



Polyoxometal cations within polyoxometalate anions.  
Seven-coordinate uranium and zirconium heteroatom  
groups in  $[(\text{UO}_2)_{12}(\mu_3\text{-O})_4(\mu_2\text{-H}_2\text{O})_{12}(\text{P}_2\text{W}_{15}\text{O}_{56})_4]^{32-}$   
and  $[\text{Zr}_4(\mu_3\text{-O})_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_4(\text{P}_2\text{W}_{16}\text{O}_{59})_2]^{14-}$

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Received 27 March 2003; revised 22 April 2003; accepted 23 April 2003

Dedicated to Professor Achim Müller on the occasion of his 65<sup>th</sup> Birthday

**Abstract**

Two new composite polyoxotungstate anions with unprecedented structural features,  $[(\text{UO}_2)_{12}(\mu_3\text{-O})_4(\mu_2\text{-H}_2\text{O})_{12}(\text{P}_2\text{W}_{15}\text{O}_{56})_4]^{32-}$  (**1**) and  $[\text{Zr}_4(\mu_3\text{-O})_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_4(\text{P}_2\text{W}_{16}\text{O}_{59})_2]^{14-}$  (**2**) contain polyoxo-uranium and -zirconium clusters as bridging units. The anions are synthesized by reaction of  $\text{Na}_{12}[\text{P}_2\text{W}_{15}\text{O}_{56}]$  with solutions of  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{ZrCl}_4$ . The structure of **1** in the sodium salt contains four  $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$  anions assembled into an overall tetrahedral cluster by means of trigonal bridging groups formed by three equatorial-edge-shared  $\text{UO}_7$  pentagonal bipyramids. The structure of anion **2** consists of a centrosymmetric assembly of two  $[\text{P}_2\text{W}_{16}\text{O}_{59}]^{12-}$  anions linked by a  $\{\text{Zr}_4\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_4\}^{10+}$  cluster. Both complexes in solution yield the expected two-line  $^{31}\text{P}$ -NMR spectra with chemical shifts of  $-2.95$ ,  $-13.58$  and  $-6.45$ ,  $-13.69$  ppm, respectively.

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**Keywords:** Polyoxometalates; Polyoxocations; Tungstophosphates; Uranyl; Zirconium

Much of the current interest in the chemistry of polyoxometalates is driven by potential applications in many fields of science and technology [1]. One such application involves the use of these complexes in the sequestration and storage of radioactive waste, and the formation and stability of polyoxometalate

complexes incorporating lanthanide and actinide heteroatoms is therefore of particular relevance. Such heteroatoms generally act as linkers between two polyoxometalate units, a role which accommodates the high coordination number preferences of the lanthanide and actinide cations [2]. In the course of our current investigations in this area we have isolated examples of new polyoxometalates in which the 'heteroatom' is itself a polyoxometal cation, i.e.  $[(\text{UO}_2)_3\text{O}(\text{H}_2\text{O})_3]^{4+}$  and  $[\text{Zr}_4\text{O}_2(\text{OH})_2(\text{H}_2\text{O})_4]^{10+}$ .

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Known polytungstates incorporating the dioxouranium(VI) cation are derived from the di- and trivacant lacunary derivatives of Keggin structure isomers,  $\gamma$ -[SiW<sub>10</sub>O<sub>36</sub>]<sup>8-</sup>, A, $\alpha$ ( $\beta$ )-[XW<sub>9</sub>O<sub>34</sub>]<sup>n-</sup> (X = P, Si); and B, $\alpha$ -[XW<sub>9</sub>O<sub>33</sub>]<sup>n-</sup> (X = As<sup>III</sup>, Sb<sup>III</sup>, Te<sup>IV</sup>) [3]. In every case the uranium atoms exhibit pentagonal bipyramidal coordination geometry and function as bridging atoms between polyoxometalate groups. The complexes reported here were prepared from the trivacant lacunary derivative of the Wells–Dawson anion,  $\alpha$ -[P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup>, which presents an open coordination site analogous to that of the B-form of [PW<sub>9</sub>O<sub>34</sub>]<sup>9-</sup>.

There are few well-characterized polyoxometalates containing zirconium as the heteroatom. With the exception of a zirconocene derivative, [(PW<sub>11</sub>NbO<sub>40</sub>)<sub>2</sub>ZrCp<sub>2</sub>]<sup>6-</sup>, [4] and the methoxy-bridged dimers, [(MeO)XW<sub>5</sub>O<sub>18</sub>]<sub>2</sub><sup>6-</sup> (X = Hf, Zr), [5] generated in nonaqueous media, the only other confirmed structure is that of the ‘sandwich’ species, [Zr<sub>3</sub>( $\mu$ -OH)<sub>3</sub>( $\beta$ -SiW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>11-</sup>, [6] which incorporates 6-coordinate Zr atoms. The structure of an anion formulated as [P<sub>2</sub>W<sub>15</sub>Zr<sub>3</sub>O<sub>62</sub>]<sup>12-</sup> prepared from the lacunary anion [P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup> was also presumed to contain 6-coordinate Zr atoms [7], but there is no unambiguous structural information to confirm this, and this anion may in fact be oligomeric, given the results of the present work, and a reinvestigation of [P<sub>2</sub>W<sub>15</sub>Ti<sub>3</sub>O<sub>62</sub>]<sup>12-</sup>, [8].

## 1. Experimental

### 1.1. Preparation of compounds

Na<sub>32</sub>[(UO<sub>2</sub>)<sub>12</sub>( $\mu$ <sub>3</sub>O)<sub>4</sub>( $\mu$ <sub>2</sub>H<sub>2</sub>O)<sub>12</sub>(P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>)<sub>4</sub>].77H<sub>2</sub>O (sodium salt of **1**). To a stirred solution of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.377 g, 0.75 mmol) in H<sub>2</sub>O (30 cm<sup>3</sup>), solid Na<sub>12</sub>[P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>].24H<sub>2</sub>O (2.21 g, 0.50 mmol) [9] was added in small portions. These slowly dissolved over approximately 30 min with magnetic stirring to give a deep yellow solution. Single crystals of the product suitable for X-ray diffraction were obtained by vapour diffusion of the solution with CH<sub>3</sub>CN over a period of 3 d. Total isolated yield, 0.66 g (53% based on uranium). Infrared (ATR): 1080, 1010, 931, 898, 871, 814, 767, 667 cm<sup>-1</sup>. Raman (powder): major peaks at 963 and 791 cm<sup>-1</sup>.

Na<sub>14</sub>[Zr<sub>4</sub>(P<sub>2</sub>W<sub>16</sub>O<sub>59</sub>)<sub>2</sub>( $\mu$ <sub>3</sub>-O)<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>].57H<sub>2</sub>O (sodium salt of **2**). Small portions of Na<sub>12</sub>[P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>].24H<sub>2</sub>O (3.6 g, 0.81 mmol) were added immediately to a freshly-prepared solution of ZrCl<sub>4</sub> (0.38 g, 1.63 mmol) in H<sub>2</sub>O (100 cm<sup>3</sup>). The resulting cloudy solution was clarified by addition of LiClO<sub>4</sub> (1.04 g, 9.78 mmol) with magnetic stirring for 20 min. Addition of NaCl (5 g, 85.56 mmol) to this solution yielded colourless plate-like crystals and microcrystalline powder after 2 d storage at 3 °C. A suitable crystal was chosen for single crystal X-ray diffraction. The rest of the solid (2.18 g, 60% yield) was collected by vacuum filtration, washed with ice cold H<sub>2</sub>O (5 cm<sup>3</sup>) and air-dried. Infrared (KBr disk): 1084, 1053, 1003, 937, 908, 765, and 516 cm<sup>-1</sup>. Anal. (powder): Na, 4.03; Zr, 3.82; P, 1.54; W, 64.45; H, 2.38. Calcd. for Na<sub>14</sub>[Zr<sub>4</sub>(P<sub>2</sub>W<sub>16</sub>O<sub>59</sub>)<sub>2</sub>( $\mu$ <sub>3</sub>-O)<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>].ca10H<sub>2</sub>O: Na, 3.61; Zr, 4.08; P, 1.39; W, 65.91; H, 2.09.

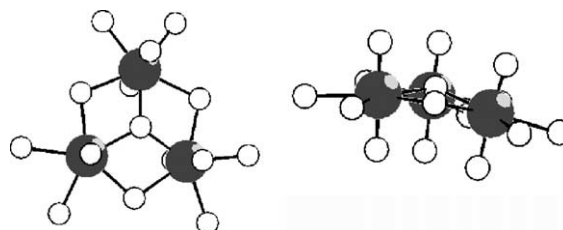
Elemental analysis was carried out using a Carlo ERBA Instruments CHNSO EA1108 Elemental Analyser, and a Fisons Horizon Elemental Analysis ICPOED spectrometer.

*Spectroscopy.* Solution NMR spectra were recorded on Bruker Avance 400 (Manchester) and Bruker WP300 (Georgetown) instruments using 5-mm tubes unless stated otherwise. Phosphorus chemical shifts are reported with reference to 85% H<sub>3</sub>PO<sub>4</sub>. Infrared (IR) and Raman spectra were recorded on a Bruker Equinox 55/Bruker FRA 106/5 with a coherent 500 mW Laser. Solid IR spectra were recorded as a KBr disk or as an Attenuated Total Reflectance (ATR) spectrum using the ‘GoldenGate’ attachment with a resolution of 2 cm<sup>-1</sup>. Solid state Raman spectra were measured by placing the sample in the path of the Laser beam. Solution UV/vis/NIR spectra were recorded using a Cary Varian 500 Scan spectrophotometer.

*Crystallography.* Bruker SMART APEX and SMART 1000 CCD diffractometers were used to determine the structures of **1** and **2** at Manchester and Georgetown, respectively. Structures were solved and refined using the SHELX-97 packages. Selected crystal data are given in Table 1. As with other structural investigations of crystals of highly hydrated large polyoxometalate complexes it was not possible to locate any of the sodium countercations in **1** and only four of these in **2**. This frequently encountered

Table 1  
Crystal data

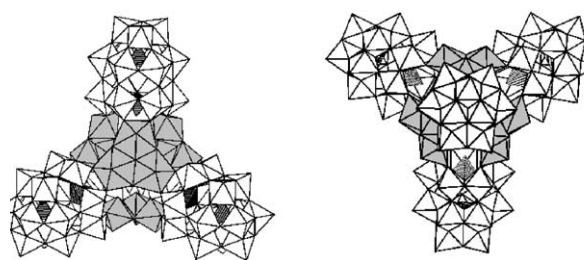
Compound	<b>1</b>	<b>2</b>
Formula	H <sub>178</sub> O <sub>341</sub> P <sub>8</sub> U <sub>12</sub> W <sub>60</sub>	H <sub>124</sub> Na <sub>4</sub> O <sub>183</sub> P <sub>4</sub> W <sub>32</sub> Zr <sub>4</sub>
Formula weight	19770.35	9516.83
Crystal System	Monoclinic	Triclinic
Space group	C2/c	P-1
Temperature (K)	100	173
Crystal size (mm)	0.15 × 0.1 × 0.08	0.1 × 0.1 × 0.04
<i>a, b, c</i> (Å)	40.355(4), 43.385(4), 28.573(3)	12.890(2), 14.010(2), 27.138(4)
$\alpha, \beta, \gamma$ (°)	90.00, 134.6220(10), 90.00	79.881(3), 79.571(3), 65.930(3)
Cell volume (Å <sup>3</sup> ), Z	35605(6), 4	4372.4(12), 1
Density (calc) Mg/m <sup>3</sup>	3.684	3.61
Absorption coefficient (mm <sup>-1</sup> )	24.873	21.343
<i>F</i> (000)	34,184	4210
2 $\theta_{\max}$ (°)	46.8	54
Total reflections	25,681	19,012
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	11,150	11,100
<i>R</i> <sub>int</sub>	<i>R</i> <sub>1</sub> = 0.0951, <i>wR</i> <sub>2</sub> = 0.2273	<i>R</i> <sub>1</sub> = 0.0538, <i>wR</i> <sub>2</sub> = 0.1241
Final <i>R</i> (all data)	<i>R</i> <sub>1</sub> = 0.2000, <i>wR</i> <sub>2</sub> = 0.2759	<i>R</i> <sub>1</sub> = 0.1113, <i>wR</i> <sub>2</sub> = 0.1381

Fig. 2. Ball-and-stick representations of the tris-uranyl group in **1**.

situation is attributed to extensive disorder of the cations and many of the hydrate water molecules. The uranium, tungsten, phosphorus and cluster-oxygen atoms were all refined anisotropically. The solvent oxygen atoms belonging to water molecules of crystallization were refined isotropically. In structure **2** tungsten, zirconium, and sodium atoms were refined anisotropically, and all oxygen atoms were refined isotropically.

## 2. Results and discussion

The structure of anion **1** contains four [P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup> anions assembled into an overall tetrahedral cluster by means of trigonal bridging groups formed by three equatorial-edge-shared UO<sub>7</sub> pentagonal bipyramids. Fig. 1 shows two views of the anion in polyhedral form, and ball-and-stick representations of the U<sub>3</sub> groups are shown in Fig. 2. Selected uranium coordination-sphere distances and -angles are given in Table 2. To our knowledge only two previous examples of such groups have been described, [(UO<sub>2</sub>)<sub>3</sub>.O(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>]NO<sub>3</sub>.4H<sub>2</sub>O [10] and (Et<sub>3</sub>NH)<sub>2</sub>[(UO<sub>2</sub>)<sub>3</sub>.O(dpa)<sub>3</sub>] where dpa is the triketonate ligand 2,2',8,8'-tetramethyl-3,5,7-nonanetrionato(1-) [11]. In the

Fig. 1. Two views of **1** showing UO<sub>7</sub> polyhedra in grey.Table 2  
Selected bond distances (Å) and angles (°) for **1**

U–O (axial)	1.74(3)–1.82(4)
U–O (W)	2.32(4)–2.43(4)
U–O (μ <sub>3</sub> )	2.18(3)–2.30(4)
U–O (μ <sub>2</sub> )	2.33(4)–2.51(4)
O–U–O (axial)	175.2(16)–178.7(17)
O (μ <sub>3</sub> )–U–O (μ <sub>2</sub> )	66.2(12)–70.5(13)
O (W)–U–O (W)	70.4(15)–73.3(15)
O (W)–U–O (μ <sub>2</sub> )	73.2(11)–79.2(11)

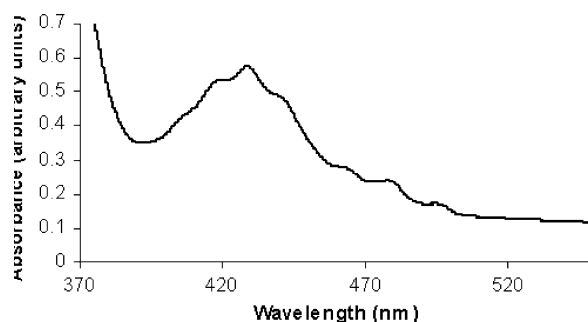


Fig. 3. Electronic absorption spectrum of an aqueous solution of **1**.

present case, owing to the invisibility of the sodium counteranions in the crystal structure, the extent of anion protonation is not certain. Although the metrical details of the  $P_2W_{15}$  groups are unexceptional and reveal no locations of localized protons, bond valence sum (BVS) considerations [12] provide some insight for the  $U_3$  groups. The results of BVS calculations for the bridging oxygen atoms in the two crystallographically-independent  $U_3$  groups are, for  $\mu_3$ -O: 1.96, 1.98, and for  $\mu_2$ -O: 0.78, 0.87, 0.87, 0.83, 0.89, 0.69. These values demonstrate that the central  $\mu_3$ -oxygen is unprotonated and that the other bridging oxygens are either hydroxo groups (BVS  $\sim 1$ ) or water molecules (BVS  $\sim 0.67$ ). We have chosen to formulate the anion with bridging water molecules, but recognize that other (disordered) protonation sites are possible.

As shown in Fig. 2 the ‘axial’ uranyl groups are not parallel and the central oxo-oxygen lies out of the plane defined by the uranium atoms by 0.47 and 0.51 Å in the two crystallographically-independent groups. This is a significant difference from the other two reported tris-uranyl structures in which the oxygen is almost coplanar (+0.18 Å [10] and +0.14 Å [11]) and the uranyl groups are close to parallel. The non-planar nature of the  $U_3$  bridging

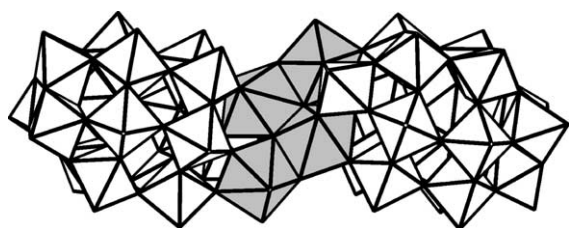


Fig. 4. Polyhedral representation of **2**.  $ZrO_7$  polyhedra are shown in grey.

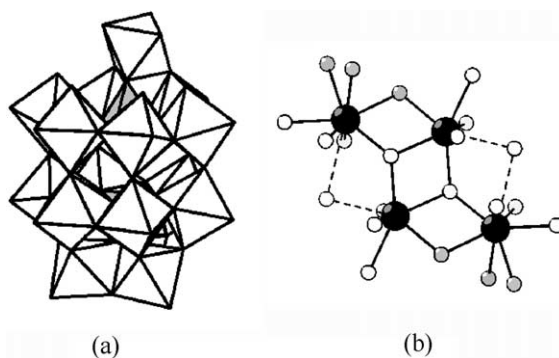


Fig. 5. (a) The  $\{P_2W_{16}O_{59}\}$  unit in polyhedral form. (b) Ball-and-stick representation of the  $\{Zr_4O_4\}$  cluster. Broken lines represent weak bonding interactions (2.456, 2.811 Å) with the oxygen atom shared between phosphorus and the remaining cap tungsten of the  $P_2W_{16}$  groups. Grey circles are terminal aqua and bridging hydroxo ligands; all other nonbridging oxygens are attached to tungsten atoms.

groups in **1** is presumed to be a consequence of the steric demands of the  $P_2W_{15}$  anions.

The formation of **1** by linking four polyoxometalate groups into a tetrahedral shape is highly unusual and is reminiscent of the tungstoniobate  $[Nb_4O_6(SiW_9Nb_3O_{40})_4]^{20-}$  reported by Hill et al. [13] A more closely related structure is the tetrameric assembly of  $[P_2W_{15}Ti_3O_{62}]^{12-}$  [8(b)].

A solution of the sodium salt of **1** in  $D_2O$  yields the expected two-line  $^{31}P$ -NMR spectrum with chemical shifts of  $-2.95$  and  $-13.58$  ppm, the former of which is assigned to the phosphorus atoms nearest to the uranium clusters. The corresponding chemical shifts in uncomplexed  $[P_2W_{15}O_{56}]^{12-}$  are  $+0.1$  and  $-13.3$  ppm [9].

Since **1** was isolated from a reaction mixture with a  $UO_2/P_2W_{15}$  ratio of 3:2 (anticipating the formation of a sandwich type structure) spectra were also recorded

Table 3  
Selected interatomic distances (Å) for **2**

Zr–O(P)	2.456(11), 2.811(12)
Zr–O(W)	2.088(10)–2.198(9)
Zr–O ( $\mu_3$ )	2.041(11), 2.083(10), 2.129(11)
Zr–O ( $\mu_2$ )	2.140(12), 2.178(12)
Zr–OH <sub>2</sub>	2.210(12), 2.328(11)
W–O(Zr)	1.778(10)–1.866(11)

Table 4  
<sup>31</sup>P Chemical shifts in some Wells-Dawson-derived tungstophosphates

Anion	Cap occupancy	Chemical shifts	Reference
$\alpha$ -[P <sub>2</sub> W <sub>15</sub> O <sub>56</sub> ] <sup>12-</sup>	none	+0.1, -13.3	9
$\alpha_2$ -[P <sub>2</sub> W <sub>17</sub> O <sub>61</sub> ] <sup>10-</sup>	W <sub>2</sub>	-7.1, -13.6	9
$\alpha_2$ -[P <sub>2</sub> W <sub>17</sub> VO <sub>62</sub> ] <sup>7-</sup>	W <sub>2</sub> V	-11.4, -13.5	14
$\alpha$ -[P <sub>2</sub> W <sub>16</sub> V <sub>2</sub> O <sub>62</sub> ] <sup>8-</sup>	WV <sub>2</sub>	-9.3, -13.9	14
$\alpha$ -[P <sub>2</sub> W <sub>15</sub> V <sub>3</sub> O <sub>62</sub> ] <sup>9-</sup>	V <sub>3</sub>	-6.8, -14.4	14
[Zr <sub>4</sub> (P <sub>2</sub> W <sub>16</sub> O <sub>59</sub> ) <sub>2</sub> ( $\mu_3$ O) <sub>2</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sup>14-</sup>	WZr <sub>2</sub>	-6.45, -13.8	This work

for solutions in which the ratio was 3:1, stoichiometric for **1**. Two-line spectra were observed, but with different chemical shifts, -4.50 and -13.13 ppm (pH 4.0) and -2.0 and -13.0 ppm (pH 6.8). These results suggest the existence of other UO<sub>2</sub>-P<sub>2</sub>W<sub>15</sub> complexes.

The UV/vis spectrum of an aqueous solution of **1** shows the characteristic absorption band for UO<sub>2</sub><sup>2+</sup> resulting from oxygen-to-uranium charge transfer with vibrational fine structure, Fig. 3. The peak with maximum intensity appears at 428 nm, and the average fine structure splitting is 583 cm<sup>-1</sup>. This value indicates a weakening of the O=U=O bonds in the excited state relative to the aquocation which has a splitting of 706 cm<sup>-1</sup>. A similar conclusion for the electronic ground state may be drawn from the Raman band at 791 cm<sup>-1</sup> versus that of the aquo cation at 871 cm<sup>-1</sup>.

The structure of anion **2** (Fig. 4) consists of a centrosymmetric assembly of two [P<sub>2</sub>W<sub>16</sub>O<sub>59</sub>]<sup>12-</sup> anions linked by a {Zr<sub>4</sub>O<sub>4</sub>}<sup>8+</sup> group. The tungstophosphate moieties are divacant lacunary versions of the Wells-Dawson ( $\alpha$ -P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>) anion from which two of the 'cap' tungstens have been removed, see Fig. 5(a). Thus anion **2** differs from the well-known sandwich complexes [M<sub>4</sub>(P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>)<sub>2</sub>]<sup>n-</sup> which incorporate a slab of octahedrally-coordinated M<sup>2/3+</sup> cations between *trivacant* lacunary derivatives of the Wells-Dawson structure. Details of the bridging group in **2**, which contains two different Zr atom environments, are shown in Fig. 5(b) and interatomic distances are given in Table 3. A search of the Cambridge Structural Database (3512 Zr-O bonds in 865 structures) revealed very few interatomic distances longer than 2.5 Å and none longer than 2.8 Å. The two longest Zr...O distances (2.456 and 2.811 Å)

are shown as broken lines in Fig. 5(b). We have chosen, somewhat arbitrarily, to ignore the longer of these as part of the relevant Zr coordination sphere, so that both zirconium atoms can be considered as 7-coordinate. The coordination geometries of both Zr(1) and Zr(2) are quite irregular and only approximately conform either to a capped trigonal prism or to a 4:3 geometry (square antiprism with one vertex removed). The results of bond valence sum calculations (0.47, 0.34) confirm that the two 'unshared' oxygen atoms attached to Zr(2), shown as grey spheres in Fig. 5(b), correspond to water molecules. The  $\mu_3$ -O atoms with bond valence sums of 1.98 are unprotonated, and the  $\mu_2$ -O atoms (1.07) are OH groups.

The <sup>31</sup>P-NMR spectrum of a solution of **2** shows the expected two lines, at -6.45 and -13.8 ppm with traces (<5%) of another species at -6.63 and -14.08 ppm. The chemical shift of the 'unsaturated' phosphorus in Wells-Dawson-derived polytungstates is sensitive to the number and type of the atoms in the reconstituted cap. Some examples are shown in Table 4.

### 3. Conclusions

The two new complexes reported here confirm that polyoxometal *cations*, which are generally only recognized in the solid state, can be incorporated in polyoxometalate assemblies. To our knowledge the only other example is {Sb<sub>4</sub>O<sub>4</sub>}<sup>4+</sup> in the recently-reported structure of [( $\alpha$ -SbW<sub>9</sub>O<sub>33</sub>)<sub>4</sub>(WO<sub>2</sub>(H<sub>2</sub>O))<sub>2</sub>{Ce<sub>3</sub>(H<sub>2</sub>O)<sub>8</sub>}(Sb<sub>4</sub>O<sub>4</sub>)]<sup>19-</sup> [14]. This raises possibilities for the development of a solution chemistry of these and other polycations. Anion **1** with U/W = 1:5

offers prospects for facile conversion to uranium-rich tungsten bronzes [15] for use as possible nuclear waste forms.

#### 4. Supporting information

X-ray crystallographic files in CIF format can be ordered from Fachinformationszentrum Karlsruhe, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany (<http://www.fiz-informationsdienste.de/en/DB/icsd/index.html>) by quoting the depository numbers CSD-391212 (2) and 391213 (1).

#### Acknowledgements

We thank EPSRC, BNFL, and NSF (CHE97-47217) for financial support, and Professor Kortz for advance information on Ref. 8(b).

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