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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 $[W_7O_{24}H]^{5-}$, containing a $\{W_5\}$ 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 $[W_r O_v H_z]^{n-}$ by acidification of aqueous $[WO_4]^{2-}$ 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)

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by basic hydrolysis of metal alkoxides in organic solvents, including the synthesis of $[W_6O_{19}]^{2-}$ 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 $[W_2O_7]^{2-1}$ as its ${}^{n}\text{Bu}_{4}\text{N}^{+}$ (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 nonaqueous studies of heterometal-containing {MW₅} Lindqvist-type POMs have involved syntheses from putative lacunary precursors $[W_5O_{18}H_2]^{(6-2)-}$, targeted either by the controlled hydrolysis of $WO(OMe)_4$ in the presence of $[WO_4]^{2-}$ as in eqn (2) and (3) or, more recently, by base-degradation of $[W_6O_{19}]^{2-}$ 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 $[W_6O_{19}]^{2-}$. Direct treatment of these dynamic reaction mixtures with heterometal precursors $M(OR)_4$ (z = 3) or MX_2 (z = 1) provides versatile access to a series of reactive Lindqvist polyoxometalates $[(RO)MW_5O_{18}]^{3-}$ or $[(MW_5O_{18}H)_2]^{6-}$ respectively.⁷⁻¹¹

$$[WO_4]^{2-} + WO(OMe)_4 + 2 H_2O \rightarrow [W_2O_7]^{2-} + 4 MeOH$$
(1)
3 $[WO_4]^{2-} + 7 WO(OMe)_4 + 17 H_2O$

 $\rightarrow 2 "[W_5 O_{18} H_3]^{3-}" + 28 \text{ MeOH}$ (2)

$$5 [WO_4]^{2-} + 5 WO(OMe)_4 + 11 H_2O$$

$$\rightarrow 2 "[W_5 O_{18} H]^{5-}" + 20 MeOH$$
 (3)

$$5 \left[W_6 O_{19} \right]^{2-} + 8 \text{ OH}^- + 5 \text{ H}_2 \text{O} \rightarrow 6 " \left[W_5 O_{18} \text{H}_3 \right]^{3-} " \qquad (4)$$

$$5 \left[W_6 O_{19} \right]^{2-} + 20 \text{ OH}^- \to 6 \text{ ``} \left[W_5 O_{18} \text{H} \right]^{5-} \text{''} + 7 \text{ H}_2 \text{O}$$
 (5)

In attempts to identify the species generated in non-aqueous reactions targeting "virtual" lacunary $[W_5O_{18}H_2]^{(6-2)-}$ precursors, we have examined the solutions by ¹⁸³W and ¹⁷O NMR spectroscopy. Degradation of $[W_6O_{19}]^{2-}$ 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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 $(TBA)_{2}[W_{6}O_{19}]$ with 4 equivalents of (TBA)OH in MeCN.

(ESI[†]), where the two sets of broad peaks 721–642 ppm and 395– 328 ppm are characteristic of terminal W=O and bridging WOW respectively. The peaks at 437 and -1.6 ppm are assigned to $[WO_4]^{2-}$ and H₂O respectively. The ¹⁸³W NMR spectrum of this solution shown in Fig. 1 contains a peak at -5 ppm due to $[WO_4]^{2-}$ 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 7*n* tungsten atoms in five unique environments. These spectra are remarkably similar to those obtained during our attempts to prepare $[W_2O_7]^{2-}$ by reaction (1),⁶ although peaks in previous ¹⁸³W NMR spectra were ~ 9 ppm upfield of those in the current studies. This further indicated that the 5-line ¹⁸³W NMR spectrum with 1:2:1:1:2 peak intensities is associated with a fundamental polytungstate structure in nonaqueous solutions of $[W_xO_yH_z]^{n-}$ with n/x = 1.0.

Details of our extensive investigations into non-aqueous tungstate speciation will be reported elsewhere, but ¹⁷O and ¹⁸³W NMR spectra from the degradation of (TBA)₂[W₆O₁₉] with varying amounts of TBA(OH) are shown in Fig. S2-S11 (ESI[†]). Note that the spectrum of (TBA)₂[W₆O₁₉] (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 ~ $55(\pm 1)$ s due to the absence of an electric field gradient and associated relaxation mechanism for the quadrupolar ¹⁷O in the centre of the highly symmetrical $[W_6O_{19}]^{2-}$ anion. After addition of 0.4 mole-equivalent of TBA(OH) to (TBA)₂[W₆O₁₉] a complex ¹⁷O NMR spectrum was observed with several broad peaks in both terminal W=O and bridging W-O-W regions. The more intense, narrow peaks at 416 ppm and 776 ppm are characteristic of $[W_6O_{19}]^{2-}$, indicating incomplete degradation of the hexatungstate. With increasing amounts of base, the spectra simplified somewhat as the residual [W₆O₁₉]²⁻ was consumed, while the peak assigned to $[WO_4]^{2-}$ at 437-439 ppm steadily increased in intensity with a concomitant decrease in the intensity of the broad W=O and W-O-W features. The complexity of ¹⁷O NMR spectra prevented definitive peak assignments for the species responsible for the ¹⁸³W NMR spectrum shown in Fig. 1.

Vapour diffusion of diethyl ether into the NMR solution for the reaction between $(TBA)_2[W_6O_{19}]$ and 1 mole-equivalent of TBA(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 $[W_6O_{19}]^{2-}$ and the new isopolytungstate $[W_7O_{24}H]^{5-}$ **1** shown in Fig. 3. The average n/xvalue 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 (TBA)71. [W6O19] 3MeCN, 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 [W7O24]⁶⁻ obtained from aqueous solutions, and can be regarded as a fusion of lacunary {W₅O₁₈} and ditungstic {W₂O₅OH} fragments, a feature similar to that observed in (W₂)-capped lacunary {BW₁₁O₃₉} 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 M=O bonds.¹³ The longer terminal W=O bond lengths in the W₅ unit of **1** (W1–W4, average *ca.* 1.73 Å) compared with those for the $[W_6O_{19}]^{2-}$ anion in the co-crystal (average ca. 1.69 Å) can be ascribed to the higher charge associated with 1. The bridging W-O bond lengths in 1 show significant distortions compared with those in [W₆O₁₉]²⁻ (average bridging W-O of ca. 1.92 Å). The asymmetric links between the $\{W_5\}$ and $\{W_2\}$ units in 1 have WOW angles of 146.8° and 146.1°, with shorter W-O bonds to the {W₅} unit (W2-O15, W3-O16 and W5–O18, average ca. 1.88 Å), while the lengthening of W2–O2, W3-O3, W4-O4 and W5-O5 bonds within the $\{W_5\}$ unit (average *ca.*1.99 Å) is consistent with a *trans* effect from more strongly π bonding oxygens. Bridging W-O bonds in the {W₅} equatorial plane and those to W1 are similar to those observed in $[W_6O_{19}]^{2-}$, 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 ($V_{O20} = 1.18 \text{ vs. } V_{O17} = 1.58$). Together with the short W4–O17 bond length of 1.750(7) Å, indicating significant W=O π -bonding, this implies that this linkage is best described as W=O···HOW₂ rather than $WOH \cdots OW_2$ involving terminal W-OH. The capping {W₂} unit contains two *cis*-WO₂ fragments with average terminal W=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 W-O bonds (1.940(7) and 1.949(7) Å) are to O23, which is μ_2 -O, while those to O20 (μ_2 -OH) and O15 (μ_3 -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 $\{W_5\}$ unit, with equivalent W atoms in the {W₂} capping unit. This is consistent with the 5-line pattern of the ¹⁸³W NMR spectrum in Fig. 1, and also with the ${}^{2}J_{WW}$ coupling previously observed for the two most intense peaks, as ²J_{WW} values of ~ 20 Hz are associated with larger WOW angles.¹⁴ The numbers of W=O and WOW peaks observed in ¹⁷O 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 $[W_7O_{24}H]^{5-}$ and calculate ¹⁸³W NMR parameters, including ${}^2J_{WW}$ between W3/W5 and W6/W7 (ESI†). The computed ¹⁸³W 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 ¹⁸³W NMR spectrum of **1** is OPBE/TZP//PBE/

Table 1 Computed and observed $^{183}\rm{W}$ NMR chemical shifts and $^2J_{\rm WW}$ (W3OW7/W5OW6) using different methodologies for 1 as shown in Fig. 3

	Chemical shift/ppm						
Procedure (NMR//OPT)	W1	W4	W5/3	W2	W6/7	MAE	$^{2}J_{WW}/Hz$
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
^{<i>a</i>} Value taken from ref. 6.							

TZ2P, with a MAE of 34 ppm compared to the values shown in Fig. 1. Calculated values for ${}^{2}J_{WW}$ 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 ¹⁸³W chemical shifts for different samples, this led us to believe that anion **1** was indeed responsible for the 5-line ¹⁸³W and complex ¹⁷O 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 $[WO_4]^{2-}$, ¹⁸³W NMR studies of the degradation mixture from (5) after removal of the volatiles were repeated with a capillary insert containing 2 M Na₂WO₄·2H₂O in D₂O (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



Fig. 2 ¹⁸³W NMR spectra of (a) $(TBA)_2[W_6O_{19}] + 4 \text{ eq. of TBA}(OH)$, (b) 2 M $(TBA)_2[WO_4]$, (c) 1 M $(TBA)_2[WO_4]$, (d) 1 M $(TBA)_2[WO_4] + 1 \text{ eq. H}_2O$, 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 Na_2WO_4·2H_2O in D_2O.

was the *ca.* 20 ppm variation in the $[WO_4]^{2-}$ chemical shift (Fig. 2a). The effects of concentration and the presence of water on the chemical shift of $[WO_4]^{2-}$ were therefore investigated. ¹⁸³W NMR spectra of 2 M and 1 M solutions of $(TBA)_2[WO_4]$ 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 ¹⁸³W NMR spectra shown in Fig. 1b and 2a contained similar relative amounts of $[WO_4]^{2-}$, 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 (TBA)₂[WO₄] in MeCN (Fig. 2d) produced an upfield shift of >9 ppm. Given that water is an expected product from basedegradation of $[W_6O_{19}]^{2-}$, it is likely that this is the cause of the variation in the $[WO_4]^{2-}$ peak position, which is not surprising in view of the high basicity of the $[WO_4]^{2-}$ anion as exemplified by the hydrogen-bonded water in the crystal structure of $(BTMA)_2[WO_4] \cdot H_2O$ (BTMA = PhCH₂Me₃N⁺).¹⁵ The presence of H₂O 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 $[WO_4]^{2-}$ peak is significantly broader in reaction mixtures produced by basedegradation of (TBA)₂[W₆O₁₉] than in spectra of (TBA)₂[WO₄] 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 ¹⁸³W spectrum in Fig. 2a with the 1 M (TBA)₂[WO₄] solution containing one equivalent of water. In the ¹⁸³W NMR spectrum of the resulting mixture (Fig. 2e), the chemical shift of $[WO_4]^{2-1}$ is approximately the mean of the corresponding shifts in the original solutions, which may be explained by the lowered H₂O: $[WO_4]^{2-}$ ratio in the mixture. The broadened $[WO_4]^{2-}$ peak in Fig. 1 and 2a compared with that for the 1 M solution of $(TBA)_2[WO_4]$ with 1 eq. of water also suggests exchange between $[WO_4]^{2-}$ and **1**. Peaks in the ¹⁸³W NMR spectra of **1** from our previous studies were notably narrower than those from these current studies, and a ²J_{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. 3 Structure of $[W_7O_{24}H]^{5-}$ 1 in the co-crystal $(TBA)_71\cdot [W_6O_{19}]\cdot$ 3MeCN.

and 2a may be explained by either (i) exchange involving $[WO_4]^{2-}$ 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 ¹⁸³W 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 (TBA)₇1. [W₆O₁₉]·3MeCN co-crystals were obtained to record confirmatory ¹⁸³W and ¹⁷O 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 ¹⁸³W NMR spectrum. The high solubility in organic solvents of (TBA)₅1 obtained from reactions (1) and (5) precluded its crystallisation and separation from any (TBA)₂[WO₄] formed in degradation reactions. In order to isolate crystals containing 1 in the absence $[W_6O_{19}]^{2-}$, we therefore treated $(TBA)_2[W_6O_{19}]$ with four mole-equivalents of (BTMA)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 (BTMA)₅[W₇O₂₄H]·2DMSO·1.71H₂O 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 ¹⁸³W NMR spectrum of (BTMA)₅1 due to its low solubility in organic solvents. To prove that the 5-line ¹⁸³W 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 ¹⁸³W NMR spectrum in DMSO to confirm the retention of a 5-line spectrum (Fig. S10 and S11, ESI⁺). Subsequent addition of (BTMA)Br and recrystallisation of the resulting precipitate from hot DMSO/DMF gave crystals that were shown by X-ray crystallography to be (BTMA)₅1·2DMSO 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 $[W_6O_{19}]^{2-}$ and $[W_{10}O_{32}]^{4-}$ as the only isopolytungstates to be isolated and characterised from non-aqueous solutions. In the FTIR spectrum of $(BTMA)_51$ (Fig. S17, ESI[†]), the band for $\nu(W=O)$ at 922 cm⁻¹ is lower than that for $(TBA)_2[W_6O_{19}]$ and $(TBA)_4[W_{10}O_{32}]$ at 967 and 953 cm⁻¹ respectively due to the greater anionic charge of **1**. By analogy with the FTIR spectra of $(TBA)_2[MO_6O_{19}]$ and $(TBA)_2$ - $[MO_2O_7]$, either of the bands at 863 or 821 cm⁻¹ may be associated with $\nu(W=O)$ for *cis*-WO₂ in **1**.

We have demonstrated conclusively that the new isopolytungstate $[W_7O_{24}H]^{5-}$ **1** is formed by both hydrolytic aggregation reaction (1) and by degradation reaction (5). Crucially, this means that **1** is present in non-aqueous $[W_xO_yH_z]^{n-}$ mixtures with n/x = 1.0, *i.e.* those used in our attempts to prepare $(TBA)_2[W_2O_7]$ or lacunary Lindqvist-type $(TBA)_5[W_5O_{18}H]$ species, and for the synthesis of a wide range of heterometal-substituted Lindqvist $\{MW_5O_{18}\}$ anions, suggesting that the $\{W_5\}$ 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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