

A new structural family of heteropolytungstate lacunary complexes with the uranyl, UO_2^{2+} , cation

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The reaction of UO_2^{2+} with the trivalent lacunary polyoxometalate anions, $[\text{SbW}_9\text{O}_{33}]^{9-}$ and $[\text{TeW}_9\text{O}_{33}]^{8-}$, yields the novel isostructural complexes $[(\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{SbW}_9\text{O}_{33})_2]^{14-}$ (**1**) and $[(\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{TeW}_9\text{O}_{33})_2]^{12-}$ (**2**), respectively. The complex anions contain two $[\text{XW}_9\text{O}_{33}]^{n-}$ ($\text{X} = \text{Sb}^{\text{III}}$ or Te^{IV}) anions linked by two UO_2^{2+} cations. Each uranyl moiety bonds to two unsaturated oxygen atoms of each lacunary anion in the complex. Each $[\text{XW}_9\text{O}_{33}]^{n-}$ anion has six unsaturated oxygen atoms meaning that in **1** and **2** each $[\text{XW}_9\text{O}_{33}]^{n-}$ anion has two unsaturated oxygen atoms which remain uncoordinated to uranium with the result being the formation of an 'open' sandwich structure. The fact that a third UO_2^{2+} cation is not coordinated to form a 'closed' sandwich structure (as is observed for first row d-block transition metals) is attributed to the steric hindrance of the axial 'yl' oxygen atoms of the uranyl group. The products, prepared as NH_4^+ salts, have been characterised by single crystal X-ray diffraction, elemental analysis, TGA analysis, IR, Raman and UV/vis spectroscopy, which indicate that the O donor atoms of the lacunary heteropolytungstate anions are strongly coordinating to U(vi) in the equatorial plane, weakening the uranyl U–O axial bonds.

Introduction

The synthesis and characterisation of heteropoly compounds containing uranium is of current interest because of their potential use for nuclear waste sequestration and storage.¹ Until recently the chemistry of the uranyl cation, UO_2^{2+} , with polyoxometalates has been largely neglected. Actinyl species are thought to be weakly coordinating to monovacant lacunary anions, such as $[\text{PW}_{11}\text{O}_{39}]^{7-}$, because of the steric constraints of the linear dioxo group.² However, Pope and co-workers have reported several structural characterisations of complexes of UO_2^{2+} with various di- and trivalent lacunary heteropolyanions. The first structurally characterised uranyl–polyoxometalate complex was from the reaction with $[\text{PW}_9\text{O}_{34}]^{9-}$ yielding the sandwich complex $[\text{Na}_2(\text{UO}_2)_2(\text{PW}_9\text{O}_{34})_2]^{12-}$ in which two UO_2^{2+} ions are sandwiched between two $[\text{PW}_9\text{O}_{34}]^{9-}$ ions and are also linked to each other through Na^+ ions.³ More recently the crystal structure and characterisation of the NpO_2^+ analogue has been reported.⁴ $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ reacts with UO_2^{2+} to form the tetrameric complex $\{[\text{Na}(\text{OH}_2)]_4(\text{UO}_2)_4(\text{SiW}_{10}\text{O}_{36})_4\}^{22-}$, which contains a U–O–Na array that links the four $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ anions and four UO_2^{2+} cations.⁵ Of most interest to this present study was that of the interaction between UO_2^{2+} and $[\text{NaAs}_4\text{W}_{40}\text{O}_{140}]^{27-}$ (a cyclic assembly of four $[\text{AsW}_9\text{O}_{33}]^{9-}$ anions linked by WO_6 octahedra), in which both plenary, $[(\text{UO}_2)_3(\text{H}_2\text{O})_6\text{As}_3\text{W}_{30}\text{O}_{105}]^{15-}$, and lacunary, $[(\text{UO}_2)_3(\text{H}_2\text{O})_5\text{As}_3\text{W}_{29}\text{O}_{104}]^{19-}$, complexes are formed.⁶ The plenary anion consists of three $B\text{-}[\text{AsW}_9\text{O}_{33}]^{9-}$ anions linked by three uranyl cations. The $[\text{AsW}_9\text{O}_{33}]^{9-}$ anions are also linked through three corner shared WO_6 octahedra.

First row transition metal ions react with lone pair containing $[\text{XW}_9\text{O}_{33}]^{n-}$ anions to yield closed dimeric structures in which three metal cations are sandwiched between two lacunary polyoxometalate anions with general formula $[(\text{XW}_9\text{O}_{33})_2\text{M}_3(\text{H}_2\text{O})_3]^{n-}$ ($n = 12$, $\text{X} = \text{As}^{\text{III}}$, Sb^{III} , $\text{M} = \text{Cu}^{2+}$, Zn^{2+} ; $n = 10$, $\text{X} = \text{Se}^{\text{IV}}$, Te^{IV} , $\text{M} = \text{Cu}^{2+}$).⁷ Trivalent polyoxoanions also form

novel structural types with 4f-elements such as $[\text{Eu}_3(\text{H}_2\text{O})_3(\text{SbW}_9\text{O}_{33})(\text{W}_5\text{O}_{18})_3]^{18-}$,⁸ and very recently the crown shaped ring complexes $[\text{K}\{\text{Eu}(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{33})\}_6]^{35-}$ and $[\text{Cs}\{\text{Eu}(\text{H}_2\text{O})_2(\text{AsW}_9\text{O}_{33})\}_4]^{23-}$ in which Eu^{3+} ions link a cyclic array of lacunary anions with encapsulation of the alkali metal ion.⁹

We report here the interaction of UO_2^{2+} with $[\text{SbW}_9\text{O}_{33}]^{9-}$ and $[\text{TeW}_9\text{O}_{33}]^{8-}$ resulting, not in complexes analogous to those with $[\text{AsW}_9\text{O}_{33}]^{9-}$, but unexpectedly dimeric lacunary complexes with formulae $[(\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{SbW}_9\text{O}_{33})_2]^{14-}$ and $[(\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{TeW}_9\text{O}_{33})_2]^{12-}$.

Experimental

General

Chemicals were obtained from commercial suppliers and used without further purification. Water was purified by distillation.

Syntheses

$\text{Na}_9[\text{SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$ was prepared according to a published literature method.¹⁰

$\text{Na}_8[\text{TeW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$ was prepared using the same method as for $\text{Na}_9[\text{SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$, but replacing Sb_2O_3 with TeO_2 as follows: $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (40 g, 121 mmol) was dissolved in boiling H_2O (80 cm^3). TeO_2 (2.14 g, 13.44 mmol) was dissolved in concentrated HCl (10 cm^3) and the resulting solution added dropwise to the tungsten containing solution. The mixture was refluxed for 1 h then allowed to cool to room temperature. Slow evaporation in air over several days yielded colourless crystals of the target compound (25.39 g, 66% yield), which were washed with ice-cold H_2O (5 cm^3) and dried in air.

$(\text{NH}_4)_{14}[(\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{SbW}_9\text{O}_{33})_2] \cdot 24\text{H}_2\text{O}$. $\text{Na}_9[\text{SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$ (1.14 g, 0.40 mmol) was suspended in H_2O (100 cm^3)

and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.20 g, 0.40 mmol) and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.13 g, 0.40 mmol) successively added with magnetic stirring. The solution was heated at reflux for 2 h (pH recorded as 6.4). Ammonium chloride (5.5 g, 102.8 mmol) was then added to the hot yellow solution (70–80 °C) and the solution stirred for a further 10 min. Following filtration under gravity the solution was left to evaporate in air overnight to yield a yellow powder (anion **1**), which was collected by vacuum filtration and air dried (0.74 g, 63% yield). Elemental analysis: calc. (found) (%) for $(\text{NH}_4)_{14}[(\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{SbW}_9\text{O}_{33})_2] \cdot 26\text{H}_2\text{O}$: U, 8.06 (8.21); Sb, 4.12 (3.93); W, 56.05 (55.92); N, 3.32 (3.17); H, 1.91 (1.79). Crystals suitable for X-ray diffraction were grown from a sample prepared for ^{183}W NMR spectroscopy (0.45 g of product in 2 cm³ H₂O), which was left to evaporate slowly over several days yielding yellow plate crystals.

$(\text{NH}_4)_{12}[(\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{TeW}_9\text{O}_{33})] \cdot 25\text{H}_2\text{O}$. *Method A:* $\text{Na}_8[\text{TeW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$ (1.13 g, 0.40 mmol) was dissolved in H₂O (100 cm³) with magnetic stirring. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.2 g, 0.40 mmol) and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.13 g, 0.40 mmol) were successively added to the resultant green–yellow solution, which was heated at reflux for 2 h. Ammonium chloride (5.5 g, 102.8 mmol) was added to the hot (70–80 °C) green–yellow solution. Following filtration under gravity the solution was allowed to evaporate in air over several days giving a small amount of green–yellow crystals (**2**) (<0.1 g) suitable for X-ray diffraction, in addition to the formation of some colourless crystals.

Method B: $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (2.00 g, 6.06 mmol) was dissolved in H₂O (80 cm³) and heated to boiling. TeO_2 (0.107 g, 0.67 mmol) was dissolved in concentrated HCl (0.5 cm³) and added dropwise to the boiling tungsten-containing solution. The resulting colourless solution was refluxed for 1 h. $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.34 g, 0.68 mmol) and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.221 g, 0.67 mmol) were successively added to the hot solution, which became cloudy, and was refluxed for 3 h, allowed to cool then centrifuged to remove small amounts of solid material. Ammonium chloride (3.62 g, 67.7 mmol) was added to the supernate with magnetic stirring and the clear yellow solution allowed to evaporate slowly in air yielding a yellow powder (**2**) after 6 d, which was collected by vacuum filtration and air dried (1.21 g, 63% yield). Elemental analysis: calc. (found) (%) for $(\text{NH}_4)_{12}[(\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{TeW}_9\text{O}_{33})_2] \cdot 26\text{H}_2\text{O}$: U, 8.02 (7.51); W, 55.74 (53.83); N, 2.83 (3.12); H, 1.86 (1.52).

The attempted synthesis of the UO_2^{2+} complex with $[\text{SeW}_9\text{O}_{33}]^{8-}$ failed to produce a pure identifiable product because of the formation of a yellow precipitate immediately upon addition of UO_2^{2+} to the Se containing solution despite variations of pH, ionic strength, temperature and attempts to prepare $[\text{SeW}_9\text{O}_{33}]^{8-}$ both as a precursor and *in situ* from stoichiometric quantities of Se and W. The yellow precipitate has not been characterised, but is probably a uranyl selenite, which are polymeric solids (prepared hydrothermally).¹¹ It is not clear why the same situation does not occur for Te, for which there are also reports of polymeric uranyl tellurite.¹²

Crystallography

Suitable crystals were chosen by examination under mineral oil using a polarising microscope and mounted on a glass fibre, then quickly placed under a stream of cold dinitrogen. Data were collected at 100(2) K for **1** on a Bruker SMART APEX CCD diffractometer and at 173(2) K for **2** on a Siemens SMART CCD platform diffractometer using graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods to locate the heaviest atoms and the remaining atoms found in the refinement with full-matrix least-squares on F^2 Fourier syntheses using the SHELXTL package of software.¹³ For both **1** and **2** the uranium, tungsten, antimony/tellurium and oxygen atoms of the anionic cluster were refined anisotropically. The nitrogen atoms and oxygen

atoms from solvent molecules were refined isotropically. The data did not allow distinction between oxygen and nitrogen atoms so, in the latter stages of refinement, oxygen atoms with the highest thermal motion were assigned as nitrogen atoms.¹⁴

CCDC reference numbers 206057 and 206058.

See <http://www.rsc.org/suppdata/dt/b3/b302955g/> for crystallographic data in CIF or other electronic format.

Physical measurements

IR/Raman spectra were recorded using a Bruker Equinox 55/Bruker FRA 106/5 spectrophotometer with a coherent 500 mW Laser, with a 2 cm⁻¹ resolution. IR spectra were recorded as KBr discs and Raman spectra obtained on solid and aqueous samples. Electronic absorption spectra were recorded on a Cary Varian 500 Scan UV-Vis-NIR spectrophotometer using a scan rate of 50 nm min⁻¹. Solid-state diffuse reflectance UV/vis spectra were recorded on an Ocean Optics SD2000 spectrometer with a fibre optic probe using a Deuterium-Halogen DH-200 light source and BaSO₄ used as a background. Thermogravimetric curves were recorded on a Mettler Toledo TGA/SDTA 851^e analyser over the temperature range of 25–1000 °C at a heating rate of 5 °C min⁻¹ under a continuous stream of dinitrogen at 100 cm³ min⁻¹. Elemental analysis: H and N was analysed for by a Carlo ERBA Instruments CHNS-O EA1108 Elemental Analyser. Metal analysis was by a Fisons Horizon Elemental Analysis ICP-OED spectrometer. No ^{183}W NMR spectra are presented here because the concentrations required to record well resolved spectra could not be achieved even with saturated solutions of **1** and **2**.

Results and discussion

Syntheses

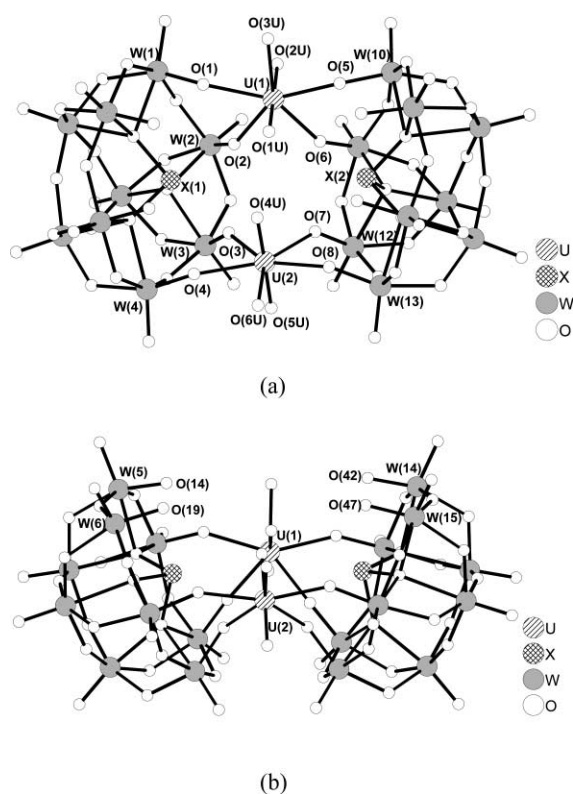
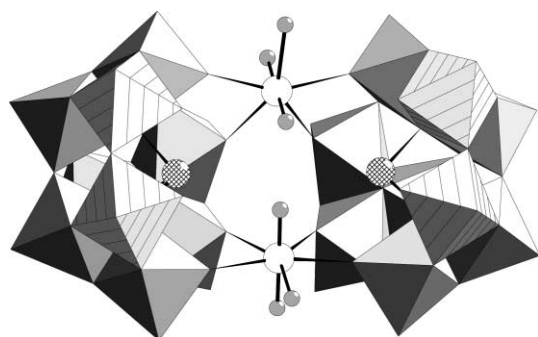
The ammonium salt of **1** was synthesised from the reaction between UO_2^{2+} and $[\text{SbW}_9\text{O}_{33}]^{9-}$ in aqueous solution under reflux conditions. After addition of NH_4Cl and filtration the resultant solution yielded **1** as a microcrystalline yellow powder, which could be recrystallised from water. The ammonium salt of **2** was prepared by two different methods. Method A was suitable for growing diffraction quality crystals and involved the preparation of $[\text{TeW}_9\text{O}_{33}]^{8-}$ as a precursor, for which there is no standard literature procedure and so was synthesised using the same method as for $\text{Na}_9[\text{SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$ and the product assumed to be $\text{Na}_9[\text{TeW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$ from the analogous profile of the IR spectrum (bands at 937, 882, 813 and 725 cm⁻¹) to that of $\text{Na}_9[\text{SbW}_9\text{O}_{33}] \cdot 19.5\text{H}_2\text{O}$. Method B was more convenient for producing a bulk quantity of the product by using stoichiometric amounts of the constituent heavier elements. IR spectroscopy was used to confirm that the products produced from both methods A and B were identical.

Structure

Compounds **1** and **2** are isostructural (Table 1, Figs. 1 and 2), differing only in the charge of the anion, which arises from the different oxidation states of the heteroatoms in $[\text{Sb}^{\text{III}}\text{W}_9\text{O}_{33}]^{9-}$ and $[\text{Te}^{\text{IV}}\text{W}_9\text{O}_{33}]^{8-}$. The structures comprise two $[\text{XW}_9\text{O}_{33}]^{n-}$ ($\text{X} = \text{Sb}^{\text{III}}$ or Te^{IV}) anions linked by two UO_2^{2+} ions. $[\text{XW}_9\text{O}_{33}]^{n-}$ polyanions are so-called trivacant and have six unsaturated oxygen atoms available for coordination to a positive metal species. In **1** and **2** both UO_2^{2+} ions are chemically equivalent and each is coordinated to both $[\text{XW}_9\text{O}_{33}]^{n-}$ anions through two unsaturated oxygen atoms. The fifth equatorial position is occupied by the coordinated oxygen atom of a water molecule, which completes the pentagonal bipyramidal geometry of the U(vi) centres. The linear dioxo groups of the two UO_2^{2+} cations are aligned approximately perpendicular to each other. Each $[\text{XW}_9\text{O}_{33}]^{n-}$ anion in **1** and **2** still have two unsaturated oxygen atoms. This is in contrast to the reported trimeric UO_2^{2+}

Table 1 Crystal data for **1** and **2**

Compound	1	2
Formula	H ₁₀₈ N ₁₄ O ₉₆ Sb ₂ U ₂ W ₁₈	H ₁₀₂ N ₁₂ O ₉₇ Te ₂ U ₂ W ₁₈
M _r	5869.86	5863.46
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
a/Å	17.2397(18)	17.244(2)
b/Å	11.5314(12)	11.5781(14)
c/Å	47.916(5)	47.682(6)
β/°	99.757(3)	99.706(2)
Z	4	4
μ/mm ⁻¹	26.135	26.138
Reflections collected/unique (R _{int})	67810/16553 (0.0592)	85184/16590 (0.1019)
F(000)	10368	10312
Final R indices [I > 2σ(I)]	R1 = 0.0403, wR2 = 0.0813	R1 = 0.0495, wR2 = 0.0991
R indices (all data)	R1 = 0.0540, wR2 = 0.0856	R1 = 0.0789, wR2 = 0.1094

**Fig. 1** (a) Ball-and-stick representation (top-down view) of the anion of **1** and **2**. (b) Side-on view clearly showing the oxygen atoms, O(14), O(19), O(42) and O(47), that remain unsaturated. (X = Sb^{III} or Te^{IV}).**Fig. 2** Polyhedral representation of the anion of **1** and **2**. The hatched polyhedra represent those which have unsaturated oxygen atoms.

complex with [AsW₉O₃₃]⁹⁻ in which the two unsaturated oxygen atoms not coordinated to the uranyl moiety form part of the WO₆ octahedra which link together the three [AsW₉O₃₃]⁹⁻ anions.⁶

For **1** the bond lengths (Table 2) within the two uranium(vi) dioxo groups are U(1)–O(1U) at 1.767(9) Å, U(1)–O(2U) at

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

	1	2
U(1)–O(1U)	1.767(9)	1.784(11)
U(1)–O(2U)	1.783(9)	1.780(11)
U(2)–O(4U)	1.773(9)	1.768(12)
U(2)–O(5U)	1.769(9)	1.779(12)
U(1)–O(3U)	2.508(9)	2.518(11)
U(2)–O(6U)	2.485(9)	2.517(11)
U(1)–O(1)	2.338(9)	2.364(11)
U(1)–O(2)	2.311(9)	2.329(12)
U(1)–O(5)	2.353(9)	2.338(12)
U(1)–O(6)	2.376(9)	2.315(11)
U(2)–O(3)	2.301(9)	2.339(12)
U(2)–O(4)	2.356(9)	2.359(12)
U(2)–O(7)	2.378(9)	2.365(12)
U(2)–O(8)	2.339(10)	2.315(13)
W(1)–O(1)	1.794(9)	1.793(12)
W(2)–O(2)	1.822(9)	1.821(12)
W(3)–O(3)	1.813(9)	1.809(13)
W(4)–O(4)	1.810(9)	1.797(13)
W(10)–O(5)	1.783(9)	1.796(12)
W(11)–O(6)	1.871(9)	1.794(11)
W(12)–O(7)	1.888(9)	1.805(12)
W(13)–O(8)	1.802(10)	1.805(12)
W(5)–O(14)	1.740(9)	1.729(12)
W(6)–O(19)	1.758(9)	1.752(12)
W(14)–O(42)	1.726(10)	1.739(13)
W(15)–O(47)	1.762(10)	1.745(12)
O(1U)–U(1)–O(2U)	176.7(4)	177.3(5)
O(4U)–U(2)–O(5U)	176.1(4)	177.3(5)
O(1)–U(1)–O(2)	70.0(3)	68.4(4)
O(1)–U(1)–O(3U)	75.5(3)	74.0(4)
O(2)–U(1)–O(6)	70.1(3)	74.8(4)
O(3U)–U(1)–O(5)	74.0(3)	73.6(4)
O(5)–U(1)–O(6)	70.5(3)	69.3(4)
O(3)–U(2)–O(4)	70.2(3)	68.4(4)
O(3)–U(2)–O(7)	70.6(3)	74.9(4)
O(4)–U(2)–O(6U)	77.6(3)	75.8(4)
O(6U)–U(2)–O(8)	72.8(3)	73.5(5)
O(7)–U(2)–O(8)	69.0(3)	67.8(5)

1.783(9) Å, U(2)–O(4U) at 1.773(9) Å and U(2)–O(5U) at 1.769(9) Å, which are all consistent with bond distances commonly observed for the UO₂²⁺ entity. The uranyl groups have a small deviation from linearity with angles of 176.7(4) and 176.1(4)° for O(1U)–U(1)–O(2U) and O(4U)–U(2)–O(5U), respectively, and are again within the expected range. The oxygen atom of the water molecule in the equatorial plane of each uranium atom is bonded at 2.508(9) Å for U(1)–O(3U) and 2.485(9) Å for U(2)–O(6U). The other four oxygen atoms in the equatorial plane, of each uranium atom, from the [SbW₉O₃₃]⁹⁻ anions have an average U–O distance of 2.344 Å. The corresponding W–O bond distances for the four equatorial oxygen atoms have an average value of 1.823 Å, whereas the four oxygen atoms that remain unsaturated have a shorter average W–O

distance of 1.747 Å, which is expected because of the effect of uranyl coordination to unsaturated oxygen atoms weakening the associated W–O bond. The average W–O bond distance for the unsaturated oxygen atoms of 1.747 Å is comparable to W=O(terminal) double bond distances observed in polyoxoanions. The O(axial)–U–O(equatorial) bond angles range from 86.6(4)° for O(4U)–U(2)–O(8) to 94.1(4)° for O(4U)–U(2)–O(7). The adjacent equatorial O–U–O bond angles can be split into two groups: (1) those angles involving oxygen atoms from the [SbW₉O₃₃]⁹⁻ anion only, which range from 69.0(3)° for O(7)–U(2)–O(8) to 70.6(3)° for O(3)–U(2)–O(7). (2) Those angles involving the oxygen atom of the water molecule, which range from 72.8(3)° for O(8)–U(2)–O(6U) to 77.6(3)° for O(4)–U(2)–O(6U). The idealised equatorial angles for a pentagonal bipyramidal arrangement are 72°. Therefore the geometry of the uranyl(vi) centre is best described as distorted pentagonal bipyramidal.

The U–O bond distances of the two uranyl groups for **2** are U(1)–O(1U) at 1.784(11) Å, U(1)–O(2U) at 1.780(11) Å, U(2)–O(4U) at 1.768(12) Å and U(2)–O(5U) at 1.779(12) Å. These distances fall within the standard range for uranyl bonds, as also found for **1**. Both uranyl groups have identical angles of 177.3(5)° for O(1U)–U(1)–O(2U) and O(4U)–U(2)–O(5U), which are closer to linearity than for those in **1**, although accounting for errors does not allow the conclusion of any significant difference between the uranyl angles of **1** and **2**. In the equatorial plane of the uranium atoms in **2** the oxygen atoms of the water molecules lie at 2.518(11) and 2.517(12) Å for U(1)–O(3U) and U(2)–O(6U), respectively, which are closely comparable to those in **1**. The remaining equatorial oxygen atoms from the [TeW₉O₃₃]⁸⁻ are at an average distance of 2.341 Å from the uranium atoms, which is not significantly different (accounting for experimental errors) from the value of 2.36 Å for compound **1**. The corresponding W–O bond distances for the four equatorial oxygen atoms of each uranium atom have an average value of 1.803 Å. The four remaining unsaturated oxygen atoms have a shorter average W–O bond distance of 1.741 Å as also found in **1**. The O(axial)–U–O(equatorial) bond angles range from 87.1(5)° for O(5U)–U(2)–O(6U) to 94.1(5)° for O(4U)–U(2)–O(7). Hence the equatorial oxygen atoms represent a slight deviation from planarity. As with **1**, the most acute equatorial O–U–O bond angles belong to those between oxygen atoms of the same [TeW₉O₃₃]⁸⁻ anion, ranging from 67.8(5)° for O(7)–U(2)–O(8) to 69.3(4)° for O(5)–U(1)–O(6). The other equatorial angles are more obtuse ranging from 73.5(5)° for O(6U)–U(2)–O(8) to 75.8(4)° for O(4)–U(2)–O(6U). This difference is dictated by the geometrical constraints on the flexibility of the unsaturated oxygen atom imposed by the whole structure of the [TeW₉O₃₃]⁸⁻ anion. For both **1** and **2** despite the lacunary anion not offering idealised geometrically placed O donor atoms the strength of the complexation is sufficient to override unfavourable distortion of the U(vi) equatorial geometry.

As mentioned in the introduction, “bare” metal ions, such as first row transition metal cations, react with [XW₉O₃₃]ⁿ⁻ (X = As^{III}, Sb^{III}, Te^{IV} and Se^{IV}) to form sandwich complexes of formula [M₃(H₂O)₃(XW₉O₃₃)₂]ⁿ⁻ (M = Cu²⁺, Zn²⁺). The steric demands of the UO₂²⁺ cation prevent it forming similar sandwich complexes because there is not enough room to accommodate three uranyl groups between two [XW₉O₃₃]ⁿ⁻ anions. The exact reason for the structures of **1** and **2** instead of an analogous structure to [(UO₂)₃(H₂O)₆As₃W₃₀O₁₀₅]¹⁵⁻ is unclear. However, when the product from the reaction of UO₂²⁺ with [SbW₉O₃₃]⁹⁻ was synthesized as a Na⁺ salt, single-crystal X-ray diffraction revealed a structure in which the framework was based on three [SbW₉O₃₃]⁹⁻ anions linked by three UO₂²⁺ ions, suggesting the nature of the cation is a factor in the assembly of the complex. The structure was too disordered to allow a full characterisation with acceptable final R indices.

From the available polyoxometalate–uranyl complexes now known, in the literature and in this report, a trend can be observed in which U(vi) always adopts its favoured seven-coordinate pentagonal-bipyramidal geometry, but with distortion in order to accommodate the positions of the unsaturated oxygen donor atoms of the polyoxoanion. The mechanism by which U(vi) then achieves a coordination number of seven, within the limitations of its steric constraints, results in the diversity of the structural architecture of the complexes formed. Associated with this is the importance of the presence of moieties that can act as anion linkers such as [WO₄]²⁻ and counter cations which impact on complex formation. For example in **1** and **2** there are no suitably placed oxygen atoms on the [XW₉O₃₃]ⁿ⁻ anions to allow UO₂²⁺ to fill the fifth equatorial position which is subsequently occupied by a water molecule. Contrastingly in [Na₂(UO₂)₂(PW₉O₃₄)₂]¹²⁻ the fifth equatorial position is occupied by a bridging oxygen atom on [PW₉O₃₄]⁹⁻ and the Na⁺ cations form an integral structural feature of the complex. Changing the cation to NH₄⁺ results in isomerisation because the different cations have different bonding interactions with the uranyl–polyoxometalate complex.³

Vibrational spectroscopy

1 has characteristic bands in the metal–oxygen stretching region of the IR spectrum at 935, 881, 773 and 681 cm⁻¹ and **2** at 948, 877, 783 and 700 cm⁻¹. The bands at 935 and 948 cm⁻¹ are assigned to the ν(W–O_{terminal}) stretching vibration (Fig. 3). The bands at 881 and 877 cm⁻¹ are assigned to ν(W–O_{edge-shared}) stretching vibrations and the bands at 773 and 783 cm⁻¹ assigned to ν(W–O_{corner-shared}) stretching vibrations. The uranyl stretch is obscured by the W–O stretching region.

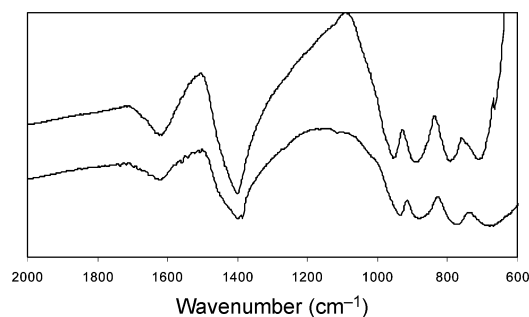


Fig. 3 IR spectra (solid ATR) of **1** (bottom) and **2** (top).

The Raman spectra of **1** and **2** (Fig. 4) have principal bands at 955 and 965 cm⁻¹, respectively, corresponding to the ν_{sym}(W=O_{terminal}) mode, which are shifted from values of 941 and 961 cm⁻¹ in ‘free’ [SbW₉O₃₃]⁹⁻ and [TeW₉O₃₃]⁸⁻, respectively.¹⁵ The Raman shift for the UO₂²⁺ symmetric stretching vibration is attributed to the band centred at 796 cm⁻¹ for **1** and 804 cm⁻¹ for **2**, with both assignments representing a significant weakening of the bonding in [O=U=O]²⁺ compared to the hydrated aquo UO₂²⁺ ion,¹⁶ which has a Raman shift at 870 cm⁻¹. The apparent greater degree of weakening in **1** than **2**

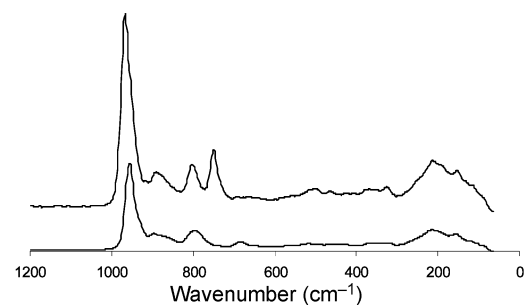


Fig. 4 Raman spectra (solid) of **1** (bottom) and **2** (top).

is probably because of the larger anionic charge for $[\text{SbW}_9\text{O}_{33}]^{9-}$ than for $[\text{TeW}_9\text{O}_{33}]^{8-}$, resulting in a greater degree of interaction with the uranyl cation in the equatorial plane and a larger decrease in the strength of the axial bonding. It should be noted that there is a low intensity feature centred at 794 cm^{-1} in the Raman spectrum of $[\text{SbW}_9\text{O}_{33}]^{9-}$, which coincides with the band at 796 cm^{-1} for **1**. However, we are confident in our assignment of this band to UO_2^{2+} because (i) it is of a much higher intensity for **1** than for 'free' $[\text{SbW}_9\text{O}_{33}]^{9-}$. (ii) there is no band in this region in the Raman spectrum of 'free' $[\text{TeW}_9\text{O}_{33}]^{9-}$, but there is one at 804 cm^{-1} for **2**. (iii) A band has been assigned to UO_2^{2+} at 791 cm^{-1} for a $\text{UO}_2^{2+}\text{-}[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ complex¹⁷ for which there is no band in this region in the spectrum of 'free' $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$. There are also bands at 685 and 750 cm^{-1} in the Raman spectra of **1** and **2**, respectively, which are tentatively assigned to $\text{W-O}_{\text{bridging}}\text{-W}$ vibrations.

Evidence for the stability of the complex anions of **1** and **2** in aqueous solution is provided by Raman spectroscopy with a principal shift at 954 cm^{-1} and a less well resolved band centred at 796 cm^{-1} for **1** and bands at 966 , 804 and 753 cm^{-1} for **2**. These values recorded for aqueous solutions of **1** and **2** compare favourably with those recorded in the solid state.

Raman spectroscopy is a much more sensitive probe of the $\text{O}=\text{U}=\text{O}$ bond strength than X-ray crystallography. Bands shifted to lower energy than the aquo uranyl ion, at 870 cm^{-1} , are rationalised as arising from an increase in the strength of the uranium–ligand interactions in the equatorial plane, which increases the electron density at the $\text{U}(\text{VI})$ centre, which in turn results in a larger electrostatic repulsion with the negative axial oxygen atoms and hence, weaker $\text{U}=\text{O}$ bonds. The lowest recorded Raman shift attributed to uranyl is at 786 cm^{-1} for an aqueous solution of the hydroxide complex $[\text{Co}(\text{NH}_3)_6]_2\text{-}[\text{UO}_2(\text{OH})_4]_3\cdot\text{H}_2\text{O}$ ¹⁶ in which OH^- ligands provide strong σ -donation to $\text{U}(\text{VI})$ in the equatorial plane. The greatly weakened $\text{O}=\text{U}=\text{O}$ bonding in **1** and **2** is comparable to the hydroxide complex and indicative of the strong complexing effect of $[\text{SbW}_9\text{O}_{33}]^{9-}$ and $[\text{TeW}_9\text{O}_{33}]^{8-}$ and explains why UO_2^{2+} is able to accommodate the distortion from idealised bond angles for pentagonal bipyramidal coordination.

Electronic absorption spectroscopy

$\text{U}(\text{VI})$ has no electrons in $5f$ orbitals and so no $f\text{-}f$ electronic transitions are possible. The observed bands in the electronic absorption spectrum for UO_2^{2+} , in the region of $350\text{--}550\text{ nm}$, arise from a charge transfer process of electrons from occupied oxygen atom orbitals to the vacant $5f$ orbitals.¹⁸ Vibrational fine structure is superimposed upon the charge-transfer band from which information about the $\text{O}=\text{U}=\text{O}$ symmetric stretching frequency in the excited state can be obtained. The UV/vis spectrum of **1** (Fig. 5) has the highest intensity band centred at 429 nm which is red shifted from the UO_2^{2+} 'aquo' ion at 409 nm .¹⁶ The average splitting between the band at 429 nm and the two adjacent bands is 566 cm^{-1} which suggests a weakening of the $\text{U}=\text{O}$ bond in the excited state compared to that in the aquo ion (706 cm^{-1}) which is expected given that there are

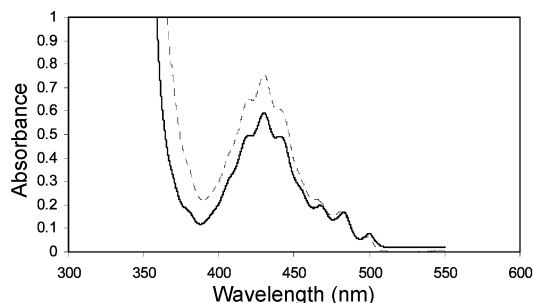


Fig. 5 UV/vis spectra of **1** (bottom) and **2** (top), dissolved in H_2O , in the $\text{L}\rightarrow\text{M}$ charge transfer region of the UO_2^{2+} cation.

negatively charged oxygen atoms strongly coordinated in the equatorial plane of UO_2^{2+} in **1**. The UV/vis spectrum of **2** is similar to that of **1** with the highest intensity band centred at 428 nm and an average splitting value of 592 cm^{-1} . There is also a $\text{O}\rightarrow\text{W}$ charge transfer band at lower wavelengths. The solid-state diffuse reflectance UV/vis spectra of **1** and **2** display similarly red shifted maxima (435 nm for **1** and 432 nm for **2**) compared to the aquo ion, but the resolution of the bands was not sufficient to make any comparisons of the vibrational fine structure.

Thermogravimetric analysis

The TGA curves of **1** and **2** show fairly continuous weight loss up to about $500\text{ }^\circ\text{C}$ and two further smaller weight losses between 600 and $1000\text{ }^\circ\text{C}$. The total weight loss over the entire range, $25\text{--}1000\text{ }^\circ\text{C}$, was 11.31% for **1** and 16.36% for **2**. The weight loss steps up to $350\text{ }^\circ\text{C}$ correspond to loss of water indicating 26 water molecules in the bulk solid for both **1** and **2**, which is in reasonable agreement with the crystallographically determined values of 24 and 25 water molecules for **1** and **2**, respectively. The weight loss in the region of $400\text{--}500\text{ }^\circ\text{C}$ (1.20% for **1** and 2.37% for **2**) is probably due to decomposition of the NH_4^+ cations to NH_3 gas although the values are lower than those expected to account for all the NH_4^+ cations in **1** and **2** (3.54% and 3.67% , respectively).

Conclusions

The reaction of UO_2^{2+} with $[\text{SbW}_9\text{O}_{33}]^{9-}$ or $[\text{TeW}_9\text{O}_{33}]^{8-}$ forms the novel dimeric anionic complexes of formulae $[(\text{UO}_2)_2\text{-}(\text{H}_2\text{O})_2(\text{SbW}_9\text{O}_{33})_2]^{14-}$ and $[(\text{UO}_2)_2(\text{H}_2\text{O})_2(\text{TeW}_9\text{O}_{33})_2]^{12-}$ in which $\text{U}(\text{VI})$ has distorted pentagonal-bipyramidal geometry in order to accommodate the coordination preferences of the polyoxometalate lacunary anions. The structure of the complexes are of an unprecedented type having 'open' structures with four unsaturated oxygen atoms, which have the potential for further coordination. Closed sandwich type structures are not formed because of the presence of a lone pair of electrons on the Sb^{III} and Te^{IV} atoms and the steric constraints of the uranyl groups. The weakening of the axial $\text{U}=\text{O}$ bonding as evidenced from the Raman and UV/vis spectra, of **1** and **2**, demonstrates that the strength of the uranium–polyoxometalate bonding in the equatorial $\text{U}(\text{VI})$ plane is comparable to that of hydroxide complexes, which have the lowest recorded UO_2^{2+} Raman stretching frequency to date. In summary, this work has not only displayed the diversity of UO_2^{2+} in forming new classes of polyoxometalate complexes, but has also elucidated, for the first time, the strength of polyoxoanion bonding to uranium in the equatorial plane by studying concomitant weakening of $\text{U}=\text{O}$ bonding in the axial plane.

Acknowledgements

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Notes and references

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- 15 'Free' $[\text{SbW}_9\text{O}_{33}]^{9-}$ and $[\text{TeW}_9\text{O}_{33}]^{8-}$ refers to these anions as the Na^+ salts, which were used in the syntheses of **1** and **2**. They cannot be strictly viewed as being 'free' because of the interaction of the Na^+ cations with the unsaturated O atoms of the lacunary anions.
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