

## Expanding molecular transition metal cubane clusters of the form $[M_4(\mu_3-O)_4]^{12+}$ : syntheses, spectroscopic and structural characterizations of molecules $M_4(\mu_3-O)_4(O_2P(Bn)_2)_4(O_4)$ , $M = V^V$ and $W^V$ †

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Received 21st July 2011, Accepted 12th September 2011

DOI: 10.1039/c1dt11375e

**Oxidizing the trimer  $V_3(\mu_3-O)(O_2)(\mu_2-O_2P(Bn)_2)_6(H_2O)$  in the presence of excess  ${}^1BuOOH$  results in  $V_4(\mu_3-O)_4(\mu_2-O_2P(Bn)_2)_4(O_4)$  and heating  $W(CO)_6$  and bis(benzyl)phosphonic acid in 1:1 EtOH/THF at 120 °C produces  $W_4(\mu_3-O)_4(\mu_2-O_2P(Bn)_2)_4(O_4)$ .**

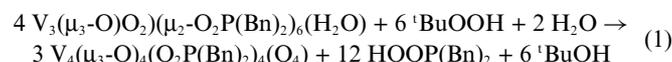
In contrast to the large number of sulfur-containing clusters known for a wide range of transition metals of the form  $[M_4(\mu_3-S)_4]^{n+}$ ,<sup>1</sup> which also extends to heterometallic formulations,<sup>2</sup> there has not been an equivalent number of reports of molecular oxygen-containing clusters of the type  $[M_4(\mu_3-O)_4]^{n+}$ . Notable exceptions are tin<sup>3</sup> (*i.e.*,  $[Sn_4O_4]^{8+}$ ), titanium<sup>4</sup>  $[Ti_4O_4]^{8+}$  and manganese  $[Mn_4O_4]^{6+}$  clusters<sup>5</sup> due to their relevance to the oxygen-evolving complex in photosystem II.<sup>6</sup> There are several reports of vanadium(IV) in sulfite polyoxometalates,<sup>7</sup> and as  $[P_2V_4O_{16}]^{6-}$  in the mineral phosphovanadylite<sup>8</sup> and as vanadium(V) in two other layered phosphovanadate structures.<sup>9</sup> For tungsten, reports of planar aggregates, *e.g.*  $[WO_2Cl_2(THF)]_4$ ,<sup>10</sup> and of cubane-like clusters with tetrameric tungstate(VI) units have been detailed. The  $[W_4O_{16}]^{8-}$  cores were stabilized by metal-containing units such as  $[(1,5-COD)Ir]^+$ ,<sup>11</sup>  $[Cp^*Rh]^{2+}$ ,<sup>12</sup>  $[Ru(\eta^6-C_6Me_6)]^{2+}$ ,<sup>13</sup> and  $[Cr(cyclam)]^{3+}$ .<sup>14</sup> So far, dimeric complexes featuring a  $[W_2O_4]^{2+}$  core have been produced only with tungsten(V)<sup>15</sup> exhibiting  $W^V-W^V$  single bond distances in the range 2.537(1)<sup>15b</sup>–2.568(1) Å.<sup>15e</sup> Our report<sup>16</sup> of a readily available route to the previously reported  $Mo_4(\mu_3-O)_4(\mu_2-O_2P(C_6H_5)_2)_4(O_4)$ <sup>17</sup> followed by the syntheses of this molybdenum tetrameric core stabilized by other phosphinate ligands, including dibenzylphosphinate,<sup>18</sup> raised the obvious question as to whether phosphinate ligands (also utilized in many of the complexes referred to above) would be capable of extending the number of transition metals that can exhibit this type of bonding in molecular form. This paper details our success at producing vanadium and the first reported tungsten(V) tetrameric cubane clusters of the form  $M_4(\mu_3-O)_4(O_2P(Bn)_2)_4(O_4)$ .

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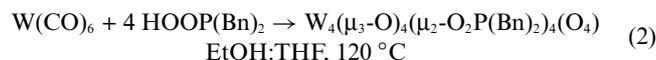
† Electronic supplementary information (ESI) available: Elemental analyses, IR, <sup>1</sup>H and <sup>31</sup>P NMR spectra, TGA plots for 1–3 and X-ray data for 1 and 2. CCDC reference numbers 834511 and 834512. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt11375e

The synthesis of these compounds turned out to be much more difficult than one would have predicted, given the various ways in which the analogous molybdenum tetramers were produced.<sup>16</sup> Essentially, the only reliable way we have discovered to produce the vanadium tetramer,  $V_4(\mu_3-O)_4(O_2P(Bn)_2)_4(O_4)$ , **1**, consists of the oxidation of the trimer  $V_3(\mu_3-O)(O_2)(\mu_2-O_2P(Bn)_2)_6(H_2O)$ <sup>19</sup> in the presence of excess  ${}^1BuOOH$  followed by self assembly of the desired compound, possibly as outlined in eqn (1).‡



The production of HOOP(Bn)<sub>2</sub> was verified by IR spectroscopy and the reaction requires water for it to be successful. The synthesis of complex **1** *via* this procedure is based on elemental analysis, IR, <sup>1</sup>H and <sup>31</sup>P NMR spectra (see ESI†) and the fact that the spectra are similar to those for tungsten (see below) and the molybdenum<sup>16</sup> analogs. Routes involving the reaction of starting vanadium complexes such as  $V_2O_5$  or  $[Bu_4N]_3[H_3V_{10}O_{28}]$  and HOOP(Bn)<sub>2</sub> in  $CH_3CN$  with or without  $[Bu_4N][OH]$  either resulted in intractable products or the trimer  $V_3(\mu_3-O)(O_2)(\mu_2-O_2P(Bn)_2)_6(H_2O)$ . Reactions with VO(acac)<sub>2</sub> in EtOH under solvothermal conditions or in THF at room temperature in the presence of HOOP(Bn)<sub>2</sub> and either  ${}^1BuOOH$  or  $H_2O_2$  were not successful, as the EtOH reduces V(V) to V(IV); these reactions also resulted in the aforementioned trimer. However, oxidizing a solution of VO(acac)<sub>2</sub> in EtOH with  ${}^1BuOOH$  and then adding HOOP(Bn)<sub>2</sub> in  $CH_2Cl_2$  (followed by stirring for 5 h at room temperature) leads to mixtures (38.5% yield) of the desired tetramer, the aforementioned trimer and/or some other complex. The desired orange tetramer may be obtained in pure form by selective crystallization consisting of the diffusion of hexane into  $CH_2Cl_2$  solutions of the crude mixture.

The tungsten tetramer,  $W_4(\mu_3-O)_4(\mu_2-O_2P(Bn)_2)_4(O_4)$ , **2**, was synthesized from  $W(CO)_6$  and was not obtained using a high oxidation state compound, *e.g.*,  $Na_2WO_4$ .§ As shown in eqn (2), this reaction was conducted under solvothermal conditions in a solvent mixture consisting of equal amounts of EtOH and THF.



$W(CO)_6$  is known to oxidize in solution under  $O_2$ .<sup>20</sup> In pure EtOH, **2** was obtained on occasion but this is not as reproducible compared to using the mixture of solvents. Complexes **1** and **2** have very characteristic IR patterns in the range 1012–978  $cm^{-1}$ .

This takes the form of two sharp outer peaks with a shoulder peak in the middle (1012, 1000 and 990  $\text{cm}^{-1}$  for **1**; 1012, 1000 and 979  $\text{cm}^{-1}$  for **2**) and this pattern was also observed for the molybdenum analogue (1011, 998 and 980  $\text{cm}^{-1}$ ).<sup>18a</sup> The complexes yielded distinctive peaks in their  $^1\text{H}$  NMR spectra consisting of AB patterns for the diastereotopic  $\text{CH}_2$  protons of the benzylic ligand at  $\delta$  2.86 and 2.90 for **1** and  $\delta$  2.93 and 3.06 for **2**. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra consist of single resonances at  $\delta$  60.6 and 68.4 for **1** and **2** respectively.

We initially observed crystals of **1** growing in a tube consisting of a mixture of the trimers  $\text{V}_3(\mu_3\text{-O})(\text{O}_2)(\mu_2\text{-O}_2\text{P}(\text{Bn})_2)_6(\text{H}_2\text{O})$  and  $\text{V}_3(\mu_3\text{-O})(\text{O}_2)(\mu_2\text{-O}_2\text{P}(\text{Bn})_2)_6(\text{py})^{19}$  in wet  $\text{CH}_2\text{Cl}_2$  and hexane.† The observation of orange crystals prompted a single crystal X-ray study, which revealed that **1** was produced and crystallized as a tetrahydrate, with one crystallographically independent water molecule of solvation per asymmetric unit, disordered over three positions; this was refined with the sum of the occupancies constrained to one. Crystals of **2**·3(THF) were obtained by layering a solution of **2** in THF with hexane. For both **1** and **2**, single crystal X-ray diffraction studies¶ reveal cubane core structures consisting of four diagonally arranged metal atoms and four triply bridging oxygen atoms at the vertices, with terminal oxygen atoms on each metal atom (arranged so that the four metal to oxygen atom bonds are all parallel), and dibenzylphosphinate ligands bridging the four faces of the cube; see Fig. 1 and 2. We have previously described these structures as consisting of two  $[\text{M}_2\text{O}_4]^{2+}$  halves held together by the bridging phosphinate ligands.<sup>18a</sup> With these electron deficient materials, we have distortions from perfect cubane core geometries resulting in elongations along the axes formed by the bridging phosphinate groups, in contrast to the almost perfect geometries exhibited by more electron rich clusters.<sup>22</sup>

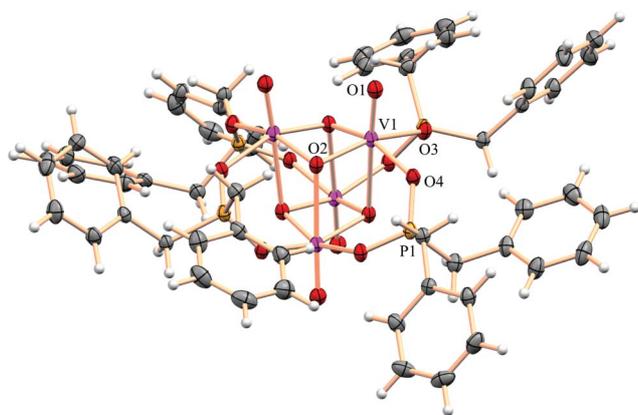


Fig. 1 Mercury<sup>21</sup> drawing of **1** with 50% probability ellipsoids.

Table 1 lists selected bond distances and angles for **1** and **2** and for the complex  $\text{Mo}_4(\mu_3\text{-O})_4(\mu_2\text{-O}_2\text{P}(\text{Bn})_2)_4(\text{O}_4)$ , **3**.<sup>18a</sup> Complex **3** did crystallize in the form of two different solvates, namely **3**·2.75 $\text{C}_7\text{H}_8$  and **3**·2 $\text{CH}_2\text{Cl}_2$  and the latter solvate crystallized in a monoclinic  $I4_1/a$  setting, equivalent to that of **1**·4( $\text{H}_2\text{O}$ ) and **2**·3(THF) and thus the data listed in Table 1 are for isomorphous compounds, as an examination of the arrangement in the benzyl groups depicted in Fig. 1 and 2 (and that of **3**·2 $\text{CH}_2\text{Cl}_2$ <sup>18a</sup>) would attest. The data in Table 1 show that while the metal to metal distance ( $\text{M}_1 \cdots \text{M}_2$ ) is short for **1**, that for **2** at 2.6354(5) Å represents a long W–W bond in contrast to those in dimeric

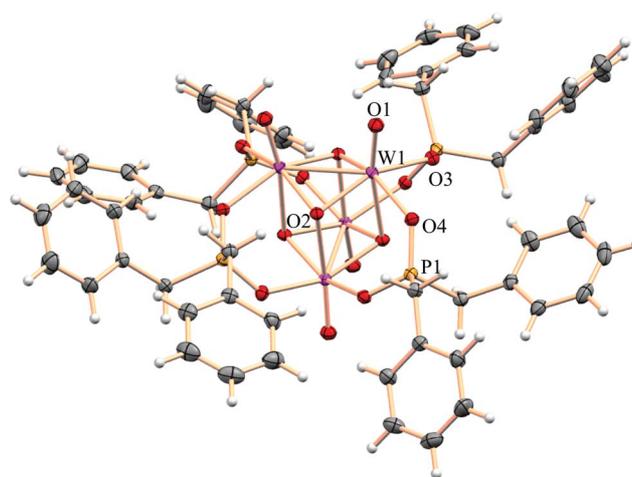


Fig. 2 Mercury<sup>21</sup> drawing of **2** with 50% probability ellipsoids.

Table 1 Selected distances and bond angles for **1**, **3** and **2**

	<b>1</b> (V)	<b>3</b> (Mo)	<b>2</b> (W)
Distances/Å			
$\text{M}_1 \cdots \text{M}_2$	2.7610(8)	2.6261(5)	2.6354(5)
$\text{O}_2 \cdots \text{O}_5$	2.419(2)	2.7560(2)	2.7970(4)
$\text{M}_1 \cdots \text{M}_3$	3.3300(6)	3.4091(2)	3.4019(4)
$\text{O}_2 \cdots \text{O}_6$	2.761(2)	2.7482(2)	2.7262(3)
$\text{M}_1\text{-O}_1$	1.5786(16)	1.668(2)	1.6964(19)
$\text{M}_1\text{-O}_2$	1.8161(13)	1.9555(19)	1.9809(16)
$\text{M}_1\text{-O}_5$	1.8919(13)	1.9612(19)	1.9825(16)
$\text{M}_1\text{-O}_7$	2.4392(15)	2.399(2)	2.3626(19)
$\text{M}_1\text{-O}_3$	1.9697(13)	2.0793(19)	2.0521(17)
$\text{M}_1\text{-O}_4$	1.9427(13)	2.0586(19)	2.0742(17)
$\text{O}_3' \cdots \text{O}_4$	2.561(2)	2.5823(2)	2.5871(3)
Bond angles/°			
$\text{O}_1\text{-M}_1\text{-O}_7$	177.40(6)	170.36(8)	168.99(7)
$\text{M}_1\text{-O}_2\text{-M}_2$	96.23(6)	84.21(7)	83.35(6)
$\text{O}_2\text{-M}_1\text{-O}_5$	81.41(6)	89.44(8)	89.77(7)
$\text{O}_1\text{-M}_1\text{-O}_2$	103.16(7)	109.09(9)	110.23(8)
$\text{O}_1\text{-M}_1\text{-O}_3$	99.44(7)	97.61(9)	97.66(8)
$\text{O}_1\text{-M}_1\text{-O}_4$	99.74(7)	98.92(9)	96.55(8)
$\text{O}_1\text{-M}_1\text{-O}_5$	102.31(7)	109.10(9)	110.29(8)

W(v) species (e.g., anti- $[\text{L}_2\text{W}_2\text{O}_4]^{2+}$ ) where shorter distances of 2.565(1) Å were noted.<sup>15c</sup> This distance is much shorter than that for the tungsten(vi) cubane clusters<sup>11–14</sup> mentioned above, where distances averaging 3.29(4) Å (indicative of no interaction between the metal atoms) were observed. Evidence of this interaction is also present in the UV-vis absorption. In this regard complex **3** displays two absorptions in  $\text{CH}_2\text{Cl}_2$  at 314 and 450 nm where the second transition can be assigned to a Mo–Mo  $\sigma \rightarrow \sigma^*$  transition. Notably complex **1** only displays one intense absorption at 340 nm, which is presumably a ligand to metal charge transfer band. That for **2** is at 374 nm with the  $\sigma \rightarrow \sigma^*$  transition appearing as a nondescript buried peak on this large absorption.

As expected, the  $M_1-O_1$  distance in **1** at 1.5786(16) Å and the corresponding *trans*  $M_1-O_7$  at 2.4392(15) Å are the shortest and the longest, respectively, out of the three complexes in Table 1. The distortion from perfect cubane cores is evident in that there are much larger distances observed for  $M_1 \cdots M_3$  compared to the  $M_1 \cdots M_2$  interactions; see Table 1. The distance labeled as  $O_2 \cdots O_5$  also varies among the three cubes with that for **1** being the shortest at 2.419(2) Å, compared to those in **3** and **2** at 2.7560(2) and 2.7970(4) Å, respectively. Somewhat related is the fact that the  $O_1-M_1-O_7$  angle for **1** at 177.40(6)° is very nearly linear whereas those for **2** and **3** at 168.99(7) and 170.36(8)°, respectively, deviate more. These effects may be attributed to the repulsive effects of the metal to metal atom interaction or more simply the fact that as the metal atoms form bonds, the oxygen atoms move apart as a consequence. This also results in the  $M_1-O_2-M_2$  and  $O_2-M_1-O_5$  angles being the largest and smallest, respectively, for **1** compared to **2** and **3**; see Table 1. The last four rows of data in Table 1 illustrate the fact that the geometry at each metal center can be considered as distorted square pyramidal, with the metal centers being raised out of the plane defined by the four pseudo-equatorial oxygen atoms. The listings for the corresponding distances reveal that those for the oxygen to metal atoms are significantly shorter in **1** compared to **2** and **3** with the exception of the bond *trans* to the multiply bonded oxo ligand. The  $O_3' \cdots O_4$  listing in Table 1 illustrates the accommodating nature of the phosphinate bridge ranging from 2.561(2) Å in **1** to 2.5871(3) Å in **3**.

In summary, we detail the synthetic routes leading to vanadium and tungsten tetrameric complexes of the stoichiometry  $[M_4(\mu_3-O)_4]^{2+}$ . While complexes containing this core were previously reported for vanadium, albeit in the form of extended clusters, this is the first report for a tungsten(v) cluster with this core geometry.

## Notes and references

† Synthesis of **1**:  $V_3(\mu_3-O)_2(\mu_2-O)_2P(Bn)_6(H_2O)^{19}$  (0.0500 g, 0.0295 mmol) was dissolved in 10 mL of  $CH_2Cl_2$  at 20 °C. To this light blue-green solution was added  $tBuOOH$  (0.016 mL of 5.5 M) in decane upon which the solution turned dark purple. About 5 drops of de-ionized  $H_2O$  were then added. After 3 h of stirring, the solution had turned reddish-orange in color. The solvent was reduced to about 1 mL, kept at -20 °C overnight and then filtered. To the filtrate was added 30 mL of hexane and this mixture was kept at -20 °C for 2 d resulting in an orange crystalline precipitate, which was then filtered off, rinsed with hexane and then dried under a vacuum to give 0.0050 g of **1** (0.0038 mmol, 17.2% yield with respect to  $V_3(\mu_3-O)_2(\mu_2-O)_2P(Bn)_6(H_2O)$ ). Anal. (Galbraith Laboratories, Knoxville, TN) calcd for  $C_{56}H_{56}V_4O_{16}P_4$ : C 51.24, H 4.30. Found: C 50.84, H 4.58%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) = 2.86 (dd, 8,  $^2J_{HP} = 23.3$ ,  $^2J_{HaHb} = 14.7$  Hz,  $CH_3P$ ), 2.90 (dd, 8,  $^2J_{HP} = 27.7$ ,  $^2J_{HaHb} = 14.7$  Hz,  $CH_bP$ ), 7.05–7.36 (m, 40, ( $C_6H_5CH_2$ )).  $^{31}P\{^1H\}$  NMR (162 MHz,  $CDCl_3$ , relative to  $H_3PO_4$ ):  $\delta$  (ppm) = 60.6 (s, 1P). UV-vis spectrum ( $CH_2Cl_2$ ) 340 nm. IR (neat,  $cm^{-1}$ ): 3062 (vw), 3029 (vw), 1602 (vw), 1496 (m), 1454 (m), 1398 (vw), 1245 (vw), 1190 (vw), 1145 (vw), 1101 (m), 1070 (m), 1012 (s), 1000 (s), 990 (s), 914 (vw), 847 (br), 779 (w), 698 (s).

§ Synthesis of **2**:  $W(CO)_6$  (0.100 g, 0.284 mmol) and bis(benzyl)phosphinic acid (0.070 g, 0.283 mmol) were placed in a sealed tube with 6 mL of a 1:1 mixture of ethanol and THF and heated at 120 °C for 36 h. The resulting dark black-blue solution was then cooled to 20 °C. After 1 d the yellow crystals that had formed were filtered off, rinsed with ethanol and then dried under vacuum to yield **2** (0.018 g, 0.010 mmol, 13.75% yield based on  $W(CO)_6$ ). Anal. (Galbraith Laboratories, Knoxville, TN) calcd for  $C_{56}H_{56}W_4O_{16}P_4$ : C 36.47, H 3.06. Found: C 36.63, H 3.23%.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) = 2.93 (dd, 8,  $^2J_{HP} = 19.5$ ,  $^2J_{HaHb} = 14.8$  Hz,  $CH_3P$ ), 3.06 (dd, 8,  $^2J_{HP} = 14.9$ ,  $^2J_{HaHb} = 14.8$  Hz,  $CH_bP$ ), 7.04–7.22 (m, 40, ( $C_6H_5CH_2$ )).  $^{31}P\{^1H\}$  NMR (162 MHz,  $CH_2Cl_2$ , relative to  $H_3PO_4$ ):  $\delta$  (ppm) = 68.4 (s, 1P). UV-vis spectrum ( $CH_2Cl_2$ ) 374 nm. IR (neat,  $cm^{-1}$ ):

3062 (vw), 3030 (vw), 1602 (vw), 1496 (m), 1454 (m), 1398 (vw), 1248 (w), 1194 (vw), 1143 (vw), 1087 (m), 1071 (m), 1043 (w), 1012 (s), 1000 (s), 979 (s), 916 (m), 854 (m,br), 779 (m), 694 (s).

¶ Crystal data for **1**:  $C_{56}H_{56}O_{16}P_4V_4 \cdot 4(H_2O)$ ,  $M = 1376.65$ , tetragonal,  $a = 22.306(4)$  Å,  $b = 22.306(4)$  Å,  $c = 12.824(2)$  Å,  $V = 6380.7(19)$  Å<sup>3</sup>,  $T = 100(2)$  K, space group  $I4_1/a$ ,  $Z = 4$ ,  $\mu = 0.738$  mm<sup>-1</sup>, 22 239 reflections measured, 4828 independent reflections ( $R_{int} = 0.0504$ ).  $R_1 = 0.0397$  ( $I > 2\sigma(I)$ ).  $wR(F^2) = 0.0899$  ( $I > 2\sigma(I)$ ).  $R_1 = 0.0691$  (all data).  $wR(F^2) = 0.102$  (all data). Crystal data for **2**:  $C_{56}H_{56}O_{16}P_4W_4 \cdot 3(C_4H_8O)$ ,  $M = 2060.56$ , tetragonal,  $a = 22.771(4)$  Å,  $b = 22.771(4)$  Å,  $c = 13.107(2)$  Å,  $V = 6796(2)$  Å<sup>3</sup>,  $T = 100(2)$  K, space group  $I4_1/a$ ,  $Z = 4$ ,  $\mu = 6.915$  mm<sup>-1</sup>, 17 299 reflections measured, 5083 independent reflections ( $R_{int} = 0.0225$ ).  $R_1 = 0.0189$  ( $I > 2\sigma(I)$ ).  $wR(F^2) = 0.0425$  ( $I > 2\sigma(I)$ ).  $R_1 = 0.0241$  (all data).  $wR(F^2) = 0.0457$  (all data).

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