

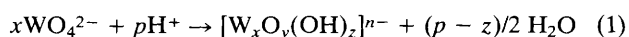
## Non-Aqueous Routes to a New Polyoxotungstate

R. John Errington,\* Martin D. Kerlogue and David G. Richards

Department of Chemistry, The University of Newcastle upon Tyne, Newcastle upon Tyne, UK NE1 7RU

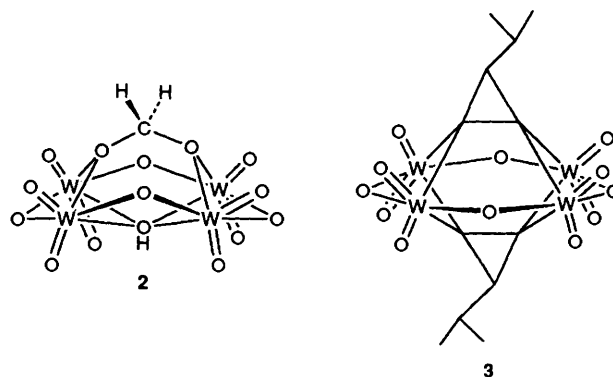
$^{183}\text{W}$  NMR studies of non-aqueous associative and dissociative reactions designed to produce  $[\text{W}_2\text{O}_7]^{2-}$  have instead revealed the formation of a new polytungstate which contains five types of tungsten and reacts with a variety of organic substrates to produce functionalised polyoxotungstates.

Activity in the area of non-aqueous polyoxometallate chemistry has increased in recent years since the recognition that these molecular oxides might display novel reactivity in organic media and that structures may be accessible that are otherwise unstable in aqueous solution.<sup>1</sup> Despite this, however, most polyoxometallate starting materials are usually synthesised in aqueous solution<sup>2</sup> and it is clear that the aggregative processes involved in the formation of these molecules are still poorly understood. In addition, there are remarkably few structurally characterised isopolytungstates  $[\text{W}_x\text{O}_y]^{n-}$ . If we consider the conceptual formation of polytungstates by acidification of monotungstate  $[\text{WO}_4]^{2-}$  eqn. (1), then the known isopolytungstates can be assigned theoretical values of  $\text{H}^+/\text{W}$  (*i.e.*  $p/x$ ) on an acidification scale from 0.0 to 2.0 as shown in Fig. 1.



NMR studies<sup>3</sup> have shown that acidification of aqueous  $[\text{WO}_4]^{2-}$  results in an equilibrium involving  $[\text{W}_7\text{O}_{24}]^{6-}$  and  $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ . More detailed investigations<sup>4</sup> have demonstrated the subsequent formation of various  $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$  'Keggin' anions and of a  $\text{W}_{11}$  species which is converted to  $[\text{W}_{10}\text{O}_{32}]^{4-}$  on increased acidification, while the crystallo-

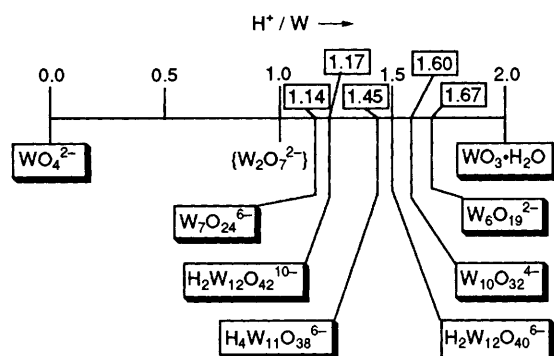
graphically characterised  $[\text{H}_4\text{W}_{11}\text{O}_{38}]^{6-}$  was obtained from a similarly acidified aqueous solution as a potassium salt.<sup>5</sup> Tetraalkylammonium salts of  $[\text{W}_6\text{O}_{19}]^{2-}$  and  $[\text{W}_{10}\text{O}_{32}]^{4-}$  which are soluble in polar organic solvents are readily prepared,<sup>2</sup> and the hexanuclear anion in particular is often the product of non-aqueous reactions. One noteworthy absentee from this list of tungstates is the ditungstate  $[\text{W}_2\text{O}_7]^{2-}$  which has not been prepared or detected in solution in the molecular



**Table 1**  $^{183}\text{W}$  NMR data for tungstates

Anion	$\delta_{\text{W}}^a$	Cations	Solvent	Ref.
$[\text{WO}_4]^{2-}$	+6	$[\text{NBu}^n_4]^+$	MeCN	This work
$[\text{W}_7\text{O}_{24}]^{6-}$	+268 [1], -106 [4], -189 [2]	$\text{Li}^+$	$\text{H}_2\text{O}$	4
$[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$	-109 [2], -114 [2], -116 [4], -147 [4]	$\text{Li}^+$	$\text{H}_2\text{O}$	4
$[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$	-107	$[\text{NBu}^n_4]^+$	MeCN	This work
$[\text{W}_{10}\text{O}_{32}]^{4-}$	-30 [4], -174 [1] <sup>b</sup>	$[\text{NBu}^n_4]^+$	MeCN	This work
$[\text{W}_6\text{O}_{19}]^{2-}$	+47	$[\text{NBu}^n_4]^+$	MeCN	This work
<b>1</b>	+44 [1], +40 [2], +29 [1], -70 [1], -85 [2]	$[\text{NBu}^n_4]^+$	MeCN	This work

<sup>a</sup> Values referenced to 2 mol dm<sup>-3</sup> aqueous  $\text{Na}_2[\text{WO}_4]$  with peak integrations in parentheses. <sup>b</sup> Chemical shifts of -98 [4] and -105 [1] were reported for this compound in ref. 4.



**Fig. 1** Diagram showing the theoretical amount of acid required to form polytungstate  $[\text{W}_x\text{O}_y(\text{OH})_z]^{n-}$  from  $[\text{WO}_4]^{2-}$  according to eqn. (1). Structurally characterised species are in shaded boxes.

form. This contrasts with the structurally characterised dimolybdate, which must be prepared in non-aqueous solvents,<sup>2,6</sup> and dichromate which is usually prepared in aqueous solution.

Jahr *et al.* were the first to demonstrate the formation of polyoxometallates by alkaline hydrolysis of metal alkoxides and thereby prepared the hexatungstate  $[\text{W}_6\text{O}_{19}]^{2-}$  from  $[\text{WO}(\text{OMe})_4]$  eqn. (2).<sup>7</sup> We have been studying the solid-state and solution properties of tungsten oxoalkoxides  $[\text{WO}(\text{OR})_4]$ <sup>8</sup> and have found that  $[\text{W}_6\text{O}_{19}]^{2-}$  can be synthesised by hydrolysis of a mixture of  $[\text{WO}_4]^{2-}$  and  $[\text{WO}(\text{OMe})_4]$  as in eqn. (3).<sup>9</sup> This led us to believe that other tungstates should be accessible by this route whereby the average anionic charge per tungsten is determined by the  $[\text{WO}_4]^{2-} : [\text{WO}(\text{OMe})_4]$  ratio and, in particular, that  $[\text{W}_2\text{O}_7]^{2-}$  might be prepared by the reaction shown in eqn. (4). As indicated in Fig. 1,  $[\text{W}_2\text{O}_7]^{2-}$  should also be accessible by protonation of  $[\text{WO}_4]^{2-}$  or from higher nuclearity tungstates by base degradation in an organic solvent, by analogy with the preparation of  $[\text{Mo}_2\text{O}_7]^{2-}$  from  $[\text{Mo}_8\text{O}_{26}]^{4-}$ .<sup>2,6</sup>

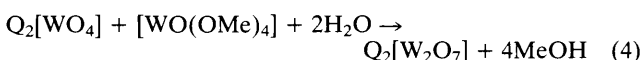
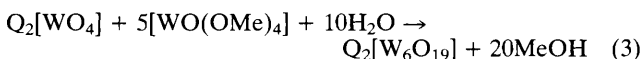
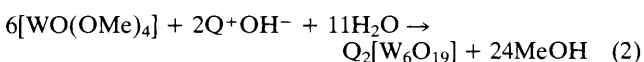
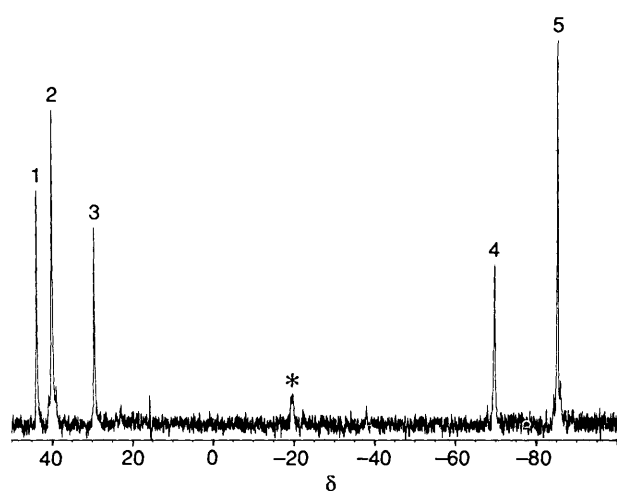


Fig. 2 shows the  $^{183}\text{W}$  NMR spectrum of the product from the hydrolysis of a 1:1 mixture of  $(\text{Bu}^n_4\text{N})_2[\text{WO}_4]$  and  $[\text{WO}(\text{OMe})_4]$  in acetonitrile after removal of the volatiles. We propose that this five-line spectrum is due to a single compound **1**, since products from a variety of non-aqueous reactions of mononuclear  $[\text{WO}_4]^{2-}$  and of polynuclear  $\text{WO}_3 \cdot \text{H}_2\text{O}$ ,  $[\text{W}_6\text{O}_{19}]^{2-}$  or  $[\text{W}_{10}\text{O}_{32}]^{4-}$  (summarised in Scheme 1) give the same  $^{183}\text{W}$  NMR spectrum.

Solution  $^{183}\text{W}$  NMR data for the structurally characterised tungstates mentioned above are given in Table 1, and the

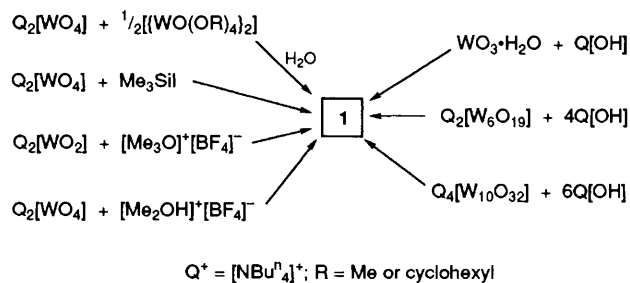


**Fig. 2**  $^{183}\text{W}$  NMR spectrum of **1** (prepared by the hydrolysis of  $[\text{NBu}^n_4]_2[\text{W}_2\text{O}_5(\text{OMe})_4]$  in MeCN. The peak marked with an asterisk is an impurity).

spectrum of **1** clearly does not correspond to any of these anions. In addition, the peaks in the spectrum of **1** occur in two distinct regions. The three low-field peaks have positive chemical shifts, which are notably rare in unreduced polyoxotungstates, while the two high-field peaks have more typical negative values. The peak integration gives a ratio of close to 1 : 2 : 1 : 1 : 2, suggesting that the anion has a nuclearity of  $7n$  and contains five types of tungsten. Satellite peaks associated with the two larger signals 2 and 5 are easily visible and the  $J_{\text{WW}}$  value of 22.6 Hz is indicative of tungstens linked by a single W-O-W bridge in a 'corner-shared' fashion. The only other couplings detected unambiguously from an INADEQUATE  $^{183}\text{W}$  NMR experiment were  $J_{1,2}$  and  $J_{2,4}$  with values of 2.5 and 3.3 Hz, respectively. Elemental microanalysis of a sample obtained from  $(\text{NBu}^n_4)[\text{WO}_4]$  and  $[\text{WO}(\text{OMe})_4]$  gave results very close to those expected for  $(\text{NBu}^n_4)_2[\text{W}_2\text{O}_7]$ , and the only features in the  $^1\text{H}$  NMR spectrum apart from those due to tetrabutylammonium were very small peaks at  $\delta$  8.5 and 14.3. In the  $^{17}\text{O}$  NMR spectrum of **1**,<sup>†</sup> there are five resonances in the terminal W=O region, three in the  $\mu_2$ -O region, one at  $\delta$  198 which may be due to  $\mu_3$ -O and a peak near  $\delta$  0 which may be due to water, while the peak at  $\delta$  -9 could be  $\mu_4$ - or  $\mu_5$ -O or -OH. Unfortunately, we have not yet obtained single crystals of **1** for an X-ray crystal structure determination, nor have we been able to propose a structure which is consistent with the symmetry and connectivity requirements of the spectroscopic data.

When the reaction between equimolar amounts of  $(\text{NBu}^n_4)[\text{WO}_4]$  and  $[\text{WO}(\text{OMe})_4]$  is monitored by  $^{183}\text{W}$  NMR, the initial product is a species having a single-line spectrum ( $\delta_{\text{W}} -109$ ). We presume that this is the tetrabutylammonium salt of the binuclear oxoalkoxide

<sup>†</sup>  $^{17}\text{O}$  NMR data for **1**:  $\delta_{\text{O}}$  (67.83 MHz, MeCN) 722, 689, 683, 678, 657, 396, 387, 360, 198, -1 and -9.



Scheme 1

$[W_2O_4(OMe)_2(\mu-O)(\mu-OMe)_2]^{2-}$  (which we have isolated and structurally characterised as a benzyltrimethylammonium salt during our work on the non-aqueous reactivity of  $[NMe_3(CH_2Ph)]_2[WO_4]^{10}$  and that hydrolysis on subsequent addition of water produces **1**. The formation of **1** in the range of diverse reactions shown in Scheme 1 was initially somewhat surprising, but presumably the oxoalkoxides  $[WO_3(OR)]^-$  produced in reactions between  $[WO_4]^{2-}$  and  $Me_3SiI$  or  $Me_3O^+$  condense due to hydrolysis or elimination of  $Me_3OSiMe_3$  ( $R = Me_3Si$ ). Alternatively, trace hydrolysis in the reaction with  $Me_3SiI$  might generate catalytic amounts of  $HI$  and **1** is then formed by condensation of  $[WO_3(OH)]^-$  with elimination of water, as in the reaction with  $HBF_4$ . Since it is difficult to completely dehydrate  $(NBu_4)_2[WO_4]$ , it is possible that some water was present in the initial reaction mixture. The formation of similar hydroxoanions by nucleophilic attack of polyoxotungstates by  $OH^-$  can be envisaged, although such reactions would be expected to be slower.

We have found **1** to be remarkably reactive towards a variety of substrates. For example, on attempted recrystallisation from dichloromethane or methanol the colourless tetrabutylammonium salts of  $[W_4O_8(\mu-O)_4(O_2CH_2)(\mu_4-OH)]^{3-}$  **2** or  $[W_6O_{19}]^{2-}$  respectively were obtained. The crystal structure of **2**, which we have also prepared from  $(NBu_4)_2[WO_4]$  by recrystallisation from dichloromethane,<sup>9</sup> show it to be isostructural with the molybdate analogue previously described by Klemperer *et al.*<sup>11</sup> The yellow solution produced when **1** is dissolved in nitromethane gave suitable crystals for an X-ray crystal structure determination. This revealed a new functionalised polytungstate **3** with a planar, tetranuclear tungsten oxide framework and two organic fragments, one on each side of the plane, but we have been unable to determine the exact nature of the organic groups because of disorder problems. <sup>183</sup>W, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy<sup>‡</sup> and elemen-

<sup>‡</sup> NMR data for **3**:  $\delta_W$  (12.5 MHz, MeCN)  $-63$ ;  $\delta_H$  (200.1 MHz,  $CD_3CN$ ) 8.71 (d, 2 H,  $J_{HH}$  9.6 Hz, CH), 7.11 (d, 2 H,  $J_{HH}$  9.6 Hz, CH), 3.14 (m, 32 H,  $NCH_2$ ), 1.61 (m, 32 H,  $NCH_2CH_2$ ), 1.36 [m, 32 H,  $N(CH_2)_2CH_2$ ], 0.96 (t, 24 H,  $CH_3$ );  $\delta_C$  (125.8 MHz,  $CD_3CN$ ,  $\{^1H\}$ ) 162.0 (CH), 109.3 (CH), 58.4 ( $NCH_2$ ), 23.6 ( $CH_2$ ), 19.4 ( $CH_2$ ) and 13.0 ( $CH_3$ ).

tal microanalysis suggest a formula such as  $(NBu_4)_4[W_4O_8(\mu-O)_4(NCH_2CHNO_2)_2]$  for **3** and we are hopeful that a low-temperature structure determination will resolve the ambiguity.

These studies demonstrate that even in non-aqueous solvents  $[W_2O_7]^{2-}$  is apparently unstable with respect to higher nuclearity species. This is in contrast with the behaviour of dimolybdate, although this has been shown<sup>12</sup> to react with water to form  $[Mo_5O_{16}(OH)]^{3-}$ , which has a structure similar to **2** in which  $\mu-MoO_4^{2-}$  replaces  $\mu-O_2CH_2^{2-}$ . This comparative instability of ditungstate may be due to the greater electrophilicity of tungsten compared with molybdenum, with the result that even trace amounts of water result in formation of **1**. Further studies of **1**, which will hopefully reveal its structure, and of similar polytungstate systems are in progress. Given the enormous potential of oxoalkoxoanions as precursors in polyoxometallate synthesis, we are also now extending this research to include a range of transition-metal and main-group elements.

We are grateful to the SERC for providing studentships (to M. D. K. and D. G. R.) and to Professor W. McFarlane, Dr M. N. S. Hill (Newcastle University), Professor W. G. Klemperer and Mrs Jie Chen (University of Illinois) for assistance with NMR experiments. R. J. E. also thanks NATO (for a Collaborative Research Grant), Newcastle University (for a Small Research Grant) and The Royal Society for additional funding.

Received, 18th January 1993; Com. 3/00304C

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