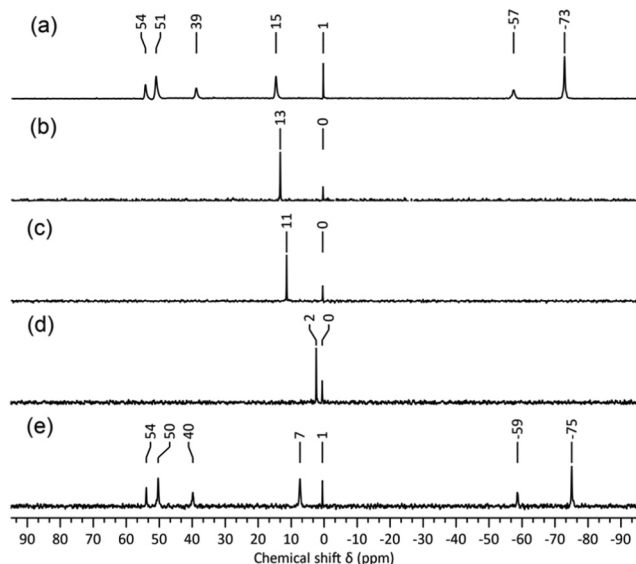


Fig. 2 ^{183}W NMR spectra of (a) $(\text{TBA})_2[\text{W}_6\text{O}_{19}] + 4$ eq. of $\text{TBA}(\text{OH})$, (b) 2 M $(\text{TBA})_2[\text{WO}_4]$, (c) 1 M $(\text{TBA})_2[\text{WO}_4]$, (d) 1 M $(\text{TBA})_2[\text{WO}_4] + 1$ eq. H_2O , and (e) a combination of solutions responsible for the spectra in (a) and (d). All spectra recorded in MeCN with an internal co-axial capillary containing 2 M $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ in D_2O .

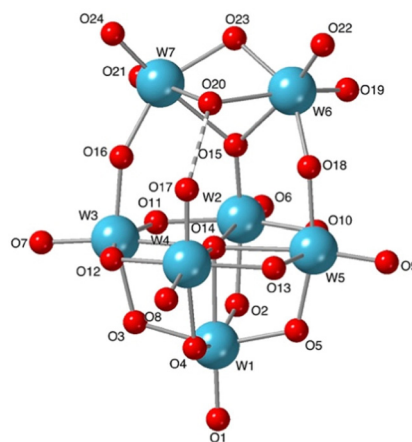


Fig. 3 Structure of $[\text{W}_7\text{O}_{24}\text{H}]^{5-}$ **1** in the co-crystal $(\text{TBA})_1 \cdot [\text{W}_6\text{O}_{19}] \cdot 3\text{MeCN}$.



and 2a may be explained by either (i) exchange involving $[\text{WO}_4]^{2-}$ formed in base degradation reactions or (ii) line broadening due to chemical shift anisotropy, which is expected to be more problematic with the low-gamma broad-band probe and 11.7 T magnet than with the dedicated ^{183}W probe and 7.05 T magnet used in previous studies.

While these combined NMR, structural and computational data suggested strongly that **1** is the main species produced in non-aqueous tungstate solutions with $n/x = 1.0$, insufficient $(\text{TBA})_7\text{1} \cdot [\text{W}_6\text{O}_{19}] \cdot 3\text{MeCN}$ co-crystals were obtained to record confirmatory ^{183}W and ^{17}O NMR spectra and we sought to obtain X-ray structural data on crystals of a salt of **1** obtained from a solution with the characteristic 5-line ^{183}W NMR spectrum. The high solubility in organic solvents of $(\text{TBA})_5\text{1}$ obtained from reactions (1) and (5) precluded its crystallisation and separation from any $(\text{TBA})_2[\text{WO}_4]$ formed in degradation reactions. In order to isolate crystals containing **1** in the absence $[\text{W}_6\text{O}_{19}]^{2-}$, we therefore treated $(\text{TBA})_2[\text{W}_6\text{O}_{19}]$ with four mole-equivalents of $(\text{BTMA})\text{OH}$ in a mixture of MeOH and MeCN. The white precipitate obtained after stirring at room temperature overnight was recrystallised from hot DMSO/DMF to give a mixture of amorphous solid and colourless crystals, which were shown to be $(\text{BTMA})_5[\text{W}_7\text{O}_{24}\text{H}] \cdot 2\text{DMSO} \cdot 1.71\text{H}_2\text{O}$ by single-crystal X-ray diffraction (Fig. S14, ESI†). FTIR spectra of the crystalline material and the amorphous solid were identical (Fig. S17 and S18, ESI†), but we were unable to record a ^{183}W NMR spectrum of $(\text{BTMA})_5\text{1}$ due to its low solubility in organic solvents. To prove that the 5-line ^{183}W NMR spectra obtained from reactions (1) and (5) were both due to **1** we first carried out reaction (5) in MeCN to obtain a spectrum analogous to that shown in Fig. 1, then removed the solvent and re-recorded the ^{183}W NMR spectrum in DMSO to confirm the retention of a 5-line spectrum (Fig. S10 and S11, ESI†). Subsequent addition of $(\text{BTMA})\text{Br}$ and recrystallisation of the resulting precipitate from hot DMSO/DMF gave crystals that were shown by X-ray crystallography to be $(\text{BTMA})_5\text{1} \cdot 2\text{DMSO}$ by comparison of unit cell parameters with the previous sample (Table S2, ESI†). Elemental microanalysis was consistent with a formula having five BTMA cations and hence a protonated anion.

To our knowledge, **1** joins $[\text{W}_6\text{O}_{19}]^{2-}$ and $[\text{W}_{10}\text{O}_{32}]^{4-}$ as the only isopolytungstates to be isolated and characterised from non-aqueous solutions. In the FTIR spectrum of $(\text{BTMA})_5\text{1}$ (Fig. S17, ESI†), the band for $\nu(\text{W}=\text{O})$ at 922 cm^{-1} is lower than that for $(\text{TBA})_2[\text{W}_6\text{O}_{19}]$ and $(\text{TBA})_4[\text{W}_{10}\text{O}_{32}]$ at 967 and 953 cm^{-1} respectively due to the greater anionic charge of **1**. By analogy with the FTIR spectra of $(\text{TBA})_2[\text{Mo}_6\text{O}_{19}]$ and $(\text{TBA})_2[\text{Mo}_2\text{O}_7]$, either of the bands at 863 or 821 cm^{-1} may be associated with $\nu(\text{W}=\text{O})$ for *cis*- WO_2 in **1**.

We have demonstrated conclusively that the new isopolytungstate $[\text{W}_7\text{O}_{24}\text{H}]^{5-}$ **1** is formed by both hydrolytic aggregation reaction (1) and by degradation reaction (5). Crucially, this means that **1** is present in non-aqueous $[\text{W}_x\text{O}_y\text{H}_z]^{n-}$ mixtures

with $n/x = 1.0$, i.e. those used in our attempts to prepare $(\text{TBA})_2[\text{W}_2\text{O}_7]$ or lacunary Lindqvist-type $(\text{TBA})_5[\text{W}_5\text{O}_{18}\text{H}]$ species, and for the synthesis of a wide range of heterometal-substituted Lindqvist $\{\text{MW}_5\text{O}_{18}\}$ anions, suggesting that the $\{\text{W}_5\}$ fragment is retained upon treatment with a wide variety of heterometal sources. This represents a major advance in the understanding of previously ill defined “virtual” precursor solutions and will further guide our development of rational protocols for targeted POM synthesis.

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Conflicts of interest

There are no conflicts to declare.

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