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FULL PAPER

New plenary and lacunary polyoxotungstate structures assembled from nonatungstoarsenate(III) anions and uranyl cations

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A new structural family of heteropolytungstate complexes containing *trans*-dioxo uranium(VI) (uranyl) groups has been isolated in good yield by reaction of UO_2^{2+} with $[NaAs_4W_{40}O_{140}]^{27-}$ (W_{40}) in aqueous solution. The "lacunary" anion, $[(UO_2)_3(H_2O)_5As_3W_{29}O_{104}]^{19-}$ **1** is formed by the reaction of W_{40} with $UO_2(MeCO_2)_2$ at pH 7, and the crystal structure of $(NH_4)_{19}[(UO_2)_3(H_2O)_5As_3W_{29}O_{104}]\cdot 28H_2O$ [orthorhombic, $P2_12_12_1$, $a = 17.5626(2)$, $b = 24.4929(2)$, $c = 33.3019(3)$ Å] is reported. The "plenary" anion, $[(UO_2)_3(H_2O)_6As_3W_{30}O_{105}]^{15-}$ **2** is formed by reaction of W_{40} with $UO_2(NO_3)_2$ at pH 4, and the crystal structure of $(NH_4)_{15}[(UO_2)_3(H_2O)_6As_3W_{30}O_{105}]\cdot 20H_2O$ [monoclinic, $P2_1/c$, $a = 23.63520(10)$, $b = 18.0646(2)$, $c = 35.32640(10)$ Å, $\beta = 107.46°$] is reported. Both heteropolyanions contain three B-$AsW_9O_{33}^{9-}$ groups linked by uranyl cations (pentagonal bipyramids) and three (or two) additional corner-sharing WO_6 octahedra cap the structure of **2** (**1**). A six-line ^{183}W NMR spectrum of **2** is consistent with an effective C_{3v} symmetry for the anion in solution. Addition of VO^{2+} to a solution of **1** yields the V-substituted anion (**3**) confirmed by a structure determination of $(NH_4)_{17}[(UO_2)_3(H_2O)_6As_3W_{29}V^{IV}O_{105}]\cdot 44H_2O$ [orthorhombic, $Pnma$, $a = 31.1821(4)$, $b = 24.9672(3)$ Å, $c = 20.3460(3)$ Å]. The cyclic voltammogram of **3** in 0.5 M sodium acetate buffer (pH 4.7) shows the $V^{IV/V}$ couple at +0.26 V (E_{pc}) and +0.40 V (E_{pa}).

Introduction

The synthesis and reactivity of very large polyoxometalate anions[1] is of much current interest. Such complexes stand at the interface between molecular species and extended metal oxide lattices and provide unique opportunities for examining the onset of new bulk and surface properties resulting from molecular growth. Applications of polyoxometalates in areas ranging from acid- and redox-catalysis to medicine are well known and are intensively studied.[2] In recent years we have been reinvestigating the possible uses of polyoxometalate chemistry for sequestration and immobilization of nuclear wastes.[3] We report here the interaction of the uranyl cation with the large polytungstate cryptate anion, $[As_4W_{40}O_{140}]^{28-}$, which itself is a cyclic assembly of four $[AsW_9O_{33}]^{9-}$ anions linked by WO_6 octahedra.[4] Unexpectedly, the product was a new polytungstate structure based on three $[AsW_9O_{33}]^{9-}$ anions linked by UO_2^{2+} cations. Both complete ("plenary") and defect ("lacunary") versions of the new structure could be isolated depending upon solution acidity, as observed for the Keggin anions and their lacunary derivatives, *e.g.* $[PW_{12}O_{40}]^{3-}$ and $[PW_{11}O_{39}]^{7-}$. Like the Keggin anion family, the new lacunary anion is shown to bind VO^{2+} in the vacant site.

Experimental

Syntheses

Sodium tetracontatungstotetraarsenate(III), $Na_{27}[NaAs_4W_{40}O_{140}]\cdot 60H_2O$, was prepared according to Hervé and Tézé[5] and uranyl acetate dihydrate (Alfa) and uranyl nitrate hexahydrate (Atomergic Chemicals) were used as received.

Ammonium 29-tungsto(triuranyl)triarsenate(III) (anion 1). 2 g (0.17 mmol) $Na_{27}[NaAs_4W_{40}O_{140}]\cdot 60H_2O$ was dissolved in 100 mL of water. Solid $UO_2(MeCO_2)_2\cdot 2H_2O$ (0.3g, 0.7 mmol) was dissolved into the solution. The pH was 6.6 ± 0.2. The solution was heated at 90 °C for an hour with stirring. While the solution was still hot, ammonium chloride (1.2 g) was added. After cooling the solution to room temperature, a small amount of yellow precipitate was filtered off, saturated NH_4Cl was added to the filtrate, and the product was crystallized by allowing the water to evaporate at room temperature for several days. Pale yellow crystals were collected on a medium porosity sintered glass filter, washed with cold water, and air dried. Yield: 1.4 g (70%). Found: N, 2.95; As, 2.21; U, 8.14; W, 61.66. $(NH_4)_{19}As_3U_3W_{29}O_{110}\cdot 21H_2O$ requires N, 3.04; As, 2.57; U, 8.16; W, 60.92%.

Anion **1** could also be prepared by the reaction of $[NaAs_4W_{40}O_{140}]^{27-}$ with $UO_2(NO_3)_2\cdot 6H_2O$ in a molar ratio of 1 : 1. When uranyl nitrate is used instead of uranyl acetate, it is important to adjust to pH 6–7 with sodium acetate before heating the solution. The yield was 75% based on uranium. Direct reaction of $[AsW_9O_{33}]^{9-}$ (as the sodium salt) with uranyl cation in a molar ratio of 1 : 1, with the addition of sufficient WO_4^{2-} to the solution, and adjusting to pH 6–7, also led to anion **1**, but this procedure has not been optimized.

Ammonium 30-tungsto(triuranyl)triarsenate(III) (anion 2). 2.5 g (0.215 mmol) $Na_{27}[NaAs_4W_{40}O_{140}]\cdot 60H_2O$ was dissolved in 200 mL of water and $UO_2(NO_3)_2\cdot 6H_2O$ (0.43 g, 0.86 mmol) was dissolved into the solution. The pH was 5.4 ± 0.2. The solution was heated at 90 °C for 2 hours. Upon cooling to room temperature the pH had decreased to 3.8 ± 0.2. The solution was reheated to 90 °C, and ammonium chloride (11 g) was dissolved in the solution. After the solution had cooled to room temperature, a small amount of yellow precipitate was filtered off, and the product crystallized from the filtrate by allowing the water to evaporate at room temperature for several days. Pale yellow crystals were collected on a medium porosity sintered glass filter, washed with cold water, and air dried. Yield: 1.5 g (60%). Found: N, 2.40; As, 2.57; U, 7.99; W, 63.00. $(NH_4)_{15}As_3U_3W_{30}O_{111}\cdot 15H_2O$ requires N, 2.40; As, 2.56; U, 8.14; W, 62.88%. ^{183}W NMR (δ/ppm): −78.3 (6W), −92.7 (3W), −98.8 (6W), −106.4 (6W), −151.2 (6W), −206.0 (3W).

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Table 1 Crystal data

	1	2	3
Formula	$H_{142}As_3N_{19}O_{143}U_3W_{29}$	$H_{112}As_3N_{15}O_{137}U_3W_{30}$	$H_{168}As_3N_{17}O_{161}U_3VW_{29}$
Formula weight	8967.83	8969.40	9304.95
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_1/c$	*Pnma*
a/Å	17.5626(2)	23.63520(10)	31.1821(4)
b/Å	24.4929(2)	18.0646(2)	24.9672(3)
c/Å	33.3019(3)	35.32640(10)	20.3460(3)
β/°	90	107.46	90
Z	4	4	4
μ/mm^{-1}	27.366	28.034	24.819
No. reflections	160170	153940	168382
Independent reflections, R_{int}	34173, 0.0913	34757, 0.1045	19932, 0.1472
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0533, 0.1137	0.0709, 0.1604	0.0750, 0.1242

Anion **2** was also a product from the reaction of Na_{27}-$[NaAs_4W_{40}O_{140}]\cdot 60H_2O$ with UCl_4 (Pfaltz and Bauer) which is air-oxidized to UO_2^{2+} in aqueous solution. The compound was identified by single crystal X-ray analysis.

Ammonium 29-tungstomonovanado(IV)(triuranyl)triarsenate(III) (anion 3). The ammonium salt of anion **1** (1.0 g, 0.11 mmol) was dissolved in 100 mL of water, and then 12 mL of 0.01 M $VOSO_4$ was added to the solution with stirring. The solution became dark brown as soon as the vanadyl sulfate was added. Stirring was continued for 20 min, and 6 g of NH_4Cl was added to the solution. The product was crystallized by allowing the water to evaporate at room temperature. Yield: 0.83 g (83%). Found: N, 2.57; As, 2.68; U, 7.93; V, 0.32; W, 60.66. $(NH_4)_{17}U_3As_3VW_{29}O_{111}\cdot 23H_2O$ requires N, 2.70; As, 2.55; U, 8.10; V, 0.58; W, 60.46%.

Crystallography

The crystals were examined under a thin layer of mineral oil using a polarizing microscope. Selected crystals were mounted on a glass fiber and quickly placed in a stream of cold nitrogen on a Siemens SMART CCD diffractometer equipped with a sealed molybdenum anode tube and graphite monochromator. Data were collected at 173(2) K. A direct methods solution located the heaviest atoms, and the remaining atoms were found in subsequent Fourier difference syntheses using the SHELX package of software.[6] In **2** and **3**, occupancy factors were varied in early stages of refinement for two disordered capping tungsten atom sites. In the final refinement, these factors were rounded off and held fixed. For these hydrated ammonium salts, the data did not support discrimination between oxygen and nitrogen atoms, and the ammonium ions were modeled as oxygen atoms. All refinements were full-matrix least squares on F^2. Crystal and refinement data are shown in Table 1. Selected average bond distances and angles are given in Table 2.

CCDC reference number 186/2343.

Physical measurements

Tungsten-183 NMR spectra were recorded using a Bruker AM-300WB spectrometer operating at 7.05 T (resonance frequency for ^{183}W is 12.483 MHz), and the chemical shifts are given with respect to external 2 M Na_2WO_4. The ammonium salts were converted to lithium salts for the W NMR measurements using Li^+-form ion-exchange resin.

Cyclic voltammograms were recorded on a BAS-100A electroanalyzer using a glassy carbon working electrode, a platinum wire counter electrode, and a standard Ag/AgCl reference electrode (+0.22 V *vs.* NHE). Electronic absorption spectra were measured in 1-cm quartz cuvettes using a Hewlett–Packard 8451A diode array spectrophotometer. IR spectra with 2 cm^{-1} resolution were recorded using a Nicolet 170SX FTIR spectrophotometer with KBr pellet samples. Elemental analysis was performed by E & R Microanalytical Laboratory, Corona, New York. Water contents were determined using a TGA 2050 Thermogravimetric Analyzer with 15–30 mg samples in 100 µL ceramic pans under a 70 cm^3 min^{-1} $N_2(g)$ flow and heating rates of 5 °C min^{-1}.

Table 2 Selected average bond distances (Å) and angles (°) for anions **1**, **2** and **3**[a]

	1	2	3
U=O			
Range	1.74(2)–1.79(2)	1.77(2)–1.79(2)	1.758(14)–1.80(2)
Mean	1.77[2]	1.78[1]	1.78[2]
U–OD(–W)			
Range	2.30(2)–2.41(2)	2.33(2)–2.39(2)	2.348(13)–2.376(13)
Mean	2.36[4]	2.35[2]	2.36[1]
U–OH$_2$[b]			
Range	2.48(2)–2.52(2)	2.45(2)–2.48(2)	2.45(2)–2.49(2)
Mean	2.50[2]	2.46[1]	2.47[2]
W[c]=O			
Range	1.75(2)–1.78(2)	1.70(2)–1.73(2)	1.709(14)–1.71(2)
Mean	1.76[1]	1.71[1]	1.71
W[c]–OC			
Range	1.90(2)–1.97(2)	1.91(2)–1.94(2)	1.881(14)–2.005(13)
Mean	1.94[3]	1.92[1]	1.94[5]
W[c]–OH$_2$[d]			
Range	2.15(2)–2.21(2)	2.25(2)–2.34(2)	2.21(2)–2.25(2)
Mean	2.18[3]	2.29[4]	2.23[2]
W–OD–U			
Range	137.1(8)–144.8(8)	137.2(9)–144.2(9)	138.8(7)–141.9(7)
Mean	139[3]	140[2]	140.6[9]

[a] Parentheses indicate e.s.d.s.; square brackets indicate calculated standard deviations. [b] O3U1, O3U2 and O3U3. [c] W41, W42 and W43. [d] O41D, O42D and O43D.

Results and discussion

The reaction of $[As_4W_{40}O_{140}]^{28-}$ with UO_2^{2+} proved to be the most convenient method for efficient formation of **1** and **2** which are easily isolated as ammonium salts in good yields. The IR spectra of the new compounds (Fig. 1) are similar, with four strong bands in the metal–oxygen stretching region (950–550 cm^{-1}).

The structures of **1** and **2** are shown in Figs. 2 and 3. Each anion is based on an assembly of three B-α-AsW_9O_{33} units which are linked by $UO_2(O)_5$ pentagonal bipyramids to form a cluster of C_{3v} symmetry. Two terminal oxygen atoms from adjacent corner-shared WO_6 octahedra of each AsW_9 group

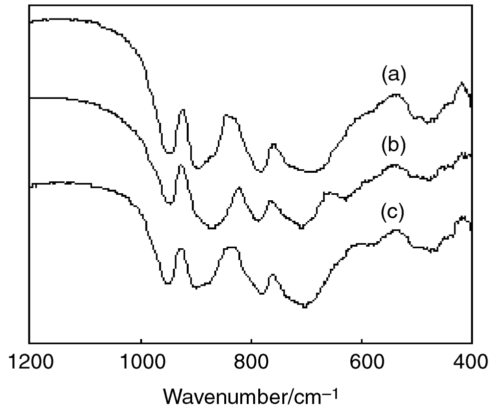

Fig. 1 IR spectra of ammonium salts of **1** (a), **2** (b) and **3** (c) in the metal–oxygen stretching region.

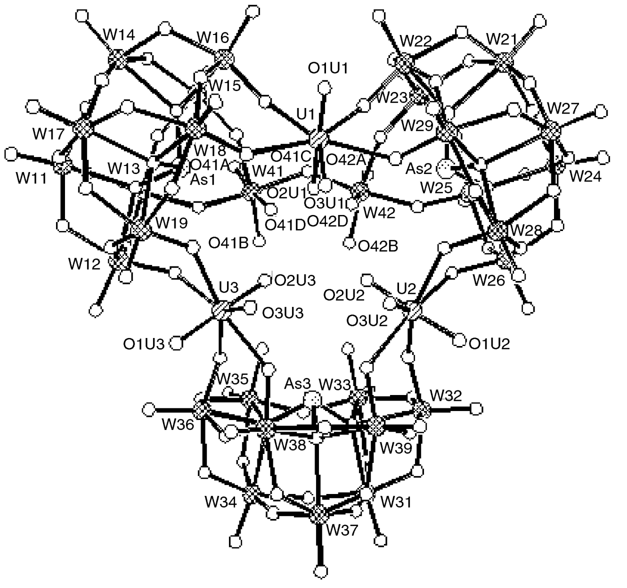

Fig. 2 Ball-and-stick representation of the structure of anion **1**, showing the atom-labelling scheme.

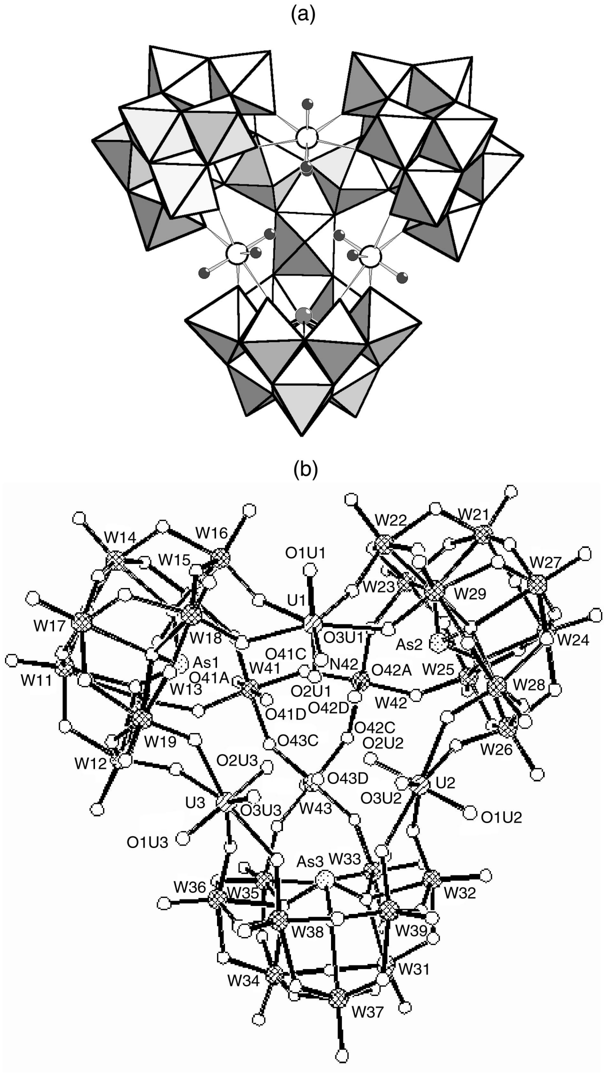

Fig. 3 Structure of anion **2** in ball-and-stick and polyhedral representations.

occupy equatorial positions of the uranium coordination spheres. The fifth equatorial site of each uranium atom is occupied by a water molecule. All three water molecules (O3U1, O3U2, O3U3 in both anions) appear on the same side ("bottom") of the anion assembly. The "top" of the structure is capped by two or three WO_6 octahedra (in anions **1** and **2** respectively) that share corners with each other and with pairs of adjacent edge-sharing WO_6 octahedra of the AsW_9 groups. Anion **1** has virtual C_s symmetry with a mirror plane bisecting the AsW_9O_{33} unit that does not have a WO_6 cap and passing through the uranium atom (U1) that bridges the other two AsW_9O_{33} units. Anion **2** has virtual C_{3v} symmetry if crystallographic disorder (see below) is ignored. The atom numbering scheme is shown in Figs. 2 and 3. Oxygen atoms, with exception of arsenate oxygens, oxo oxygens of uranyl, and water, are given the lower number of the tungsten atoms to which they are bound (except where that would duplicate an existing number; in that case, the higher number is used). This is followed by a letter (A–D) designating the type of bridging in which the oxygen is involved. The letter A indicates a terminal oxo oxygen; B indicates an oxygen bridging edge-sharing WO_6 octahedra; C indicates an oxygen bridging corner-sharing WO_6 octahedra; D indicates a terminal oxygen coordinated to uranium and tungsten. The oxygens of uranyl are labeled O*n*U*m* where $n = 1$ and 2 for oxo oxygens and $n = 3$ for a water molecule, and *m* is the number of the uranium. The arsenate oxygens are numbered O*n*A*m* where *m* is the number of the arsenic atom. Water and ammonium ions refined as oxygens are labeled O*n*W where *n* is an integer. Unless specially noted, the bond distances and angles in the AsW_9 units are not significantly different from other structures.[7] Parentheses indicate estimated standard deviations of a single datum and square brackets indicate calculated standard deviations of the mean of more than one equivalent value.

The two capping tungsten centers in **1** have octahedral coordination. Each tungsten has two *cis*-oxo oxygens with a mean distance of 1.76[1] Å. One oxygen bridges the two tungsten centers with a mean distance of 1.94[3] Å which is usual for such bonds. The sixth position on each tungsten is occupied by a water molecule with a mean distance of 2.18[3] Å. It is noteworthy that all five water ligands in **1** are on the same side (bottom) of the anion structure. An ammonium cation or a water molecule occupies the cavity formed by the "missing" WO_6 octahedron.

Anion **2** has essentially the same structure as **1** except that the vacant capping site is filled with a WO_6 octahedron (Fig. 3). The three capping WO_6 octahedra form a triangle linked by a corner sharing. Therefore, each capping WO_6 octahedron has only one terminal oxo oxygen, and a coordinated water is in *trans* position to the oxo oxygen. Two tungsten centers of the WO_6 octahedra are disordered between two positions along the oxo oxygen–water axis. One is disordered 75% in an upper site and 25% in a lower site, and the other is disordered 40% upper and 60% lower. Because of this disorder, the coordinated water and terminal oxo oxygen switch their positions. Anion **2** may have

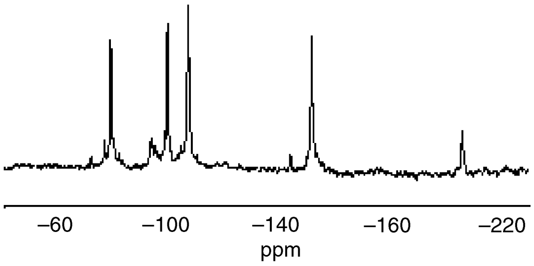

Fig. 4 12.50 MHz ^{183}W NMR spectrum of anion **2**.

C_s or C_{3v} symmetry as a result of the disorder. According to the crystal structure, there are three populations of anions with different arrangements of the three tungsten atoms (designated as W41, W42, and W43 in Fig. 3): all the three tungsten atoms are "up" (30%); two tungsten atoms are "up" and one is "down" (55%); one tungsten atom is "up" and the two are "down" (15%). In solution, the ^{183}W NMR spectrum of **2** showed six major peaks at −78.3, −92.7, −98.8, − 106.4, −151.2 and −206.0 ppm with a 2 : 1 : 2 : 2 : 2 : 1 intensity ratio, together with several minor resonances between −70 and −140 ppm (Fig. 4). A six-line spectrum would be consistent with a static structure of C_{3v} symmetry (all three tungsten atoms "up"), or with one of virtual C_{3v} symmetry as a result of rapid interconversion among the three arrangements.[8] The minor resonances are tentatively attributed to unidentified impurities, most likely derived from the As_4W_{40} framework. The ^{183}W NMR spectrum of anion **1**, which has C_s symmetry and should give 15 lines, was poorly resolved with broad lines resulting from many overlapping peaks. This was also the case for the spectrum of anion **3** (below).

The rearrangement of the 40-tungstotetraarsenate(III) anion to 29- or 30-tungstotriarsenate(III) is driven by the stereochemical requirements of the uranyl cation[9] and the presence of the lone pairs of the arsenic(III) atoms.[10] The latter prevent the formation of sandwich-like structures that were observed with uranyl complexes of A-$[PW_9O_{34}]^{9-}$.[3d] The dimensions of the bowl-shaped assembly are appropriate for the three corner-sharing WO_6 octahedra that cap the plenary structure **1**. Such a grouping of octahedra is analogous to that observed in the Keggin structure. The formation of **1** and **2** is pH-dependent; anion **2** forms exclusively at pH 4 and anion **1** at pH 7. The formation of **2** can be represented by the stoichiometry of eqn. (1) (at pH 4).

$$[As_4W_{40}O_{140}]^{28-} + 4\,UO_2^{2+} \longrightarrow \tfrac{4}{3}\,[(UO_2)_3As_3W_{30}O_{105}]^{15-} \qquad (1)$$

Although the isolated yields of **2** were good, we cannot be certain that the reaction was quantitative according to the above equation. Anion **1**, formed at pH 7, is a lacunary version of **2** and the relationship between **1** and **2** is strictly analogous to that between Keggin species as can be seen by comparison between eqns. (2) and (3).

$$[(UO_2)_3As_3W_{30}O_{105}]^{15-} + 5\,OH^- \longrightarrow [(UO_2)_3As_3W_{29}O_{104}]^{19-} + \text{"}HWO_4^-\text{"} + 2\,H_2O \qquad (2)$$

$$[PW_{12}O_{40}]^{3-} + 5\,OH^- \longrightarrow [PW_{11}O_{39}]^{7-} + \text{"}HWO_4^-\text{"} + 2\,H_2O \qquad (3)$$

One way to adjust the pH is to use different uranyl sources. When $UO_2(MeCO_2)_2$ is used, the pH is automatically adjusted (pH ≈ 7) for the formation of **1**; and with $UO_2(NO_3)_2$ the pH is appropriate (pH ≈ 4) for the assembly of **2**. This can be understood based on the buffer action of acetate ions and on the very weak conjugate basicity of nitrate ions. This self-controlled pH by the counter ions of uranyl cations gives the most clean products. Alternatively, the pH can be intentionally controlled for synthesis of **1** or **2**. In the reactions of $Na_{27}[NaAs_4W_{40}O_{140}]$ and $UO_2(NO_3)_2$ with adjustment of pH to 4.7–7.1, anion **1** is produced, and the product can be identified by a qualitative test with vanadyl cation (see below). Based on the study for the synthetic methods, anion **1** appears to be stable at pH 4.5–7.5, and anion **2** is stable at pH 3.5–6.

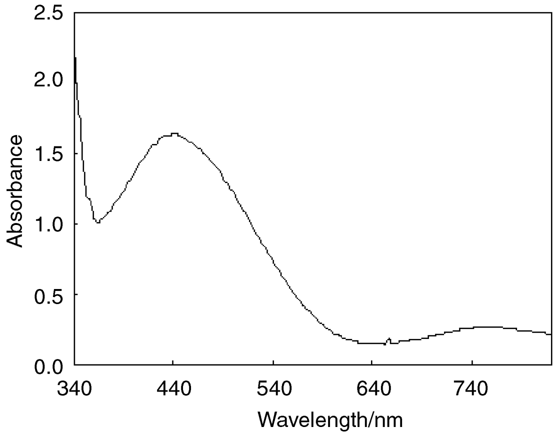

Fig. 5 Electronic absorption spectrum of anion **3**.

Thermal behavior of anion 2

The conversion of the ammonium salt of **2** to the cubic bronze U_xWO_3 ($x \approx 0.1$) has been reported elsewhere.[3e]

Reaction of anion 1 with VO^{2+}

From the crystal structure, anion **1** has a vacant site which might be suitable for coordination of various metal ions. VO^{2+} gives a dark brown color when it forms complexes with lacunary heteropolyanions, and it is often used for a qualitative test for such anions. The vanadyl cation was employed in order to investigate the reactivity of the lacunary site of anion **1**.

The visible absorption spectrum of **3** shows a maximum at 442 nm (ε = 1450 dm^3 mol^{-1} cm^{-1}) in water (Fig. 5). This strong absorption band originates from the charge transfer of $V^{IV} \rightarrow W^{VI}$. The color change to brown by addition of VO^{2+} was thus used as a qualitative test to discriminate between anions **1** and **2** during the study of synthetic methods to produce **1** and **2**.

Structure of the vanadyl derivative

Based on the crystal structure analysis of the ammonium salt, anion **3** (Fig. 6) is isostructural with **2**. The three capping sites (W41, W42, W43 in anion **2**, Fig. 3) are occupied by one vanadium and two tungsten atoms. Crystallographic disorder renders all three metal centers indistinguishable, but unlike the situation for **2** there is no metal atom disorder along the oxo oxygen–water axes; all metal atoms occupy "up" positions. The X-ray analysis shows full occupancy for the three water oxygens, and eliminates the possibility of a five-coordinate (square pyramidal) V(IV) which is often found in polyvanadates.

A cyclic voltammogram of **3** in 0.5 M $MeCO_2Na/MeCO_2H$ (pH 4.7) buffer solution shows a reversible one-electron redox process for $V^{IV/V}$; E_{pc}/E_{pa} = +0.26/+0.40 V *vs.* Ag/AgCl. This redox potential is similar to those of the 11-tungsto-1-vanadosilicates.[11] Addition of manganese(II) ions to **1** also results in a color change (to orange) and it is probable that many other transition metal cations can be coordinated to the lacunary site of **1**. However, preliminary experiments with lanthanide cations were not successful. In a reaction of **1** with Eu^{3+}, it was found by X-ray single crystal diffraction that the lacunary site was not occupied by Eu^{3+} and the structure was the same as **1**.

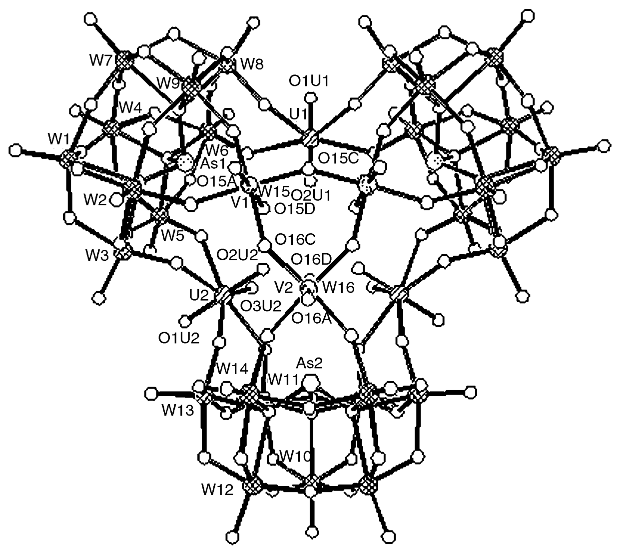

Fig. 6 Ball-and-stick representation of the structure of anion **3** showing the atom-labelling scheme.

Conclusions

New heteropolytungstodioxouranate(VI) complexes were synthesized by reaction of $[NaAs_4W_{40}O_{140}]^{27-}$ with uranyl cations. Because the lone pair of As(III) in $[AsW_9O_{33}]^{9-}$ is directed toward the outside of the shell, this anion cannot form the sandwich-type complexes with uranyl cations, as observed with $[PW_9O_{34}]^{9-}$ (and $[SiW_9O_{34}]^{10-}$). Instead, uranyl ions react with $[AsW_9O_{33}]^{9-}$ ions by functioning as linkers, and lead to formation of larger polyoxoanion assemblies. The assembly of four $[AsW_9O_{33}]^{9-}$ units joined by octahedral tungsten centers in $[NaAs_4W_{40}O_{140}]^{27-}$, rearranges to an assembly of three $[AsW_9O_{33}]^{9-}$ units linked by pentagonal bipyramidal uranium centers.

Formation of the plenary anion, $[(UO_2)_3(H_2O)_6As_3W_{30}O_{105}]^{15-}$ **2** and the lacunary version, $[(UO_2)_3(H_2O)_5As_3W_{29}O_{104}]^{19-}$ **1** critically depends on the pH: the plenary anion forms at pH 3.7–4.2, and the lacunary version forms at pH 4.7–7. Anion **2** is converted to the lacunary anion **1** by hydrolytic degradation above pH 7.

The lacunary anion **1** functions as a multidentate ligand for transition metal ions. Reaction of **1** with VO^{2+} ions gives a characteristic brown color which originates from $V^{IV}\rightarrow W^{VI}$ charge transfer.

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