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Alkoxide hydrolysis as a route to early transition-metal polyoxometalates: synthesis and crystal structures of heteronuclear hexametalate derivatives†

William Clegg, Mark R. J. Elsegood, R. John Errington* and Joanne Havelock
Department of Chemistry, The University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK

Oxygen-17 NMR studies indicated that the hexametalates $[MW_5O_{19}]^{n-}$ or their derivatives $[(MeO)MW_5O_{18}]^{(n-1)-}$ (M = Ti, Zr, V, Nb, Ta, Mo or W) can be obtained by hydrolysis of the appropriate mixture of metal alkoxides in the presence of $M'O_4{}^{2-}$ (M′ = W or Mo) with remarkable selectivity in some cases, giving a very efficient method of preparing ^{17}O-enriched polyoxometalates. The crystal structure of $[NBu^n{}_4]_3[(MeO)TiW_5O_{18}]\cdot0.5MeCN$ shows the terminal Ti–OMe bond in the anion to have Ti–O 1.760(10) Å and Ti–O–C 150.1(12)° and also reveals W–O bridging bond length alternations due to the substitution of $Ti(OMe)^{3+}$ for WO^{4+} in the $[W_6O_{19}]^{2-}$ structure. Hydrolysis of $[NBu^n{}_4]_2[(MeO)NbW_5O_{18}]$ gives $[NBu^n{}_4]_4[(NbW_5O_{18})_2O]$ and the crystal structure revealed two eclipsed NbW_5O_{18} oxide fragments joined by a strictly linear Nb–O–Nb linkage with Nb–O 2.264(8) Å.

The synthesis of early transition-metal polyoxometalates by alkaline hydrolysis of metal alkoxides was first investigated by Jahr and Fuchs[1] and is related to the 'sol–gel' production of metal oxides from solutions of alkoxides. In our efforts to develop rational synthetic routes to new polyoxometalates we have adopted a modified strategy in which soluble oxoalkoxo-anions formed in reactions between mononuclear tungstate $WO_4{}^{2-}$ and metal alkoxides are hydrolysed in organic solvents. We are particularly interested in (*a*) the preparation of heteropolyanions from mixtures of different metal alkoxides and (*b*) the preparation of alkoxide-substituted polyoxoanions by controlling the hydrolysis process, since these would enable the systematic introduction of reactive surface sites into polyoxometalate structures. An additional advantage of this strategy is that when ^{17}O-enriched water is used for the hydrolysis these non-aqueous reactions are conveniently monitored by ^{17}O NMR spectroscopy.

Our attempts to synthesise the unknown molecular ditungstate $[W_2O_7]^{2-}$ by hydrolysis of a 1:1 mixture of $WO_4{}^{2-}$ and $WO(OMe)_4$ have already been reported[2,3] and we describe here the application of this strategy to the synthesis of the hexatungstate $[W_6O_{19}]^{2-}$ **1** and a range of derivatives. We chose these particular polyoxometalates as synthetic targets because of the apparent stability of the hexanuclear M_6O_{19} core structure which, since the structural characterisation of $Na_7HNb_6O_{19}\cdot15H_2O$ and $K_8Ta_6O_{19}\cdot16H_2O$ by Lindqvist,[4] has been identified in a variety of other molecular and extended oxide structures, *e.g.* $[Mo_6O_{19}]^{2-}$,[5] $[W_6O_{19}]^{2-}$,[6] $[MW_5O_{19}]^{3-}$ (M = Nb or Ta),[7,8] $[Nb_2W_4O_{19}]^{4-}$,[8] $[\{M(\eta^5\text{-}C_5Me_5)\}_4V_6O_{19}]$ (M = Rh or Ir),[9] $[V_6O_{12}(OMe)_7]^-$,[10] $[V_6O_{13}\{(OCH_2)_3CNO_2\}_2]^{2-}$,[11] $[Mo_6O(OEt)_{18}]$,[12] $[Fe_6O\{(OCH_2)_3CMe\}_6]^{2-}$,[13] $[Fe_6O(OMe)_{18}]^{2-}$,[14] $[Zr_2Co_4O(OPr^n)_{10}(acac)_4]$ (acac = acetylacetonate)[15] and the α-copper vanadate $Cu_{0.78}V_6O_{18.78}$.[16]

Our studies of non-aqueous polyoxometalate reactivity[17] have served to emphasis the inertness of anion **1** compared with $[Mo_6O_{19}]^{2-}$. We and others have shown that the hexamolybdate can be converted into organoimido derivatives by reaction with phosphinimines,[18] isocyanates[17] or aromatic amines,[19] whereas hexatungstate **1** does not react. The activation of the tungsten oxide framework by the systematic introduction of heterometal atoms and/or surface alkoxide ligands is therefore of major significance in this area, as exemplified by Klemperer and Schwartz[20] who have used this approach of surface functionalisation in the preparation of thio-derivatives $[MW_5O_{18}S]^{3-}$ from $[MW_5O_{19}]^{3-}$ (M = Nb or Ta).

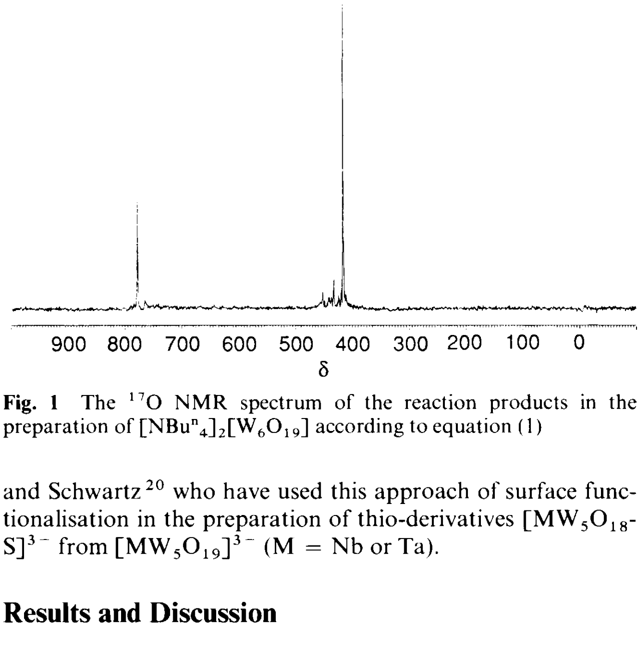

Fig. 1 The ^{17}O NMR spectrum of the reaction products in the preparation of $[NBu^n{}_4]_2[W_6O_{19}]$ according to equation (1)

Results and Discussion

The hydrolysis of a mixture of $[NBu^n{}_4]_2[WO_4]$ and $WO(OMe)_4$ in acetonitrile with the stoichiometry (1) produced

$$WO_4{}^{2-} + 5WO(OMe)_4 + 10H_2O \longrightarrow [W_6O_{19}]^{2-} + 20MeOH \quad (1)$$

$[NBu^n{}_4]_2[W_6O_{19}]$ in almost quantitative yield. When the reaction is carried out in an NMR tube most of the $[NBu^n{}_4]_2[W_6O_{19}]$ crystallises from solution and the ^{183}W NMR spectrum of the soluble fraction contains only small impurity peaks at δ −31.1 and −116.3 in addition to the peak for **1** at δ 47.8, while the ^{17}O NMR spectrum (Fig. 1) better reveals just how clean the reaction is, with only very minor impurity peaks appearing slightly above the baseline. This remarkably efficient self-assembly of **1** encouraged us to investigate the possible incorporation of other early transition metals into hexametalate structures using this strategy.

Group 4 heteroatoms

The product from the hydrolysis of a mixture of $Ti(OMe)_4$, $WO(OMe)_4$ and $WO_4{}^{2-}$ with ^{17}O-enriched water using the stoichiometry (2) gave a ^{17}O NMR spectrum consistent with

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$$3WO_4^{2-} + 7WO(OMe)_4 + 2Ti(OMe)_4 + 17H_2O \longrightarrow 2[(MeO)TiW_5O_{18}]^{3-} + 34MeOH \quad (2)$$

that of a monosubstituted $[LMW_5O_{18}]^{n-}$ species contaminated with small amounts of **1** and another unidentified polyoxoanion. The ^{183}W NMR spectrum of the recrystallised material contained two resonances at δ 64.5 (1W) and 32.3 (4W) with J_{WW} 6.2 Hz and the ^{1}H NMR spectrum contained a singlet at δ 4.10 in addition to tetrabutylammonium and solvent resonances. The ^{17}O NMR spectrum (Fig. 2) shows two types of terminal W=O, one type of TiOW bridge, two types of WOW bridge and the unique central μ_6-O, but no signal for terminal Ti=O. These spectra are consistent with the methoxide-substituted hexametalate $[(MeO)TiW_5O_{18}]^{3-}$ **2** and this formulation was confirmed by crystal structure determination (see below). Surprisingly, an attempted hydrolysis of this alkoxoanion with a stoichiometric amount of water at room temperature did not produce a significant amount of the expected product, $[(TiW_5O_{18})_2O]^{6-}$, since the OMe singlet was still present in the ^{1}H NMR spectrum. This suggests that **2** possesses a certain degree of kinetic stability and we are presently investigating the optimum conditions for this hydrolysis (*e.g.* higher concentration of water, increased temperature). However, the niobium analogue of this hydrolysate has been obtained and is described later in this paper.

Compounds containing terminal Ti=O ('titanyl') bonds are comparatively rare and to our knowledge $[TiW_5O_{19}]^{4-}$ has not been reported. We therefore adjusted the stoichiometry to that shown in equation (3) in an attempt to prepare this

$$2WO_4^{2-} + 3WO(OMe)_4 + Ti(OR)_4 + 8H_2O \longrightarrow [TiW_5O_{19}]^{4-} + 12MeOH + 4ROH \quad (3)$$

heteropolyanion but the reaction did not proceed as cleanly as the preparation of anion **2**. Of the two or three main products observed by NMR spectroscopy, one is the methoxide-substituted anion **2** and another appears to be a related TiW$_5$ species **3**. The ^{183}W NMR spectrum of the solid from a reaction involving $Ti(OPr^i)_4$ contained peaks at δ 64.9 and 32.9 due to **2**, at δ 69.7 (1W) and 36.5 (4W) due to **3** and a peak at δ 72.0 in addition to a few small peaks near δ 0 (Fig. 3). While this suggested that **3** might be $[(Pr^iO)TiW_5O_{18}]^{3-}$, ^{17}O NMR studies of reactions with R = Me or Pr^i in equation (3) showed the same mixture from both titanium alkoxide starting materials. We have not yet been able to isolate a sufficiently pure sample of **3** for full characterisation since crystallisation has only yielded crystals of $[NBu^n_4]_3[(MeO)TiW_5O_{18}]$ (which were used for the crystal structure determination), but it seems likely that it is either $[TiW_5O_{19}]^{4-}$, the protonated $[(HO)TiW_5O_{18}]^{3-}$ or the Ti–O–Ti bridged derivative $[(TiW_5O_{18})_2O]^{6-}$. There is no overwhelming evidence in favour of any one of these formulae, although ^{17}O NMR spectra of the more soluble fractions from these reactions contain a small peak at δ 947 which might be assigned to Ti–OH or Ti=O, whereas no obvious TiOTi peak is present. Most of the compounds containing terminal Ti=O bonds that have been characterised[21] contain fairly rigid polydentate ligands such as phthalocyanine or porphyrin derivatives, or the tridentate 1,4,7-trimethyl-1,4,7-triazacyclononane, and in this regard it is worth noting that the $W_5O_{18}^{6-}$ fragment is effectively a pentadentate oxygen-donor ligand towards the heterometal in $[LMW_5O_{18}]^{n-}$ hexametalates.

In the crystal structure of $[NBu^n_4]_3[(MeO)TiW_5O_{18}]$ the asymmetric unit contains two unique anions $[(MeO)TiW_5O_{18}]^{3-}$ **2**, six discrete $NBu^n_4{}^+$ cations and one molecule of acetonitrile solvate. Angles at W are typical of those in $[W_6O_{19}]^{2-}$ and related polytungstates while M–O–M angles lie in the range 114.1(4)–119.7(5)°. The different O–Ti–O–C torsion angles in the two anions are visible in the views shown in Fig. 4(*a*) and (*b*). Selected bond lengths and angles are given in Table 1. The methoxide ligand is terminally bonded to titanium with an average Ti–O bond length of 1.758(10) Å and a Ti–O–C angle of 148.6(15)°. The bond length is in the middle of the range of Ti–OMe values reported by Wieghardt and co-workers[21a] for a series of octahedral titanium(IV) complexes $[Ti(tmtacn)(OMe)_xBr_{3-x}]^+$ (tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane; x = 1–3) in which competition for metal π orbitals results in an increase in the Ti–O bond length from 1.723(12) to 1.795(6) Å. By comparison, the Ti=O bond length in $[Ti(tmtacn)OCl_2]$ is 1.637(3) Å.[21a] As such, the Ti–O π bonding in **2** is substantially less than would be expected for terminal Ti=O in this situation and this is reflected in the internal M–O bond lengths along the Ti–O–W axis where Ti–O [2.221(10) Å (average)] is shorter than W–O [2.353(10) Å (average)]. Systematic variations in the bridging M–O bond lengths in **2** are discussed later in a comparison with similar effects observed in other examples of MW$_5$-substituted hexametalates.

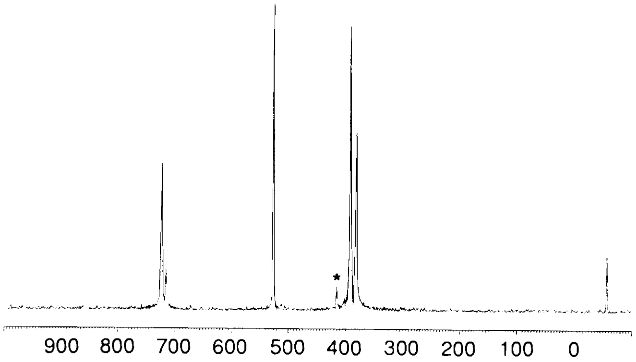


Fig. 2 The ^{17}O NMR spectrum of $[(MeO)TiW_5O_{18}]^{3-}$ **2**. The peak marked with an asterisk is due to an impurity

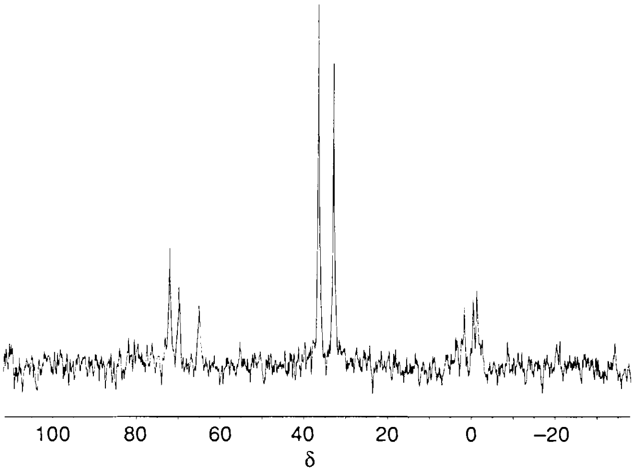


Fig. 3 The ^{183}W NMR spectrum of the products from a reaction to prepare $[TiW_5O_{19}]^{4-}$ according to equation (3)

The lack of zirconium-substituted hexametalates in the literature suggested that the aqueous synthetic routes used for other derivatives may be unsuitable for this metal and prompted us to attempt the preparation of $[(MeO)ZrW_5O_{18}]^{3-}$ *via* an alkoxide hydrolysis method analogous to that used for **2**. The compound $Zr(OPr^n)_4$ was used in the reaction on the assumption that methanol produced by hydrolysis would cause metathesis of the propoxide ligands. The ^{183}W NMR spectrum of the product **4** (Fig. 5) contains no significant impurity peaks, suggesting that the reaction proceeds cleanly to give the expected ZrW$_5$ hexametalate structure. Despite broadening of several peaks, the ^{17}O NMR

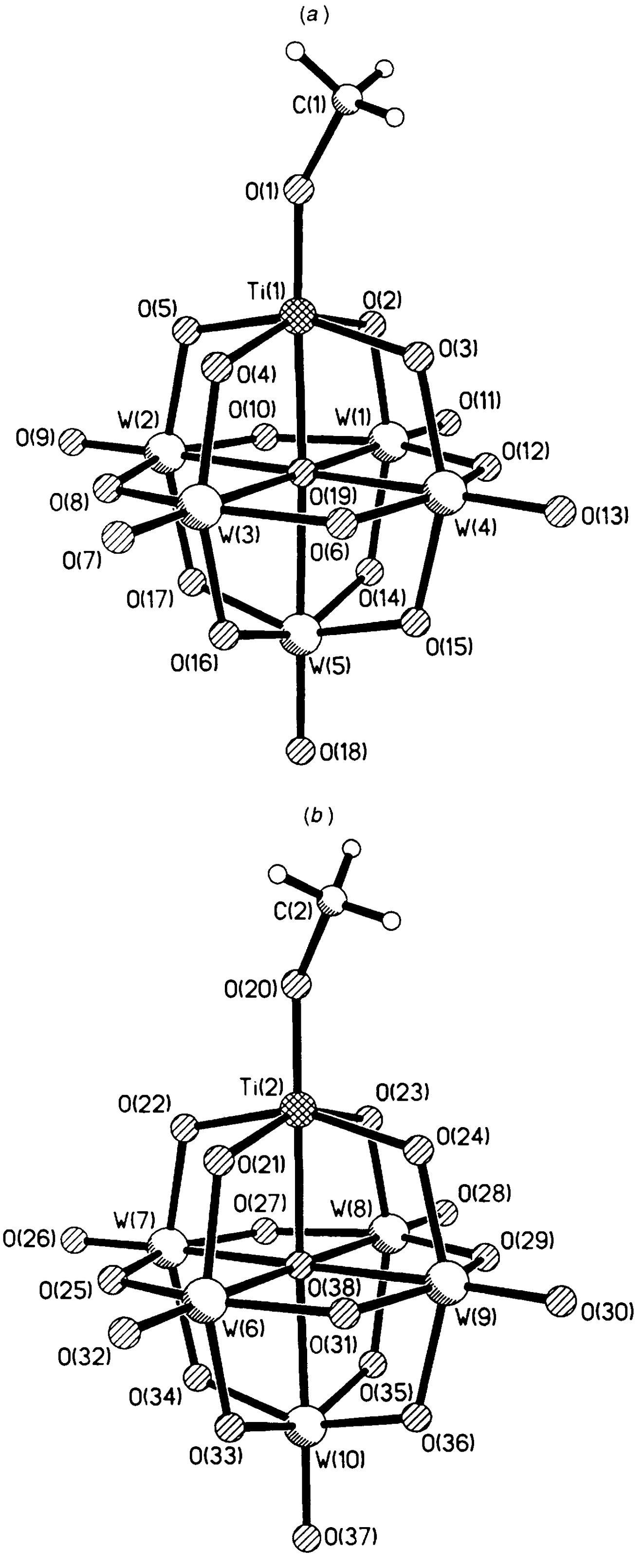


Fig. 4 Views (*a*) and (*b*) of the two unique $[(MeO)TiW_5O_{18}]^{3-}$ **2** anions in the crystal structure of $[NBu^n_4]_3[(MeO)TiW_5O_{18}]\cdot 0.5MeCN$ with the atom labelling scheme. Torsion angles: C(1)–O(1)–Ti(1)–O(3) 4.4, C(2)–O(20)–Ti(2)–O(24) −19°

spectrum (Table 4) is also consistent with the required metal oxide framework, as is the IR spectrum, which is similar to that of **2**. The presence of alkoxide groups is suggested by the ^1H NMR spectrum; broad peaks between δ 3.9 and 4.2 (possibly due to OCH_2 of propoxide) and a sharp peak at δ 3.77 integrate for a total of 6 H for every three cations, although these may also be due to co-ordinated propanol, water or hydroxide. In this regard, it is noteworthy that no band due to ν(OH) is present in the IR spectrum of **4**, but there is a band at 1660 cm^{-1} which may be due to OH bend. These differences between **2** and **4** are presumably due to different co-ordination environments at the heteratoms and reflect the greater covalent radius of zirconium.

Group 5 heteroatoms

Tetraalkylammonium salts of $[VW_5O_{19}]^{3-}$ **5** have previously been prepared from Na_2WO_4 and $NaVO_3$ in aqueous media[22] or, when ^{17}O-enriched material was required, by a non-aqueous route involving the treatment of ^{17}O-enriched $[W_{10}O_{32}]^{4-}$ with a vanadate solution obtained by dissolving V_2O_5 in methanolic NBu^n_4OH.[23] Using our hydrolytic method, ^{17}O-enriched **5** is readily prepared in high yield by hydrolysis of an acetonitrile solution of $[NBu^n_4]_2[WO_4]$, $WO(OMe)_4$ and $VO(OMe)_3$ with ^{17}O-enriched water [equation (4)]. The ^{17}O

$$3WO_4^{2-} + 7WO(OMe)_4 + 2VO(OMe)_3 + 17H_2O \longrightarrow 2[VW_5O_{19}]^{3-} + 34MeOH \quad (4)$$

and ^{51}V NMR spectra show that the minor amounts of hexatungstate **1** and other vanadates formed in this reaction are removed on recrystallisation. However, we have been unable so far to isolate the methoxide derivative $[(MeO)VW_5O_{18}]^{2-}$, ^{17}O and ^{51}V NMR spectra of the solid product from the reaction [equation (5)] showing a significant amount of **1** with

$$WO_4^{2-} + 4WO(OMe)_4 + VO(OMe)_3 + 9H_2O \longrightarrow [(MeO)VW_5O_{18}]^{2-} + 18MeOH \quad (5)$$

smaller amounts of **5** and three other unidentified vanadates.

In our attempts to prepare tungstoniobates from $Nb(OMe)_5$, ^{17}O NMR studies showed that the theoretical stoichiometry required for $[NbW_5O_{19}]^{3-}$ **6** [equation (6)] gave a yield of

$$3WO_4^{2-} + 7WO(OMe)_4 + 2Nb(OMe)_5 + 19H_2O \longrightarrow 2[NbW_5O_{19}]^{3-} + 38MeOH \quad (6)$$

about 80% based on tungsten with **1** as the only other significant polyoxoanion product. As in the vanadate system, an attempt to synthesise the methoxide derivative $[(MeO)NbW_5O_{18}]^{2-}$ **7** [equation (7)] gave a more complex

$$WO_4^{2-} + 4WO(OMe)_4 + Nb(OMe)_5 + 10H_2O \longrightarrow [(MeO)NbW_5O_{18}]^{2-} + 20MeOH \quad (7)$$

mixture although, in this case, the peaks in the ^{17}O NMR spectra could be assigned to roughly equal amounts of **1** and a new NbW_5 species in addition to a small amount of **6**. The new compound was isolated by crystallisation and, in addition to tetrabutylammonium resonances, peaks were observed at δ 4.40 in the ^1H NMR spectrum and δ 65.9 in the ^{13}C NMR spectrum of this colourless crystalline solid. This suggests that the methoxide **7** is indeed formed in this reaction and, moreover, since the ^{17}O NMR spectrum (Fig. 6) is consistent with C_{4v} symmetry, that the methoxide is terminally bound to the niobium. If the methoxide occupied one of the bridging positions between niobium and tungsten a more complex spectrum with one NbO, four WO (2 : 1 : 1 : 1), two NbOW (2 : 1), five WOW (2 : 2 : 2 : 1 : 1) and a single μ_6-O peak would be expected.

It was noticeable that the ^1H NMR sample of the methoxide **7** showed signs of hydrolysis, with methanol signals at δ 3.28 and 2.21 and a combined Me integration of three protons for every two cations and this moisture sensitivity was evident on attempted recrystallisation. Crystals obtained by slow diffusion of diethyl ether vapour into an acetonitrile solution of this compound over several weeks were shown to be $[NBu^n_4]_4$-

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

Ti(1)–O(1)	1.760(10)	Ti(1)–O(5)	1.931(10)	Ti(2)–O(24)	1.935(10)	Ti(2)–O(23)	1.937(10)
Ti(1)–O(3)	1.941(11)	Ti(1)–O(4)	1.948(10)	Ti(2)–O(21)	1.955(9)	Ti(2)–O(22)	1.982(11)
Ti(1)–O(2)	1.967(10)	Ti(1)–O(19)	2.211(11)	Ti(2)–O(38)	2.231(10)	O(20)–C(2)	1.42(2)
O(1)–C(1)	1.44(2)	W(1)–O(11)	1.697(10)	W(6)–O(32)	1.754(9)	W(6)–O(21)	1.872(9)
W(1)–O(2)	1.849(9)	W(1)–O(10)	1.928(10)	W(6)–O(25)	1.923(9)	W(6)–O(33)	1.929(10)
W(1)–O(14)	1.935(9)	W(1)–O(12)	1.956(10)	W(6)–O(31)	1.941(10)	W(6)–O(38)	2.309(11)
W(1)–O(19)	2.325(9)	W(2)–O(9)	1.726(10)	W(7)–O(26)	1.722(10)	W(7)–O(22)	1.858(10)
W(2)–O(5)	1.879(9)	W(2)–O(10)	1.910(10)	W(7)–O(27)	1.919(10)	W(7)–O(25)	1.939(8)
W(2)–O(17)	1.925(9)	W(2)–O(8)	1.956(9)	W(7)–O(34)	1.947(10)	W(7)–O(38)	2.293(10)
W(2)–O(19)	2.355(9)	W(3)–O(7)	1.709(10)	W(8)–O(28)	1.694(8)	W(8)–O(23)	1.844(10)
W(3)–O(4)	1.851(9)	W(3)–O(8)	1.923(10)	W(8)–O(29)	1.920(9)	W(8)–O(27)	1.955(10)
W(3)–O(16)	1.945(10)	W(3)–O(6)	1.959(11)	W(8)–O(35)	1.957(10)	W(8)–O(38)	2.342(11)
W(3)–O(19)	2.349(9)	W(4)–O(13)	1.723(11)	W(9)–O(30)	1.722(10)	W(9)–O(24)	1.845(9)
W(4)–O(3)	1.859(10)	W(4)–O(6)	1.925(9)	W(9)–O(31)	1.933(9)	W(9)–O(29)	1.937(9)
W(4)–O(12)	1.925(9)	W(4)–O(15)	1.940(9)	W(9)–O(36)	1.999(9)	W(9)–O(38)	2.352(10)
W(4)–O(19)	2.288(9)	W(5)–O(18)	1.740(10)	W(10)–O(37)	1.698(10)	W(10)–O(34)	1.908(9)
W(5)–O(16)	1.874(10)	W(5)–O(15)	1.909(10)	W(10)–O(36)	1.912(10)	W(10)–O(35)	1.917(10)
W(5)–O(14)	1.932(9)	W(5)–O(17)	1.947(10)	W(10)–O(33)	1.932(9)	W(10)–O(38)	2.358(10)
W(5)–O(19)	2.348(10)	Ti(2)–O(20)	1.755(10)				
O(1)–Ti(1)–O(5)	103.3(5)	O(1)–Ti(1)–O(3)	99.9(5)	O(20)–Ti(2)–O(24)	101.4(4)	O(20)–Ti(2)–O(23)	103.9(5)
O(5)–Ti(1)–O(3)	156.8(4)	O(1)–Ti(1)–O(4)	100.8(5)	O(24)–Ti(2)–O(23)	87.0(4)	O(20)–Ti(2)–O(21)	101.0(4)
O(5)–Ti(1)–O(4)	88.1(4)	O(3)–Ti(1)–O(4)	88.2(4)	O(24)–Ti(2)–O(21)	88.5(4)	O(23)–Ti(2)–O(21)	155.1(4)
O(1)–Ti(1)–O(2)	103.5(5)	O(5)–Ti(1)–O(2)	86.9(4)	O(20)–Ti(2)–O(22)	103.4(4)	O(24)–Ti(2)–O(22)	155.2(4)
O(3)–Ti(1)–O(2)	87.2(4)	O(4)–Ti(1)–O(2)	155.7(4)	O(23)–Ti(2)–O(22)	86.4(4)	O(21)–Ti(2)–O(22)	87.5(4)
O(1)–Ti(1)–O(19)	176.8(5)	O(5)–Ti(1)–O(19)	79.7(4)	O(20)–Ti(2)–O(38)	178.9(5)	O(24)–Ti(2)–O(38)	78.2(4)
O(3)–Ti(1)–O(19)	77.2(4)	O(4)–Ti(1)–O(19)	78.1(4)	O(23)–Ti(2)–O(38)	77.1(4)	O(21)–Ti(2)–O(38)	78.0(4)
O(2)–Ti(1)–O(19)	77.6(4)	C(1)–O(1)–Ti(1)	150.1(12)	O(22)–Ti(2)–O(38)	77.0(4)	C(2)–O(20)–Ti(2)	147.1(11)

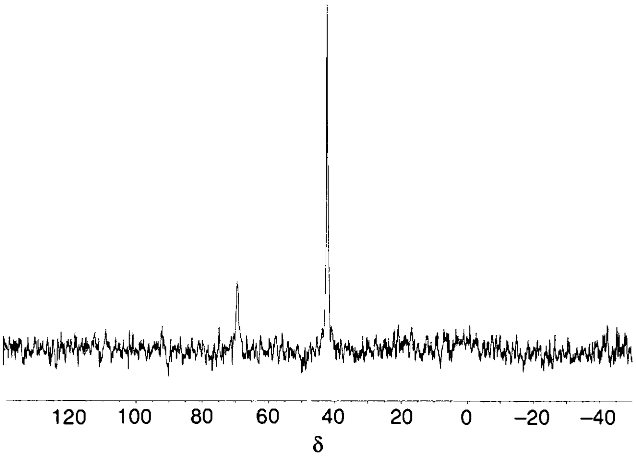


Fig. 5 The ^{183}W NMR spectrum of anion **4**

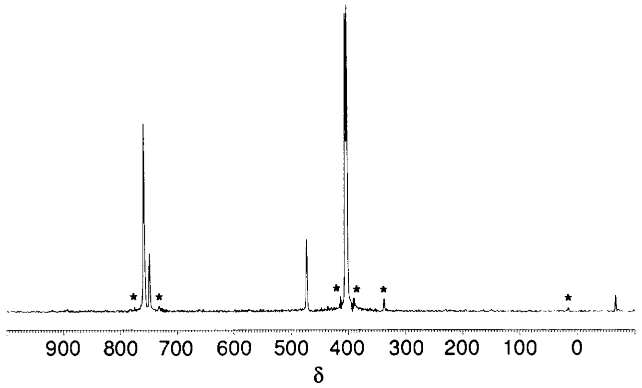


Fig. 6 The ^{17}O NMR spectrum of $[(MeO)NbW_5O_{18}]^{2-}$ **7**. Impurity peaks are marked with an asterisk

$[(NbW_5O_{18})_2O]$ by an X-ray structure determination. This is the first structural characterisation of an anion in which two polyoxometalate units are linked by a single oxide bridge, although $[(Nb_2W_4O_{18})_2O]^{6-}$ has been characterised spectroscopically.[24] The asymmetric unit contains one half of the anion $[(NbW_5O_{18})_2O]^{4-}$ **8** and two discrete tetrabutylammonium cations. Angles at W are again typical of those in $[W_6O_{19}]^{2-}$ and related polytungstates, while M–O–M bridges within the NbW_5O_{18} unit lie in the range 114.1(4)–118.7(4)°. Fig. 7 shows the linear Nb–O–Nb linkage between two NbW_5O_{18} fragments in **8** and a selection of other bond lengths and angles is given in Table 2.

To our knowledge, the only crystal structure of a polyoxoanion containing the NbW_5O_{19} fragment is that of $[(C_5H_5)_3U(NbW_5O_{19})_2]^{5-}$ **9** in which the pentatungstoniobate fragments bond to uranium through the terminal NbO oxygens.[25] The only other related structure is that of the tetratungstodiniobate $[(Bu^tMe_2SiO)Nb_2W_4O_{18}]^{3-}$ **10** which contains a terminal bulky siloxide ligand at one of the two niobium sites.[24] The Nb(1)–O(1) bond in **8** [1.8882(11) Å] is similar to the Nb–OSi bond in **10** [1.86(2) Å] but is significantly longer than the $Nb–O\cdots U$ bond in **9** [1.78(3) Å]. This indicates a greater degree of Nb–O π bonding in **9**, whereas in **8** and **10** π overlap with another Nb or Si respectively is also possible, reducing the Nb–O bond order. The linear Nb–O–Nb linkage and eclipsed geometry of the two NbW_5O_{18} fragments in **8** optimise the overlap of oxygen p_x and p_y orbitals respectively with the d_{xz} orbital of one niobium and the d_{yz} orbital of the other (where the z axis is coincident with the Nb–O–Nb bridge). This variation in the terminal Nb–O π bonding results in an increase in the Nb–O distance to the central μ_6-O from 2.264(8) and 2.27(1) Å in **8** and **10** respectively to 2.33(3) Å in **9**, consistent with the general phenomenon of bond lengthening *trans* to strong π-donor ligands (*i.e. trans* influence) at d^0 metal centres[26] and analogous to the situation in **2** described above.

In common with the other structurally characterised NbW_5 hexametalate **9** and with **2** discussed above, the electronic effects of this substitution are manifested in M–O bridging bond-length variations within MW_3O_4 rings. Average values for the bonds labelled as in Fig. 8 are given in Table 3 and clearly show a variation from short to long single bonds as indicated by the dashed and solid lines. This effect is less marked for **8**, possibly because $[W{=}O]^{4+}$ has effectively been replaced by $[NbL]^{4+}$ in **8** and not $[ML]^{3+}$ as in the other examples in Table 3, resulting in stronger Nb–O bonds (*a*) and weaker W–O bonds (*b*) within the NbW_3O_4 ring. Day and Klemperer[28] have discussed this type of bond-length alternation in terms of charge distribution in hexametalates and related it to variations in ^{17}O chemical shifts. We discuss its relevance to ^{183}W NMR chemical shifts below.

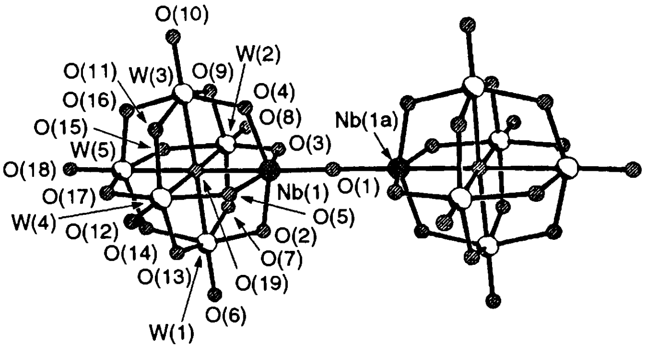


Fig. 7 View of the $[(NbW_5O_{18})_2O]^{4-}$ anion **8** in the crystal structure of $[NBu^n_4]_4[(NbW_5O_{18})_2O]$ with the atom labelling scheme. Torsion angles: O(2)–Nb(1)–Nb(1a)–O(4a) −0.5, O(5)–Nb(1)–Nb(1a)–O(3a) −0.3°

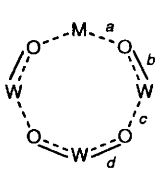


Fig. 8 Bond-length variation within the MW_3O_4 rings of MW_5 hexametalates

Table 2 Selected bond lengths (Å) and angles (°) for complex **8**

W(1)–O(6)	1.701(9)	W(1)–O(2)	1.902(9)
W(1)–O(7)	1.909(8)	W(1)–O(14)	1.924(9)
W(1)–O(13)	1.926(9)	W(1)–O(19)	2.328(7)
W(2)–O(8)	1.688(8)	W(2)–O(3)	1.908(8)
W(2)–O(9)	1.926(8)	W(2)–O(15)	1.930(7)
W(2)–O(7)	1.942(8)	W(2)–O(19)	2.349(7)
W(3)–O(10)	1.695(9)	W(3)–O(4)	1.888(8)
W(3)–O(9)	1.919(8)	W(3)–O(16)	1.928(8)
W(3)–O(11)	1.934(9)	W(3)–O(19)	2.343(7)
W(4)–O(12)	1.691(9)	W(4)–O(5)	1.908(8)
W(4)–O(13)	1.924(8)	W(4)–O(11)	1.932(9)
W(4)–O(17)	1.936(8)	W(4)–O(19)	2.320(7)
W(5)–O(18)	1.711(8)	W(5)–O(16)	1.920(8)
W(5)–O(17)	1.921(9)	W(5)–O(15)	1.924(8)
W(5)–O(14)	1.925(8)	W(5)–O(19)	2.377(8)
Nb(1)–O(1)	1.8882(11)	Nb(1)–O(3)	1.953(8)
Nb(1)–O(2)	1.959(9)	Nb(1)–O(4)	1.964(8)
Nb(1)–O(5)	1.968(8)	Nb(1)–O(19)	2.264(8)
O(1)–Nb(1)–O(3)	101.5(2)	O(1)–Nb(1)–O(2)	103.9(2)
O(3)–Nb(1)–O(2)	86.6(3)	O(1)–Nb(1)–O(4)	103.4(2)
O(3)–Nb(1)–O(4)	87.6(3)	O(2)–Nb(1)–O(4)	152.7(3)
O(1)–Nb(1)–O(5)	104.8(2)	O(3)–Nb(1)–O(5)	153.7(3)
O(2)–Nb(1)–O(5)	86.9(3)	O(4)–Nb(1)–O(5)	86.6(3)
O(1)–Nb(1)–O(19)	178.5(2)	O(3)–Nb(1)–O(19)	77.0(3)
O(2)–Nb(1)–O(19)	76.4(3)	O(4)–Nb(1)–O(19)	76.4(3)
O(5)–Nb(1)–O(19)	76.6(3)	Nb(1)–O(1)–Nb(1a)	180

Symmetry transformation used to generate equivalent atom Nb(1a): $-x + 1, -y, -z$.

We were curious to see if by increasing slightly the amount of water in the reaction designed to produce anion **7** [equation (7)] we might instead obtain **8**. After hydrolysis according to equation (8) and removal of the volatiles, the ^{17}O NMR

$$2WO_4^{2-} + 8WO(OMe)_4 + 2Nb(OMe)_5 + 21H_2O \longrightarrow [(NbW_5O_{18})_2O]^{4-} + 42MeOH \quad (8)$$

spectrum revealed a mixture of **1**, **6** and a third component with chemical shifts similar to those of **7** but with an additional broad peak at δ 500 (Table 4). By comparison with the ^{17}O NMR spectrum of $[(Nb_2W_4O_{18})_2O]^{6-}$ reported previously,[24] we can tentatively assign this peak to the NbONb oxygen of **8**, which on this basis is formed in roughly 30% yield based on tungsten.

An attempted synthesis of $[(MeO)TaW_5O_{18}]^{2-}$ **11** according to equation (9) resulted in the production of a small amount of

$$WO_4^{2-} + 4WO(OMe)_4 + Ta(OR)_5 + 10H_2O \longrightarrow [(MeO)TaW_5O_{18}]^{2-} + 5ROH + 15MeOH \quad (9)$$

crystalline complex **1** and a soluble fraction containing one major component and small amounts of two other species. The ^{17}O and ^{183}W NMR spectra of the major component (Tables 4 and 5) are consistent with TaW_5 monosubstitution[7] and, in the absence of peaks due to Ta=O or TaOTa, we have tentatively assigned this to **11**, although further characterisation is in progress.

A reaction designed to produce $[Ta_2W_4O_{19}]^{4-}$ [equation (10)] gave a mixture of species, but with much less of the

$$2WO_4^{2-} + 2WO(OMe)_4 + 2Ta(OMe)_5 + 9H_2O \longrightarrow [Ta_2W_4O_{19}]^{4-} + 18MeOH \quad (10)$$

hexatungstate **1** than was formed in the previous reaction. The ^{183}W NMR spectrum is shown in Fig. 9 and the complex ^{17}O NMR spectrum contains peaks in the region expected for TaOTa, suggesting that a *cis*-disubstituted product was present.

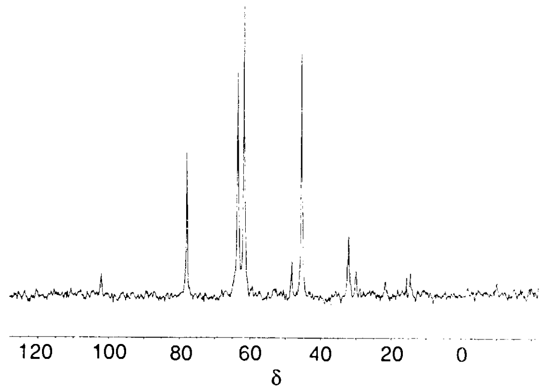


Fig. 9 The ^{183}W NMR spectrum of the reaction products from an attempted preparation of $[Ta_2W_4O_{19}]^{4-}$ according to equation (10)

Table 3 Average bond lengths (Å) within MW_3O_4 rings in MW_5 hexametalate derivatives*

Anion	*a*	*b*	*c*	*d*	*n*	Ref.
2 $[(MeO)TiW_5O_{18}]^{3-}$	1.95(2)	1.86(1)	1.95(2)	1.91(3)	8	This work
$[(\eta\text{-}C_5H_5)TiW_5O_{18}]^{3-}$	1.95(2)	1.87(1)	1.93(2)	1.91(3)	4	27
8 $[(NbW_5O_{18})_2O]^{4-}$	1.961(6)	1.902(8)	1.930(4)	1.923(2)	4	This work
9 $[(\eta\text{-}C_5H_5)_3U(NbW_5O_{19})_2]^{6-}$	1.97(3)	1.86(3)	1.93(3)	1.90(3)	4	25

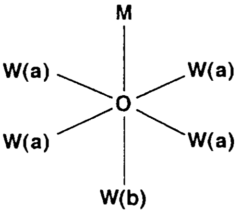
* For bond labels see Fig. 8; averages of *n* numerical values with estimated standard deviations in parentheses.

Table 4 Oxygen-17 NMR data for MW_5 hexametalate derivatives

anion[b]	δ_O[a] (linewidth/Hz) M=O	W=O	MOM	MOW	WOW	μ_6-O
1 $[W_6O_{19}]^{2-}$		774(98)			414(98)	−80
2 $[(MeO)TiW_5O_{18}]^{3-}$		721(258), 713(284)		525(64)	390(129), 380(271)	−58(52)
3[c] $[LTiW_5O_{18}]^{n-}$	*d*	693(258), 690(258)		499(85)	378(206), 365(903)	−66(77)
4[e] $[(RO)ZrW_5O_{18}]^{3-}$		727(1160), 715(774)		530(245)	387(1096), 375(1520)	−56(85)
5 $[VW_5O_{19}]^{3-}$	1224(784)	737(217), 734(199)		565(415)	399(119), 392(119)	−72(99)
6 $[NbW_5O_{19}]^{3-}$	*f*	732(232), 730(192)		456(1160)	394(142), 392(142)	−67(39)
7 $[(MeO)NbW_5O_{18}]^{2-}$		758(206), 748(181)		472(181)	405(103), 402(103)	−71(77)
8 $[(NbW_5O_{18})_2O]^{4-}$		758(774), 748(490)	500(4130)	470(1160)	405(258), 403(387)	−73(103)
11 $[(MeO)TaW_5O_{18}]^{2-}$		756(264), 744(209)		425(110)	404(120), 403(176)	−68(66)
12 $[TaW_5O_{19}]^{3-}$	666(257)	739(206), 736(193)		426(64)	397(257)	−71(26)
13 $[MoW_5O_{19}]^{2-}$	935(69)	775(65)		488(15), 486(15), 482(15)	414(10), 412(10)	−74(69)

[a] Positive values downfield from water reference. [b] All are $NBu^n{}_4{}^+$ salts. [c] See the text for a discussion of the identity of this species. [d] A small peak was observed at δ 947 which might be due to Ti=O or Ti–OH. [e] The ^{183}W NMR spectrum supports the formulation of this anion as an alkoxide derivative. [f] A small broad peak was on occasion observed in the region of δ 800.

Table 5 Tungsten-183, ^{51}V and ^{95}Mo NMR data for MW_5 hexametalate species



Anion[b]	δ[a] (linewidth/Hz) W(a)	W(b)	M
1	47.8		
2	32.3	64.5	
3	36.5	69.7	
4	42.1	69.4	
5	70 (74)	Not observed	−509 (221)
6	65.2	20.3	
7	26.5	69.4	
11	24.8	53.2	
12	63.5	32.2	
13	47.4	55.0	116 (176)

[a] Positive values downfield of reference (2 mol dm^{-3} aqueous Na_2MO_4 for ^{183}W or ^{95}Mo, neat $VOCl_3$ for ^{51}V). [b] All as $NBu^n{}_4{}^+$ salts.

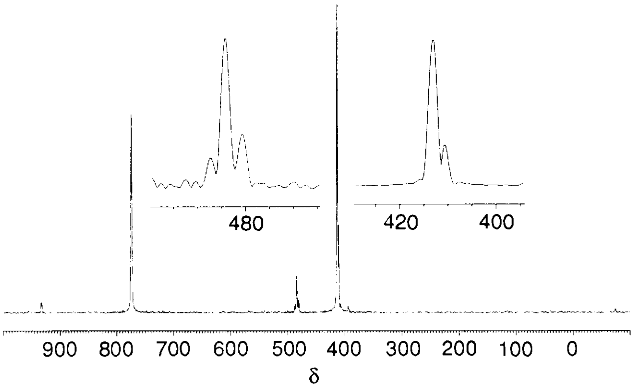


Fig. 10 The ^{17}O NMR spectrum of a mixture of $[W_6O_{19}]^{2-}$ **1** and $[MoW_5O_{19}]^{2-}$ **11**

On further work-up a small amount of crystalline material was obtained which from microanalysis and ^{17}O NMR data appeared to be $[NBu^n{}_4]_3[TaW_5O_{19}]$. This suggests that the major peaks in Fig. 9 are due to three main reaction products. A *cis*-disubstituted Ta_2W_4 species would have a 1 : 1 ^{183}W NMR spectrum, possibly the peaks at δ 61.7 and 45.4, whereas the 4 : 1 pattern expected for $[TaW_5O_{19}]^{3-}$ **12** is most likely to comprise the peaks at δ 63.5 and 32.2, which leaves peaks at δ 77.9 and 102.1 unassigned. Work is going on to isolate and characterise further these species.

Group 6 heteroatoms

In a previously published procedure, treatment of an aqueous solution of $MoO_4{}^{2-}$ with an active form of $WO_3 \cdot H_2O$ at pH > 6 and subsequent addition of $NBu^n{}_4Br$ precipitated a mixture of the tetrabutylammonium salts of anion **1** and $[MoW_5O_{19}]^{2-}$ **13** in a ratio of 4:1. Separation was subsequently achieved by selectively reducing the MoW_5 anion electrochemically and then crystallising the reduced compound $[NBu^n{}_4]_3[MoW_5O_{19}]$.[29] We recognised that a hydrolytic route using $[NBu^n{}_4]_2[MoO_4]$ as the source of molybdenum and of anionic charge may be a more convenient alternative synthesis of **13** [equation (11)]. Similarly, we reasoned that

$$MoO_4{}^{2-} + 5WO(OMe)_4 + 10H_2O \longrightarrow [MoW_5O_{19}]^{2-} + 20MeOH \quad (11)$$

$[(MeO)MoW_5O_{18}]^-$ and $[(MoW_5O_{18})_2O]^{2-}$ may also be accessible from reactions involving the readily prepared dimolybdate $[Mo_2O_7]^{2-}$ [equations (12) and (13)]. In the

$$[Mo_2O_7]^{2-} + 10WO(OMe)_4 + 19H_2O \longrightarrow 2[(MeO)MoW_5O_{18}]^- + 38MeOH \quad (12)$$

$$[Mo_2O_7]^{2-} + 10WO(OMe)_4 + 20\,H_2O \longrightarrow [(MoW_5O_{18})_2O]^{2-} + 40MeOH \quad (13)$$

event, ^{17}O NMR spectra (Fig. 10) of the pale greenish yellow crystalline products obtained from all three of these reactions contained the same peaks (Table 4), which are consistent with a MoW_5 derivative. In addition to the terminal MoO peak at δ 935, the terminal WO and the WOW peaks have similar chemical shifts to those of **1**, while the μ_6-O signal was not visible for all samples of **13**. Inductively coupled plasma (ICP) spectrophotometric analysis gave a ratio of W:Mo of 5.9:1, suggesting that hexatungstate **1** cocrystallises with **13** (in a ratio of 0.15:1). Overlap of ^{17}O NMR peaks from the two species would then explain the relative intensities of the two WOW peaks shown in Fig. 10. The substitution of one of the W=O sites in **1** for Mo=O would not be expected to have as great an effect on the electronic environment of the unique tungsten in a MoW_5 compound as would the incorporation of Group 4 or 5 elements in the TiW_5 or NbW_5 anions, so the observation of only one terminal WO peak is not surprising. However, a curious feature in these spectra is the appearance of three peaks in the region for MoOW instead of one. These peaks at δ 488, 486 and 482 are not equally intense but have similar relative intensities in spectra of samples from different reactions and there doesn't appear to be an obvious explanation for this pattern. A ^{183}W NMR spectrum of this material contains two peaks at δ 55.0 and 47.4 with an approximate intensity ratio of 1 : 4 (this is difficult to measure with any precision because the low solubility of the compound resulted in a poor signal-to-noise ratio) while the ^{95}Mo NMR spectrum contains only one peak at δ 116 with a linewidth of 176 Hz. Consistent with the presence of **13** in this product, ν(W=O) and ν(Mo=O) appear in the IR spectrum at 976 and 930 cm^{-1} compared with 976 and 954 cm^{-1} for **1** and $[Mo_6O_{19}]^{2-}$ respectively.

The ^{183}W NMR spectra were obtained for all of the hexametalates except **8** (for which insufficient material was available). For $[VW_5O_{19}]^{3-}$ **5** only one broad resonance was observed, consistent with previous reports of line broadening in ^{183}W NMR spectra of vanadium-substituted tungstates for the W atoms in proximity to vanadium.[30] This broad peak was assigned to W(a) since this should be the largest peak in the spectrum, although it is possible that a larger peak might be sufficiently broadened so as not to be visible. The relationship between electronic structure and δ_W in heteronuclear polyoxometalates has been discussed in terms of an upfield shift relative to the analogous homonuclear anion due to a decreased availability of excited states, countered by a downfield shift due to an increase in electronic anisotropy when distortion from the octahedral WO_6 co-ordination geometry occurs. For example, Baker and co-workers[30] noted that in substituted α-Keggin anions $[EMW_{11}O_{40}]^{n-}$ (E, M = P, V; P, Ti; Si, V or B, V) and $[(H_2O)ZnEW_{11}O_{39}]^{n-}$ (E = P, n = 5; E = Si, n = 6) the resonances of W atoms which are bridged through two O atoms to the heteroatom (*i.e.* the tungsten and heteroatom co-ordination octahedra are edge-shared) shift downfield, while corner-shared W atoms shift upfield relative to the unsubstituted α-Keggin anions. From the data shown in Table 5 for the MW_5 hexametalates, a discernible trend emerges in which W atoms *cis* to the heteroatom in $[MW_5O_{19}]^{n-}$ anions are deshielded relative to **1** while the *trans* W atoms are shielded, but in the titanium and niobium alkoxide derivatives **2** and **7** respectively, this effect is reversed so that *cis* W atoms are shielded relative to **1** and the *trans* W atoms are deshielded. This implies that the greatest electronic anisotropy is at W(a) in $[MW_5O_{19}]^{n-}$ anions and at W(b) in the alkoxide derivatives $[(MeO)MW_5O_{18}]^{n-}$. In **13** substitution has a smaller effect on δ_W values (as might be expected when W is replaced by Mo) but unlike the other $[MW_5O_{19}]^{n-}$ anions, W(b) appears to have the largest electronic anisotropy. As mentioned earlier, structural distortions in hexametalates have been related to δ_O for terminal WO groups[28] and, although more experimental results are needed, it seems that similar correlations are possible with δ_W values. Assuming that the above trends in δ_W are generally applicable to MW_5 hexametalates containing Group 4 and 5 heteroatoms, they lend support to the assignment of alkoxide structures to the zirconium and tantalum derivatives **4** and **11** respectively, and would also suggest that the titanium species **3** is not $[TiW_5O_{19}]^{4-}$. However, δ_O values for terminal WO in Table 4 move upfield with increasing charge on any particular MW_5 hexametalate unit, and on this basis **3** is more likely to be $[TiW_5O_{19}]^{4-}$. Clearly, more results are needed to clarify the relationships between spectroscopic trends, electronic charge distribution and structure in these species.

In contrast to the complex equilibria established during the aqueous acidification of MO_4^{2-} (M = Mo or W), especially when other early transition metals are present,[31] the reactions discussed here demonstrate that it is possible to generate relatively simple non-aqueous systems in which only a few species are formed. In particular, the almost quantitative formation of $[NBu^n_4]_2[W_6O_{19}]$ from $[NBu_4{}^n]_2[WO_4]$ and $WO(OMe)_4$ is striking and provides a convenient route to ^{17}O-enriched material using only a stoichiometric amount of enriched water, which is more efficient than the previously published method.[23] Similarly, the hydrolytic routes to heterometalates $[MW_5O_{19}]^{3-}$ (M = V, Nb or Ta) described here are more straightforward than previously published methods,[7,22,23] and ^{17}O enrichment is readily achieved without modification to the procedure. In addition, this synthetic strategy appears to be particularly well suited to the preparation of reactive alkoxide derivatives $[(RO)MW_5O_{18}]^{n-}$ (M = Ti or Zr, n = 3; M = Nb or Ta, n = 2), although conditions have yet to be optimised for niobium and tantalum compounds. It is interesting that spectroscopic evidence requires a terminal Nb–OMe bond in **7** since alkylation of *cis*-$[Nb_2W_4O_{19}]^{4-}$ has been shown to occur at bridging sites in the absence of steric hindrance.[24] This difference is likely to be a reflection of the aggregation mechanism in which Nb–O–W bridges are formed in preference to terminal Nb=O bonds during hydrolysis. We have shown that ligand redistribution follows the initial associative step in the homonuclear reaction between WO_4^{2-} and $WO(OMe)_4$ to form $[W_2O_5(OMe)_4]^{2-}$.[3] Analogous interactions with $Nb(OMe)_5$ would lead to heteronuclear species such as $[WNbO_4(OMe)_5]^{2-}$ which, on hydrolysis in the presence of $WO(OMe)_4$, generate the NbW_5 hexametalates. Similar considerations apply to the formation of the other MW_5 polyanions from the appropriate alkoxides. However, it is still unclear what factors are responsible for selectivity during aggregation to these hexanuclear anions and further studies are in progress to uncover more of the fundamental growth steps.

We are exploring the chemistry of these derivatised tungstates, including the simple hydrolysis of the alkoxides to produce linked hexametalates such as **8** and ligand metathesis reactions. We are also investigating the range of other polyoxometalate structures that might be accessible using this hydrolytic method.

Experimental

All manipulations were carried out under dry, oxygen-free nitrogen using standard Schlenk techniques, or in a dry-box fitted with a recirculation system. Hydrocarbon and ether solvents were dried over and distilled from sodium–benzophenone and acetonitrile was dried over and distilled from calcium hydride immediately prior to use. Tungsten alkoxides,[32] $Ti(OMe)_4$, $Nb(OMe)_4$, $Ta(OMe)_5$[33] and $[NBu^n_4]_2[Mo_2O_7]$[34] were prepared by literature procedures, $VO(OMe)_3$ was prepared from $[VOCl_3(dme)]$ (dme = 1,2-dimethoxyethane)[35] other titanium and zirconium alkoxides were supplied by Tioxide Specialities Ltd. and $[(NBu^n_4)_2][WO_4]$ was prepared by a modification of the method described by Klemperer and co-workers.[36] The salt $[NBu^n_4]_2[W_2O_5(OMe)_4]$ was prepared by mixing equimolar amounts of $[NBu^n_4]_2[WO_4]$ and $WO(OMe)_4$ in acetonitrile.[3] Infrared spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 598 spectrometer, NMR spectra on Bruker WP 200 (^{1}H and ^{13}C-{^{1}H}), WM 300 (^{183}W and ^{95}Mo) or AM 500 (^{17}O) spectrometers. Elemental analyses were performed by the University of Newcastle upon Tyne microanalytical service. Resonances due to $NBu^n_4{}^+$ cations are not listed and appear as multiplets centred at about δ 1.0, 1.4, 1.7 and 3.2 in ^{1}H NMR spectra and as singlets at about δ 13, 19, 24 and 58 in ^{13}C-{^{1}H} NMR spectra.

Preparations

$[NBu^n_4]_2[W_6O_{19}]$. A solution of $[NBu^n_4]_2[WO_4]$ (0.23 g, 0.31 mmol) and $WO(OMe)_4$ (0.50 g, 1.54 mmol) in acetonitrile (3 cm^3) was treated with water (56 μl, 3.11 mmol) with thorough mixing. Well formed colourless prisms formed overnight and, after cooling to −20 °C, these were isolated and dried *in vacuo*

(0.36 g, 61%). Further material could be isolated from the mother-liquor, but the yield was not optimised in this experiment.

[NBu$^n{}_4$]$_3$[(MeO)TiW$_5$O$_{18}$]. The salt [NBu$^n{}_4$]$_2$[WO$_4$] (6.00 g, 8.19 mmol) in acetonitrile (40 cm^3) was transferred *via* cannula to Ti(OMe)$_4$ (0.94 g, 5.46 mmol) and the mixture stirred for 2 h. The remaining white solid dissolved on heating and after cooling to room temperature a solution of WO(OMe)$_4$ (6.19 g, 19.11 mmol) in acetonitrile (10 cm^3) was added. The solution was stirred for 30 min and filtered to remove some remaining white precipitate before the addition of water (836 μl, 46.4 mmol, 2% ^{17}O enrichment) in acetonitrile (10 cm^3). After stirring for 1 h, the solution subsequently turned from a straw colour to pale green on standing overnight. No crystalline material was obtained overnight after reduction of the volume to 10 cm^3 but addition of diethyl ether (40 cm^3) caused precipitation of a sticky solid which was triturated with further portions of ether (3 × 10 cm^3) and dried *in vacuo*. Recrystallisation from acetonitrile afforded first [NBu$^n{}_4$]$_2$[W$_6$O$_{19}$], then pale green single crystals of [NBu$^n{}_4$]$_3$[(MeO)TiW$_5$O$_{18}$]·0.5MeCN, which were used for an X-ray determination (5.79 g, 53%) (Found: C, 29.9; H, 5.75; N, 2.2. C$_{50}$H$_{112.5}$N$_{3.5}$O$_{19}$TiW$_5$ requires C, 29.5; H, 5.6; N, 2.4%); $\tilde{\nu}_{max}$/cm^{-1} 1144m, 1090m, 1050w, 1020w, 966w, 947s, 925 (sh), 882m, 795s (br), 735m, 619m, 600m, 575w, 540w, 445s, 425s, 366w and 350w; δ_H(200.13 MHz, CD$_3$CN) 4.10 (s, OMe); δ_C(75.47 MHz, CD$_3$CN) 62.35 (OMe).

[NBu$^n{}_4$]$_4$[TiW$_5$O$_{19}$] (attempted). (*a*) A solution of [NBu$^n{}_4$]$_2$[WO$_4$] (1.43 g, 1.95 mmol) in acetonitrile (10 cm^3) was transferred *via* cannula to WO(OMe)$_4$ (0.95 g, 2.93 mmol), with simultaneous addition of Ti(OPr^i)$_4$ (0.29 cm^3, 0.98 mmol) from a syringe, with stirring. ^{17}O-Enriched water (141 μl, 7.82 mmol, 5% enrichment) was added. After stirring for 36 h, the solvent was removed *in vacuo*. Fractional recrystallisation from acetonitrile at −20 °C produced crystals of [NBu$^n{}_4$]$_3$-[(MeO)TiW$_5$O$_{18}$] and then anion **3**.

(*b*) The salt [NBu$^n{}_4$]$_2$[WO$_4$] (6.00 g, 8.19 mmol) dissolved in acetonitrile (40 cm^3) was transferred *via* cannula to Ti(OMe)$_4$ (0.70 g, 4.07 mmol) in acetonitrile (10 cm^{-3}). After stirring for 2 h the solution was heated to dissolve the remaining white solid, then a solution of WO(OMe)$_4$ (3.98 g, 12.28 mmol) in acetonitrile was added. The solution was stirred for 30 min and then filtered. A solution of water (590 μl, 32.8 mmol, 2% ^{17}O enrichment) in acetonitrile (10 cm^3) was added and stirred for 1 h. After 24 h a small quantity of insoluble material had settled and the mother-liquor was transferred *via* cannula to a clean flask. The solvent was removed under reduced pressure and the resultant oil was triturated with diethyl ether (5 × 10 cm^3) to give a colourless solid which was pumped dry (yield 8.25 g). Fractional recrystallisation from acetonitrile (10 cm^3) at −20 °C produced crystals of [NBu$^n{}_4$]$_3$[(MeO)-TiW$_5$O$_{18}$] and then anion **3** (1.62 g).

[NBu$^n{}_4$]$_6$[(TiW$_5$O$_{18}$)$_2$O] (attempted). A solution of water (4.5 μl, 0.25 mmol, 10% ^{17}O enrichment) in acetonitrile (10 cm^3) was transferred to [NBu$^n{}_4$]$_3$[(MeO)TiW$_5$O$_{18}$] (1.00 g, 0.5 mmol) in acetonitrile (10 cm^3), with stirring. The solution was left ovenight, then the solvents were removed *in vacuo*, triturated with diethyl ether and dried *in vacuo* to produce a white solid (0.93 g) which was shown by ^{1}H NMR spectroscopy to be starting material.

[NBu$^n{}_4$]$_3$[(MeO)ZrW$_5$O$_{18}$] (attempted). A solution of [NBu$^n{}_4$]$_2$[WO$_4$] (0.87 g, 1.19 mmol) in acetonitrile (10 cm^3) was added to an immiscible mixture of a propan-1-ol solution of Zr(OPr^n)$_4$ (73%, 0.36 g, 0.79 mmol) and acetonitrile (10 cm^3). After stirring for 1 h some white solid remained, but after removal of the volatiles *in vacuo* the residue dissolved in acetonitrile (10 cm^3). The compound WO(OMe)$_4$ (0.90 g, 2.77 mmol) in acetonitrile (10 cm^3) was added and the solution stirred for 1 h before addition of water (121 μl, 6.73 mmol, 5% ^{17}O enrichment) in acetonitrile (5 cm^3). The mixture was stirred for 1 h and then left for 10 d, over which time a small quantity of insoluble material settled out. The solution was decanted into a clean flask and the solvent removed *in vacuo* to leave a white solid. Colourless needles were obtained from acetonitrile (5 cm^3) at −20 °C. $\tilde{\nu}_{max}$/cm^{-1} 1660m, 1150m, 1105w, 1065m, 1029m, 945s, 890m, 800s (br), 740s, 646w, 560w, 500w, 475w, 430s and 340w; δ_H(200.13 MHz, CD$_3$CN) 3.62–4.20 (several peaks).

[NBu$^n{}_4$]$_2$[(MeO)VW$_5$O$_{18}$] (attempted). A solution of VO(OMe)$_3$ (0.10 g, 0.62 mmol) in acetonitrile (20 cm^3) was transferred *via* cannula to [NBu$^n{}_4$]$_2$[WO$_4$] (0.46 g, 0.62 mmol) with stirring to give a pale yellow solution. After 10 min a solution of WO(OMe)$_4$ (0.81 g, 2.50 mmol) in acetonitrile (10 cm^3) was added, and stirring continued for 1 h. The solution turned orange on addition of water (101 μl, 5.61 mmol, 5% ^{17}O enrichment) in acetonitrile (5 cm^3). It was left overnight and then the solvent removed *in vacuo* to leave a brown oil.

[NBu$^n{}_4$]$_3$[VW$_5$O$_{19}$]. The salt [NBu$^n{}_4$]$_2$[WO$_4$] (0.69 g, 0.94 mmol) in acetonitrile (10 cm^3) was transferred *via* cannula to a stirred solution of VO(OMe)$_3$ (0.10 g, 0.62 mmol) in acetonitrile (10 cm^3) to give a pale yellow solution. After 15 min WO(OMe)$_4$ (0.71 g, 2.19 mmol) in acetonitrile (10 cm^3) was added and stirring was continued for 1 h. Addition of water (96 μl, 5.31 mmol, 5% ^{17}O enrichment) in acetonitrile (5 cm^3) gave an orange solution, which was used for spectroscopic characterisation: δ_V(131.55 MHz, MeCN) −509.

[NBu$^n{}_4$]$_2$[(MeO)NbW$_5$O$_{18}$]. (*a*) A mixture of WO(OPr^i)$_4$ (2.05 g, 4.7 mmol), [NBu$^n{}_4$]$_2$[WO$_4$] (0.86 g, 1.17 mmol) and Nb(OMe)$_5$ (0.29 g, 1.17 mmol) was stirred in acetonitrile (40 cm^3) for 1 h and then heated to dissolve some remaining solid. A solution of ^{17}O-enriched water (210 μl, 11.7 mmol, 5% ^{17}O enrichment) in acetonitrile (15 cm^3) was added *via* cannula with stirring and the solution turned from brown to straw coloured. After stirring for 90 min the solvent was removed *in vacuo* to give a green oily solid. Recrystallisation from acetonitrile at −20 °C produced first [NBu$^n{}_4$]$_2$[W$_6$O$_{19}$] then a second colourless crystalline fraction. δ_H(200.13 MHz, CD$_3$CN) 3.28 (s, 1 H) and 4.40 (s, 2 H); δ_C(125.76 MHz, CD$_3$CN) 65.91 (OMe).

(*b*) A solution of [NBu$^n{}_4$]$_2$[WO$_4$] (1.70 g, 2.32 mmol) in acetonitrile (10 cm^3) was added to a solution of Nb(OMe)$_5$ (0.57 g, 2.29 mmol) in acetonitrile (10 cm^3), and after 1 h of stirring WO(OMe)$_4$ (3.00 g, 9.26 mmol) in acetonitrile (10 cm^3) was also added. The solution was stirred for 4 h before addition of water (417 μl, 23.17 mmol, 2% ^{17}O enrichment) in acetonitrile (10 cm^3). A small quantity of fine precipitate was allowed to settle over approximately 48 h and then the mother-liquor was decanted into a clean flask. The solution was reduced in volume for NMR studies which showed a mixture of the same three products obtained by method (*a*).

[NBu$^n{}_4$]$_3$[NbW$_5$O$_{19}$]. A solution of [NBu$^n{}_4$]$_2$[WO$_4$] (3.32 g, 4.53 mmol) in acetonitrile (20 cm^3) was transferred *via* cannula to Nb(OMe)$_5$ (0.75 g, 3.02 mmol) with stirring. A solution of WO(OMe)$_4$ (3.43 g, 10.58 mmol) in acetonitrile (20 cm^3) was added after 1 h followed, after 3 h, by a solution of water (517 μl, 28.72 mmol, 5% ^{17}O enrichment) in acetonitrile (10 cm^3). After 10 min the solution was filtered and solvent removed *in vacuo* to leave a green oil which was triturated with diethyl ether (2 × 10 cm^3) and dried *in vacuo* to give a blue-white solid. Recrystallisation from acetonitrile (5 cm^3) at −20 °C produced first [NBu$^n{}_4$]$_2$[W$_6$O$_{19}$] and then colourless cubic crystals of [NBu$^n{}_4$]$_3$[NbW$_5$O$_{19}$].

Table 6 Crystallographic data[a]

	$[NBu^n_4]_3[(MeO)TiW_5O_{18}]\cdot 0.5MeCN$	$[NBu^n_4]_4[(NbW_5O_{18})_2O]$
Formula	$C_{50}H_{112.5}N_{3.5}O_{19}TiW_5$	$C_{64}H_{144}N_4Nb_2O_{37}W_{10}$
M	2034.08	1793.08
Crystal system	Monoclinic	Orthorhombic
Space group	*Pc*	*Pccn*
Crystal size/mm	0.34 × 0.28 × 0.24	0.57 × 0.48 × 0.34
a/Å	24.283(2)	35.022(2)
b/Å	17.1798(12)	15.4860(11)
c/Å	16.5903(12)	17.6990(12)
β/°	98.095(2)	90
U/Å^3	6852(8)	9599.0(11)
No. reflections for cell refinement	23 424	24 367
Z	4	4
D_c/g cm^{-3}	1.972	2.481
μ/mm^{-1}	8.534	12.233
F(000)	3924	6696
Crystal colour	Colourless	Colourless
2θ Range/°	2.38–51.28	2.88–51.38
Maximum *hkl* indices	−29 to 28, −20 to 19, −19 to 10	−41 to 31, −18 to 16, −21 to 21
No. reflections measured	29 642	39 601
No. unique reflections	17 063	8323
No. with $F^2 > 2\sigma(F^2)$	16 330	7238
Transmission factors	0.394–0.694	0.180–0.756
R_{int} (on F^2)	0.0458	0.0883
Weighting parameters *a*, *b*	0.0260, 68.9512	0.0184, 202.3139
$R1$ [$F^2 > 2\sigma(F^2)$]	0.0350	0.0489
$wR2$ (all data)[b]	0.0848	0.1141
No. parameters	1464	575
Goodness of fit on F^2	1.075	1.191
Extinction coefficient	0.000 050(7)	0.000 084(6)
Maximum, minimum in difference map/e Å^{-3}	1.418, −1.319	1.756, −1.763

[a] The standard deviation of the last significant figure(s) is given in parentheses. [b] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$.

$[NBu^n_4]_4[(NbW_5O_{18})_2O]$ (attempted). A solution of $[NBu^n_4]_2[WO_4]$ (1.02 g, 1.39 mmol) in acetonitrile (10 cm^3) was transferred to $Nb(OMe)_5$ (0.35 g, 1.41 mmol) with stirring. After 60 min a solution of $WO(OMe)_4$ (1.80 g, 5.56 mmol) in acetonitrile (10 cm^3) was added followed, after 2 h, by a solution of water (263 μl, 14.6 mmol, 4% ^{17}O enrichment) in acetonitrile (5 cm^3). The solvent was removed *in vacuo* and the residue used for spectroscopic studies. Note: crystals shown to be $[NBu^n_4]_4[(NbW_5O_{18})_2O]$ by X-ray diffraction studies, were isolated from the attempted preparation of $[NBu^n_4]_2[(MeO)NbW_5O_{18}]$.

$[NBu^n_4]_2[(MeO)TaW_5O_{18}]$ (attempted). Acetonitrile (40 cm^3) was added to a mixture of $WO(OC_6H_{11})_4$ (1.77 g, 2.95 mmol), $[NBu^n_4]_2[WO_4]$ (0.54 g, 0.74 mmol) and $Ta(OMe)_5$ (0.25 g, 0.74 mmol). The solution was heated and stirred for 2 h before addition of water (134 μl, 7.4 mmol, 5% ^{17}O enrichment) in acetonitrile (15 cm^3) *via* cannula. Stirring was continued for 90 min after which time all of the product dissolved to give a greenish solution. The solution was filtered and the solvent removed *in vacuo*. Fractional recrystallisation from acetonitrile at −20 °C removed $[NBu^n_4]_2[W_6O_{19}]$ and the residue was used for spectroscopic studies.

$[NBu^n_4]_4[Ta_2W_4O_{19}]$ (attempted). The salt $[NBu^n_4]_2[W_2O_5(OMe)_4]$ (1.33 g, 1.26 mmol) in acetonitrile (20 cm^3) was transferred *via* cannula to $Ta(OMe)_5$ (0.42 g, 1.26 mmol), with stirring at room temperature. After 24 h, water (204 μl, 11.33 mmol, 5% ^{17}O enrichment) was added with stirring, then the solvent removed *in vacuo*. The salt $[NBu^n_4]_3[TaW_5O_{19}]$ crystallised from an acetonitrile (10 cm^3) solution of the product mixture at −20 °C (0.4 g, 15%) (Found: C, 27.0; H, 5.0; N, 2.0. $C_{48}H_{108}N_3O_{19}TaW_5$ requires C, 27.0; H, 5.1; N, 2.0%); $\tilde{\nu}_{max}$/cm^{-1} 1160w, 1150w, 1105w, 1059w, 1025w, 977 (sh), 964 (sh), 959s, 910m, 884m, 805s, 736m, 723m, 591m, 581m, 447s, 437s and 305w.

$[NBu^n_4]_2[MoW_5O_{19}]$. A mixture of $WO(OMe)_4$ (2.90 g, 8.95 mmol) and $[NBu^n_4]_2[MoO_4]$ (1.15 g, 1.78 mmol) in acetonitrile (20 cm^3) was stirred for 30 min. After addition of a solution of water (323 μl, 17.9 mmol, 5% ^{17}O enrichment) in acetonitrile (15 cm^3) the solution turned pale green. The solvent was removed *in vacuo* to give an oil which was triturated with diethyl ether (2 × 10 cm^3) and pumped dry to give a pale green solid. Pale green single crystals were obtained from hot acetonitrile on cooling to room temperature (1.24 g) (Found: C, 21.4; H, 3.9; N, 1.6. $C_{32}H_{72}MoN_2O_{19}W_5$ requires C, 21.3; H, 4.0; N, 1.55%); $\tilde{\nu}_{max}$/cm^{-1} 1164m, 1108w, 1072w, 1062w, 1035w, 1029w, 994(sh), 976s, 971s, 930m, 889m, 875m, 812s (br), 755w, 738m, 592m, 451s and 372m.

$[NBu^n_4][(MeO)MoW_5O_{18}]$ (attempted). A solution of $WO(OMe)_4$ (1.00 g, 3.09 mmol) in acetonitrile (5 cm^3) was transferred to a stirred solution of $[NBu^n_4]_2[Mo_2O_7]$ (0.24 g, 0.31 mmol) in acetonitrile (5 cm^3). After 15 min, water (106 μl, 5.88 mmol, 5% ^{17}O enrichment) in acetonitrile (5 cm^3) was added and stirring continued for 90 min, during which time the solution turned green. The solvent was removed under reduced pressure to give a greenish oil which was shown by ^{17}O NMR spectroscopy to be $[NBu^n_4]_2[MoW_5O_{19}]$.

$[NBu^n_4]_2[(MoW_5O_{18})_2O]$ (attempted). The compound $WO(OMe)_4$ (1.00 g, 3.09 mmol) in acetonitrile (10 cm^3) was transferred *via* cannula to a stirred solution of $[NBu^n_4]_2[Mo_2O_7]$ (0.24 g, 0.31 mmol) in acetonitrile (5 cm^3). After 15 min, water (111 μl, 6.17 mmol, 5% ^{17}O enrichment) in acetonitrile (5 cm^3) was added and the resultant pale green solution was stirred for 20 min. The solvent was removed *in* *vacuo* to leave a green oil which was shown by ^{17}O NMR spectroscopy to be $[NBu^n{}_4]_2[MoW_5O_{19}]$.

X-Ray crystallography

Crystal data for the compounds $[NBu^n{}_4]_3[(MeO)TiW_5O_{18}]\cdot 0.5MeCN$ and $[NBu^n{}_4]_4[(NbW_5O_{18})_2O]$ are presented in Table 6. All measurements were made at 160(2) K on a Siemens SMART CCD area-detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) with narrow frames (0.3°) and three-dimensional profile fitting. The data were corrected semiempirically for absorption by ψ scans. Structure solution was by direct methods, refinement by full-matrix least-squares analysis on F^2 for all independent reflections, with weighting $w^{-1} = \sigma^2(F_o{}^2) + (aP)^2 + bP$, where $P = (F_o{}^2 + 2F_c{}^2)/3$. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were constrained. Siemens SHELXTL,[37] SMART[38] and SAINT[38] software for data collection and reduction, and local programs, were employed.

The structure of $[NBu^n{}_4]_3[(MeO)TiW_5O_{18}]\cdot 0.5MeCN$ was refined as a racemic twin with a ratio of 91.07(11):8.91(11)% for the two components. For three of the *n*-butyl chains the terminal carbon atom was disordered over two positions with refined site occupancies as follows: C(42):C(42a), 78(4):22(4); C(50):C(50a), 66(3):34(3); C(62):C(62a), 30(3):70(3)%. Some N–C and C–C distance and anisotropic displacement parameter restraints were used in these cases. Anisotropic displacement parameters were also restrained for the fragment N(6)–C(95)–C(96) which is part of a $[NBu^n{}_4]^+$ cation.

In the structure of $[NBu^n{}_4]_4[(NbW_5O_{18})_2O]$ one *n*-butyl chain in one of the $[NBu^n{}_4]^+$ cations is disordered over two sets of positions: C(17)–C(18)–C(19)–C(20):C(17a)–C(18a)–C(19a)–C(20a), 59(4):41(4)%. The N–C and C–C distance and anisotropic displacement parameter restraints were used for this part of the model. Anisotropic displacement parameter restraints were also applied to atoms O(15), O(18), W(2) and W(5).

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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