



Cite this: *Inorg. Chem. Front.*, 2015, 2, 254

## Two new members of the niobium-substituted polytungstophosphate family based on hexalacunary $[H_2P_2W_{12}O_{48}]^{12-}$ building blocks†

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Two structurally novel nanoscale clusters  $\{[Nb_6(O_2)_4P_2W_{12}O_{57}]_2\}^{20-}$  (**1**) and  $\{[P_2W_{12}Nb_7O_{63}(H_2O)_2]_4-Nb_4O_4(OH)_6\}^{30-}$  (**2**) were synthesized under specific reaction conditions. Cluster **1** displays an unprecedented di-Nb–O–Nb-linked Wells–Dawson dimer, whilst cluster **2** contains the highest nuclearity niobium containing heteropolyoxometalate to date. Furthermore, <sup>31</sup>P and <sup>183</sup>W NMR spectra indicate that the polyanion **2** remains stable in solution. The photocatalytic activities of the respective salts **1a**, **2a** and  $K_6[\alpha-P_2W_{18}O_{62}]\cdot 14H_2O$  for H<sub>2</sub> evolution were evaluated. The enhanced photocatalytic activity of **2a** may be attributed to the incorporation of Nb into the polyoxotungstate framework.

Received 18th October 2014,  
Accepted 17th December 2014

DOI: 10.1039/c4qi00169a

rsc.li/frontiers-inorganic

### Introduction

Polyoxometalates (POMs)<sup>1</sup> are an exceptional family of metal-oxo clusters, primarily constructed of Mo, W, V and Nb in their high oxidation states.<sup>2</sup> This class of compounds has attracted great attention during the last two decades, not only due to their intriguing structural diversity<sup>3</sup> and remarkable chemical properties,<sup>4</sup> but also due to their various potential applications ranging from catalysis, magnetism, biomedicine, and materials science, to nanotechnology.<sup>5</sup> The sustained interest in POM chemistry is reflected by the near exponential increase in the number of publications pertaining to new POM species over the last decade.<sup>2–5</sup>

Among the vast POM family, transition-metal-substituted POMs constitute the most expanding subfield, chiefly due to

well-established synthetic strategies, which utilize various lacunary POM species as secondary building units to construct target compounds with various properties.<sup>6</sup> In particular, the hexalacunary  $[H_2P_2W_{12}O_{48}]^{12-}$  ( $P_2W_{12}$ ) fragment has shown tremendous potential for the assembly of larger transition-metal-substituted POMs.<sup>7–11</sup> To date, a considerable number of polyoxotungstate architectures have been synthesized, such as the monomeric, dimeric and tetrameric aggregates reported by Gouzerh and co-workers,<sup>7a,b</sup> and the  $P_2W_{12}$ -based trimeric family prepared by Wang and co-workers.<sup>8a,9b</sup> Fang and co-workers also recently communicated a spectacular structure, which can be described as the assembly of 16 Wells–Dawson subunits.<sup>8c</sup> A comprehensive literature survey of transition-metal-substituted POMs synthesized from  $P_2W_{12}$  precursors is shown in Table 1.

In contrast to the rapid development of reported 3d transition metal containing species, the synthesis and characterisation of niobium-substituted polyoxotungstates remains relatively unexplored,<sup>11–19</sup> with the first Nb-substituted POM obtained in 1984.<sup>12</sup> The substitution of  $W^{VI}$  in polyoxotungstates with  $Nb^V$  is of particular interest, because of the expected enhanced basicity and nucleophilicity of the Nb-bound oxygen atoms, as well as the higher reactivity of the resulting polyanion.<sup>20</sup> We have already demonstrated that niobium atoms incorporated in  $P_2W_{12}$  are reactive sites with a strong tendency towards oligomer formation through Nb–O–Nb bonds,<sup>11c</sup> as seen in the Keggin type analogues.<sup>13–15</sup>

Herein, we present an important expansion of this family with two Nb-containing tungstophosphates, the dimeric Nb<sub>12</sub>-containing 24-tungsto-4-phosphate  $[H_{13}\{Nb_6(O_2)_4P_2W_{12}O_{57}\}_2]^{7-}$  (**1**) and the tetrameric Nb<sub>32</sub>-containing 48-tungsto-8-phosphate

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†Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format, Fig. S1–S8, and BVS results of all of the oxygen atoms on polyanions **1** and **2**. CSD 426569 (**1**) and 426570 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4qi00169a

Table 1 Survey of coordination chemistry of the hexavacant tungstophosphate

Polyanion	The nuclearity of M <sup>a</sup>	Reference
Iron-substituted derivatives		
[H <sub>4</sub> P <sub>2</sub> W <sub>12</sub> Fe <sub>9</sub> O <sub>56</sub> (OAc) <sub>7</sub> ] <sup>6-</sup>	9	Gouzerh <i>et al.</i> (2005) <sup>7a</sup>
[H <sub>5.5</sub> P <sub>8</sub> W <sub>49</sub> Fe <sub>27</sub> O <sub>248</sub> ] <sup>26-</sup>	27	Gouzerh <i>et al.</i> (2005) <sup>7a</sup>
[H <sub>12</sub> P <sub>4</sub> W <sub>28</sub> Fe <sub>8</sub> O <sub>120</sub> ] <sup>16-</sup>	8	Gouzerh <i>et al.</i> (2005) <sup>7b</sup>
[(H <sub>2</sub> Fe <sub>2</sub> P <sub>2</sub> W <sub>16</sub> O <sub>60</sub> ) <sub>3</sub> ] <sup>24-</sup>	6	Cronin <i>et al.</i> (2010) <sup>7c</sup>
Manganese-substituted derivatives		
[[Mn(H <sub>2</sub> O) <sub>4</sub> ] <sub>2</sub> {WO <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> {WO(H <sub>2</sub> O)} <sub>3</sub> (P <sub>2</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ] <sup>22-</sup>	2	Wang <i>et al.</i> (2008) <sup>8a</sup>
[Ce <sub>3</sub> Mn <sub>2</sub> O <sub>6</sub> (OAc) <sub>6</sub> (H <sub>2</sub> O) <sub>9</sub> ] <sub>2</sub> {Mn <sub>2</sub> P <sub>2</sub> W <sub>16</sub> O <sub>60</sub> ] <sub>3</sub> <sup>20-</sup>	6	Wang <i>et al.</i> (2009) <sup>8b</sup>
[Mn <sub>40</sub> P <sub>32</sub> W <sub>224</sub> O <sub>888</sub> ] <sup>144-</sup>	40	Fang, Kögerler <i>et al.</i> (2011) <sup>8c</sup>
Cobalt-substituted derivatives		
[[W <sub>2</sub> Co <sub>2</sub> O <sub>8</sub> (H <sub>2</sub> O) <sub>2</sub> ](P <sub>2</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>2</sub> ] <sup>20-</sup>	2	Wang <i>et al.</i> (2008) <sup>9a</sup>
[[Co(H <sub>2</sub> O) <sub>4</sub> ] <sub>6</sub> {WO(H <sub>2</sub> O)} <sub>3</sub> (P <sub>2</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ] <sup>18-</sup>	6	Wang <i>et al.</i> (2010) <sup>9b</sup>
[(Co <sub>2</sub> P <sub>2</sub> W <sub>16</sub> O <sub>60</sub> ) <sub>3</sub> ] <sup>24-</sup>	6	Cronin <i>et al.</i> (2009) <sup>9c</sup>
Nickel-substituted derivatives		
[(Ni <sub>2</sub> P <sub>2</sub> W <sub>16</sub> O <sub>60</sub> ) <sub>3</sub> ] <sup>30-</sup>	6	Cronin <i>et al.</i> (2010) <sup>7c</sup>
[[Ni <sub>3.5</sub> (H <sub>2</sub> O) <sub>13</sub> ]{WO <sub>2</sub> (H <sub>2</sub> O)} <sub>2</sub> {WO(H <sub>2</sub> O)} <sub>3</sub> (P <sub>2</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ] <sup>18.75-</sup>	3.5	Wang <i>et al.</i> (2008) <sup>9a</sup>
[[Ni(H <sub>2</sub> O) <sub>4</sub> ] <sub>6</sub> {WO(H <sub>2</sub> O)} <sub>3</sub> (P <sub>2</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ] <sup>18-</sup>	6	Wang <i>et al.</i> (2010) <sup>9b</sup>
Copper-substituted derivative		
[[Cu <sub>3</sub> (H <sub>2</sub> O) <sub>9</sub> ]{WO <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> }{WO(H <sub>2</sub> O)} <sub>3</sub> (P <sub>2</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ] <sup>20-</sup>	3	Wang <i>et al.</i> (2008) <sup>8a</sup>
Uranium-substituted derivative		
[Li(H <sub>2</sub> O)K <sub>4</sub> (H <sub>2</sub> O) <sub>3</sub> ]{(UO <sub>2</sub> ) <sub>4</sub> (O <sub>2</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> }(PO <sub>3</sub> OH) <sub>2</sub> P <sub>6</sub> W <sub>36</sub> O <sub>136</sub> ] <sup>25-</sup>	4	Kortz <i>et al.</i> (2008) <sup>10</sup>
Niobium-substituted derivatives		
[P <sub>2</sub> W <sub>12</sub> O <sub>56</sub> (NbO <sub>2</sub> ) <sub>6</sub> ] <sup>12-</sup>	6	Hill <i>et al.</i> (1997) <sup>11a</sup>
[H <sub>6</sub> P <sub>2</sub> W <sub>12</sub> Nb <sub>4</sub> O <sub>59</sub> (NbO <sub>2</sub> ) <sub>2</sub> ] <sup>8-</sup>	12	Yue <i>et al.</i> (2014) <sup>11b</sup>
[(Nb <sub>4</sub> O <sub>6</sub> (OH) <sub>4</sub> ]{Nb <sub>6</sub> P <sub>2</sub> W <sub>12</sub> O <sub>61</sub> }] <sup>36-</sup>	28	Niu <i>et al.</i> (2014) <sup>11c</sup>

<sup>a</sup> The number of transition metal ions encapsulated within the polyanion structure.

[H<sub>14</sub>{P<sub>2</sub>W<sub>12</sub>Nb<sub>7</sub>O<sub>63</sub>(H<sub>2</sub>O)<sub>2</sub>}]<sub>4</sub>{Nb<sub>4</sub>O<sub>4</sub>(OH)<sub>6</sub>}]<sup>16-</sup> (**2**), which were isolated as the salts K<sub>7</sub>[H<sub>13</sub>{Nb<sub>6</sub>(O<sub>2</sub>)<sub>4</sub>P<sub>2</sub>W<sub>12</sub>O<sub>57</sub>}]<sub>2</sub>·31H<sub>2</sub>O (**1a**) and (NH<sub>4</sub>)<sub>16</sub>[H<sub>14</sub>{P<sub>2</sub>W<sub>12</sub>Nb<sub>7</sub>O<sub>63</sub>(H<sub>2</sub>O)<sub>2</sub>}]<sub>4</sub>{Nb<sub>4</sub>O<sub>4</sub>(OH)<sub>6</sub>}]·16H<sub>2</sub>O (**2a**), respectively. Furthermore, preliminary photocatalytic properties indicated that both compounds **1a** and **2a** exhibit significantly enhanced photocatalytic activity compared to similar structures.

## Results and discussion

### Synthesis

Typically, lacunary POMs are inorganic ligands derived from parent plenary structures, and can effectively bind transition metals with large range of nuclearities and diverse structural topologies currently realised.<sup>21</sup> Incorporation of transition metal ions into lacunary cluster sites is a well-performed strategy for the construction of macromolecular POM assemblies.

In this context, multi-vacant Wells–Dawson polyoxoanions are of particular interest, as they possess vacant sites that could capture more transition metal ions and link them together to form large molecular architectures.<sup>7–11,22</sup> It is worth noting that the monomeric, peroxo-niobium containing 12-tungsto-2-phosphate [(NbO<sub>2</sub>)<sub>6</sub>P<sub>2</sub>W<sub>12</sub>O<sub>56</sub>]<sup>12-</sup> (abbreviated as {(NbO<sub>2</sub>)<sub>6</sub>P<sub>2</sub>W<sub>12</sub>}), reported first by Hill and coworkers as early as 1997, has received little attention.<sup>11a</sup> To date, there is only one dimeric derivative reported, in which a {Nb<sub>12</sub>} assembly is wrapped by two P<sub>2</sub>W<sub>12</sub> units.<sup>11b</sup> Recently, a direct method using a new one-pot synthetic strategy, enabled the study of the [Nb<sub>6</sub>O<sub>19</sub>]<sup>8-</sup> interaction with P<sub>2</sub>W<sub>12</sub>, which resulted in a

tetrameric Nb<sub>28</sub>-containing polyanion.<sup>11c</sup> This indicated that it is possible to extend and grow this family following a systematic control of a combination of components, such as pH and temperature, to obtain large architectures.

The synthetic procedures for **1** and **2** are simple, and both compounds could be formed by carefully controlling the reaction parameters. It is well known that P<sub>2</sub>W<sub>12</sub> is a metastable precursor that easily transforms in aqueous solution to other Wells–Dawson derivatives,<sup>7b,c,8b,9a,c,23</sup> however, after insertion of six Nb ions, a more stable subunit is formed, which is evident in both **1** and **2**.

An interesting aspect in the molecular growth of **1** and **2** is the possible formation of {(NbO<sub>2</sub>)<sub>x</sub>Nb<sub>6-x</sub>P<sub>2</sub>W<sub>12</sub>} *in situ*, in which the oxoniobium(v) surface is more basic and reactive than its oxotungsten(vi) counterpart. If so, the Nb<sup>v</sup>-substituted Wells–Dawson species serves as a likely starting point of aggregation, which is seldom for plenary POM structures.<sup>8c</sup> To rationalize the molecular growth, we postulate three concurrent reactions central to the formation of **1** and **2** under the selected reaction conditions (Fig. 1):

(1) The decomposition of [Nb<sub>6</sub>O<sub>19</sub>]<sup>8-</sup> in H<sub>2</sub>O<sub>2</sub> aqueous solution, resulting in the release of intermediate {NbO<sub>2</sub>} species.

(2) The incorporation of {NbO<sub>2</sub>} into P<sub>2</sub>W<sub>12</sub> at room temperature, and the formation of the peroxo precursor {(NbO<sub>2</sub>)<sub>6</sub>P<sub>2</sub>W<sub>12</sub>}.<sup>11a</sup>

(3) The stepwise cleavage of the O–O bonds followed by condensation to Nb–O–Nb bridges in acid solution on heating, which stabilizes these highly charged species.

The balanced chemical reaction for the formation of **1** and **2** is presented in eqn (1) and (2), respectively.

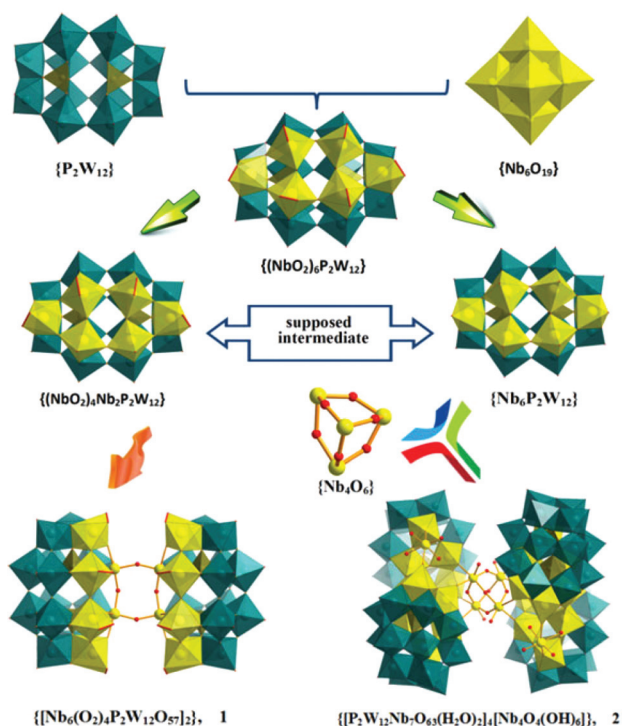
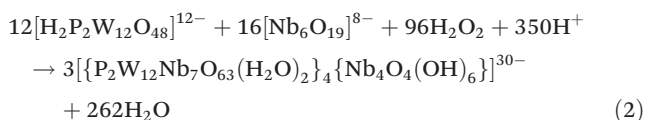
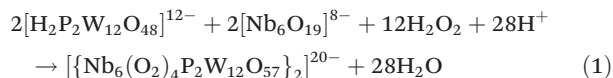


Fig. 1 Postulated steps in the formation of **1** and **2**.



It is worth noting that the color of the starting solution turns from bright-yellow to light-yellow and finally colorless upon heating, suggesting the thermal decomposition of the peroxy groups. As expected, the reaction at 70 °C for 6 h gave a pale yellow solution with **1** as the major product, and **2** could be obtained with prolonged heating at 80 °C until the solution turned colorless. Moreover, the lower the pH, the shorter the required heating time. If the reaction is performed at pH 2.0, it takes about 36 h to turn colorless, whereas this can be done in about just 10 h when the pH value is 1.7. This demonstrates that small changes in the synthetic conditions can have considerable effect on the formation reaction thermodynamics of the product.

### Structure of the polyanions

The structure of **1** (Fig. 2) comprises two hexalacunary  $\text{P}_2\text{W}_{12}$  fragments with the vacant sites occupied by four peroxo-terminal  $\{\text{NbO}_2\}$  groups (yellow polyhedra) and two oxo-bridging  $\{\text{NbO}\}$  groups (yellow balls), resulting in an assembly with idealized  $C_{2v}$  symmetry. Each of the four peroxo-Nb atoms is coordinated by four  $\mu_2$ -oxo, one  $\mu_4$ -oxo (cap sites) or  $\mu_3$ -oxo

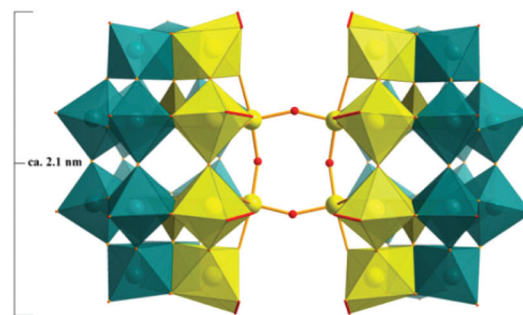


Fig. 2 Combined polyhedral/ball-and-stick representation of polyanion **1**. All cations and crystal waters are omitted for clarity. Teal polyhedra  $\{\text{WO}_6\}$ ; yellow polyhedra  $\{\text{Nb}(\text{O}_2)\text{O}_5\}$ ; yellow balls Nb; dark-yellow polyhedra  $\{\text{PO}_4\}$ ; red balls O.

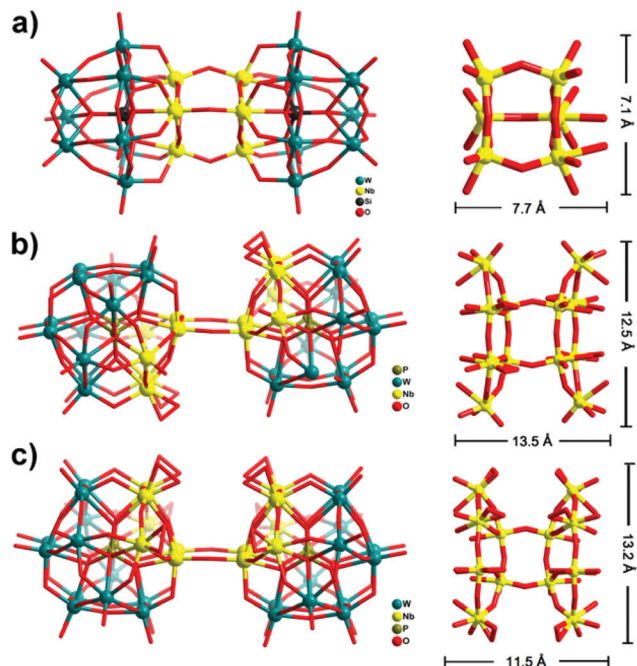
(belt sites), and one terminal  $\eta^2$ -coordinated peroxy ligand, leading to a distorted pentagonal-bipyramidal coordination sphere, whereas the two oxo-Nb atoms exhibit octahedral coordination. The two half-units  $[\text{Nb}_6(\text{O}_2)_4\text{P}_2\text{W}_{12}\text{O}_{57}]^{10-}$  (Fig. S1†) are hence fused *via* the two parallel, equatorial Nb–O–Nb bridges (Fig. S2†), and are related by a mirror plane.

The structure of **1** suggests that the peroxy groups in the belt sites of the all-peroxy precursor  $\{(\text{NbO}_2)_6\text{P}_2\text{W}_{12}\}$  are preferentially reduced to hydroxy groups with respect to the cap sites, which then initiates dimerization.

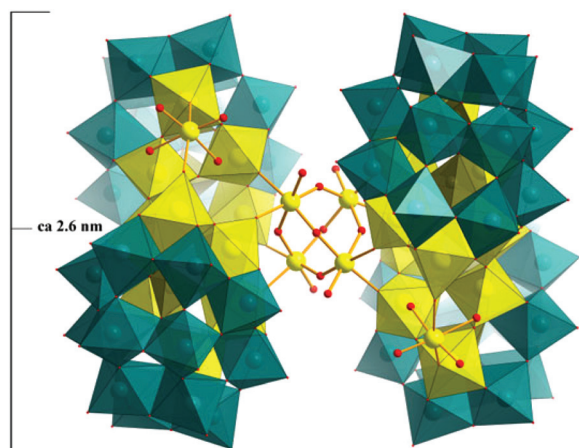
Such dimerization through Nb–O–Nb bridges is known for the Nb-substituted Keggin anions (Fig. 3a).<sup>12,13a,c,14a</sup> As mentioned above, only one di-Nb–O–Nb-linked Wells–Dawson-dimer,  $[\{\text{H}_6\text{P}_2\text{W}_{12}\text{Nb}_4\text{O}_{59}(\text{NbO}_2)_2\}_2]^{8-}$  (**1'**) has so far been reported very recently, with the peroxy groups '*trans*' to each other (Fig. 3b).<sup>11b</sup> We now present a different di-Nb–O–Nb-bridged Wells–Dawson-dimer with '*cis*' peroxy groups (**1**), which represents a previously unreported structure type. This *cis*-dimeric configuration seems especially relevant from a mechanistic point of view, providing a second perspective on the possible Nb–O–Nb linkage growth, and leading to further aggregation of more subunits with the Nb atoms from the equatorial sites, as in the case of polyanion **2**.

The crystal structure of **2** shows a large  $\text{Nb}_{32}$ -containing 48-tungsto-8-phosphate (Fig. 4), comprising the dimeric  $[\text{P}_4\text{W}_{24}\text{Nb}_{14}\text{O}_{126}(\text{H}_2\text{O})_4]^{18-}$  subunits (Fig. 5a), connected by four Nb–O–Nb bridges in a perpendicular arrangement, and resulting in an adamantane-like  $\{\text{Nb}_4\text{O}_6\}$  core (Fig. S3a†). All four Nb ions within  $\{\text{Nb}_4\text{O}_6\}$  exhibit octahedral geometry coordinated by five  $\mu_2$ -oxygen atoms and one terminal oxygen atom with an average Nb–O bond length of 1.990 (8) Å. The O–Nb–O bond angles are between 85.5(5) and 95.0(5). Fig. 5a/b illustrates the connectivity within each dimeric subunit, in which two peroxy-free derivatives,  $[\text{Nb}_6\text{P}_2\text{W}_{12}\text{O}_{61}]^{10-}$  ( $\{\text{Nb}_6\text{P}_2\text{W}_{12}\}$ ), are linked by two Nb–O–Nb bridges and 'capped' by two extra Nb centers. Each of the latter (Nb8 in Fig. 5b) is linked to two oxo ligands of each Wells–Dawson unit, and the coordination sphere is completed by two terminal oxo and two aqua ligands.



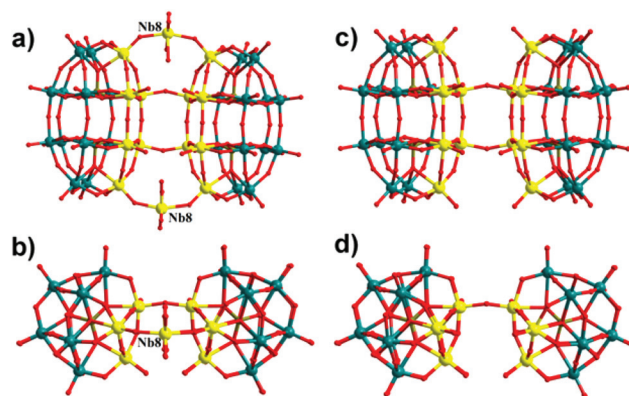


**Fig. 3** Comparison of the Nb–O–Nb bridges to polyanions **1** and **1'** and the Keggin-based niobium-substituted polyanions. (a) The 'double Keggin' structure of  $[\text{Si}_2\text{Nb}_6\text{W}_{18}\text{O}_{77}]^{8-}$ , in which two  $\{\text{Nb}_3\text{SiW}_9\text{O}_{40}\}$  subunits are linked through three Nb–O–Nb bridges.<sup>13c</sup> In the case of the 'double Wells–Dawson' structure, it can clearly be seen how the  $\{\text{Nb}_6(\text{O}_2)_2\text{P}_2\text{W}_{12}\text{O}_{59}\}^{11b}$  or  $\{\text{Nb}_6(\text{O}_2)_4\text{P}_2\text{W}_{12}\text{O}_{57}\}$  subunits are fused together by two Nb–O–Nb bridges, forming (b) **1'** *trans*- or (c) **1** *cis*-dimer, respectively.

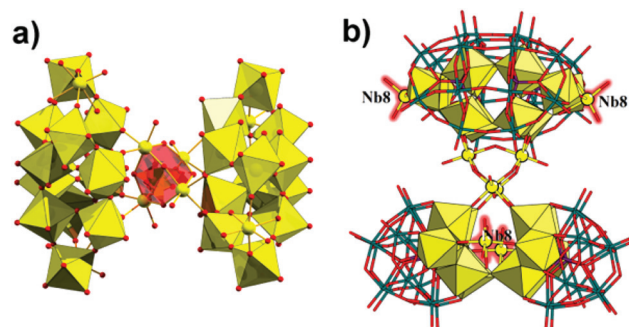


**Fig. 4** Combined polyhedral/ball-and-stick representation of polyanion **2**. All cations and crystal waters are omitted for clarity. Teal polyhedra  $\{\text{WO}_6\}$ ; yellow polyhedra  $\{\text{NbO}_6\}$ ; yellow balls Nb; dark-yellow polyhedra  $\{\text{PO}_4\}$ ; red balls O.

Alternatively, **2** can be viewed as four  $\{\text{P}_2\text{W}_{12}\}$  fragments supporting an unprecedented  $\{\text{Nb}_{32}\}$  core (Fig. 6a), the maximum nuclearity of Nb observed in heteropolyoxometalate chemistry. Such Wells–Dawson-based tetrameric structures have so far been characterized for few compounds,<sup>11c,24–28</sup>



**Fig. 5** Comparisons of the subunit (a/b)  $[\text{P}_4\text{W}_{24}\text{Nb}_{14}\text{O}_{126}]^{18-}$  in **2** and (c/d)  $[\text{P}_4\text{W}_{24}\text{Nb}_{12}\text{O}_{122}]^{20-}$  in  $\{\text{Nb}_{28}(\text{P}_2\text{W}_{12})_4\}^{11b}$  from different directions. Teal balls W; yellow balls Nb; dark-yellow balls P; red balls O.



**Fig. 6** (a) Representation of the unprecedented  $\{\text{Nb}_{32}\}$  cluster in polyanion **2**. (b) The Nb8 atoms in polyanion **2** are highlighted in red rendering.

among which only for  $\{\text{Fe}_{27}\text{P}_8\text{W}_{49}\}^{25}$  and  $\{\text{Nb}_{28}(\text{P}_2\text{W}_{12})_4\}^{11c}$  the hexalacunary  $\{\text{P}_2\text{W}_{12}\}$  fragment is maintained.

Structural analysis reveals that the structure of  $[\text{H}_{14}(\text{P}_2\text{W}_{12}\text{Nb}_7\text{O}_{63}(\text{H}_2\text{O})_2)_4[\text{Nb}_4\text{O}_4(\text{OH})_6]]^{16-}$  is very similar to that of the recently reported cluster  $\{\text{Nb}_{28}(\text{P}_2\text{W}_{12})_4\}^{11c}$  but with subtle differences. For instance, both polyanions form tetrahedrally shaped structures containing four  $\{\text{Nb}_6\text{P}_2\text{W}_{12}\}$  Wells–Dawson units linked together *via* an  $\{\text{Nb}_4\text{O}_6\}$  adamantane core. Despite the fact that  $\text{P}_2\text{W}_{12}$  is metastable, both polyanions have retained this entity throughout the synthetic process. In the previous  $\{\text{Nb}_{28}(\text{P}_2\text{W}_{12})_4\}$ , the subunit is  $[\text{P}_4\text{W}_{24}\text{Nb}_{12}\text{O}_{122}]^{20-}$  in which two  $\{\text{Nb}_6\text{P}_2\text{W}_{12}\}$  moieties are linked by two Nb–O–Nb bridges (Fig. 5c). However, polyanion **2** comprises a  $[\text{P}_4\text{W}_{24}\text{Nb}_{14}\text{O}_{126}]^{18-}$  subunit in which the two  $\{\text{Nb}_6\text{P}_2\text{W}_{12}\}$  moieties are fused together by two Nb–O–Nb bridges and the two additional Nb8 atoms. This result indicates that the subunit may be able to react further with adjacent subunits *via* these exposed axial Nb8 centers, subsequently forming a large structure.

Moreover, the similarity in the fragmentation patterns of **1**,  $\{\text{Nb}_{28}(\text{P}_2\text{W}_{12})_4\}$  and **2** allow the assumption that these clusters share a similar assembly pathway. The three complexes show how it is possible to increase the number of the encapsulated

Nb nuclearity (from 12 and 28 to 32) by slightly changing the synthetic conditions. This result suggests that the new architectures based on the plenary  $\{\text{Nb}_{28}(\text{P}_2\text{W}_{12})_4\}$  species may be successfully accessed.

Bond valence sum (BVS) calculations for **1** and **2** are consistent with W and Nb being in the +6 and +5 oxidation states, respectively.<sup>29</sup> BVS calculations for all oxygen atoms in **2** suggest that all the four terminal ligands in the  $\{\text{Nb}_4\text{O}_6\}$  core are monoprotonated, as well as the two bridging oxygen atoms resulting in an  $\{\text{Nb}_4(\text{OH})_6\}$  core (Fig. S3b<sup>†</sup>). Charge-balance considerations with counter cations suggested that compounds **1a** and **2a** contain some protons, namely  $\text{K}_7[\text{H}_{13}\{\text{Nb}_6(\text{O}_2)_4\text{P}_2\text{W}_{12}\text{O}_{57}\}_2]\cdot 31\text{H}_2\text{O}$  and  $(\text{NH}_4)_{16}[\text{H}_{14}\{\text{P}_2\text{W}_{12}\text{Nb}_7\text{O}_{63}(\text{H}_2\text{O})_2\}_4\{\text{Nb}_4\text{O}_4(\text{OH})_6\}]\cdot 16\text{H}_2\text{O}$ . It should be noted that the very large number of crystallographically independent atoms and parameters makes the direct location of protons from the Fourier maps difficult, as stated already by Nyman and us.<sup>30</sup> Thus, we believe that the thirteen protons in **1a** are delocalized, whereas six protons are localized and fourteen protons are delocalized in **2a**.

### IR spectroscopy

The IR spectra of **1a** and **2a** are similar to that of the plenary Wells–Dawson  $\text{K}_{3.5}\text{Na}_4[\text{H}_{4.5}(\text{NbO}_2)_6\text{P}_2\text{W}_{12}\text{O}_{56}]\cdot 12.5\text{H}_2\text{O}$  (**3a**) (Fig. S4<sup>†</sup>).<sup>11c</sup> Interestingly, the characteristic vibration peak of  $\nu(\text{P}-\text{O})$  at about  $1074\text{ cm}^{-1}$  for **1a** and **2a** shows splitting as compared to the IR spectrum of **3a**, which might be attributed to the structural distortion and the consequent lowering of the symmetry. The medium band around  $712\text{ cm}^{-1}$  for **1a** and **2a** originate from Nb–O–Nb stretching vibrations,<sup>12,13a,d,14,31</sup> whilst absent in the IR spectrum of **3a**. Additionally, the main difference between **1a** and **2a** is the weak intensity band at  $871\text{ cm}^{-1}$  for **1a**, characteristic of the antisymmetric stretching vibrations of peroxy groups.<sup>13a,32</sup> These results are in complete agreement with the solid-state structure.

### NMR spectroscopy

The structural novelty of polyanion **2**, containing an unprecedented  $\{\text{Nb}_{32}\}$  cluster, is very intriguing. We hence explored the solution properties of **2a** redissolved in  $\text{H}_2\text{O}-\text{D}_2\text{O}$  by multinuclear NMR spectroscopy. The  $^{31}\text{P}$  NMR spectrum showed a singlet at  $\delta = -8.1$  ppm, consistent with the eight equivalent phosphate groups. In addition, several weak peaks are also observed, and probably attributed to small transformation or decomposition products, such as previously reported in  $[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{9-}$  reaction system.<sup>19c,33</sup> On the other hand, the  $^{183}\text{W}$  NMR spectrum exhibits six peaks of equal intensity at  $\delta = -124.4, -135.9, -141.5, -165.4, -192.7,$  and  $-195.6$  ppm, corresponding to the six inequivalent tungstens of the solid-state structure (Fig. S5<sup>†</sup>).

### Photocatalytic properties

Photocatalytic water-splitting offers a promising way for environmentally friendly solar-hydrogen production. Great efforts have been made on POM-based photocatalysts over the past few years.<sup>34</sup> Two tantalotungstates have shown photocatalytic

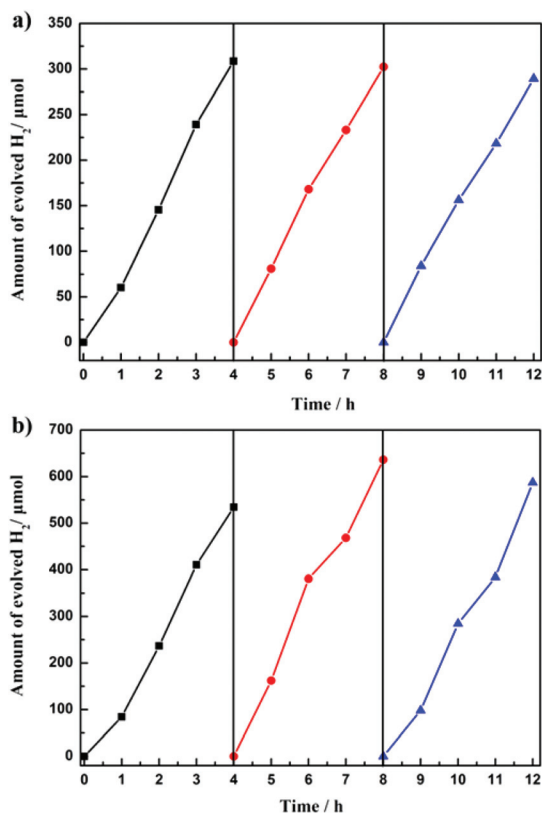
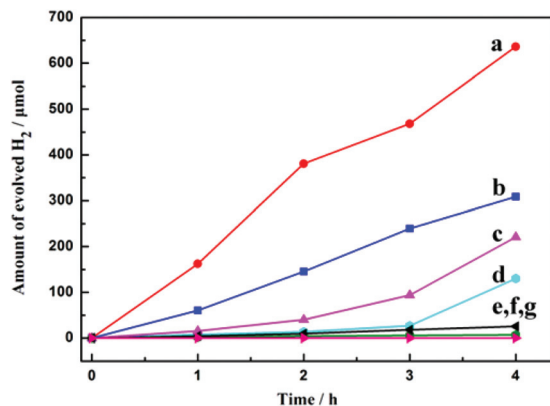


Fig. 7 Time courses of H<sub>2</sub> evolution from 100 mg photocatalyst **1a** (a) and **2a** (b) under UV irradiation in 100 mL of 10% methanol aqueous solution.

properties in the production of H<sub>2</sub>, as demonstrated by Liu *et al.*,<sup>35</sup> showing the potential activities of mixed-metal POMs.

To demonstrate the photocatalytic H<sub>2</sub> evolution activities of the title compounds, 100 mg of **1a** or **2a** and 0.05 mg of H<sub>2</sub>PtCl<sub>6</sub> were dissolved in 100 mL of 10% methanol, which was irradiated under UV using a 500 W mercury lamp. In this system, **1a** or **2a** was used as light photosensitizers and catalysts in the presence of a Pt co-catalyst,<sup>36</sup> and methanol was employed as a sacrificial electron donor, which is the source of the electrons required in the reduction half-reaction of water.<sup>34c,e,35,37</sup> As shown in Fig. 7b, the H<sub>2</sub> evolution rates in the three runs were 1336, 1590 and 1468 μmol h<sup>-1</sup> g<sup>-1</sup> for compound **2a**, respectively. The total evolved H<sub>2</sub> over a 12 h span was 1757.7 μmol, with a corresponding turnover number of 298 (moles of H<sub>2</sub> formed/moles of **2a**). However, for compound **1a**, the H<sub>2</sub> evolution rates in the three runs were 771, 756 and 723 μmol h<sup>-1</sup> g<sup>-1</sup>, respectively, and the total evolved H<sub>2</sub> over the same 12 h span was 900.2 μmol (Fig. 7a).

For comparison, the use of K<sub>6</sub>[α-P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>] $\cdot$ 14H<sub>2</sub>O (**P<sub>2</sub>W<sub>18</sub>**) (control) and K<sub>3.5</sub>Na<sub>4</sub>[H<sub>4.5</sub>(NbO<sub>2</sub>)<sub>6</sub>P<sub>2</sub>W<sub>12</sub>O<sub>56</sub>] $\cdot$ 12.5H<sub>2</sub>O (**3a**) was tested under otherwise identical reaction conditions (lines c and d in Fig. 8). Evolution of H<sub>2</sub> was continuous in 4 h at a rate of 553 and 325 μmol h<sup>-1</sup> g<sup>-1</sup>, respectively, which is significantly smaller than that of **2a**. To investigate the important role of **2a** in the photocatalytic process, three blank experi-



**Fig. 8** Time courses of photocatalytic H<sub>2</sub> evolution over different photocatalytic systems: (lines a–d) compounds **2a** (red), **1a** (blue), **P<sub>2</sub>W<sub>18</sub>** (pink) and **3a** (cyan) as photocatalysts; (lines e–g) the absence of Pt-co-catalyst (black), **2a** (green), CH<sub>3</sub>OH (purple).

ments were performed with no H<sub>2</sub> evolution observed (line e–g in Fig. 8). On the one hand, relatively no H<sub>2</sub> is detected when the Pt-co-catalyst or **2a** is absent, indicating that both play a crucial role in light harvesting for photocatalysis. On the other hand, when the sacrificial solvent (CH<sub>3</sub>OH) is absent, no H<sub>2</sub> production was also observed.

Furthermore, the photocatalysis of **1a**, **2a**, **3a**, and **P<sub>2</sub>W<sub>18</sub>** was accompanied by a color change of the reaction mixture from colorless to deep blue, indicating reduction of W<sup>VI</sup> to W<sup>V</sup>. The color however remained unchanged when the mixture was left under an oxygen-free atmosphere. However, reoxidation of W<sup>V</sup> to W<sup>VI</sup> occurred within hours of air exposure, accompanied with the disappearance of the deep blue color (Fig. S6†). In addition, the significantly higher rates when using **1a** or **2a** versus the **P<sub>2</sub>W<sub>18</sub>** control clearly indicate a positive photocatalytic effect upon Nb incorporation into heteropolytungstates, which is in agreement with the reduced band gaps of 2.58 and 2.43 eV for **1a** and **2a**, respectively, (Fig. S7 and S8†).<sup>38</sup> Finally, the prominently lower H<sub>2</sub> production rates in the case of **1a** and **3a** compared to **2a** may be attributed to the peroxo moieties in their structures, which appear to decrease the catalytic activity. We plan to further study this hypothesis at a later stage.

## Conclusion

In conclusion, two multi-Nb-substituted POMs were synthesized using similar reaction conditions. Our work demonstrates that the {Nb<sub>6</sub>P<sub>2</sub>W<sub>12</sub>} fragment can be stabilized as a dimer or a tetramer by careful synthetic control. Polyanion **1** consists of two oxo bridged [Nb<sub>6</sub>(O<sub>2</sub>)<sub>4</sub>P<sub>2</sub>W<sub>12</sub>O<sub>57</sub>]<sup>10-</sup> units, leading to a dimeric structure. On the other hand, polyanion **2** encapsulates 32 Nb centers, representing the largest transition metal-containing P<sub>2</sub>W<sub>12</sub>-based POM characterized so far. Furthermore, **2a** exhibits good photocatalytic H<sub>2</sub> evolution activity compared to other similar structures. We are currently exploring if other derivatives of **1** and **2** can be prepared.

## Experimental section

### Materials and methods

All reagents were used as purchased without further purification. K<sub>7</sub>[HNb<sub>6</sub>O<sub>19</sub>]·13H<sub>2</sub>O and K<sub>12</sub>[H<sub>2</sub>P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>]·24H<sub>2</sub>O were synthesized according to published procedures.<sup>39</sup> The purity of both compounds was confirmed by infrared spectroscopy. Infrared (IR) spectra were recorded on a AVATAR360 FT-IR spectrophotometer using KBr pellets in the range of 4000–400 cm<sup>-1</sup>. The following abbreviations were used to assign the peak intensities: s = strong, m = medium, and w = weak. C, H and N elemental analyses were measured on a PerkinElmer 2400 II CHNS/O analyzer. Nb and W elemental analyses were obtained by PerkinElmer Optima 2100 DV inductively coupled plasma optical emission spectrometry. NMR spectroscopy for compound **2a** was carried out at room temperature on a 400 MHz JEOL ECS instrument, Jacobs University, Bremen, Germany. The <sup>31</sup>P NMR measurements were performed in 5 mm tubes at a working frequency of 162.1 MHz and H<sub>3</sub>PO<sub>4</sub> (85%) as a reference, whereas the <sup>183</sup>W NMR measurements were performed in 10 mm tubes at a working frequency of 16.7 MHz and 1 M Na<sub>2</sub>WO<sub>4</sub> as a reference. Photocatalytic reactions were carried out in a Pyrex inner-irradiation-type reaction vessel with a magnetic stirrer at room temperature. The reactant solution was evacuated using N<sub>2</sub> several times to ensure complete air removal and then irradiated using a 500 W mercury lamp. The produced H<sub>2</sub> was analyzed by a GC9800 instrument with a thermal conductivity detector and a 5 Å molecular sieve column (2 mm × 2 m) using N<sub>2</sub> as a carrier gas.

**Synthesis of K<sub>7</sub>[H<sub>13</sub>{Nb<sub>6</sub>(O<sub>2</sub>)<sub>4</sub>P<sub>2</sub>W<sub>12</sub>O<sub>57</sub>}<sub>2</sub>]-31H<sub>2</sub>O (**1a**).** K<sub>7</sub>[HNb<sub>6</sub>O<sub>19</sub>]·13H<sub>2</sub>O (1.60 g, 1.17 mmol) was dissolved in a solution consisting of 13.5 mL of 30% aqueous H<sub>2</sub>O<sub>2</sub> and 165 mL of water with moderate stirring. Next, 1 M HCl<sub>aq</sub> (12.5 mL, 12.5 mmol) was added dropwise to give a bright yellow, effervescent solution. (Caution: If at this stage the reaction solution became cloudy, due to a suspension of Nb<sub>2</sub>O<sub>5</sub>, the solution was discarded.) Immediately after the addition of HCl<sub>aq</sub>, and while the mixture was rapidly stirred, finely powdered K<sub>12</sub>[H<sub>2</sub>P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>]·24H<sub>2</sub>O (4.80 g, 1.22 mmol) was added in a single step, resulting in a clear, yellow solution (at this point pH was about 2.2). Fifteen minutes later, the pH was adjusted to ca. 2.0 by adding 0.5 M HCl<sub>aq</sub>. Stirring of the suspension was continued for approximately 1 h and filtered through a filter paper (when necessary) to obtain a clear solution. The filtrate was then heated to 70 °C for 6 hours. A pale yellow precipitate formed upon cooling was removed by filtration, followed by the addition of KCl (2.65 g, 35.6 mmol). The solution was then stirred for 30 min and filtered. The resulting pale yellow filtrate was kept at room temperature to allow slow evaporation. Yellow needle-shaped crystals formed within four weeks. Yield: 0.51 g, 0.06 mmol (10% based on Nb). IR (cm<sup>-1</sup>): 1397(s), 1082(s), 1059(m), 1002(w), 954(s), 898(m), 871(w), 784(s), 712(m), 650(m). Elemental analysis for **1a** (M<sub>w</sub> 8576.1 g mol<sup>-1</sup>), % calculated: K 3.2, P 1.4, Nb 13.0, W 51.4; % found: K 3.4, P 1.4, Nb 12.8, W 51.9.



**Synthesis of  $(\text{NH}_4)_{16}[\text{H}_{14}\{\text{P}_2\text{W}_{12}\text{Nb}_7\text{O}_{63}(\text{H}_2\text{O})_2\}_4\{\text{Nb}_4\text{O}_4(\text{OH})_6\}] \cdot 16\text{H}_2\text{O}$  (2a).**  $\text{K}_7[\text{HNb}_6\text{O}_{19}] \cdot 13\text{H}_2\text{O}$  (2.00 g, 1.47 mmol) was dissolved in a solution consisting of 13.5 mL of 30% aqueous  $\text{H}_2\text{O}_2$  and 165 mL of water with moderate stirring. Next, 1 M  $\text{HCl}_{\text{aq}}$  (12.5 mL, 12.5 mmol) was added dropwise to give a bright yellow, effervescent solution. Finely powdered  $\text{K}_{12}[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}] \cdot 24\text{H}_2\text{O}$  (4.80 g, 1.22 mmol) was added quickly in a single step, resulting in a clear, yellow solution. Fifteen minutes later, the pH was adjusted to *ca.* 2.0 by adding 0.5 M  $\text{HCl}_{\text{aq}}$ . Stirring of the suspension was continued for approximately 1 h and filtered through a filter paper (when necessary) to obtain a clear solution. The filtrate was adjusted to 1.7 by the addition of  $\text{HCl}_{\text{aq}}$  and then heated to 80 °C until the yellow color disappeared. Then  $\text{NH}_4\text{Cl}$  (1.90 g, 35.6 mmol) was added to the filtrate. Pale yellow block-shaped crystals formed within four weeks. Yield: 1.32 g, 0.10 mmol (35% based on Nb). IR ( $\text{cm}^{-1}$ ): 1402(s), 1086(s), 1059(m), 1002(w), 955(s), 900(m), 871(w), 781(s), 712(s), 590(w), 555(s), 493(m), 427(w). Elemental analysis for 2a ( $M_w$  16978.1 g mol $^{-1}$ ), % calculated: N 1.3, P 1.5, Nb 17.5, W 52.0; % found: N 1.3, P 1.5, Nb 17.8, W 52.5.

### X-ray crystallography

Suitable single crystals were selected and placed in a thin glass tube due to efflorescence. X-ray diffraction intensity data were recorded at 296(2) K on a Bruker Apex-II CCD diffractometer using Mo  $\text{K}\alpha$  monochromated radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Structure solution and refinement were carried out with SHELXS-97 and SHELXL-97 program packages.<sup>40</sup> No hydrogen atoms associated with the water molecules were located from the difference Fourier map. All hydrogen atoms were refined isotropically as a riding mode using the default SHELXTL parameters. Selected details of the data collection and structural refinement of compounds 1a and 2a can be found in Table 2

**Table 2** Crystal data and structure refinement

	1a	2a
Empirical formula	$\text{K}_7\text{H}_{75}\text{Nb}_{12}\text{P}_4\text{W}_{24}\text{O}_{161}$	$\text{N}_{16}\text{H}_{132}\text{P}_8\text{W}_{48}\text{Nb}_{32}\text{O}_{286}$
Formula weight	8576.1	16978.1
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/c$	$Fddd$
$a/\text{\AA}$	42.852(3)	24.0163(8)
$b/\text{\AA}$	12.6794(8)	44.0686(14)
$c/\text{\AA}$	29.4933(18)	72.836(2)
$\beta/^\circ$	101.4760(10)	90
$V/\text{\AA}^3$	15 704.4(17)	77 087(4)
$Z$	4	8
$D_c/\text{g cm}^{-3}$	3.620	2.923
$\mu/\text{mm}^{-1}$	18.681	15.288
$F_{000}$	15 228	60 000
Crystal size/ $\text{mm}^3$	$0.47 \times 0.28 \times 0.23$	$0.22 \times 0.15 \times 0.12$
Reflns collected	37 625	97 316
Indep reflns	13 691	16 835
$R_{\text{int}}$	0.1227	0.1026
Goodness-of-fit on $F^2$	1.024	1.010
$R_1 [I > 2\sigma(I)]^a$	0.0982	0.0548
$wR_2$ (all data) <sup>b</sup>	0.2599	0.1557

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

and full details are available in the corresponding CIF files. CSD-426569 (1a) and CSD-426570 (2a) can be obtained free of charge from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request\_for\_deposited\_data.html).

## Acknowledgements

We gratefully acknowledge support from the NSFC (grant numbers 91222102 and 21371048) and the NSF from Henan Province (grant numbers 122300410126, 13A150058 and 142300410009).

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