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ARTICLE TYPE

Protonolysis of $[(^i\text{PrO})\text{TiMo}_5\text{O}_{18}]^{3-}$: access to a family of TiMo_5 Lindqvist type polyoxometalates†

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The tetra-*n*-butylammonium (TBA) salts of $[(^i\text{PrO})\text{TiMo}_5\text{O}_{18}]^{3-}$ **1** and $[(^i\text{BuO})\text{TiMo}_5\text{O}_{18}]^{3-}$ **2** were prepared by hydrolysis of mixtures of $(\text{TBA})_2[\text{Mo}_2\text{O}_7]$, $(\text{TBA})_4\alpha\text{-}[\text{Mo}_8\text{O}_{26}]$ and $\text{Ti}(\text{OR})_4$ ($\text{R} = ^i\text{Pr}$ or ^iBu) in acetonitrile. Treatment of $(\text{TBA})_3\textbf{1}$ with alcohols ROH afforded primary and tertiary alkoxide derivatives $[(\text{RO})\text{TiMo}_5\text{O}_{18}]^{3-}$ ($\text{R} = \text{Me}$ **3**, ^iBu **4**), whilst aryloxides $[(\text{ArO})\text{TiMo}_5\text{O}_{18}]^{3-}$ were prepared by reacting **1** with phenols ArOH ($\text{Ar} = \text{C}_6\text{H}_4\text{Me}$ -4 **5**, and $\text{C}_6\text{H}_4\text{CHO}$ -2 **6**). Oxo-bridged $[(\mu\text{-O})(\text{TiMo}_5\text{O}_{18})_2]^{6-}$ **7** rather than the hydroxo derivative $[(\text{HO})\text{TiMo}_5\text{O}_{18}]^{3-}$ was obtained upon hydrolysis of **1**. X-ray crystal structures of TBA salts of anions **3–7** show that titanium is six-coordinate in all cases, although titanium sites are disordered over two *trans* positions in **3**. Mo–O bond length alternation is observed in the Mo_4O_4 planes of **4** and **7** and in one of the two independent anions in the structure of **3**. In solution, ^{17}O NMR spectra are consistent with the higher anionic charge compared to $[\text{Mo}_6\text{O}_{19}]^{2-}$ and reveal an order of basicity for the anions $[\text{LM}'\text{Mo}_5\text{O}_{18}]^{3-}$ associated with the ability of $\{\text{LM}'\}^{3+}$ to donate/withdraw electron density from $\{\text{Mo}_5\text{O}_{18}\}^{6-}$. Protonolysis reactions of **1** and **3** were slower than for tungstate analogues and the possibility of initial protonation at TiOM ($\text{M} = \text{Mo}$) rather than TiOR ($\text{M} = \text{W}$) in a proton-assisted $\text{S}_{\text{N}}1$ mechanism for ligand exchange in $[(\text{RO})\text{TiMo}_5\text{O}_{18}]^{3-}$ is discussed.

Introduction

Polyoxometalates (POMs) are unrivalled in their chemical and structural diversity and provide a versatile platform for nanoscale molecular metal oxide science,¹ but the rational synthesis of POMs with pre-determined composition and structure remains a major challenge. This fundamental capability is essential for the development of systematic POM chemistry and the main approaches to date have involved (a) the aggregation of small molecular precursors, (b) direct functionalisation, *i.e.* reactions in which oxido ligands of the POM are replaced with other ligands without disruption of the core metal oxide structure and (c) incorporation of electrophilic groups into lacunary species with high surface charge densities. As part of our programme to develop the metalorganic chemistry of POMs,^{2–8} we chose as basic structural units the comparatively simple 6 Lindqvist type hexametalates $[\text{M}_6\text{O}_{19}]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$) because of their ready formation in organic solvents.⁹ Metathesis of oxido ligands in $[\text{Mo}_6\text{O}_{19}]^{2-}$ has been achieved in reactions involving $\text{Ph}_3\text{P}=\text{NX}$ ($\text{X} = \text{Ar}, \text{N}=\text{C}(\text{Me})\text{Ar}$),¹⁰ ArNCO ,¹¹ $\text{RNCO}^{2(\text{b})}$ or ArNH_2 ,³ and the latter reaction has subsequently been adapted to provide general access to arylimido and diazoalkane derivatives,^{12,13} but the tungstate $[\text{W}_6\text{O}_{19}]^{2-}$ is inert under similar reaction conditions. The limited reactivity of these hexametalates has been ascribed to their low surface charge density and many of the reported organic derivatives have been prepared by indirect routes *i.e.* from

$[\text{WO}_4]^{2-}$, $[\text{Mo}_2\text{O}_7]^{2-}$ or $\alpha\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ rather than from $[\text{M}_6\text{O}_{19}]^{2-}$.¹⁴

An established approach to the design of reactive Lindqvist type hexametalates is the replacement of M^{VI} in the relatively inert hexametalates $[\text{M}_6\text{O}_{19}]^{2-}$ ($\text{M} = \text{Mo}, \text{W}$) by lower-valent metals, thereby increasing the charge density at the surface of the resulting heterometallic anions $[\text{M}'_x\text{M}_{(6-x)}\text{O}_{19}]^{n-}$, but detailed structure-reactivity correlations for these heterometalates are difficult to establish because of frequent problematic disorder of the anions in the solid state. The introduction of $\{\text{M}'\text{L}\}^{x+}$ instead of $\{\text{M}'=\text{O}\}^{x+}$, where $x < 4$, provides a means of circumventing this problem by using ligands L with sufficient steric bulk to prevent disorder. This approach was first exploited by Klemperer for the synthesis of $(\text{TBA})_3[(\eta^5\text{-C}_5\text{H}_5)\text{TiM}_5\text{O}_{18}]$ ($\text{M} = \text{Mo}, \text{W}$) and $(\text{TBA})_3[(\eta^5\text{-C}_5\text{Me}_5)\text{TiW}_5\text{O}_{18}]$,¹⁵ and subsequently by Yagasaki who reported $(\text{TBA})_3[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMo}_5\text{O}_{18}]$.¹⁶ To our knowledge, the only other structurally characterised examples of $[\text{LM}'\text{M}_5\text{O}_{18}]^{n-}$ where $n > 2$ are from our work involving early transition metal alkoxido species and their derivatives,^{5,6} and the cobalt-substituted anion $[(\text{py})\text{CoW}_5\text{O}_{18}\text{H}]^{3-}$, which was derived from dimeric $[(\text{CoW}_5\text{O}_{18}\text{H})_2]^{6-}$.⁷

Our strategy to expand the metalorganic chemistry of POMs has been to target heterometalates $[\text{LM}'\text{M}_5\text{O}_{18}]^{n-}$ which not only have higher surface basicity than the parent $[\text{M}_6\text{O}_{19}]^{2-}$ but also possess labile $\text{M}'\text{-L}$ bonds, thereby opening up access to reactivity at the heterometal site. By employing a non-aqueous approach, which provides some control over hydrolytic aggregation reactions, we have prepared the alkoxido-substituted

tungstate derivatives $[(RO)MW_5O_{18}]^{n-}$ from alkoxide precursors and demonstrated that functionality can be manipulated in a rational fashion through straightforward reactions at the $M(OR)$ site,^{5(b), 5(c)} including the first covalent immobilisation of $\{TiW_5O_{18}\}$ molecular metal oxide units on derivatised silicon surfaces.⁸ We have now extended this methodology to analogous molybdate systems and recently reported the synthesis of $[(^iPrO)TiMo_5O_{18}]^{3-}$ **1** as its tetra-*n*-butylammonium (TBA) salt.⁶ We describe here the synthesis of the *iso*-butoxide $[(^iBuO)TiMo_5O_{18}]^{3-}$ **2** and the reactivity of **1** towards a range of protic reagents to give a family of alkoxido- and aryloxido-derivatised titanomolybdates as well as the oxido-bridged condensation product from hydrolysis. Structural and spectroscopic data are discussed in terms of electronic properties and comparisons are made with related $[LM'M_5O_{18}]^{3-}$ anions.

Results

$(TBA)_3\mathbf{2}$ was prepared by a hydrolytic aggregation reaction from $(TBA)_2[Mo_2O_7]$, $(TBA)_4\alpha-[Mo_8O_{26}]$ and $Ti(O^iBu)_4$ according to eqn. (1) as described previously for $(TBA)_3\mathbf{1}$.⁶ The FTIR, 1H , ^{13}C and ^{17}O NMR spectra of $(TBA)_3\mathbf{2}$ are all consistent with a structure that is analogous to that of **1**, although its high solubility has so far prevented the growth of single crystals for single-crystal X-ray crystallography and purification for elemental analysis.

The *iso*-propoxide **1** was chosen for protonolysis studies because of the ready availability of $Ti(O^iPr)_4$ and the easier purification of $(TBA)_3\mathbf{1}$. Hence, treatment of $(TBA)_3\mathbf{1}$ with methanol or *tert*-butanol gave the primary and tertiary alkoxido derivatives $[(MeO)TiMo_5O_{18}]^{3-}$ **3** and $[(^iBuO)TiMo_5O_{18}]^{3-}$ **4** respectively, and similar exchange reactions with phenols 4-MeC₆H₄OH and 2-(CHO)C₆H₄OH gave the aryloxides $[(4-MeC_6H_4O)TiMo_5O_{18}]^{3-}$ **5** and $[(2-CHO)C_6H_4O]TiMo_5O_{18}]^{3-}$ **6**. Hydrolysis of **1** resulted in formation of the oxido-bridged species $[(\mu-O)(TiMo_5O_{18})_2]^{3-}$ **7**. Reactions were readily monitored in solution by 1H and ^{17}O NMR spectroscopy and the structures of **3–7** have been determined by single-crystal X-ray diffraction.

Alcoholysis and hydrolysis of $(TBA)_3\mathbf{1}$

A significant ionic contribution to $M-OR$ bonding in metal alkoxides has been proposed to account for their susceptibility to protonolysis and subsequent ligand exchange *via* loss of alcohol,¹⁷ and the archetypal reaction of this type is that between $M-OR$ and ROH , resulting in OR exchange between the metal and the alcohol. In order to assess the lability of the alkoxido group in **1**, we therefore monitored the reaction between $(TBA)_3\mathbf{1}$ and iPrOH by 1H NMR spectroscopy. Separate, well resolved TiO^iPr and iPrOH methine and methyl peaks were observed at temperatures up to 70 °C, as shown in Fig. 1(b), and the lack of line broadening demonstrates that exchange is slow on the NMR timescale. In general, the replacement of tertiary and secondary alkoxido groups in exchange reactions by less sterically demanding primary alcohols is a favourable process,¹⁷ so we expected the reaction between $(TBA)_3\mathbf{1}$ and MeOH to proceed

Fig. 1 1H NMR spectra of $(TBA)_3\mathbf{1}$ at 25 °C (a), reaction between $(TBA)_3\mathbf{1}$ and iPrOH at 70 °C (b), reaction between $(TBA)_3\mathbf{1}$ and MeOH, after 3 h at 25 °C then 20 min at 60 °C, recorded at 25 °C (c), and reaction between $(TBA)_3\mathbf{1}$ and H_2O at 24 °C (d).

more readily. After addition of approximately one equivalent of MeOH to a sample of $(TBA)_3\mathbf{1}$ the 1H NMR spectrum showed the expected doublet and septet of iPrOH as well as a new singlet at 4.01 ppm, which was assigned to the methoxido ligand of $(TBA)_3\mathbf{3}$. As shown in Fig. 1(c) the reaction had proceeded to 50 % completion upon heating to 60 °C for 20 min after 3 h at room temperature. In the light of these NMR results, we were able to obtain good yields of the methoxido $(TBA)_3\mathbf{3}$ and the *tert*-butoxide $(TBA)_3\mathbf{4}$ by heating $(TBA)_3\mathbf{1}$ with an excess of the respective alcohol. Our previous studies of OMe exchange between methanol and the methoxido sites in the pentatungstates $[(MeO)TiW_5O_{18}]^{3-}$ and $[(MeO)ZrW_5O_{18}]^{6-}$ by 2D 1H EXSY NMR spectroscopy showed that the rate of exchange is slow (*ca.* $0.03\ s^{-1}$ at 75 °C),^{5(b),5(c)} but in the case of $(TBA)_3\mathbf{3}$ we were surprised when the 2D 1H EXSY NMR spectrum of a mixture of $(TBA)_3\mathbf{3}$ and MeOH showed only off-diagonal NOE cross-polarisation peaks for the TBA cations and no exchange peaks,

Fig. 2 2D ^1H EXSY NMR spectrum of a mixture of $(\text{TBA})_3\mathbf{3}$ and MeOH at 75 $^\circ\text{C}$, showing the absence of off-diagonal peaks for OMe exchange.

Fig. 3 ^{17}O NMR spectrum of $(\text{TBA})_3\mathbf{4}$ with the labelling scheme for the oxometalate framework.

even at 75 $^\circ\text{C}$ (Fig. 2). This implies that exchange in $(\text{TBA})_3\mathbf{3}$ is significantly slower than for the TiW_5 and ZrW_5 analogues, despite the fact that polyoxomolybdates are usually regarded as being more labile than polyoxotungstates. A possible explanation for this apparent anomaly is discussed below.

^1H NMR studies of reactions between $(\text{TBA})_3\mathbf{1}$ and stoichiometric amounts of phenols showed incomplete exchange of O i Pr ligands at 25 $^\circ\text{C}$, but complete conversion to aryloxido

Fig. 4 ^{17}O NMR spectrum of $(\text{TBA})_6\mathbf{7}$. The peak marked with an asterisk is due to terminal $\text{Mo}=\text{O}$ of $[\text{Mo}_2\text{O}_7]^{2-}$.

derivatives at 60 $^\circ\text{C}$, enabling high yields of $(\text{TBA})_3\mathbf{5}$ and $(\text{TBA})_3\mathbf{6}$ to be obtained by treatment of $(\text{TBA})_3\mathbf{1}$ with *p*-cresol or salicylaldehyde respectively.

The moisture sensitivity of alkoxido derivatives **1–4** was evident from the presence of alcohol peaks in ^1H NMR spectra of samples prepared without the rigorous exclusion of trace moisture, whereas the aryloxides **5** and **6** are less readily hydrolysed by atmospheric moisture. Fig. 1(d) shows the ^1H NMR spectrum of a sample of $(\text{TBA})_3\mathbf{1}$ after addition of *ca.* one mole-equivalent of water under ambient conditions and it is evident from the presence of the TiO i Pr peaks that hydrolysis was incomplete. However, the *iso*-propoxido ligand was removed completely by repeated treatment with an excess of water.

^{17}O NMR spectra

^{17}O -enriched **1** and **2** were prepared from $(\text{TBA})_2[\text{Mo}_2\text{O}_7]$, $(\text{TBA})_4\alpha\text{-}[\text{Mo}_8\text{O}_{26}]$, $\text{Ti}(\text{OR})_4$ ($\text{R} = ^i\text{Pr}$ or ^tBu respectively) and ^{17}O -enriched H_2O , while enriched alkoxides and aryloxides **3–6** were prepared from ^{17}O -enriched $(\text{TBA})_3\mathbf{1}$. The ^{17}O NMR spectra of **1–6** are all consistent with averaged C_{4v} symmetry in solution (Table 1) and a representative spectrum of $(\text{TBA})_3\mathbf{4}$ is shown in Fig. 3 together with a diagram of the core structure. The peak intensities indicate non-statistical enrichment of the different sites during the aggregation process. Using established correlations between M–O bond strengths and ^{17}O NMR chemical shifts in POMs,¹⁸ the well resolved peaks can be assigned to terminal $\text{Mo}_{\text{eq}}=\text{O}_a$ and $\text{Mo}_{\text{ax}}=\text{O}_b$, bridging TiO_cMo , bridging $\text{Mo}_{\text{eq}}\text{O}_d\text{Mo}_{\text{eq}}$ and $\text{Mo}_{\text{ax}}\text{O}_e\text{Mo}_{\text{eq}}$ (although the two peaks in this region cannot be unambiguously assigned to either O_d or O_e) and central O_f .

The ^{17}O NMR spectrum of the product isolated after hydrolysis of $(\text{TBA})_3\mathbf{1}$ and subsequent treatment with ^{17}O -enriched water showed a peak at 704 ppm for TiOTi in addition to the characteristic peaks for the C_{4v} $\text{TiMo}_5\text{O}_{18}$ structure (Fig. 4). Peaks at 717 and 248 ppm which were sometimes present in ^{17}O NMR spectra of hydrolysis products or of impure samples of $(\text{TBA})_3\mathbf{2}$

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Table 1 ¹⁷O NMR data for Lindqvist-type polyoxomolybdates

Anion ^a	¹⁷ O chemical shift/ppm ^b						Solvent	Reference
	V=O	Mo=O	TiOTi	M'OMo	MoOMo	μ ₆ -O		
[Mo ₆ O ₁₉] ²⁻	-	927	-	-	559	-32	DMF	18
[VMo ₅ O ₁₉] ³⁻	1200	885 ^c	-	665	541, 531	-22	MeCN	18
[(η ⁵ -C ₅ H ₅)TiMo ₅ O ₁₈] ³⁻	-	863, 834	-	641	535, 516	5	MeCN	15(a), 15(c)
[(η ⁵ -C ₅ Me ₅)TiMo ₅ O ₁₈] ³⁻	-	859, 832	-	649	537, 515	-10	MeCN	16(b)
[(ⁱ PrO)TiMo ₅ O ₁₈] ³⁻ 1	-	876, 857	-	622	537, 521	10	MeCN	6
[(ⁱ BuO)TiMo ₅ O ₁₈] ³⁻ 2	-	879, 859	-	626	538, 522	10	MeCN	This work
[(MeO)TiMo ₅ O ₁₈] ³⁻ 3	-	877, 858	-	619	538, 520	12	MeCN	“
[(ⁱ BuO)TiMo ₅ O ₁₈] ³⁻ 4	-	880, 855	-	621	536, 520	9	MeCN	“
[(4-MeC ₆ H ₄ O)TiMo ₅ O ₁₈] ³⁻ 5	-	882, 861	-	622	540, 524	10	MeCN	“
[{2-(CHO)C ₆ H ₄ O}TiMo ₅ O ₁₈] ³⁻ 6	-	886, 863	-	629	541, 526	4	MeCN	“
[(μ-O)(TiMo ₅ O ₁₈) ₂] ⁶⁻ 7	-	879, 867	704	626	538, 522	10	MeCN	“

^a As ⁿBu₄N⁺ salts. ^b Positive shifts to high frequency of external H₂O reference. ^c Only one value reported

Table 2 Crystallographic data

	(TBA) ₃ 3	(TBA) ₃ 4 ·0.5MeCN	(TBA) ₃ 5	(TBA) ₃ 6	(TBA) ₆ 7 ·2MeCN
Chemical formula	3C ₁₆ H ₃₆ N ⁺ CH ₃ Mo ₅ O ₁₉ Ti ³⁻	3C ₁₆ H ₃₆ N ⁺ C ₄ H ₉ Mo ₅ O ₁₉ Ti ³⁻ ·0.5C ₂ H ₃ N	3C ₁₆ H ₃₆ N ⁺ C ₇ H ₇ Mo ₅ O ₁₉ Ti ³⁻	3C ₁₆ H ₃₆ N ⁺ C ₇ H ₅ Mo ₅ O ₂₀ Ti ³⁻	6C ₁₆ H ₃₆ N ⁺ Mo ₁₀ O ₃₇ Ti ₂ ⁶⁻ · 2C ₂ H ₃ N
Formula mass	1574.0	1636.6	1650.1	1664.1	3184.1
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Tetragonal
<i>a</i> / Å	29.4619(7)	24.9233(5)	23.8573(14)	24.049(4)	16.1864(17)
<i>b</i> / Å	18.6123(7)	33.6182(8)	16.9901(10)	17.521(3)	
<i>c</i> / Å	27.2737(9)	16.8302(3)	17.3090(10)	17.242(3)	50.752(7)
β / °	113.343(2)	90.915(2)			
Unit cell volume / Å ³	13731.5(8)	14099.8(5)	7016.0(7)	7265(2)	13297(3)
Space group	C2/c	P2 ₁ /c	Pnma	Pnma	P4 ₁ 2 ₁ 2
<i>Z</i>	8	8	4	4	4
μ / mm ⁻¹	1.06	1.03	1.04	1.01	1.09
Crystal size / mm	0.62 × 0.44 × 0.42	0.22 × 0.20 × 0.15	0.50 × 0.32 × 0.20	0.30 × 0.20 × 0.20	0.60 × 0.48 × 0.35
Transmission range	0.560–0.665	0.800–0.860	0.625–0.820	0.750–0.825	0.560–0.700
Reflections measured	48667	134551	50872	61909	114405
Unique reflections	12093	34144	8322	9237	15970
<i>R</i> _{int} (on <i>F</i> ²)	0.0394	0.0531	0.0513	0.1493	0.0540
No. of refined parameters	756	1535	421	428	724
No. of restraints	261	3238	117	520	0
<i>R</i> [<i>F</i> , <i>F</i> ² > 2σ(<i>F</i> ²)]	0.0682	0.0586	0.0964	0.0748	0.0400
<i>R</i> _w (<i>F</i> ² , all data)	0.1389	0.1048	0.1843	0.2420	0.0907
Goodness of fit on <i>F</i> ²	1.273	1.029	1.334	0.990	1.114
Difference map extremes / e Å ⁻³	2.42, −2.48	1.38, −1.33	1.59, −1.69	1.00, −0.88	0.89, −1.33

^a Footnote text.

or (TBA)₃**4** were assigned to Mo=O and MoOMo respectively of [Mo₂O₇]²⁻, suggesting that the dimolybdate anion is produced upon degradation of the TiMo₅ structures, although we have yet to investigate this further.

X-ray crystal structures

X-ray crystal structural analyses (Table 2) confirmed the hexanuclear [LTiMo₅O₁₈]³⁻ nature of **3–6** (Figs. 5–8) and the presence of a TiOTi bridge between two TiMo₅O₁₈ fragments in the structure of **7** (Fig. 9). All anions were well separated from each other in the structures by discrete TBA cations. Bond

lengths averaged to C_{4v} symmetry for the TiMo₅O₁₈ units in **1** and **3–7** are given in Table 3 along with TiOC and TiOTi angles, while individual bond lengths in the equatorial Mo₄O₄ rings of these anions are shown in Fig. 10.

The crystal structure of methoxide (TBA)₃**3** contains two independent hexametalate anions **3A** and **3B** with crystallographic symmetries of C_i and C₂ respectively, and **3A** is shown in Fig. 5. In both cases TiOMe and Mo_{ax}=O groups are disordered over two *trans* axial sites of the anion and, although this disorder prevents any meaningful discussion of the bond

Fig. 5 Structure of one of the independent anions **3A** in the crystal structure of $(\text{TBA})_3[(\text{MeO})\text{TiMo}_5\text{O}_{18}]$, showing the axial disorder

Fig. 6 Structure of one of the independent anions **4A** in the crystal structure of $(\text{TBA})_3[(\text{tBuO})\text{TiMo}_5\text{O}_{18}]$

lengths and angles associated with the individual Ti and Mo_{ax} sites, a comparison of $\text{Ti}/\text{Mo}_{\text{ax}}\text{-OC}$ and $\text{Ti}/\text{Mo}_{\text{ax}}\text{-O}_f$ distances, TiOC angles and average $\text{Ti}/\text{Mo}_{\text{ax}}\text{-O}(\text{Mo})$ distances for the two independent anions (1.744(4) and 2.2586(7) Å, 132.1(8)° and 1.940(4) Å respectively for **3A** and 1.761(6) and 2.2330(8) Å, 156.9(11)° and 1.928(6) Å for **3B**) suggests that the alkoxide orientation is sensitive to the lattice environment and not solely determined by electronic factors. Notably, bond length alternation is observed in the equatorial Mo_4O_4 ring of **3A**, with average short and long distances of 1.877(4) and 2.027(4) Å, but this bonding pattern does not occur in **3B**.

Two independent anions were also present in the acetonitrile-solvated crystal structure of the *tert*-butoxide $(\text{TBA})_3\mathbf{4}$ but, in this case, these are not disordered. Anions **4A** and **4B** both have C_1 symmetry and **4A** is shown in Fig. 6. The TiOC angle is larger in **4A** than in **4B** but the difference is not as great as that between the $\text{Ti}/\text{Mo}_{\text{ax}}\text{OC}$ angles in **3A** and **3B**. Table 3 shows that the bond distances (averaged to C_{4v} symmetry) are similar for **4A** and **4B**,

Fig. 7 Structure of the anion $[(4\text{-MeC}_6\text{H}_4\text{O})\text{TiMo}_5\text{O}_{18}]^{3-}$ **5**

Fig. 8 Structure of the anion $[\{2\text{-(CHO)C}_6\text{H}_4\text{O}\}\text{TiMo}_5\text{O}_{18}]^{3-}$ **6**

Fig. 9 Structure of the anion $[(\mu\text{-O})(\text{TiMo}_5\text{O}_{18})_2]^{6-}$ **7**

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Table 3 Average bond lengths (Å) and selected angles (°) in [LTiMo₅O₁₈]³⁻ polyoxometalates.^a

	Anion							
	1	3A ^b	3B ^b	4A	4B	5	6	7
Ti–O(C)	1.794(8)	<i>n/a</i>	<i>n/a</i>	1.790(3)	1.787(3)	1.861(7)	1.890(8)	-
O–C	1.289(17)	1.490(17)	1.447(19)	1.412(6)	1.433(6)	1.353(13)	1.315(15)	-
TiOC	155.7(12)	132.1(8)	156.9(11)	154.6(4)	149.8(3)	141.7(7)	143.5(9)	-
Ti–O _c	1.956(8)	<i>n/a</i>	<i>n/a</i>	1.956(4)	1.966(4)	1.946(6)	1.941(6)	1.956(3)
Ti–O _f	2.136(5)	<i>n/a</i>	<i>n/a</i>	2.156(3)	2.148(3)	2.097(6)	2.075(6)	2.179(3)
Ti–O(Ti)	-	-	-	-	-	-	-	1.8148(7)
TiOTi	-	-	-	-	-	-	-	173.2(3)
Mo _{eq} –O _a	1.688(7)	1.695(4)	1.691(6)	1.699(4)	1.699(4)	1.696(6)	1.681(6)	1.700(3)
Mo _{ax} –O _b	1.693(7)	<i>n/a</i>	<i>n/a</i>	1.692(4)	1.699(3)	1.689(8)	1.676(7)	1.689(3)
Mo _{eq} –O _c	1.832(8)	<i>n/a</i>	<i>n/a</i>	1.849(4)	1.844(3)	1.851(5)	1.846(6)	1.856(3)
Mo _{eq} –O _d	1.945(7)	1.952(4)	1.944(6)	1.951(4)	1.951(4)	1.953(7)	1.946(6)	1.959(3)
Mo _{ax} –O _e	1.910(7)	<i>n/a</i>	<i>n/a</i>	1.913(3)	1.912(3)	1.914(6)	1.906(6)	1.920(3)
Mo _{eq} –O _e	1.943(8)	<i>n/a</i>	<i>n/a</i>	1.958(4)	1.957(3)	1.950(5)	1.954(5)	1.954(3)
Mo _{eq} –O _f	2.323(5)	2.336(5)	2.330(4)	2.329(3)	2.331(3)	2.339(5)	2.337(5)	2.336(3)
Mo _{ax} –O _f	2.341(5)	<i>n/a</i>	<i>n/a</i>	2.358(3)	2.354(3)	2.368(6)	2.385(6)	2.336(3)

^a Sites labelled as in Fig. 1. ^b Disorder prevented determination of specific bond distances to Ti, Mo_{ax}, O_c and O_e. **Fig. 10** Bond lengths (Å) in the equatorial Mo₄O₄ rings of the {TiMo₅} anions indicated **Fig. 11** Bond lengths (Å) in the TiMo₃O₄ rings of the {TiMo₅} anions indicated, averaged to C_{4v} symmetry

but note that the averaged Mo_{eq}–O_d distances shown in Table 3 hide the bond length alternations that are present in the equatorial Mo₄O₄ rings of both anions (Fig. 10). The average short and long distances within the rings are 1.862(4) and 2.042(4) Å for **4A** and 1.877(4) and 2.026(4) Å for **4B**. A molecule of acetonitrile is present in the lattice and lies close to anion **4A** with a C...O(7) distance of 3.12 Å. The aryloxido-substituted anions **5** (Fig. 7) and **6** (Fig. 8) in the crystal structures of (TBA)₃**5** and (TBA)₃**6** have C_s symmetry, and the vertical mirror planes containing the aryl rings mean that bond length alternation is not observed in the equatorial Mo₄O₄ rings of these anions. The Ti–OC distances in **5** and **6** are longer than in the alkoxido-substituted anions **1**, **3** and **4** and the TiOC angles are smaller than in all of the alkoxido anions except for **3A**. As in the analogous tungstate [(2-CHOC₆H₄O)TiW₅O₁₈]³⁻ the aldehyde group in **6** does not interact with Ti and

is oriented away from the metal, unlike in the zirconotungstate [(2-CHOC₆H₄O)ZrW₅O₁₈]³⁻ where a chelating salicylaldehyde ligand increases the coordination number of Zr to seven.^{5(b)}

Fig. 10 shows that bond alternation is also present in the Mo₄O₄ rings of **7** with average short and long distances of 1.856(3) and 2.063(3) Å. In contrast to the linear NbONb bridge in the structure of the niobotungstate [(μ-O)(NbW₅O₁₈)₂]⁴⁻ in which the {NbW₅O₁₈} units are eclipsed,^{5(a)} the TiOTi bridge in **7** is non-linear with a TiOTi angle of 173.2(3)° and a Ti–O distance of 1.8148(7) Å, and these values are similar to those in the structure of the analogous tungstate [(μ-O)(TiW₅O₁₈)₂]⁶⁻.^{5(c)} In **7** the bridging Ti–OTi distance is shorter than the average Ti–O_c distance of 1.956(3) Å indicating that this bond is stronger than the Ti–OMo bonds within the hexametalate units. In the crystal structure, two acetonitrile solvent molecules lie in the region between the two {TiMo₅O₁₈} units of each anion, with methyl groups oriented towards the TiOW oxygen atoms and the co-

Fig. 12 Methine region of the ^1H NMR spectrum of a sealed sample of $(\text{TBA})_3\mathbf{1}$ after heating to 70°C overnight

linear $\text{N}-\text{C}-\text{C}\cdots\text{O}\cdots\text{C}-\text{C}-\text{N}$ alignment with the TiOTi bridging oxygen is approximately perpendicular to the TiOTi bridge. The shortest $\text{C}\cdots\text{O}$ distance to a TiOMo bridging site is $3.18\text{ \AA}$, which is within the sum of carbon and oxygen van der Waals radii and is suggestive of a $\text{CH}\cdots\text{O}$ interaction (Supplementary Fig. S1). The crystal structure of $(\text{TBA})_6[(\mu-\text{O})(\text{TiW}_5\text{O}_{18})_2]$ also contains co-linear acetonitrile molecules in similar positions, but in this case they are aligned $\text{N}-\text{C}-\text{C}\cdots\text{O}\cdots\text{N}-\text{C}-\text{C}$ with one of the MeCN molecules rotated by 180° and the shortest $\text{C}\cdots\text{O}$ distance to TiOW is $3.22\text{ \AA}$.

The bonding pattern within the TiMo_3O_4 rings of all of these $[\text{LTiMo}_5\text{O}_{18}]^{3-}$ anions is consistent with $\text{Ti}-\text{O}_\text{c}$ bonds that are weaker than $\text{Mo}_{\text{eq}}-\text{O}_\text{c}$ bonds, and a *trans* influence from the stronger $\text{Mo}_{\text{eq}}-\text{O}_\text{c}$ bonds which induces a lengthening of $\text{Mo}_{\text{eq}}-\text{O}_\text{e}$ bonds (Fig. 11). The cumulative effect strengthens the $\text{Mo}_{\text{ax}}-\text{O}_\text{e}$ bonds and, to maintain charge balance at Mo_{ax} , the $\text{Mo}_{\text{ax}}-\text{O}_\text{f}$ bond is weaker than $\text{Mo}_{\text{eq}}-\text{O}_\text{f}$ bonds.

FTIR spectra

Strong $\nu(\text{Mo}=\text{O})$ bands are observed in the FTIR spectra of the $[\text{LTiMo}_5\text{O}_{18}]^{3-}$ anions at about 930 cm^{-1} for alkoxides **1–4** and 938 cm^{-1} for aryloxides **5** and **6**, with a corresponding band at 934 cm^{-1} for **7**, while strong bands for $\nu(\text{MoOMo})$ appear at about 790 cm^{-1} in all cases. A band at 660 cm^{-1} in the IR spectrum of **7** was assigned to $\nu(\text{TiO})$ of the TiOTi bridge by comparison with that observed at 667 cm^{-1} for the tungstate $[(\mu-\text{O})(\text{TiW}_5\text{O}_{18})_2]^{6-}$.^{5(c)} The characteristic bathochromic shifts for $\nu(\text{Mo}=\text{O})$ from the corresponding value for $[\text{Mo}_6\text{O}_{19}]^{2-}$ of 955 cm^{-1} can be attributed to the higher charges of **1–7** which, when delocalised over the hexametalate units, weaken the terminal $\text{Mo}=\text{O}$ bonding.

Thermal and photo-stabilities of **1** and **4**

During the preparation of secondary and tertiary alkoxido-titanotungstates $[(\text{RO})\text{TiW}_5\text{O}_{18}]^{3-}$ ($\text{R} = ^i\text{Pr}$ and ^tBu) from the methoxido analogue *via* alcoholysis at elevated temperatures we observed minor peaks at *ca.* 1000 ppm in ^{17}O NMR spectra which we tentatively assigned to terminal $\text{Ti}=\text{O}$. This raised the possibility that these bulkier alkoxido groups might degrade *via* H-transfer to a bridging TiOW oxygen. We therefore investigated the possible thermal and photochemical H-transfer reactivity of $(\text{TBA})_3\mathbf{1}$ by ^1H and ^{17}O NMR spectroscopy. After heating at 70°C overnight, the 500 MHz ^1H NMR spectrum of a flame-sealed sample of $(\text{TBA})_3\mathbf{1}$ showed three ^iPr resonances with Me doublets at 1.12 , 1.18 and 1.22 ppm and associated methine resonances at 3.89 , 4.58 and 4.41 ppm and $^3J(\text{HH}) = 6\text{ Hz}$ (Fig. 12). The major

species with the methine peak at 4.58 ppm is due to **1** (47%), while the double septet at 3.89 ppm with $^3J(\text{HH}) = 4\text{ Hz}$ due to coupling to OH is assigned to $^i\text{PrOH}$ (33%). The remaining ^iPr species (20%) has not been characterised but the methine chemical shift of 4.41 ppm is suggestive of a metal alkoxide. No peaks for propene, the expected product from $\gamma\text{-H}$ abstraction, were observed. Upon heating at 110°C for 16 h , a solution of $(\text{TBA})_3\mathbf{1}$ in MeCN changed from yellow to blue-ish and the ^{17}O NMR spectrum showed evidence of structural degradation, with the appearance of peaks due to $\alpha\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ and $[\text{Mo}_2\text{O}_7]^{2-}$ as well as a small amount of **7** (Supplementary Fig. S2). No peaks were observed in the chemical shift range for $\text{Ti}=\text{O}$, although it should be borne in mind that such a group generated from TiO^iPr by H-abstraction would not be ^{17}O -enriched unless it were involved in site exchange. In a similar thermal treatment of a sample of $(\text{TBA})_3\mathbf{4}$, a singlet for $^t\text{BuOH}$ appeared in the ^1H NMR spectrum while in the ^{17}O NMR spectrum there was again no evidence for $\text{Ti}=\text{O}$ formation but peaks due to the hydrolysis product **7** were present. We are currently investigating these thermal decomposition reactions in more detail.

In a preliminary experiment, the only changes to the ^1H NMR spectrum of a sample of $(\text{TBA})_3\mathbf{1}$ upon UV irradiation (254 nm) for 4 h was the appearance of peaks due to a small amount of $^i\text{PrOH}$, which may be due simply to trace hydrolysis.

Discussion

The successful synthesis of these $\{\text{TiMo}_5\}$ oxoanions provides the opportunity to assess the effects of variations in L, M' and M on the properties of Lindqvist-type POMs of the type $[\text{LM}'\text{M}_5\text{O}_{18}]^{3-}$. In particular, information regarding charge distribution and surface basicity gained from ^{17}O NMR chemical shifts and bond lengths can then be related to observed reactivity.

Spectroscopic comparisons and reactivity

^{17}O NMR chemical shifts for all of the oxygen sites except the central $\mu_6\text{-O}$ are lower for **1–7** than corresponding peaks for $[\text{Mo}_6\text{O}_{19}]^{2-}$ (Table 1) because of the higher charge on the heterometalates and the consequent $\text{Mo}-\text{O}$ bond weakening/negative charge build-up on oxygen atoms, as described previously for the cyclopentadienyl derivatives $[(\eta^5\text{-C}_5\text{R}_5)\text{TiMo}_5\text{O}_{18}]^{3-}$ ($\text{R} = \text{H}, \text{Me}$).^{15, 16} The weighted average ^{17}O NMR chemical shifts for the $\{\text{Mo}_5\text{O}_{18}\}$ cage in the $[\text{LTiMo}_5\text{O}_{18}]^{3-}$ anions vary from 614 ppm for $[(\eta^5\text{-C}_5\text{H}_5)\text{TiMo}_5\text{O}_{18}]^{3-}$ to 622 ppm for **6**, which is consistent with increasing electron donation from L in $\{\text{LTi}\}^{3+}$ in the order $\text{ArO} < \mu\text{-O} < \text{RO} < \eta^5\text{-C}_5\text{R}_5$. This order is also reflected in the IR spectra of these POMs, where $\nu(\text{Mo}=\text{O})$ decreases from 939 cm^{-1} for the aryloxide **6** to 916 cm^{-1} for $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMo}_5\text{O}_{18}]^{3-}$. By comparison, the weighted average ^{17}O chemical shift for the $\{\text{Mo}_5\text{O}_{18}\}$ cage in $[\text{VMo}_5\text{O}_{19}]^{3-}$ is 631 ppm , reflecting the ability of $\{\text{VO}\}^{3+}$ to withdraw electron density from the $\{\text{M}_5\text{O}_{18}\}^{6-}$ oxometalate 'ligand' more effectively than the $\{\text{LTi}\}^{3+}$ groups. Given this trend, the oxometalate oxygen atoms in POMs **1–7** should be less susceptible to protonation than those in $[(\eta^5\text{-C}_5\text{R}_5)\text{TiMo}_5\text{O}_{18}]^{3-}$ but more readily protonated than $[\text{VMo}_5\text{O}_{19}]^{3-}$. This is apparently borne out in that the hydrolytic reactivity described above for **1** is intermediate between that of $[\text{VMo}_5\text{O}_{19}]^{3-}$, which is stable towards hydrolysis, and that of $[(\eta^5\text{-C}_5\text{R}_5)\text{TiMo}_5\text{O}_{18}]^{3-}$.

Scheme 1 Possible mechanisms for protonolysis of the Ti–OR bond in $[(\text{RO})\text{TiMo}_5\text{O}_{18}]^{3-}$ polyoxometalates with HL involving either direct protonation of the alkoxido ligand (a) or protonation of the oxometalate cage at TiOM with subsequent proton transfer to the alkoxido ligand (b)

$\text{C}_5\text{H}_5\text{TiMo}_5\text{O}_{18}]^{3-}$, which decomposes upon exposure to atmospheric moisture.^{15(a),15(b)} Note that although $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMo}_5\text{O}_{18}]^{3-}$ is even more basic, the bulkier $\eta^5\text{-C}_5\text{Me}_5$ ligand appears to protect the O_c sites from protonation and subsequent loss of $\text{C}_5\text{Me}_5\text{H}$ and degradation, so that protonated $[(\eta^5\text{-C}_5\text{Me}_5)\text{TiMo}_5\text{O}_{18}\text{H}_x]^{(3-x)-}$ ($x = 1, 2$) can be isolated.¹⁶ It is also worth noting that the tungstate analogues were shown to be less basic and consequently more stable towards degradation, and protonated derivatives $[(\eta^5\text{-C}_5\text{R}_5)\text{TiMo}_5\text{O}_{18}\text{H}_x]^{(3-x)-}$ were isolated and characterised for $\text{R} = \text{H}$ and Me and $x = 1$ and 2 .^{15(d)}

From the comparative hydrolytic behaviours of $[\text{LTiMo}_5\text{O}_{18}]^{3-}$ and the trends in surface oxygen basicity, it would appear that the oxometalate cage may be involved in protonolysis reactions, and this should be taken into account when the mechanism of ligand exchange is considered. Ti–OR bond hydrolysis is fundamental to the conversion of soluble alkoxides to solid titanium oxide materials by the ‘sol-gel’ process but, despite the widespread use of metal alkoxides in materials chemistry and organic synthesis, remarkably little effort has been devoted to a detailed mechanistic understanding of protonolysis reactions. Although once regarded as $\text{S}_{\text{N}}2$, it has recently been proposed that the mechanism for protonolysis of alkoxido ligands in metal alkoxides should be more generally viewed as a proton-assisted $\text{S}_{\text{N}}1$ process.¹⁹ In the single-site alkoxides $[(\text{RO})\text{TiMo}_5\text{O}_{18}]^{3-}$, the reluctance of Ti to increase its coordination number beyond six, as demonstrated by the absence of an interaction between the salicylaldehyde carbonyl group and Ti in the solid state structure of **6**, makes it even more likely that ligand exchange proceeds *via* a proton-assisted $\text{S}_{\text{N}}1$ mechanism. However, the basicity of TiOM bridging oxygens in these POMs provides an additional complication in that the initial interaction with a protic reagent HL may occur at either OR or TiOM sites (Scheme 1), so that the mechanism of Ti–OR protonolysis in $[(\text{RO})\text{TiMo}_5\text{O}_{18}]^{3-}$ POMs might be determined by the relative basicities of the OR and TiOM sites. The greater basicity of TiOMo compared to TiOW may therefore result in protonation at TiOMo in $[(\text{RO})\text{TiMo}_5\text{O}_{18}]^{3-}$ but at the OR group in the less basic $[(\text{RO})\text{TiW}_5\text{O}_{18}]^{3-}$ and, given that an extra proton-transfer step would then be required before ROH could be lost from $[(\text{RO})\text{TiMo}_5\text{O}_{18}\text{H}]^{2-}$, dissociation would likely be slower than from $[(\text{ROH})\text{TiW}_5\text{O}_{18}]^{2-}$. This may explain why alcohol exchange was too slow to be observed by 2D ^1H EXSY NMR in the reaction between $(\text{TBA})_3\mathbf{3}$ and MeOH, whereas an

exchange peak was observed in the tungstate system.

The formation of the oxo-bridged **7** upon hydrolysis of these alkoxido-derivatised $\{\text{TiMo}_5\}$ POMs once again demonstrates the instability of the Ti–OH group at the surface of Lindqvist-type $\{\text{TiMo}_5\}$ oxoanions towards condensation, as we previously observed in the hydrolysis of the tungstates $[(\text{RO})\text{TiW}_5\text{O}_{18}]^{3-}$,^{5(c)} and is similar to the formation of $[(\mu\text{-O})(\text{NbW}_5\text{O}_{18})_2]^{4-}$ upon hydrolysis of $[(\text{MeO})\text{NbW}_5\text{O}_{18}]^{2-}$.^{5(a)} In the latter case, we observed that hydrolysis is more facile than for the more highly charged $\{\text{TiMo}_5\}$ POMs, and this can be explained in terms of comparative charge distributions, where a greater negative charge associated with the NbOMe oxygen atom relative to NbOW sites of the less basic $[(\text{MeO})\text{NbW}_5\text{O}_{18}]^{2-}$ will lower the energy of a proton-assisted $\text{S}_{\text{N}}1$ pathway involving direct proton transfer to the alkoxide.

Structural comparisons

A comparison of the titanium environments in the structures of these TiMo_5 Lindqvist-type hexametalates with those of the tungstate analogues described previously shows that the average Ti– O_c distances are similar in both families, but the Ti– $\text{O}(\text{C})$ or Ti– $\text{O}(\text{Ti})$ bonds are longer and the Ti– O_f bonds are shorter in the molybdates **1**, **4A**, **4B**, **5**, **6**, and **7**,^{5(c)} indicating that the $\{\text{Mo}_5\text{O}_{18}\}^{6-}$ oxometalate ligand has a larger *trans* influence than the corresponding $\{\text{W}_5\text{O}_{18}\}^{6-}$. The slightly longer Ti– $\text{O}(\text{C})$ alkoxide bonds in the molybdates, which range from 1.787 Å for **4B** to 1.794 Å for **1**, suggest that these bonds are slightly weaker than in the tungstate analogues (1.764 to 1.777 Å) with a greater negative charge on the alkoxide ligands that would be expected to increase their susceptibility to protonolysis,¹⁹ which is in contrast to what we observed in our 2D ^1H NMR EXSY experiments. This therefore provides some support for our proposal that protonolysis in the molybdates proceeds *via* a different mechanism to the tungstates, perhaps involving initial protonation at bridging TiOMo atoms. A computational study will hopefully shed more light on this issue.

We now turn to the short and long bond length alternation in the M_4O_4 rings of Lindqvist hexametalates, first noted for $[\text{Mo}_6\text{O}_{19}]^{2-}$ in 1972 by Allcock and co-workers,²⁰ and subsequently discussed by Klempner and Yagasaki for $[(\eta^5\text{-C}_5\text{R}_5)\text{TiMo}_5\text{O}_{18}]^{3-}$ ($\text{R} = \text{H}$,^{15(c)} Me ^{16(b)}). More recently, this phenomenon has been ascribed to pseudo-Jahn-Teller vibronic instabilities arising from decreased HOMO–LUMO energy gaps in the symmetrical structures and greater metal–oxygen π -orbital mixing upon displacement of metal nuclei from higher-symmetry positions.²¹ The HOMOs in these POMs are essentially non-bonding O_p type orbitals and LUMOs are vacant $\text{M}_{d(xy)}$ type orbitals, so any factors that decrease the HOMO energies will disfavour vibronic coupling and reduce the distortion. If the amount of distortion is defined by Δd , the difference between average long and short distances, the bond length alternations shown in Fig. 9 for the Mo_4O_4 rings in anions **3A**, **4A**, **4B** and **7** show values of Δd of 0.150, 0.180, 0.149 and 0.207 respectively, while there is no bond length alternation in **3B**. It has been pointed out that ‘crystal packing effects’ can influence the degree of bond length alternation by reshaping the adiabatic potential energy surface for the motion involved in vibronic coupling, which for $[\text{Mo}_6\text{O}_{19}]^{2-}$ was shown to be fairly flat.²¹ A detailed analysis of all close contacts between the anions and

cation/solvent molecules is beyond the scope of this paper, but an inspection of the crystal structures suggests that these variations may be due to the number of C–H...O hydrogen bonding interactions in the solid state, particularly to O_d of the Mo_4O_4 rings, which would be expected to lower the energies of the orbitals based on these oxygens, reduce metal–oxygen π -orbital mixing and thereby reduce Δd .

Conclusions

We have synthesised a range of Lindqvist-type titanomolybdates $[LTiMo_5O_{18}]^{3-}$ either directly by controlled hydrolysis of a mixture of $(TBA)_2[Mo_2O_7]$, $(TBA)_4\alpha-[Mo_8O_{26}]$ and $Ti(OR)_4$ for $L = OR$, where $R = ^iPr$ (**1**) and iBu (**2**) or by protonolysis of $(TBA)_3\mathbf{1}$ with HL for $L = OMe$ (**3**), O^iBu (**4**), OC_6H_4Me -**4** (**5**) or OC_6H_4CHO -**2** (**6**), and obtained the oxido-bridged aggregate $[(\mu-O)(TiMo_5O_{18})_2]^{6-}$ (**7**) by hydrolysis of $(TBA)_3\mathbf{1}$. Rates of protonolysis reactions are fairly slow, as shown by 1H NMR spectroscopy, and the rate of OMe exchange between **3** and $MeOH$ is too slow to be observed in a 2D 1H EXSY NMR experiment. Comparison of ^{17}O NMR and X-ray structural data for these POMs with those for the few previously reported $\{TiMo_5\}$ hexametalates and $[VMo_5O_{19}]^{3-}$ provides some indication of ligand (L) effects on charge distribution within $[LTiMo_5O_{18}]^{3-}$ and on the relative abilities of $\{LTi\}^{3+}$ and $\{VO\}^{3+}$ to withdraw charge from the oxometalate ligand $\{Mo_5O_{18}\}^{6-}$. A comparison with the tungstate analogues $[LTiW_5O_{18}]^{3-}$ enables the ligand properties of the lacunary oxometalate fragments $\{M_5O_{18}\}^{6-}$ ($M = Mo, W$) to be compared, and the slower rate for methoxido ligand exchange for **3** compared to $[(MeO)TiW_5O_{18}]^{3-}$ suggests that the different charge distributions in $[(RO)TiM_5O_{18}]^{3-}$ for $M = Mo$ compared to W result in different pathways for $Ti-OR$ protonolysis. These results demonstrate that systematic access to closely related series of derivatised POMs is important for reactivity studies that are beginning to shed light on fundamental details of mixed-metal molecular oxide reactivity.

Experimental

All reactions and manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen in screw-top flasks fitted with PTFE screw valves using Schlenk and dry-box techniques. Hydrocarbon and ether solvents were dried over and distilled from sodium benzophenone ketyl, acetonitrile was dried over and distilled from calcium hydride and methanol was pre-dried over 3A molecular sieves and distilled from magnesium methoxide immediately prior to use. $(TBA)_3\mathbf{1}$ was prepared as previously described.⁶ 10 % ^{17}O -enriched water and deuterated acetonitrile were purchased from Goss Scientific Instruments, and the latter was degassed and stored under nitrogen over calcium hydride or 3A molecular sieves. $[4-MeC_6H_4OH]$ and $[2-(CHO)C_6H_4OH]$ (Aldrich) were distilled and stored under nitrogen over activated 4 Å molecular sieves. $Ti(O^iBu)_4$ was a gift from Tioxide and was used as received.

Infrared spectra were recorded on a Nicolet Avatar 370 DTGS spectrometer from Nujol mulls between CsI or KBr plates. NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300.0 MHz (1H) or 75.39 MHz (^{13}C), or a Jeol

Lamda 500 spectrometer operating at 500.0 MHz (1H), 125.65 MHz (^{13}C) or 67.63 MHz (^{17}O). Resonances due to $^nBu_4N^+$ cations are not listed below, but appear as multiplets centred at about 1.0, 1.4, 1.7 and 3.2 ppm in 1H NMR spectra and as singlets at about 13, 19, 24 and 58 ppm in $^{13}C\{^1H\}$ NMR spectra. Two-dimensional 1H EXSY NMR spectra were obtained at 500 MHz using a $90^\circ - t_1 - 90^\circ - \tau_{mix} - 90^\circ - Acq(t_2)$ sequence with appropriate phase-cycling to give a phase sensitive spectrum. The initial $512(t_2) \times 128(t_2)$ data matrix was zero-filled to 1024×512 points prior to Fourier transformation. Spectra were obtained with a mixing time (τ_{mix}) of 250 ms. Elemental analyses were performed by Newcastle University Chemical Analysis Service.

X-ray crystallography. Crystal data and other information on the data collection and structure determination for the 5 crystal structures are given in Table 2, with further details in the supplementary material. Data for the salt of anion **4** were collected on an Oxford Diffraction (now Agilent Technologies) Gemini A Ultra diffractometer at 150 K, while the other salts were examined on a Bruker SMART 1K diffractometer at 160 K; in each case $Mo K\alpha$ radiation was used, with $\lambda = 0.71073 \text{ \AA}$.²³ Data for the salts of anions **3–7** were collected on Bruker SMART 1K and Nonius Kappa CCD diffractometers with $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 150 or 160 K. Absorption corrections were based on symmetry-equivalent and repeated reflections in the highly redundant data sets. The structures were solved by direct methods and refined on all unique F^2 values.²⁴ In cases of disorder for many of the cations and solvent molecules, restraints were applied to geometric and displacement parameters. Hydrogen atoms were included as constrained riding atoms where their positions were unambiguous on the basis of purely geometrical considerations (not for the acetonitrile molecules). The major features in final difference electron density maps are close to heavy atoms and disordered components. The space group of the non-centrosymmetric structure of the salt of **7** is confirmed as $P4_12_12$ rather than the enantiomorphic $P4_32_12$ from anomalous scattering effects.²⁵ Structural diagrams were produced with CrystalMaker.

Syntheses

$(^nBu_4N)_3[(^iBuO)TiMo_5O_{18}]$, $(TBA)_3\mathbf{2}$. A solution of $(TBA)_2[Mo_2O_7]$ (1.59 g, 2.02 mmol) and $(TBA)_4\alpha-[Mo_8O_{26}]$ (4.35 g, 2.02 mmol) in MeCN (25 mL) was added to $Ti(O^iBu)_4$ (1.37 g, 4.04 mmol). The mixture was heated to dissolve the $Ti(O^iBu)_4$ and water (10 % ^{17}O -enriched, 110 μL , 6.06 mmol) was added to the resulting green solution. After stirring at 100 °C for 40 min the solvent was removed under reduced pressure and the residue was triturated with diethyl ether (30 mL). Unreacted $(TBA)_4\alpha-[Mo_8O_{26}]$ was recovered by dissolving the resulting solid in acetonitrile (18 mL), addition of diethyl ether (30 mL) and cooling to $-20^\circ C$. This process was repeated twice more to give a total of 0.92 g of $(TBA)_4\alpha-[Mo_8O_{26}]$. The remaining solution was evaporated to give a yellow-green solid after washing with diethyl ether and drying *in vacuo*. Yield 2.50 g, 38 % (based on Ti). FTIR (Nujol mull): 1151m, 1107m, 1026w, 957w, 931s, 887m, 793s, 735w, 667m and 563w cm^{-1} . δ_H (300 MHz, d_3 -MeCN) 3.95 (d, $J = 6$ Hz, 2H, OCH_2), 1.77 (m, $J = 6$ Hz, 1H, OCH_2CH), 0.91 [d, 6H, $CH(CH_3)_3$]. δ_C (75.5 MHz, d_3 -MeCN) 81.9, 31.6, 19.6.

(¹⁸Bu₄N)₃[(MeO)TiMo₅O₁₈], (TBA)₃3. MeOH (0.5 mL, 12.5 mmol) was added to (TBA)₃1 (0.40 g, 0.25 mmol) in MeCN (5 mL) and the mixture was heated at 50 °C with stirring for 1 h. The pale yellow solid remaining after removal of the volatiles was recrystallised from acetonitrile by addition of diethyl ether and cooling to –20 °C. Yield 0.34 g, 87 %. Found: C, 36.4; H, 7.0; N, 2.7. C₄₉H₁₁₁N₃O₁₉TiMo₅ requires C, 37.4; H, 7.1; N, 2.7 %. FTIR (Nujol mull): 1152m, 1105w, 1099w, 1026w, 958w, 930s, 889m, 791s, 732w, 644w, 586m, 446m cm^{–1}. δ_H (300 MHz, d₃-MeCN) 4.01 [s, 3 H, OCH₃]. δ_C (75.5 MHz, d₃-MeCN) 61.9.

(¹⁸Bu₄N)₃[(¹⁸BuO)TiMo₅O₁₈], (TBA)₃4. ¹⁸BuOH (2.0 mL, 25.0 mmol) was added to (TBA)₃1 (0.40 g, 0.25 mmol) in MeCN (5 mL) and the mixture was heated at 50 °C overnight. The pale yellow solid remaining after removal of the volatiles was recrystallised from acetonitrile by addition of diethyl ether and cooling to –20 °C. Yield 0.26 g, 65 %. Found: C, 38.7; H, 7.5; N, 2.7. C₅₂H₁₁₇N₃O₁₉TiMo₅ requires C, 38.6; H, 7.3; N, 2.6 %. FTIR (Nujol mull): 1192m, 1152m, 1013m, 954w, 930s, 889m, 787s, 732w, 581m, 439w cm^{–1}. δ_H (300 MHz, d₃-MeCN) 1.29 [s, 9H, OC(CH₃)₃]. δ_C (75.5 MHz, d₃-MeCN) 81.8, 32.2.

(¹⁸Bu₄N)₃[(4-MeC₆H₄O)TiMo₅O₁₈] (TBA)₃5. A solution of *p*-cresol (0.03 g, 0.25 mmol) in acetonitrile (5 mL) was added to (TBA)₃1 (0.40 g, 0.25 mmol) and the mixture was stirred at room temperature for 3 h and then heated to 60 °C for 15 min. The solution was dried *in vacuo* and recrystallised from acetonitrile and diethyl ether to give pale yellow crystals. Yield 0.33 g, 79 %. Found: C, 40.0; H, 6.3; N, 2.7. C₅₅H₁₁₅N₃O₁₉TiMo₅ requires C, 40.0; H, 7.0; N, 2.6 %. FTIR (Nujol mull): 1505m, 1275m, 1168w, 1153w, 962w, 938s, 896w, 876w, 827w, 792s, 775m, 740w, 668w, 645w, 573m and 459m. δ_H (300 MHz, d₃-MeCN) 6.97, 6.95, 6.74, 6.72 (4H, C₆H₄) and 2.22 (s, 3H, CH₃). δ_C (75.5 MHz, d₃-MeCN) 164.0, 130.0, 129.9, 119.4 and 20.6.

(¹⁸Bu₄N)₃[(2-CHOC₆H₄O)TiMo₅O₁₈] (TBA)₃6. Salicylaldehyde (30 μL, 0.25 mmol) was added to a solution of (TBA)₃1 (0.40 g, 0.25 mmol) in acetonitrile (5 mL) and the solution was stirred at room temperature for 3 h. After removal of the volatiles, ¹H NMR showed the reaction to be incomplete so further salicylaldehyde (30 μL, 0.125 mmol) was added and the mixture was heated to 60 °C for 15 min. After removal of the volatiles under reduced pressure, the residue was washed with ether (2 × 10 mL) and dried *in vacuo*. The product was recrystallised from acetonitrile and diethyl ether to give yellow crystals. Yield 0.39 g, 93 %. Found: C, 35.5; H, 6.4; N, 2.5. C₅₅H₁₁₃N₃O₂₀TiMo₅ requires C, 39.7; H, 6.8; N, 2.5 %. FTIR (Nujol mull): 1677s, 1597m 1562w, 1321m, 1276m, 1263w, 1250m, 1185w, 1153m, 1030w, 963w, 939s, 882m, 789s, 763w, 645w, 618m, 452w, and 404m. δ_H (300 MHz, d₃-MeCN) 10.56 (s, 1H, CHO) and C₆H₄ at 7.63 (dd, 1H), 7.48 (ddd, 1H), 7.07 (d, 1H), and 6.84 (dd, 1H). δ_C (75.5 MHz, d₃-MeCN) 193.4, 170.0, 136.6, 127.3, 126.8, 123.8 and 119.8.

(¹⁸Bu₄N)₆[(μ-O)(TiMo₅O₁₈)₂] (TBA)₆7. Water (1.43 mL, 79.0 mmol) was added to a solution of (TBA)₃1 (1.27 g, 0.79 mmol) in MeCN (5 mL) and the mixture was stirred for 30 min at room temperature before removal of the volatiles under reduced

pressure. This was repeated twice more and ¹H NMR confirmed that the alkoxido ligand had been removed. The product was dried *in vacuo* and then dissolved in MeCN (4 mL) and stirred with 10% ¹⁷O-enriched water (64 μL, 3.6 mmol) at room temperature overnight. The pale green-yellow product remaining after removal of the volatiles was recrystallised from acetonitrile and diethyl ether. Yield 0.46 g, 38 %. Found: C, 36.6; H, 7.8; N, 2.7. C₉₆H₂₁₆N₆O₃₇TiMo₁₀ requires C, 37.2; H, 7.0; N, 2.7 %. FTIR (Nujol mull): 1152m, 1107w, 1059w, 1028w, 934s, 875m, 841w, 794s, 735m, 660m, 565w and 429w.

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Notes and references

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- [†] Electronic Supplementary Information (ESI) available: Views of the structure of TBA₆7·2MeCN showing positions of MeCN molecules, ¹⁷O NMR analysis of thermal decomposition of (TBA)₃1.
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