

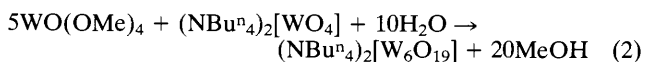
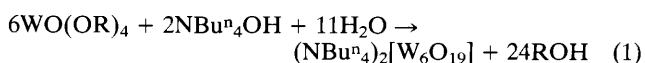
## Evidence for Rapid Ligand Redistribution in Non-aqueous Tungstate Chemistry: Rational Synthesis of the Binuclear Tungsten Oxoalkoxide $[\text{W}_2\text{O}_5(\text{OMe})_4]^{2-}$

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In the solid state, the tungstate  $[\text{NMe}_3(\text{CH}_2\text{Ph})]_2[\text{WO}_4]\cdot\text{H}_2\text{O}$  contains chains of alternating  $[\text{WO}_4]^{2-}$  anions and water molecules linked by  $\text{W}=\text{O}\cdots\text{H}-\text{O}-\text{H}$  hydrogen bonding; in organic solvents, oxo-alkoxo ligand exchange occurs readily between  $\text{Q}_2\text{WO}_4$  ( $\text{Q}^+ = \text{NBu}^n_4^+$  or  $[\text{NMe}_3(\text{CH}_2\text{Ph})]^+$ ) and  $[\{\text{WO}(\text{OMe})\}_2]$  to produce the new binuclear oxoalkoxo-tungstate  $[\text{W}_2\text{O}_5(\text{OMe})_4]^{2-}$ , which is a precursor for non-aqueous polyoxo-tungstate synthesis.

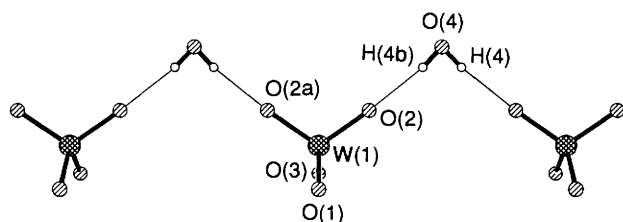
Molecular aggregation processes involved in the formation of early transition metal polyoxometalates  $\text{M}_x\text{O}_y^{n-}$  are poorly understood.<sup>1</sup> Our efforts to control molecular growth in these systems have involved the development of non-aqueous routes to polyoxotungstates<sup>2</sup> whereby, through the isolation and/or characterisation of intermediates, we hope to identify the structure-determining factors in these reactions. Metal alkoxides are becoming increasingly important as precursors for oxide preparation (the 'sol-gel' process)<sup>3</sup> and pioneering work by Fuchs<sup>4</sup> demonstrated that polyoxometalates can be formed by alkaline hydrolysis of metal alkoxides, in particular that  $(\text{NBu}^n_4)_2[\text{W}_6\text{O}_{19}]$  can be prepared from  $\text{WO}(\text{OEt})_4$  as in eqn. (1).<sup>5</sup> This prompted us to investigate more fully the potential of tungsten oxoalkoxides  $\text{WO}(\text{OR})_4$  for non-aqueous polytungstate synthesis, and by synthesising  $[\text{W}_6\text{O}_{19}]^{2-}$  from a 5 : 1 mixture of  $\text{WO}(\text{OMe})_4$  and  $[\text{WO}_4]^{2-}$  as in eqn. (2), we have established the viability of using quaternary ammonium tungstate salts  $\text{Q}_2[\text{WO}_4]$  as a source of the polyanion charge in polytungstates.<sup>6</sup>



Quaternary ammonium salts  $\text{Q}_2[\text{WO}_4]$  were prepared from  $\text{WO}_3\cdot\text{H}_2\text{O}$  and  $\text{QOH}$  in methanol, but we were not certain whether these were completely anhydrous and we were keen to obtain a crystal structure of one of these salts. In the only

previous crystal structure determinations of organic salts of  $[\text{MO}_4]^{2-}$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) extensive hydrogen-bonding interactions between the  $\text{RNH}_3^+$  cations ( $\text{R} = \text{C}_6\text{H}_{11}$  or  $\text{Bu}^t$ ) and the metalate anions were identified, and in the hydrated  $(\text{C}_6\text{H}_{11})_2\text{NH}_2^+$  salt, this also involved the water molecules.<sup>7</sup> Our attempts to recrystallise  $(\text{NBu}^n_4)_2[\text{WO}_4]$  met with little success, but the benzyltrimethylammonium salt gave suitable single crystals from acetonitrile-methanol for X-ray diffraction studies,<sup>†</sup> and was thereby shown to be a monohydrate  $[\text{NMe}_3(\text{CH}_2\text{Ph})]_2[\text{WO}_4]\cdot\text{H}_2\text{O}$  **1**. The  $[\text{WO}_4]^{2-}$  anions are linked by hydrogen bonding to water molecules into chains, as shown in Fig. 1, and there are no unusually close contacts between the cations and anions. The W-O bond lengths are

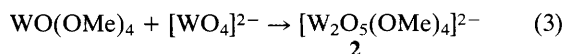
<sup>†</sup> Crystal data for **1**:  $\text{C}_{20}\text{H}_{34}\text{N}_2\text{O}_5\text{W}$ ,  $M = 566.34$ , monoclinic, space group  $P2_1/m$ ,  $a = 12.841(2)$ ,  $b = 7.0073(12)$ ,  $c = 13.697(2)$  Å,  $\beta = 112.646(12)^\circ$  at 240 K,<sup>8</sup>  $U = 1137.4(3)$  Å<sup>3</sup>,  $Z = 2$ . Intensities were measured to  $2\theta_{\text{max}} = 50^\circ$  on a Stoe-Siemens diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å)<sup>9</sup> and corrected semiempirically for absorption ( $\mu = 5.11$  mm<sup>-1</sup>, transmission 0.318–0.447). The structure was solved by heavy-atom methods and refined<sup>10</sup> on  $F^2$  with weights  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ , where  $P = (F_o^2 + 2F_c^2)/3$ ;  $a = 0.0304$ ,  $b = 0$ . Extinction effects were negligible. H atoms were refined freely with isotropic displacement parameters; anisotropic parameters were used for other atoms. All 2197 measured data were used in refinement, giving final  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} = 0.0509$  and conventional  $R = 0.0197$  based on  $F$  values for 2031 reflections with  $F_o^2 > 2\sigma(F_o^2)$ ; goodness of fit on  $F^2 = 1.106$ . All features in a final difference map were between +0.46 and  $-0.67$  e Å<sup>-3</sup>.



**Fig. 1** A view of the hydrogen-bonded  $[\{WO_4 \cdot H_2O\}_n]^{2n-}$  chains in **1**. Selected distances (Å) and angles ( $^\circ$ ): W(1)–O(1) 1.764(4); W(1)–O(2) 1.761(3); W(1)–O(3) 1.755(4); O(2)–O(4) 2.748; O(1)–W(1)–O(2) 109.46(13); O(1)–W(1)–O(3) 108.7(2); O(2)–W(1)–O(3) 110.07(14); O(2)–W(1)–O(2a) 109.1(2).

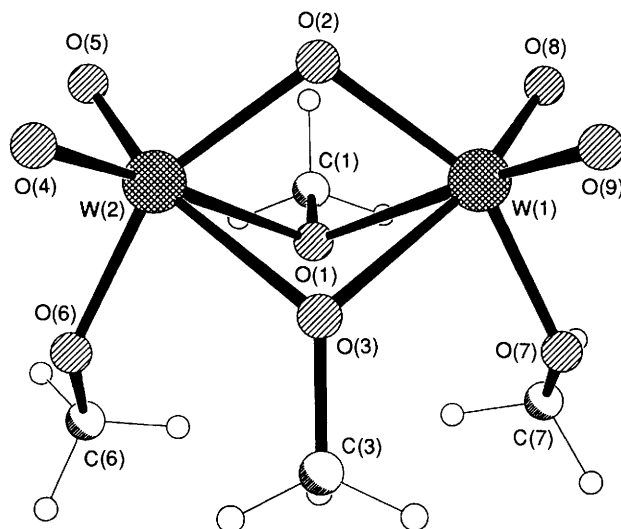
identical within experimental error [1.760(4) Å] and are not affected by the hydrogen bonding, in which the O–(H)⋯O distance (2.748 Å) is shorter than those in the structure of  $WO_3 \cdot H_2O$  (2.87, 2.97 Å) where the oxygen of the water molecule is coordinated to tungsten.<sup>11</sup>

Previously, we showed by  $^{183}W$  NMR spectroscopy that hydrolysis of a 1:2 mixture of  $[\{WO(OMe)_4\}_2]$  and  $(NBu^n)_4[WO_4]$  in acetonitrile produces a new polytungstate with a characteristic five-line spectrum.<sup>12</sup> Our investigations have now revealed that the initial reaction between  $[\{WO(OMe)_4\}_2]$  and  $Q_2[WO_4]$  in organic solvents produces a tungstate with a single line  $^{183}W$  NMR spectrum ( $Q^+ = NBu^n_4^+$ ; MeCN solvent;  $\delta_W -109$ .  $Q^+ = [NMe_3(CH_2Ph)]^+$ ; MeOH–MeCN solvent;  $\delta_W -138$ ). Again, we have been unable to crystallise the tetrabutylammonium salt, but single crystals of the benzyltrimethylammonium salt were obtained from acetonitrile–methanol and the crystal structure of the anion is shown in Fig. 2.<sup>‡</sup>

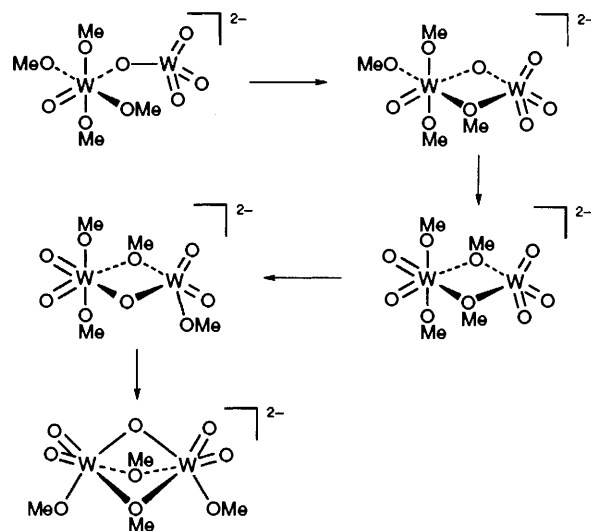


The formula of this oxoalkoxoditungstate,  $[W_2O_5(OMe)_4]^{2-}$  **2**, is that expected from the conproportionation of  $WO(OMe)_4$  and  $[WO_4]^{2-}$  in eqn. (3), and the symmetrical structure suggests that ligand redistribution occurs very readily in solution. The distorted confacial bioctahedral structure contains terminal and bridging methoxides with average W–O bond distances of 1.925 and 2.21 Å, respectively. These compare with terminal (1.888 Å av.) and asymmetric bridging (2.032 and 2.242 Å av.) W–OMe bond lengths in the two independent molecules of dimeric  $[\{WO(OMe)_4\}_2]$ .<sup>13</sup> The terminal W=O bond lengths of the *cis*-dioxo groups average 1.738 Å, which is shorter than those in the structures of monotungstates described above but longer than the single terminal W=O bond in  $[\{WO(OMe)_4\}_2]$  (1.702, 1.696 Å), reflecting the relative degrees of tungsten-oxo  $\pi$ -bonding in these compounds. The bridging W–O bonds, which are *cis* to the terminal oxides, average 1.938 Å and are typical of bridging distances in polyoxotungstates.<sup>1</sup>

Our investigations of the solution dynamics of  $[\{WO(OMe)_4\}_2]$ <sup>13</sup> suggest that dissociation of the longer W–OMe bridging bonds enables reaction with nucleophilic



**Fig. 2** A view of the oxoalkoxoanion **2** in  $[NMe_3(CH_2Ph)_2][W_2O_5(OMe)_4] \cdot MeOH \cdot MeCN$ . Selected distances (Å) and angles ( $^\circ$ ): W(1)–O(9) 1.730(4); W(1)–O(8) 1.739(4); W(1)–O(7) 1.932(4); W(1)–O(2) 1.932(4); W(1)–O(3) 2.178(4); W(1)–O(1) 2.247(4); W(2)–O(5) 1.732(4); W(2)–O(4) 1.752(4); W(2)–O(6) 1.917(4); W(2)–O(2) 1.944(4); W(2)–O(3) 2.197(4); W(2)–O(1) 2.199(4); W(1)–O(2)–W(2) 105.0(2); W(1)–O(1)–W(2) 87.48(13); W(1)–O(3)–W(2) 89.27(13).



**Scheme 1** A possible mechanism for ligand redistribution in the formation of **2** from  $[WO_4]^{2-}$  and  $[\{WO(OMe)_4\}_2]$

$[WO_4]^{2-}$  to form an adduct  $[\{WO(OMe)_4\}_2(\mu-O)(WO_3)]^{2-}$ , which appears to be very dynamic in solution and rearranges by rapid ligand transfer of the type shown in Scheme 1 to give the symmetric structure of **2** shown in Fig. 2. This is the first oxoalkoxoanion containing simple alkoxide ligands to be characterised, previous examples being molybdates containing chelating catecholate ligands.<sup>14</sup> The neutral confacial bioctahedral rhenium oxoalkoxide  $[Re_2O_3(OMe)_6]$  containing one bridging and two terminal oxides has also been reported.<sup>15</sup> Mixed metal oxoalkoxides containing tungsten have been described<sup>16</sup> but, to our knowledge, this is the first structure of an isolated anion (although we have also recently obtained the crystal structure of  $[N(PPh_3)_2][WO(OMe)_5]$ .<sup>17</sup> More significantly, however, this is the first rational synthesis of an oxoalkoxoanion precursor for polyoxometallate synthesis and, having shown that this can be converted cleanly to a new polyoxotungstate by hydrolysis, we are now extending this synthetic strategy to other elements. If this approach

<sup>‡</sup> *Crystal data*:  $C_{27}H_{51}N_3O_{10}W_2$ ,  $M = 945.41$ , triclinic, space group  $P1$ ,  $a = 10.998(6)$ ,  $b = 13.080(7)$ ,  $c = 13.847(7)$  Å,  $\alpha = 62.57(2)$ ,  $\beta = 78.78(3)$ ,  $\gamma = 82.54(4)^\circ$  at 170 K,  $U = 1732(2)$  Å<sup>3</sup>,  $Z = 2$ . Procedures were as for **1**, with  $\mu = 6.69$  mm<sup>-1</sup>, transmission 0.180–0.255; weighting parameters,  $a = 0.0463$ ,  $b = 1.794$ ; isotropic extinction coefficient  $x = 0.0017(2)$ , whereby  $F'_c = F_c/(1 + 0.001x F_c^2 \lambda^3 / \sin 2\theta)^{1/4}$ . Isotropic H atoms were constrained to give rigid methyl groups. Final  $wR2 = 0.0811$  for all 6090 data, conventional  $R = 0.0312$  for 5452  $F$  values, goodness of fit = 1.101; final difference map features between +1.36 and –2.22 e Å<sup>-3</sup>. Atomic coordinates, bond lengths and angles, and atomic displacement parameters for both structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

proves to be generally applicable, it should be possible to design and synthesise a wide range of soluble, molecular, homo- and hetero-nuclear oxides of transition and main-group elements.

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