Assembly of titanium embedded polyoxometalates with unprecedented structural features†

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Two titanium embedded polyoxometalates with unprecedented structural features are presented: a monotitanium containing tungstoantimonate $Na_{13}H_3[TiO(SbW_9O_{33})_2]\cdot 33\ H_2O$ featuring a $\{Ti{=}O\}^{2+}$ moiety (**1**) and a hexatitanium containing tungstoarsenate $K_6[Ti_4(H_2O)_{10}(AsTiW_8O_{33})_2]\cdot 30\ H_2O$ containing a $\{Ti_4(H_2O)_{10}\}^{16+}$ moiety (**2**). Both compounds have been fully characterised by single crystal X-ray diffraction, elemental analysis, IR and TGA. **1** is constructed from two α-B-$\{Sb^{III}W_9O_{33}\}$ fragments linked by five sodium cations and an unprecedented square pyramidal $Ti(O)O_4$ group with a terminal Ti=O bond, and **2** exhibits a Krebs-type structure composed of two $\{AsTiW_8O_{33}\}$ fragments, where one W(VI) centre has been substituted for a Ti(IV) centre in each, fused together *via* a belt of four additional Ti(IV) centres. This system represents the tungsten Ti-incorporated polyoxoanion with one of the highest Ti : W ratios so far reported. Additionally, **2** could also be isolated as an *n*-tetrabutylammonium salt and has been further characterised by electrochemistry and electrospray ionisation (ESI) MS studies. Due to the unique nature of these systems, both have been fully investigated using DFT calculations yielding highly interesting results. Structure **1** has been optimised with five sodium atoms in the belt position, which in addition to reducing the high charge of the cluster influence a stabilisation of the antimony lone pairs. Electrostatic potential calculations highlight the high electronegativity of the terminal oxygen on the titanium centre, enhancing real potentiality as a reactive site for catalysis.

Introduction

Polyoxometalates (POMs) are a unique class of inorganic materials due to their wide structural variety and diverse range of applications.[1–4] They are anionic metal–oxygen clusters comprising early transition metals (mainly V, Mo, W) in their highest oxidation states and are typically synthesised from low nuclearity precursors in aqueous solutions.[5,6] POMs are generally divided into two sub-classes, namely isopolyanions and heteropolyanions, and the latter, in which additional metal centres are incorporated (commonly Si, Ge, P, As, Sb, Bi), exhibit a higher degree of stability in the overall system.[7,8]

Ti(IV) containing polyoxotungstates are promising for potential applications in medicine[9,10] and catalysis, specifically selective oxidation[11–13] catalysis. Investigations of these systems, which are thermodynamically stable to oxidation, utilising related peroxo- and hydroperoxo- species have been well documented as a result of the associated use of the environmentally compatible oxidant H_2O_2, however high nuclearity inorganic POM–Ti 'hybrids', and systems containing Ti=O moieties are not yet known. Despite this, it can be reasoned that the ionic radius of Ti(IV) (0.75 Å) is close to that of W(VI) (0.74 Å), therefore incorporation of Ti(IV) into lacunary polyoxotungstates should be feasible resulting in the production of multi-centre active sites with corner or edge sharing TiO_6 polyhedra. In general, the substitution of W(VI) by lower valent Ti(IV) in aqueous solution leads to an increased basicity of the POM and hence a strong tendency towards formation of oligomers *via* Ti–O–Ti bonds.[14,15] As a result, systems with monomeric Ti(IV) sites appear difficult to obtain. Nevertheless reports of mono-, di-, tri- and tetrameric architectures with mono-, di-, and tri-Ti(IV) incorporated systems are known, and this demonstrates potential for the relatively small field of titanium-containing POMs. Furthermore, the majority of existing Ti(IV) containing POMs are based on derivatives of the Keggin cluster and the field is dominated by the polyoxotungstate family, *e.g.* $[PTiW_{11}O_{40}]^{5-}$ and $[PTi_2W_{10}O_{40}]^{7-}$,[16–18] and dimeric Ti–O–Ti bridged polyoxoanions $[X_2Ti_6W_{18}O_{77}]^{14-}$,[19–21] (X = Si, Ge, P) and $[(PTi_2W_{10}O_{39})_2]^{10-}$.[22] Later, it was shown that these types of di-Ti(IV) substituted monomeric units can be connected into extended frameworks *via* Ti–O–M bridges, where M = Co(II), Mn(II) and Ni(II).[23] Also, cyclic Keggin trimers $[(PTi_3W_9O_{38})_3(PO_4)]^{18-}$ and $[(XTi_3W_9O_{37}OH)_3(TiO_3(OH_2)_3)]^{17-}$ were prepared (X = Si, Ge),[24,25] and this was extended to tetrameric systems.[26] Although less explored, Ti(IV) has also been incorporated into the Dawson systems *e.g.* two assemblies based on the $[P_2W_{15}O_{56}]^{12-}$ fragment,[27,28] where each Dawson unit contains a trimeric cap comprised of three Ti(IV) centres allowing the tetramer formation *via* a series of

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† Electronic supplementary information (ESI) available: Thermogravimetric analysis, FT-IR spectra, catalytic experiments and detailed information regarding electrochemistry, mass spectrometry experiments, and DFT calculations. CCDC reference numbers 795796 and 795797. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01327g

Ti–O–Ti linkages. Additionally, a dimeric structure composed of two $[P_2W_{17}O_{61}]^{10-}$ clusters connected *via* a single Ti–O–Ti bond was recently reported.[29] One further related class of interest are the peroxo-titanium(IV) substituted polyoxotungstates, due to the investigation of active intermediates of H_2O_2 based oxidations catalysed by Ti(IV) containing polyoxotungstates.[30–32]

Given the context of previous work, we are interested in the preparation of Ti(IV) based polyoxotungstates containing titanium centres with unique coordination environments. One such example is the $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ cluster prepared in 2007,[11] and highlighted in Fig. 1, which contains two structurally equivalent titanium atoms that are five-coordinate, and exhibit a square pyramidal coordination geometry. It is suggested that the extended Ti–O bonds are monoprotonated from BVS (bond valence sum) calculations. Interestingly, the system was shown to be an active catalyst in the oxidation of cyclohexene with hydrogen peroxide as a TBA (*n*-tetrabutylammonium) salt and then later found to be highly active in the oxidation of other related organic substrates.[12]

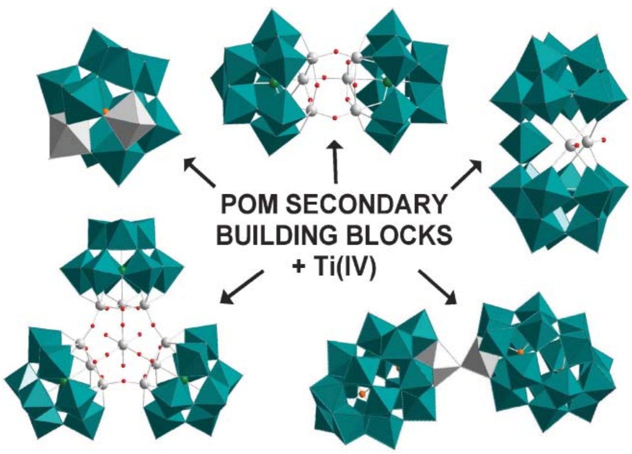

Fig. 1 Selection of reported polyoxometalate systems incorporating Ti(IV) centres. Top left: disubstituted monomeric system,[18] top middle: dimeric bridged cluster,[19] top right: a dititanium containing tungstoarsenate structure,[11] bottom left: a trimeric system[24] and bottom right: the unique Dawson based dimer linked *via* a single Ti–O–Ti bond.[29] W: teal polyhedra, Ti: silver polyhedra/silver spheres, O: red spheres, P: orange spheres, Si: green spheres, As: purple spheres.

Inspired by all of these results, we were able to adopt an approach that allowed us to effectively isolate two new cluster systems using the well defined secondary building blocks α-*B*-$[SbW_9O_{33}]^{9-}$ ($\{SbW_9\}$) and $[As_2W_{19}O_{67}(H_2O)]^{14-}$ ($\{As_2W_{19}\}$) as precursors, and these allowed the isolation of clusters incorporating the unprecedented $\{Ti{=}O\}^{2+}$ terminal oxo-containing system and the highly charged $\{Ti_4(H_2O)_{10}\}^{16+}$ moiety, respectively. The structures were determined using single crystal X-ray diffraction methods[46] and the compound formulae have been established as $Na_{13}H_3[TiO(SbW_9O_{33})_2]\cdot 33\ H_2O$ (**1**) and $K_6[Ti_4(H_2O)_{10}(AsTiW_8O_{33})_2]\cdot 30\ H_2O$ (**2**). We were also able to prepare a TBA (*n*-tetrabutylammonium) salt of **2**, $((n\text{-}C_4H_9)_4N)_4H_2[Ti_4(H_2O)_{10}(AsTiW_8O_{33})_2]$ (TBA-**2**).

Results and discussion

The monotitanium containing tungstoantimonate **1** was prepared in aqueous sodium acetate buffered solution at neutral pH using titanium oxosulfate as the titanium source and was isolated as a sodium salt. It is composed of two $\{SbW_9\}$ fragments[33] linked by five sodium ions and a unique square pyramidal $Ti(O)O_4$ group with a terminal Ti=O bond. The four Ti–O bonds linking the lacunary clusters have distances in the range 1.95–2.00 Å and the Ti=O bond has a measured distance of 1.653(9) Å. Successful isolation of this system can only be obtained by maintaining rigid synthetic parameters and these are discussed in detail. The starting $\{SbW_9\}$ fragment is reasonably stable in aqueous solution at a pH of around 7.5, and exposure to an acidic medium results in undesired condensation reactions with $[WO_4]^{2-}$ leading to the completed structures such as $[SbW_{18}O_{60}]^{9-}$. It has also been previously observed using crystallography that in neutral solutions the fragment is stabilised by a belt of six Na^+ ions to give the dimeric system displayed in Fig. 2.[33] The choice of titanium precursor is well suited to the design of systems with terminal Ti–O centres if the following equation is considered.

$$2\ Na_9[SbW_9O_{33}] + TiOSO_4 \rightarrow Na_{16}[TiO(SbW_9O_{33})_2] + Na_2SO_4$$

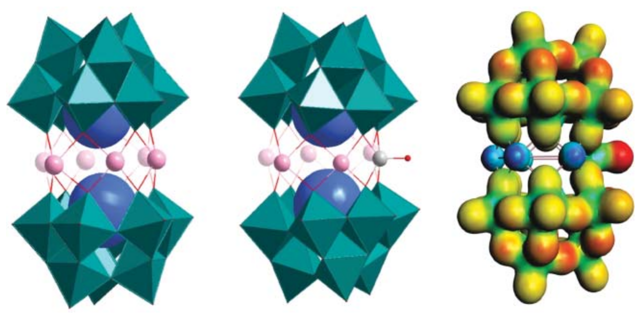

Fig. 2 Left: polyhedral representation of the dimeric system resulting from the sodium salt of α-*B*-$[SbW_9O_{33}]^{9-}$.[33] The two lacunary fragments are held together by a belt of six sodium cations. Middle: polyhedral representation of the unique system **1**. One of the six sodium cations has been replaced by a five-coordinate titanium(IV) centre with a terminal Ti=O bond extending away from the cluster. W: teal polyhedra, Na: pink spheres, Sb: blue space filling spheres, Ti: silver sphere, O: red sphere. Additional Na atoms have been omitted for clarity. Right: image of the electrostatic potential for $\{Na_5[TiO(SbW_9O_{33})_2]\}^{11-}$ highlighting the high electronegativity of the terminal Ti=O site. The coloured regions correspond to the scale being (most negative) red < yellow < green < light blue < dark blue (most positive).

The formation of sulfate salts, in this case sodium sulfate, leaves the transient $\{Ti{=}O\}$ species available to be incorporated into the POM system whilst minimising the effect of Ti–O–Ti oligomerisation. The inclusion of such sites in POMs is unique and based on BVS calculations and non-POM related Ti–O bond distances in the literature[34,35] we were able to deduce that the terminal oxygen in **1** is not protonated.

Excited by the successful isolation of this unprecedented system, we decided to carry out density functional theory (DFT) calculations in an attempt to describe the electronic properties for the Ti^{IV}-oxo portion of the molecule. Initial attempts to geometrically optimise **1** led to distorted structures with large Sb–Sb distances caused by repulsions between the $\{SbW_9O_{33}\}^{9-}$ motifs. A belt of

Na atoms between each fragment is clearly observed from the crystal structure so we decided to incorporate Na atoms in the calculations. When five Na atoms are included, the charge of the whole system is reduced, *i.e.* $\{Na_5[TiO(SbW_9O_{33})_2]\}^{11-}$, and the optimised structure has a non-bonding Sb–Sb distance which is only 0.13 Å larger than the experimental one. Hence the structure optimised with five Na atoms in the belt position, as shown in Fig. 2, gives a good approximation of the crystal structure; see also Fig. S9 and S10 (ESI†) for full data. The inclusion of Na atoms in addition to partially reducing the high charge of the cluster also influences a stabilisation of the antimony lone pairs. The importance of these five Na centres in the belt position supports the fact that all attempts to synthesise the compound with alternative cations or indeed subsequent cation exchange proved unsuccessful. A pictorial representation of the obtained electrostatic potential for $\{Na_5[TiO(SbW_9O_{33})_2]\}^{11-}$ is also shown in Fig. 2, highlighting the high electronegativity of the terminal oxygen on the titanium centre, enhancing potentiality as a reactive site for catalysis. We investigated the orbital diagrams, obtained after a single point calculation of the optimised geometry of $\{Na_5[TiO(SbW_9O_{33})_2]\}^{11-}$, with and without the presence of Na atoms and these are shown in Fig. 3. With the Na ions present, the occupied Sb orbitals are attracted to each other but, in the absence of the Na ions, this is not the case and the Sb–Sb distance is longer. Thus, the molecular orbital scheme featured in Fig. 3 demonstrates how the Na ions help to stabilise this highly anionic structure: their presence does not only result in a reduction in charge of the whole molecule, but Sb σ and σ* orbitals gain stabilisation in terms of relative orbital energy. Furthermore, some calculations were also carried out with hydrogen atoms and a structure was optimised with four protons attached, $\{TiO(H_2SbW_9O_{33})_2\}^{12-}$, see Fig. S11.† The negative charge of $\{TiO(SbW_9O_{33})_2\}^{16-}$ has now been reduced by the four protons attached to terminal W═O bonds. These results show that in acidic solution the terminal oxygen atoms may be protonated to some extent and hence the negative charge would be compensated by protons rather than sodium cations. However, this type of conclusion should be treated carefully due to the dynamic nature of the processes; *i.e.* both protons and sodium cations could be present in the inner part of the molecule.

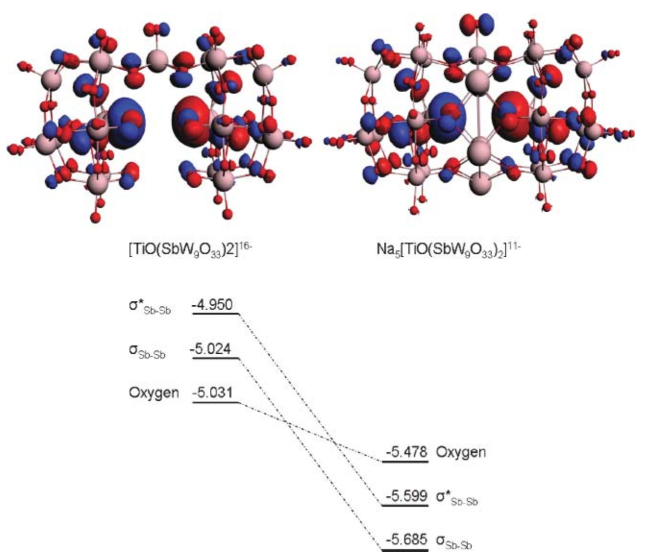

Fig. 3 Top left: $\{TiO(SbW_9O_{33})_2\}^{16-}$, orbital σ^*_{Sb-Sb}, energy = -4.945 eV. Top right: $\{Na_5[TiO(SbW_9O_{33})_2]\}^{11-}$, orbital σ^*_{Sb-Sb}, energy = –5.599 eV. Bottom: representation of the occupied molecular orbitals for $\{TiO(SbW_9O_{33})_2\}^{16-}$ with and without the sodium atoms. Energies are in eV.

So far we have been unable to identify compound **1** intact using mass spectrometry, only the presence of smaller fragments is observed in the spectrum. Furthermore, attempts to transfer the structure into organic media by introducing tetraalkylammonium salts have also failed. Given the previous discussion regarding the stabilising nature of the Na counter-ions, this result is not unexpected.

Having obtained this system using the $\{SbW_9\}$ fragment as an initial precursor, we attempted to prepare an arsenic analogue using the corresponding α-*B*-$[As^{III}W_9O_{33}]$ fragment, also without success. Subsequently, and considering the synthesis of the $[Ti_2(OH)_2As_2W_{19}O_{67}(H_2O)]^{8-}$ compound,[11] we decided to use the adaptable precursor $[As_2W_{19}O_{67}(H_2O)]^{14-}$ instead.[36] It has been previously reported that this structure can be feasibly disassembled in solution, releasing the α-*B*-$[As^{III}W_9O_{33}]$ species plus an additional tungsten fragment which can then allow further aggregation.[37] The hexatitanium tungstoarsenate **2** was prepared by reacting this precursor with titanium oxosulfate in aqueous solution at low pH and the resulting potassium salt was obtained by a slow crystallisation process. The Krebs-type structure is composed of two $\{AsTiW_8O_{33}\}$ fragments; in each case one W(VI) centre has been substituted for a Ti(IV) centre, fused together *via* a belt of four additional Ti(IV) centres. The two cluster halves are offset by a distance of *ca.* 3.4 Å with respect to the central arsenic positions and the six Ti atoms are found in two different planes, each one containing four co-planar Ti atoms. This is nicely demonstrated in Fig. S15.† Both experimental and theoretical structures for **2** are depicted in Fig. 4 and Table 1 shows relevant experimental and theoretical distances with the complete data available in the ESI.† The inner centres, Ti_B and Ti_C, see Fig. 4 and Table 1, have two Ti–O–Ti bridges with Ti–O distances of *ca.* 1.8 Å and two Ti–O–W bridges with Ti–O distances of *ca.* 2.0 Å. Two coordinated aqua ligands complete the coordination sphere with Ti–O distances of *ca.* 2.2 Å. The outer centres, Ti_A and Ti_D in Fig. 3, have two Ti–O–W bridges with Ti–O distances of *ca.* 1.8 Å, one Ti–O–Ti bridge with a Ti–O distance of 1.806(6) Å,

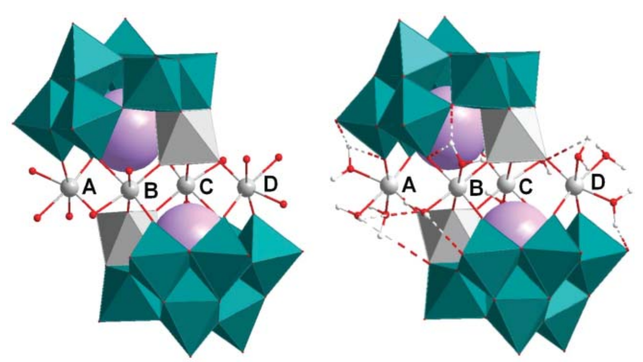

Fig. 4 Polyhedral representation of the unique system **2**. Left: experimental crystal structure, right: theoretically optimised structure showing the positions of the hydrogen atoms. The two $\{AsTiW_8O_{33}\}$ fragments are held together by a belt of four Ti(IV) centres. W: teal polyhedra, As: purple space filling spheres, Ti: silver spheres / polyhedra, O: red spheres. K cations have been omitted for clarity.

Table 1 Selected X-ray and computed Ti–O bond distances (Å) for compound **2**

Bond	X-Ray[a]	DFT[a]
$Ti_{A,D}$–O(W)	1.823(6)	1.820
	1.847(5)	1.826
$Ti_{A,D}$–O(Ti)	1.806(6)	1.808
$Ti_{A,D}$–O(H_2O)	2.142(6)	2.237
	2.179(7)	2.236
	2.096(7)	2.283
$Ti_{B,C}$–O(W)	1.932(6)	1.944
	1.954(5)	1.971
$Ti_{B,C}$–O(Ti)	1.790(6)	1.783
	1.798(6)	1.804
$Ti_{B,C}$–O(OH_2)	2.185(6)	2.351
	2.206(6)	2.323

[a] Averaged values.

and three coordinated aqua ligands with Ti–O distances of *ca.* 2.1 Å. It is clear that these are water ligands, and not any form of terminal Ti–O sites, from comparison to related distances in the literature.[38,39] The presence of water ligands has also been confirmed by DFT calculations. The values in Table 1 and Fig. S13† prove that the crystal structure is effectively reproduced when ten aqua ligands are coordinated to titanium centres A–D, and the deviation in the averaged Ti–O bond lengths is less than 0.02 Å for most of the bonds. The deviations for the more labile aqua ligands are slightly higher because in solution aqua ligands are normally stabilised by interactions with metal centres, solvent molecules and neighbouring oxo centres (as shown in Fig. 4). In general, bond distances in solution are slightly longer than in the solid state.[40] Such deviations are expected to be longer for more labile M–OH_2 bonds and we have found an average deviation for Ti–OH_2 bonds computed in water solution and observed crystal structures of 0.12 Å.

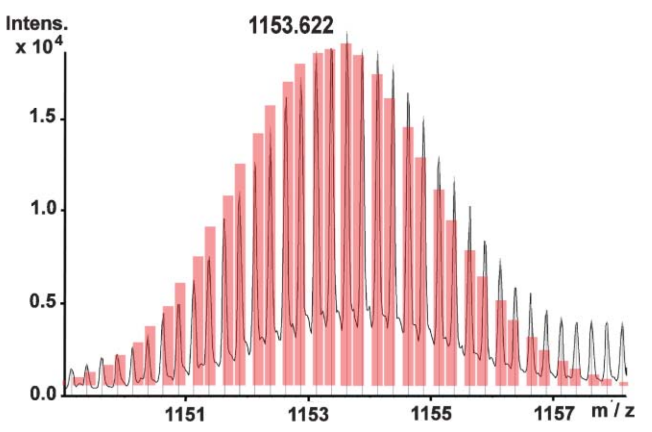

Fig. 5 Negative ion mass spectrum showing the $\{Ti_6(H_2O)_{10}(AsW^{VI}_{7+n}W^{V}_{1-n}O_{33}H_n)_2\}^{4-}$ in H_2O/CH_3CN (9 : 1). Two envelopes can be seen where $n = 0$ (with two W ions reduced to W^V) gives an envelope centered at *m/z ca.* 1153.6 and where $n = 1$ (with all the W oxidised, requiring 2 protons) gives an envelope centered at *m/z ca.* 1154.2 as confirmed by isotopic fitting of the envelopes to the bifurcated isotopic distribution shown between 1149 and 1159 *m/z*. The black line shows the actual spectrum and the red bar graph is the simulated envelop where $n = 0$.

The assembly process of **2** is quite complex and we propose a mechanism with several steps involved. First is the disassembly of the initial precursor $[As_2W_9O_{33}]$ releasing two $\{AsW_9\}$ lacunary fragments, and this is followed by specific site substitution of W(VI) centres for Ti(IV) forming $\{AsTiW_8O_{33}\}$ intermediates. These intermediates are then dimerised *via* incorporation of four additional Ti(IV) centres. The result is a $\{Ti_4\}^{16+}$ core sandwiched between two $\{AsTiW_8O_{33}\}^{11-}$ shells, with overall stabilisation by potassium cations. The mechanistic route is summarised in the following equations:

$$[As_2W_{19}O_{67}(H_2O)]^{14-} \rightarrow 2[AsW_9O_{33}]^{9-} + \{WO\}$$

$$2[AsW_9O_{33}]^{9-} + 2TiOSO_4 \rightarrow 2\{AsTiW_9O_{33}\}^{11-} + 2\{WO\}$$

$$2\{AsTiW_9O_{33}\}^{11-} + 4TiOSO_4 \rightarrow [Ti_4(H_2O)_{10}(AsTiW_8O_{33})_2]^{6-}$$

In contrast to compound **1**, this cluster is highly stable in aqueous solution and can be directly observed using mass spectrometry. The electrospray ionisation (ESI)-MS studies have proved to be a powerful tool in our effort to identify the extent of the protonation of this novel type of cluster in solution with a range of protonation (0 and 2) states observed, see Fig. 5. The direct observation of $\{Ti_6(H_2O)_{10}(HAsW_8O_{33})_2\}^{4-}$ allows us to confirm that the cluster observed in the solid state which has 6 cations associated, is carrying ten water molecules coordinated to the peripheral Ti(IV) metal centres. This observation is extremely important since it gives unambiguous proof that the sandwich type cluster is present in solution, establishes the existence of six Ti(IV) metal centres between the $\{W_8\}$ lobes and also confirms the extent of protonation of the cluster (in combination with X-ray, BVS and elemental analysis) which is almost impossible to determine directly. Also, compound **2** features one of the highest Ti : W ratios so far reported for tungsten Ti-incorporated polyoxoanions. The assignment of the cluster containing six titanium ions is unambiguous and importantly each of the terminal oxygen atoms coordinated to the peripheral titanium centres are protonated two-fold. It is noteworthy, that the determination of the protons in the oxo-coordination sphere of the titanium centres is usually problematic and the ESI-MS studies have proven very important for the explicit determination of the exact number of protons.

Using this information as a basis, we were able to successfully isolate a TBA salt of **2**, TBA-**2**, by adding an excess of TBABr to the final reaction mixture. We established the presence of four TBA cations per cluster using elemental and thermal analysis, however as of yet we have been unable to obtain a crystal structure. Having confirmed the aqueous solution stability of **2**, we investigated the associated electrochemistry in a buffered aqueous solution as well as that of TBA-**2** in CH_3CN at room temperature. The details are fully described in the ESI.† Briefly, in aqueous solution the form of the voltammograms remained identical no matter the scanning potential direction indicating that the phenomena observed in one domain had a negligible influence on those in the other domain. By scanning towards the negative region of potential values, the reduction processes of the compound occur *via* two electrochemically irreversible steps. As expected, no oxidation peaks were observed in the scanning from 0 V towards the positive region of potentials indicating that the initial oxidation state for the titanium centres is IV. Studying the electrochemical behaviour of TBA-**2** in CH_3CN, two well separated redox couples were observed similar to those observed in aqueous medium but slightly shifted towards more negative values. An additional irreversible process was observed at −0.300 V (see Fig. S3†) indicating the formation of an electro-active Ti(II) species on the surface.

Furthermore, the successful isolation of **2** as a TBA salt allowed us to carry out some preliminary catalytic studies in organic media yielding highly promising results. The test reaction used was the oxidation of benzyl alcohol to benzaldehyde and full details can be found in the ESI.†

Conclusions

In summary, we have prepared two novel titanium containing polyoxotungstates, the first based on lacunary $\{SbW_9\}$ building blocks featuring a highly unique terminal Ti=O site. The second has been prepared using the adaptable precursor $[As_2W_{19}O_{67}(H_2O)]^{14-}$ and represents the first example of the tungsten Ti-incorporated polyoxoanion with the highest Ti : W ratio, and incorporates a highly charged $\{Ti_4(H_2O)_{10}\}^{16+}$ unit. Both have been fully characterised and **2** has been directly identified using mass spectrometry in addition to featuring preliminary catalytic activity as a TBA salt (see ESI†). We are currently working towards exploiting these compounds further as oxidation catalysts for simple organic reactions as well as further extending the relatively small family of titanium containing polyoxometalates.

Experimental section

The *α-B*-$[SbW_9O_{33}]^{9-}$ fragment was prepared as a sodium salt according to the literature procedure.[33] The precursor $K_{14}[As_2W_{19}O_{67}(H_2O)]$ was synthesised according to the published procedure and the purity was confirmed by infrared spectroscopy.[36] All other chemicals and solvents were commercially purchased and used without purification. X-Ray structure analysis and crystallographic data: suitable single crystals of **1** and **2** were selected and mounted onto the end of a thin glass fibre using Fomblin oil. Structure solution and refinement was carried out with SHELXS-97[41] and SHELXL-97[41] using WinGX.[42] Computational calculations were carried out using DFT methodology with the ADF 2008 program.[43] The exchange–correlation functionals of Becke and Perdew were used.[44] Relativistic corrections were included by means of the ZORA formalism. Triple-ζ polarisation basis sets were employed to describe the valence electrons of W, O, Ti, Sb and As. All the structures were optimised in the presence of a continuous model solvent by means of the conductor-like screening model (COSMO).[45] Further information can be found in the ESI.†

Preparation of $Na_{13}H_3[TiO(SbW_9O_{33})_2]\cdot 33\ H_2O$ (1)

$TiOSO_4$·dil. H_2SO_4 15 wt.% (1.0 ml, 0.94 mmol) was added to a 1 M NaOAc solution (40 ml) and the pH adjusted to 7.0 using 4 M NaOH, resulting in the formation of white precipitate. The slurry was heated to 80 °C and finely ground $Na_9[SbW_9O_{33}]$ (0.70 g, 0.28 mmol) was slowly added. The mixture was then heated under reflux conditions at 110 °C for 10 h. After allowing to cool to room temperature, solid material comprised of mainly titanium oxide and sodium sulfate was removed by centrifugation and filtration and a clear, pale green liquor obtained. Very fine, needle-like, colourless crystals were obtained after approx. 5 days by slow diffusion of a 1 : 1 mixture of acetone and methanol at 4 °C. The crystals were collected by first sonicating the mother liquor and subsequent filtration. Yield: 73.7 mg, 13.8 μmol, 9.9 % based on W. Elemental analysis, (dried material) in wt.% for $Na_{13}H_3O_{67}Sb_2TiW_{18}$ (calculated values in brackets): Na: 6.4 (6.0), Sb: 3.9 (4.9), Ti: 0.9 (1.0), W: 68.3 (66.5). Note that the value for W is rather high despite analysis on crystallographically phase pure material. This is probably due to interference in the ICP experiment between W and Ti, although the impact here on the Ti value is not significant. However the quality of the structure is such that our formula assignment can be supported.

Preparation of $K_6[Ti_4(H_2O)_{10}(AsTiW_8O_{33})_2]\cdot 30\ H_2O$ (2)

$TiOSO_4$·dil. H_2SO_4 15 wt.% (1.4 ml, 1.31 mmol) was added to 40 ml deionised water followed by $K_{14}[As_2W_{19}O_{67}(H_2O)]$ (2.10 g, 0.40 mmol). The pH was adjusted from 1.25 to 1.31 using 1 M KOH solution and the mixture heated at 80 °C for 1 h. After allowing to cool and filtration, the clear green solution was stored in an open flask and after approx. 1 week, yellow-green rhombus shaped crystals appeared. These were collected by filtration and washed with a minimal amount of very cold water. Yield: 0.44 g, 88.8 μmol, 22.3 % based on W. Elemental analysis, (dried material) in wt.% for $As_2K_6O_{66}Ti_6W_{16}$ (calculated values in brackets): As: 2.8 (3.2), K: 5.1 (5.0), Ti: 4.1 (6.2), W: 64.0 (63.0). Note again that the value for W is high despite analysis on crystallographically phase pure material. This is probably due to interference in the ICP experiment between W and Ti, and here the suppression of the Ti value is significant. However the TBA exchange (see below), and the mass spectrometry results confirm our formula assignment.

Preparation of $((n\text{-}C_4H_9)_4N)_4H_2[Ti_4(H_2O)_{10}(AsTiW_8O_{33})_2]$ (TBA-2)

The *n*-tetrabutylammonium salt of **2** was prepared by adding TBABr (3.20 g, 9.93 mmol) dissolved in 10 ml H_2O to a freshly prepared end reaction mixture of **2**. The resulting pale green solid was filtered, washed thoroughly with H_2O, EtOH, and Et_2O and then dried in vacuum. Yield: 1.36 g, 0.25 mmol, 62.9 % yield based on $K_{14}[As_2W_{19}O_{67}(H_2O)]$. Elemental analysis, (dried material) in wt.% for $C_{64}H_{146}As_2N_4O_{66}Ti_6W_{16}$ (calculated values in brackets): C: 13.3 (14.2), H: 2.9 (2.7), N: 0.9 (1.0), Ti: 5.1 (5.3).

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46 Crystallographic data for **1**: $H_{69}Na_{13}O_{100}Sb_2TiW_{18}$, $M_r = 5569.1$ g mol^{-1}; colourless needle crystal; $0.27 \times 0.12 \times 0.08$ mm^3; $T = 150(2)$ K; triclinic, space group $P\bar{1}$, $a = 12.3948(2)$, $b = 17.4618(3)$, $c = 23.1989(4)$ Å, $\alpha = 74.019(2)$, $\beta = 78.653(2)$, $\gamma = 76.950(2)°$, $V = 4653.55(14)$ Å^3, $Z = 2$, $\rho = 3.974$ g cm^{-3}, μ(MoKα) = 22.98 mm^{-1}, $F(000) = 4936$, 66 892 reflections measured, 18 192 unique ($R_{int} = 0.0362$), 1138 refined parameters, $R_1 = 0.0335$, w$R_2 = 0.0894$ (all data). Crystallographic data for **2**: $H_{80}As_2K_6O_{106}Ti_6W_{16}$, $M_r = 5389.9$ g mol^{-1}; pale green block crystal; $0.25 \times 0.06 \times 0.06$ mm^3; $T = 150(2)$ K; triclinic, space group $P\bar{1}$, $a = 12.2625(2)$, $b = 12.6540(2)$, $c = 15.9764(3)$ Å, $\alpha = 73.571(2)$, $\beta = 76.674(2)$, $\gamma = 85.793(2)°$, $V = 2313.72(7)$ Å^3, $Z = 1$, $\rho = 3.868$ g cm^{-3}, μ(MoKα) = 21.39 mm^{-1}, $F(000) = 2424$, 42 090 reflections measured, 9085 unique ($R_{int} = 0.0454$), 606 refined parameters, $R_1 = 0.0272$, w$R_2 = 0.0689$ (all data). The cluster is basically composed of two $\{AsTiW_8O_{33}\}$ halves sandwiching a $\{Ti_4\}$ moiety in the centre. However a small portion of a ninth tungsten centre on each half is observed making the total number of tungsten atoms found in the structure slightly higher than the given 16 in the formula which is used to simplify the description. Crystal data was collected on a Gemini Oxford diffractometer using MoKα radiation ($\lambda = 0.71073$ Å) at 150(2) K.

