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The cyclic 48-tungsto-8-phosphate  $[H_7P_8W_{48}O_{184}]^{33-}$  Contant-Tézé polyanion and its derivatives  $[H_6P_4W_{24}O_{94}]^{18-}$  and  $[H_2P_2W_{12}O_{48}]^{12-}$ : structural aspects and reactivity

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Polyoxometalates (POMs) are discrete, anionic metal-oxo clusters of early transition metals in high oxidation states  $(e.q., W^{VI}, Mo^{VI}, V^{V})$  usually comprised of edge- and corner-shared  $MO_6$  octahedra. Lacunary POMs are defect heteropolyanions mainly of the Keggin or Dawson type, and they can be formed by the loss of one or more  $MO_6$  octahedra by controlled base hydrolysis. The largest subclass of POMs are tungstophosphates, and several lacunary derivatives are known, such as the Keggin-based  $[PW_{11}O_{39}]^{7-}$  and  $[P_{2}W_{17}O_{51}]^{10-}$  and the Dawson-based  $[P_{2}W_{17}O_{61}]^{10-}$  and  $[P_{2}W_{15}O_{56}]^{12-}$ . This review is based on the cyclic 48-tungsto-8-phosphate  $[H_7P_8W_{48}O_{184}]^{33-}$  ( $P_8W_{48}$ ) as well as its smaller derivatives  $[H_6P_4W_{24}O_{94}]^{18-}$  $(\mathbf{P_4W_{24}})$ , and  $[\mathrm{H_2P_2W_{12}O_{48}}]^{12-}$   $(\mathbf{P_2W_{12}})$ , with a focus on structural aspects, solution stability and reactivity. All three polyanions can be considered as inorganic multidentate O-donor ligands that coordinate with d, f or p-block metal ions. Here we provide a comprehensive overview of guest metal-containing derivatives of the  $P_8W_{48}$  wheel, the  $P_4W_{24}$  half-wheel and the  $P_2W_{12}$  quarter wheel. The structures containing  $P_2W_{12}$ as a building unit are presented in a sequence of increasing number of POM units in the resulting assembly. Transition metal-containing POMs have been of interest for decades due to their remarkable capability of forming novel and unexpected structures associated with interesting and relevant physicochemical properties (e.g., catalysis, magnetism, biomedicine, electrochemistry), and this also applies for derivatives containing P<sub>8</sub>W<sub>48</sub>, P<sub>4</sub>W<sub>24</sub> and P<sub>2</sub>W<sub>12</sub>.

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### 1. Introduction

The field of polyoxometalate (POM) chemistry has seen increased interest in recent decades due to the extensive range of chemical and physical properties of such compounds. Berzelius reported the formation of a molydophosphate polyoxoanion in 1826, and more than a decade later, Keggin identified the crystal structure of H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] using powder X-ray diffraction.<sup>1</sup> As such, POMs were elucidated as discrete anionic metal-oxo clusters formed by condensation of simple oxoanions (*e.g.*, WO<sub>4</sub><sup>2-</sup>) in aqueous media upon acidification. POMs consist of oxo-bridged early transition metal atoms of groups V and VI in high oxidation states, such as V<sup>V</sup>, Nb<sup>V</sup>, Ta<sup>V</sup>, Mo<sup>VI</sup>, or W<sup>VI</sup>.<sup>2</sup> For the formation of stable polyanions, the metal addendum atom should possess vacant d orbitals,

which allows for  $d_{\pi}$ – $p_{\pi}$  back bonding with terminal oxygen atoms. This phenomenon helps to terminate the condensation process at the level of discrete polyanions and disfavors the formation of extended metal oxide lattices.

Based on their chemical composition, POMs can be broadly subdivided into two main subclasses: (i) isopolyanions, which are composed exclusively of metal addenda M and oxo ligands, represented as  $[M_mO_v]^{n-}$ , and (ii) heteropolyanions, which contain one or more hetero atoms inside the polyanion, represented as  $[X_x M_m O_y]^{q-}$  ( $x \le m$ ), where X is usually a main group element such as P, Si, Ge, or As. Due to their high thermal and redox stability as well as their radiation-resistant nature, isopolyanions have attracted increasing attention for applications involving the separation and sequestration of radioactive species.<sup>3</sup> It is important to note that the formation of polyoxotungstates is accompanied by very slow equilibration of the reaction system, compared to molybdates and vanadates. Prime examples of heteropolyanions are the Keggin ion (e.g.  $[SiW_{12}O_{40}]^{4-}$ ) and the Wells-Dawson ion (e.g. [P<sub>2</sub>Mo<sub>18</sub>O<sub>62</sub>]<sup>6-</sup>), incorporating one or two tetrahedral XO<sub>4</sub> hetero groups, respectively. Pope and Müller reviewed the synthesis and characterization of POMs in 1991. Subsequently,

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Hill, as guest editor, highlighted popular research themes within the field of POM chemistry in a thematic issue of Chemical Reviews in 1998.4-9

POMs have generated considerable interest across all areas of chemistry due to their versatile nature with regard to shape, size, composition, redox activity, solubility, photochemistry, and charge distribution. Contemporary areas that have emerged in the multidisciplinary field of POM chemistry are mainly associated with various applications of POMs corresponding to developing new materials. 10 These have shown promise in the fields of nanotechnology, 11 biology, 12-15 surfaces, 14-17 catalysis, 18,19 supramolecular materials, 20,21 colloid science,<sup>22</sup> and electronic materials,<sup>23</sup> sensors,<sup>24,25</sup> molecular materials<sup>26,27</sup> and magnetism.<sup>28</sup> Crucial to the fast development of structural POM chemistry are advances in single-crystal X-ray diffraction (XRD), which allows for faster measurements on smaller crystals, allowing the characterization of large (with several hundred addenda atoms) polyanions.<sup>29,30</sup> Polyoxotungstates, in particular, have been observed to be effective homogeneous photocatalysts for the mineralization of organic pollutants. 31-35 As such, this review will focus on recent developments of the large, cyclic 48-tungsto-8-phosphate  $[H_7P_8W_{48}O_{184}]^{40-}$  (abbreviated as  $P_8W_{48}$ ) and its smaller fragments  $[H_2P_2W_{12}O_{48}]^{12-}$  (abbreviated as  $P_2W_{12}$ ) and  $[H_6P_4W_{24}O_{94}]^{18-}$  (abbreviated as  $P_4W_{24}$ ). Emphasis will be placed on the synthesis and structure of these polyanions.

In 1945, A. F. Wells suggested a detailed structure for the dimeric (18:2) tungstophosphate ion,36 based on Pauling's principles and the structure Keggin had shown for the 12-tungstophosphate. In 1952, the formula  $[P_2M_{18}O_{62}]^{6-}$  (M = Mo, W) proposed by Wells was experimentally established for the molybdo analogue by Tsigdinos. In 1953, Dawson investigated this polyanion using single-crystal X-ray diffraction,<sup>37</sup> and

demonstrated that the positions of the W atoms in  $[P_2W_{18}O_{62}]^{6-}$  coincided with what was postulated by Wells. In 1975 Strandberg, <sup>38</sup> and in 1976 D'Amour, <sup>39</sup> reported complete and accurate X-ray crystal structures of  $\left[\alpha - P_2 Mo_{18}O_{62}\right]^{6-}$  and  $\left[\alpha - P_2 W_{18} O_{62}\right]^{6-}$ , respectively.

## 2. The cyclic $[H_7P_8W_{48}O_{184}]^{33-}$ (P<sub>8</sub>W<sub>48</sub>) and its derivatives $[H_6P_4W_{24}W_{94}]^{18-}$ $(P_4W_{24})$ and $[\alpha-H_2P_2W_{12}O_{48}]^{12-}$ $(P_2W_{12})$

The single-crystal X-ray structure for the  $[P_2W_{18}O_{62}]^{6-}$  polyanion indicated that the eighteen metal centers are not equivalent. Thus, the distinction was made between the  $\alpha_2$  positions for the cap tungstens and the  $\alpha_1$  positions for the belt tungstens. The two caps in this Wells-Dawson structure are composed of three edge-shared MO<sub>6</sub> (M = W, Mo) octahedra, whereas the two equatorial belts are formed via alternating corner- and edge-shared MO<sub>6</sub> units. In 1979 Acerete showed by  $^{183}$ W solution NMR that the  $\beta$  geometrical isomer of  $[P_2W_{18}O_{62}]^{6-}$  differs from the  $\alpha$  isomer by a 60° rotation of one W<sub>3</sub>O<sub>13</sub> cap. 40,41 The Wells–Dawson derivative can be seen as a derivative of the Keggin structure; the removal of a cornershared  $W_3O_{13}$  triad from  $\left[\alpha\text{-PW}_{12}O_{40}\right]^{3-}$  produces a lacunary structure formulated as  $[A-\alpha-PW_9O_{34}]^{9-}$ , which combines with another equivalent moiety to form the  $\left[\alpha-P_2W_{18}O_{62}\right]^{6-}$ assembly.

Careful solution studies by Contant and Tézé on the chemistry of the complete (plenary)  $[\alpha-P_2W_{18}O_{62}]^{6-}$  polyanion showed that upon basification a hydrolytic cleavage of W-O (W) bonds occurs, resulting in a mixture of the monovacant (lacunary) species  $\left[\alpha_1 - P_2 W_{17} O_{61}\right]^{10-}$  and  $\left[\alpha_2 - P_2 W_{17} O_{61}\right]^{10-}$ ,



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respectively. Further, if the final pH is kept between 4 and 6, the  $\left[\alpha_1\text{-}P_2W_{17}O_{61}\right]^{10-}$  anion is observed to transform to the  $\left[\alpha_2\text{-}P_2W_{17}O_{61}\right]^{10-}$  anion readily. <sup>42</sup> At about pH 10, the trilacunary polyanion [P<sub>2</sub>W<sub>15</sub>O<sub>56</sub>]<sup>12-</sup> is formed. 42 Alternatively, in the presence of tris(hydroxymethyl)aminomethane (tris base), the plenary  $\left[\alpha\text{-}P_2W_{18}O_{62}\right]^{6-}$  transforms to the hexavacant polyanion  $[\alpha - H_2 P_2 W_{12} O_{48}]^{12-} (P_2 W_{12})^{42}$  This  $P_2 W_{12}$  is labile and transforms quickly in aqueous, acidic medium to either the unstable, monolacunary polyanion  $\left[\alpha_1\text{-}P_2W_{17}O_{61}\right]^{10-}$ , which successively rearranges to either the more stable  $\alpha_2$  $P_2W_{17}O_{61}$ ]<sup>10-,42</sup> or the large cyclic polyanion  $\left[H_7P_8W_{48}O_{184}\right]^{40-}$ (P8W48).43 Additionally, Contant and Tézé have revealed that two P<sub>2</sub>W<sub>12</sub> can be connected end-on to form the dimeric  $[H_6P_4W_{24}O_{94}]^{18-}$   $(P_4W_{24})$  species in aqueous solution.<sup>43</sup> However, the exact linkage of the two P2W12 units is still unknown.44

Lacunary derivatives of the plenary Wells-Dawson ion  $\left[\alpha - P_2 W_{18} O_{62}\right]^{6-}$  and their related terminology  $(\alpha, \alpha_1, \alpha_2)$  have been thoroughly investigated by Contant. 42 More recently, Poblet and Cronin have studied the different rotational isomerisms of non-classical Wells-Dawson anions with different heteroatoms based on theoretical and mass spectrometry techniques.45

### 2.1 The metastable, hexalacunary $\left[\alpha - H_2 P_2 W_{12} O_{48}\right]^{12-} \left(P_2 W_{12}\right)$

The hexalacunary 12-tungsto-2-phosphate  $P_2W_{12}$  is generated by the treatment of  $[\alpha - P_2 W_{18} O_{62}]^{6-}$  by tris(hydroxymethyl)aminomethane (tris base). The formation of P<sub>2</sub>W<sub>12</sub> can be visualized by removing six tungsten-oxo groups (W-Ot), one from each of the two caps and two from each of the two belts. The P<sub>2</sub>W<sub>12</sub> was first identified by Contant in 1985, who proved its existence by <sup>31</sup>P NMR (-8.6 ppm) in lithium chloride solution. The polyanion structure can be inferred from that of the cyclic



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Prof. Ulrich Kortz performed Ph. studies at Georgetown University in Washington, DC under the supervision of Michael T. Pope (1990-1995). Then he did postdoctoral studies with Dante Gatteschi in Florence, Italy (1995-1996) as well as André Tézé and Gilbert Hervé in Versailles, France (1996-1997). In 1997 he started his independent academic career at the American University of Beirut (AUB) in Lebanon. In 2002 he

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tetramer P8W48. This is due to the fact that P2W12 is labile and readily undergoes rearrangement in aqueous, acidic medium to the more stable monolacunary  $\left[\alpha_2 - P_2 W_{17} O_{61}\right]^{10-42}$ , or cyclic  $P_8W_{481}^{43}$  as stated earlier. As such, the <sup>183</sup>W NMR spectrum of this polyanion is not clean due to the presence of one or more transformation products in solution simultaneously, as Baker reported.46 Very recently, the polyanion P2W12 was characterized by single-crystal X-ray diffraction studies, as well as a W-bridged dimer and trimer. 47,48 Due to the presence of six lacunary sites in  $P_2W_{12}$ , the reactivity of this polyanion with guest metal ions has been explored in some detail, as will be discussed subsequently (vide infra, section 3).

### 2.2 The dimeric, multilacunary $[H_6P_4W_{24}O_{94}]^{18-}(P_4W_{24})$

The P<sub>4</sub>W<sub>24</sub> polyanion has been known since 1985, <sup>43</sup> and very likely it comprises of two P2W12 units, which are linked in a Cor S-shaped fashion, resulting in structures with  $C_{2v}$  or  $C_{2h}$ symmetry in solution (Fig. 1). 43 The 31P and 183W NMR spectra have proven the coexistence of both such forms in solution. 40,41,46,49 Only a few polyanions have been reported based on the dimeric P4W24 unit till date. In 1998, Roussel et al. investigated the structure of P4W24 by single-crystal X-ray diffraction studies and electron microscopy, which suggested P<sub>4</sub>W<sub>24</sub> to be a phosphate-containing derivative of a polyoxotungstate with the chemical formula  $(PO_4)_4(WO_3)_{2m}$   $(m = 12)^{50}$ 

### 2.3 The crown-shaped, superlacunary $[H_7P_8W_{48}O_{184}]^{33-}(P_8W_{48})$

The crown-shaped polyanion  $[H_7P_8W_{48}O_{184}]^{33-}$   $(P_8W_{48})$  comprises of four  $P_2W_{12}$  subunits, which are linked via the caps in a cyclic fashion, resulting in a structure with idealized  $D_{4h}$  symmetry (Fig. 2). The structural elucidation of the polyanion by single-crystal XRD showed the presence of eight potassium ions within the central cavity. This suggests a templating effect of the alkali ions, which may play an important role in the formation process of this cyclic polyanion. The P<sub>8</sub>W<sub>48</sub> is stable over a broad pH range (ca. 1-8), which represents a remarkable stability in POM chemistry. The presence of potassium ions inside the polyanion crown decreases the solubility of the salt and increases the tendency towards aggregation in solution, causing precipitation. Cronin reported two K-free salts of P<sub>8</sub>W<sub>48</sub>. 51

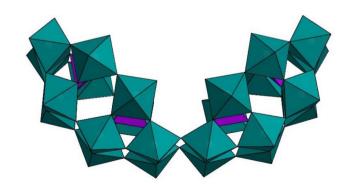


Fig. 1 Polyhedral representation of the C-shaped isomer of P<sub>4</sub>W<sub>24</sub>. Color code: WO<sub>6</sub> octahedra (green), PO<sub>4</sub> tetrahedra (pink).

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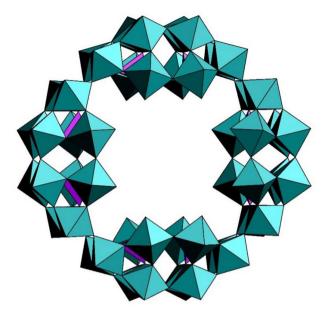


Fig. 2 Polyhedral representation of  $P_8W_{48}$ . Color code:  $WO_6$  octahedra (green),  $PO_4$  tetrahedra (pink).<sup>51</sup>

## 3. Metal complexes of $[\alpha-H_2P_2W_{12}O_{48}]^{12-}$

#### 3.1 Monomeric structures

To date, only a limited number of transition metal-containing derivatives of  $\mathbf{P_2W_{12}}$  have been reported. <sup>52</sup> Hill reported the peroxo-niobium-containing derivative  $[\mathbf{P_2W_{12}(NbO_2)_6O_{56}}]^{12-}$   $(\mathbf{P_2W_{12}(NbO_2)_6})$ , see Fig. 3. <sup>53</sup> This peroxo-polyanion was reported to be unstable both in solution and in the solid-state in the absence of hydrogen peroxide. However, the formation of  $\mathbf{P_2W_{12}(NbO_2)_6}$  in the presence of  $\mathbf{H_2O_2}$  has been demonstrated using several spectroscopic methods, such as infrared spectroscopy (IR), fast atom bombardment-mass spectroscopy (FAB-MS), and <sup>31</sup>P and <sup>183</sup>W NMR spectroscopy. The  $\mathbf{P_2W_{12}(NbO_2)_6}$  polyanion was prepared by the reaction of  $\mathbf{P_2W_{12}}$  with the Lindqvist-type isopolyanion  $[\mathbf{Nb_6O_{19}}]^{8-}$  in the presence of aqueous  $\mathbf{H_2O_2}$  as an oxidant. The six Nb atoms in  $\mathbf{P_2W_{12}(NbO_2)_6}$  are connected by  $\eta^2$ -O ligands, and each has a terminal, side-on peroxo ligand.

In 2002, Nadjo reported the synthesis and characterization of five mixed 3d (Fe, Cu)-4d (Mo) metal-containing  $P_2W_{12}$ -based polyanions:  $\alpha_2$ -[ $P_2W_{12}$ Fe(OH<sub>2</sub>)Mo<sub>5</sub>O<sub>61</sub>]<sup>7-</sup> ( $P_2W_{12}$ FeMo<sub>5</sub>) and  $\alpha_2$ -[ $P_2W_{13}$ Fe(OH<sub>2</sub>)Mo<sub>4</sub>O<sub>61</sub>]<sup>7-</sup> ( $P_2W_{13}$ FeMo<sub>4</sub>),  $\alpha_1$ - and  $\alpha_2$ -[ $P_2W_{12}$ Cu(OH<sub>2</sub>)Mo<sub>5</sub>O<sub>61</sub>]<sup>8-</sup> ( $P_2W_{12}$ CuMo<sub>5</sub>) and  $\alpha_2$ -[ $P_2W_{13}$ Cu (OH<sub>2</sub>)Mo<sub>4</sub>O<sub>61</sub>]<sup>8-</sup> ( $P_2W_{13}$ CuMo<sub>4</sub>). These compounds were characterized by IR, UV-vis, and <sup>31</sup>P NMR spectroscopy. No XRD structures could be obtained, but in particular, IR and <sup>31</sup>P NMR spectroscopy were useful tools for purifying the Fe<sup>3+</sup> and Cu<sup>2+</sup>-substituted derivatives. The authors have also studied the electrocatalytic properties of these polyanions, and the Cu and Fe-substituted derivatives showed good activity for the electrocatalytic reduction of nitrate. <sup>55-57</sup>

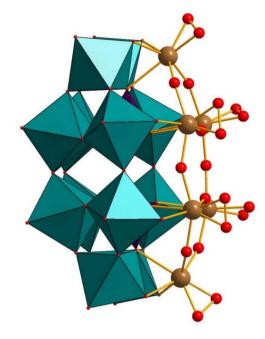


Fig. 3 Combined polyhedral/ball-and-stick representation of the peroxo-Nb polyanion  $[P_2W_{12}(NbO_2)_6O_{56}]^{12-}$   $(P_2W_{12}(NbO_2)_6)$ . Color code: WO<sub>6</sub> octahedra (green), PO<sub>4</sub> tetrahedra (pink), O (red), Nb (brown).<sup>53</sup>

Gouzerh reported dimeric 3d transition metal ( $Fe^{3+}$ ,  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ) containing derivatives of  $P_2W_{12}$ . The iron( $\mathfrak{m}$ )-containing polyanion [ $H_4P_2W_{12}Fe_9O_{56}(CH_3COO)_7$ ]<sup>6-</sup> ( $Fe_9P_2W_{12}$ ), see Fig. 4a, was prepared by a simple one-pot reaction of  $P_2W_{12}$  with an excess of iron( $\mathfrak{m}$ ) chloride in aqueous solution containing lithium chloride and lithium acetate, at room temperature.<sup>58</sup> The monomeric  $Fe_9P_2W_{12}$  structure is derived from  $P_2W_{12}$  by filling the six vacant sites with iron atoms, with the now-formed plenary Wells–Dawson type species { $P_2W_{12}Fe_6$ } having three additional iron( $\mathfrak{m}$ ) atoms grafted onto the hexa-iron-oxo face of the polyanion, resulting in  $Fe_9P_2W_{12}$ , which has idealized  $C_2$  symmetry. Magnetic susceptibility measurements on  $Fe_9P_2W_{12}$  showed intramolecular antiferromagnetic coupling between the two high-spin  $Fe^{3+}$  centers.

#### 3.2 Dimeric structures

Upon further investigation of the Fe³+ and  $P_2W_{12}$  system by Gouzerh, it was observed that lowering the Fe³+:  $P_2W_{12}$  ratio and the solution pH, as well as prolonged heating, led to the formation of dimeric polyanions with the general formula  $[H_yP_4W_{28+x}Fe_{8-x}O_{120}]^{(28-y-3x)-}$ . These species have extra tungsten atoms in the new polyanions (with slight variations in the value of x), which have been isolated as different salts. The polyanion  $[H_{12}P_4W_{28}Fe_8O_{120}]^{16-}$  (Fe<sub>8</sub>P<sub>4</sub>W<sub>28</sub>) comprises two {P<sub>2</sub>W<sub>14</sub>Fe<sub>4</sub>} units linked via Fe-O-Fe′ bonds, resulting in a cubic Fe<sub>8</sub> topology. The Fe<sub>8</sub>P<sub>4</sub>W<sub>28</sub> is formed by reaction of P<sub>2</sub>W<sub>12</sub> with hydrous iron(III) oxide or iron(III) acetate [Fe<sub>3</sub>O (OAc)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>]Cl·5H<sub>2</sub>O. Fe

An extra tungsten atom arising from the decomposition of  $P_2W_{12}$  in situ or upon deliberate addition of tungstate to the

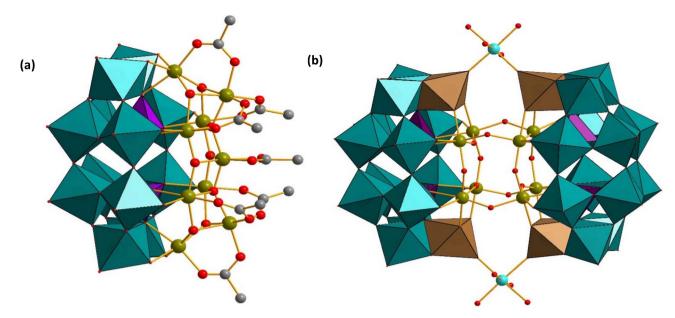


Fig. 4 Combined polyhedral/ball-and-stick representations of (a)  $[H_4P_2W_{12}Fe_9O_{56}(CH_3COO)_7]_6^ (Fe_9P_2W_{12}),$  $(H_2O)_4)_2(H_{12}P_4W_{28}Fe_8O_{120})]^{12-}$  (M =  $Co^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ). Color code: WO<sub>6</sub> octahedra (green and brown), PO<sub>4</sub> tetrahedra (pink), Fe (green), M (turquoise), O (red), C (grey). H atoms on carbon have been omitted for clarity. 58,59

reaction mixture competes with the added metal ions, as has been observed in the reactions with lanthanide ions. 60,61 Frequently, adding of extra tungstate to the reaction mixture is not essential for the formation of such structures. 61 The cyclic voltammogram (CV) of the polyanion Fe<sub>8</sub>P<sub>4</sub>W<sub>28</sub> displays four reduction waves. The first one at -0.32 V vs. SCE is attributed to the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>.

A polyanion with the composition  $[H_yP_4W_{28+x}Fe_{8-x}O_{120}]^{(28-y-3x)-}$   $(x\approx 2)$  was characterized among the products obtained from a 1:4:2 aqueous mixture of P<sub>2</sub>W<sub>12</sub>, sodium tungstate, and iron(III) chloride at pH 4.2.<sup>59</sup> When  $P_2W_{12}$  is reacted with the mixed-metal complexes  $[Fe_2^{III}M^{II}O(OAc)_6(H_2O)_3]$  (M = Co<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>), the polyanions  $\left[ \{ M(H_2O)_4 \}_2 \{ H_{12}P_4W_{28}Fe_8O_{120} \} \right]^{12-} \left( M_2Fe_8P_4W_{28} \right) (Fig. 4b) (M = 1)^{-1} \left[ \{ M_1P_2O_{12} \}_2 \{ H_{12}P_4W_{28}Fe_8O_{120} \} \right]^{12-} \left( M_2Fe_8P_4W_{28} \right) (Fig. 4b) (M = 1)^{-1} \left[ \{ M_1P_2O_{12} \}_2 \{ H_{12}P_4W_{28}Fe_8O_{120} \} \right]^{12-} \left( M_2Fe_8P_4W_{28} \right) (Fig. 4b) (M = 1)^{-1} \left[ \{ M_1P_2O_{12} \}_2 \{ H_{12}P_4W_{28}Fe_8O_{120} \} \right]^{12-} \left( M_2Fe_8P_4W_{28} \} \right) (Fig. 4b) (M = 1)^{-1} \left[ \{ M_1P_2O_{12} \}_2 \{ H_{12}P_4W_{28} \} \right]^{-1} \left( M_2Fe_8P_4W_{28} \} \right) (Fig. 4b) (M = 1)^{-1} \left[ \{ M_1P_2O_{12} \}_2 \{ H_{12}P_4W_{28} \} \right]^{-1} \left( M_2Fe_8P_4W_{28} \} \right) (Fig. 4b) (M = 1)^{-1} \left[ \{ M_1P_2O_{12} \}_2 \{ H_{12}P_4W_{28} \} \right]^{-1} \left( M_2Fe_8P_4W_{28} \} (Fig. 4b) (M = 1)^{-1} \left( M_2Fe_8P_4W_{28} \} \right) (Fig. 4b) (M = 1)^{-1} \left( M_2Fe_8P_4W_{28} \} (Fig. 4b) (M = 1)^{-1} \left( M_2Fe_8P_4W_{28} \} \right) (Fig. 4b) (M = 1)^{-1} \left( M_2Fe_8P_4W_{28} \} (Fig. 4b) (M = 1)^{-1} \left( M_2Fe_8P_4W_{28} \} \right) (Fig. 4b) (M = 1)^{-1} \left( M_2Fe_8P_4W_{28} \} (Fig. 4b) (M = 1)^{-1} \left( M_2Fe_8P_4W_{28} \right) (M$ Co<sup>2+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>) are obtained, together with Fe<sub>8</sub>P<sub>4</sub>W<sub>28</sub>.<sup>59</sup> These compounds were isolated as potassium salts. Magnetic susceptibility measurements on Co2Fe8P4W28 are consistent with two non-interacting Co<sup>2+</sup> centers, suggesting that the ground state of the Fe<sub>8</sub>P<sub>4</sub>W<sub>28</sub> unit is diamagnetic, along with the intramolecular antiferromagnetic coupling of the eight Fe3+ centers. In contrast, the parent polyanion Fe8P4W28 showed weak magnetization, arising either from paramagnetic impurities or a partial substitution of Fe for W.59 The cyclic voltammogram indicated that the Co<sup>2+</sup> centers are not electrochemically active in the potential range investigated.

Wang and coworkers investigated the reactivity of P2W12 with Co2+ ions in an aqueous acidic medium. A new heartshaped dimeric Co<sup>2+</sup>-containing polyanion [{W<sub>2</sub>Co<sub>2</sub>O<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub>}  $(P_2W_{12}O_{46})_2|^{20-}$   $(W_2Co_2(P_2W_{12})_2)$  was synthesized and structurally characterized by IR spectroscopy, thermogravimetry, electrochemistry, and single-crystal X-ray diffraction.<sup>62</sup> The

polyanion W<sub>2</sub>Co<sub>2</sub>(P<sub>2</sub>W<sub>12</sub>)<sub>2</sub> comprises two subunits of P<sub>2</sub>W<sub>12</sub>, which are fused via four W-O-W bonds and grafting of two W and two Co atoms in the vacant positions. This type of W-O-W connectivity was observed for the first time by Kortz and coworkers in the dimethyletin-containing tungstophosphate [{Sn  $(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2\big]^{28-}$  (vide infra, section 4). Notably, all the addenda positions in  $W_2Co_2(P_2W_{12})_2$  are disordered in the cluster.

Very recently, a dimeric mixed-addenda Nb/W polyanion,  $[H_6P_2W_{12}Nb_4O_{59}(NbO_2)_2]_2^{8-}$   $(P_2W_{12}Nb_4(NbO_2)_2)_2$ , has been isolated under acidic condition by Yue, He, and coworkers. 63 This Nb-peroxo-containing polyanion was synthesized by the reaction of  $K_7H[Nb_6O_{19}]\cdot 13H_2O$  and  $P_2W_{12}$  in sodium formate buffer in the presence of H2O2. The polyanion was characterized by single-crystal X-ray diffraction and elemental analysis. The structure revealed that six Nb atoms occupy the vacant sites of the hexalacunary P2W12 precursor to form a  $\{P_2W_{12}Nb_6(O_2)_2\}$ mixed-addenda subunit. Two {P<sub>2</sub>W<sub>12</sub>Nb<sub>6</sub>(O<sub>2</sub>)<sub>2</sub>} subunits are joined by two Nb-O-Nb bridges at the belt positions to form a dimeric unit. This polyanion, (P<sub>2</sub>W<sub>12</sub>Nb<sub>4</sub>(NbO<sub>2</sub>)<sub>2</sub>)<sub>2</sub>, is structurally different from the Nbperoxo polyanions reported by Hill and coworkers, for example, P2W12(NbO2)6, as discussed in section 3.1 (vide supra).<sup>53</sup> In P<sub>2</sub>W<sub>12</sub>(NbO<sub>2</sub>)<sub>6</sub> structure, all niobium atoms have terminal peroxo ligands and exist as a six-membered Nbperoxo monomer; whereas in (P<sub>2</sub>W<sub>12</sub>Nb<sub>4</sub>(NbO<sub>2</sub>)<sub>2</sub>)<sub>2</sub>, only two niobium ions have peroxo ligands, and the polyanion is a dimer. A common feature for both polyanions was that the polyanions aggregated to larger species when the peroxo groups in either P2W12Nb4(NbO2)2 or P2W12(NbO2)6 were removed by heating or chemical reduction. 64-66

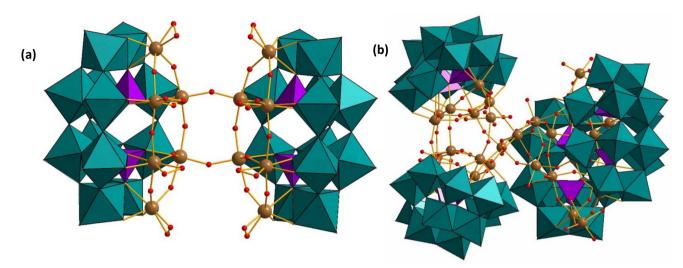


Fig. 5 Combined polyhedral, ball-and-stick representations of (a)  $[H_{13}\{Nb_6(O_2)_4P_2W_{12}O_{57}\}_2]^{7-}$  and (b)  $[H_{14}\{P_2W_{12}Nb_7O_{63}(H_2O)_2\}_4\{Nb_4O_4(OH)_6\}]^{16-}$ , respectively. Color code:  $WO_6$  octahedra (green),  $PO_4$  tetrahedra (pink), Nb (brown), O (red).

In 2015, Niu, Wang, and coworkers reported two new multi-Nb-containing POM structures,  $[H_{13}\{Nb_6(O_2)_4P_2W_{12}O_{57}\}_2]^{7-}$  $(P_2W_{12}Nb_6(O_2)_4)_2$  (Fig. 5a) and  $[H_{14}\{P_2W_{12}Nb_7O_{63}(H_2O)_2\}_4]_4$  $\{Nb_4O_4(OH)_6\}\}^{16-} (P_2W_{12}Nb_7)_4Nb_4 \text{ (Fig. 5b).}^{67} \text{ Interestingly,}$ (P2W12Nb7)4Nb4 has the highest nuclearity of all niobium-conheteropolyanions to date. polyanion taining The  $\{P_2W_{12}Nb_6(O_2)_4\}_2$  is a di-Nb-O-Nb-linked dimer of two  $P_2W_{12}$ units with the six vacant sites of each P2W12 unit occupied by four niobium-peroxo groups (NbO2) and two niobium-oxo groups (Nb-O). Further, (P<sub>2</sub>W<sub>12</sub>Nb<sub>7</sub>)<sub>4</sub>Nb<sub>4</sub> comprises dimeric  $[P_4W_{24}Nb_{14}O_{126}(H_2O)_4]^{18-}$  subunits and an adamantane-like  $Nb_4O_6$  core. The  $[P_4W_{24}Nb_{14}O_{126}(H_2O)_4]^{18-}$  subunit in  $(P_2W_{12}Nb_7)_4Nb_4$  comprises two  $[Nb_6P_2W_{12}O_{61}]^{10-}$ without any niobium-peroxo groups. The [Nb<sub>6</sub>P<sub>2</sub>W<sub>12</sub>O<sub>61</sub>]<sup>10-</sup> units are connected through Nb-O-Nb bridges. The adamantane-like {Nb<sub>4</sub>O<sub>6</sub>} core is composed of four niobium metal atoms connected by oxo ligands. The authors have demonstrated that careful synthetic control can stabilize the (Nb<sub>6</sub>P<sub>2</sub>W<sub>12</sub>) fragment in both polyanions as a dimer or a tetramer. Moreover, 31P and 183W NMR spectra indicated that (P<sub>2</sub>W<sub>12</sub>Nb<sub>7</sub>)<sub>4</sub>Nb<sub>4</sub> is stable in solution. The photocatalytic activity for H2 evolution has been studied for both polyanions, and (P<sub>2</sub>W<sub>12</sub>Nb<sub>7</sub>)<sub>4</sub>Nb<sub>4</sub> exhibited good activity.

In 2018, Kögerler and coworkers reported an open dimeric structure based on the  $P_4W_{24}$  unit with  $\{P_4W_{24}O_{29}\}$  being capped by two phenyl phosphonate or -arsonate ligands,  $[(PhXO)_2P_4W_{24}O_{92}]^{16-}$  (X = P, As)  $(PhXOP_4W_{24})^{.68}$  In 2006, Kortz and coworkers have also reported  $P_4W_{24}$  units in the dimethyltin-grafted polyanion  $[\{Sn(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2]^{28-}$  (Sn  $(CH_3)_2P_4W_{24})$  (vide infra). The PhXOP4W24, the PhXOP4W24 unit due to the presence of the two phoshonate/arsonate ligands. Further studies on the incorporation of  $Co^{2+}$  ions into the central cavity of  $PhXOP_4W_{24}$  resulted in the formation of  $[\{(H_2O)_4Co\}$ 

 $(PhXO)_2P_4W_{24}O_{92}]^{14-}$  units linked into an infinite 1D chain in the solid state *via* additional "outer"  $Co^{2+}$  centers.

Very recently, the same group reported an unprecedented discrete dimeric polyanion [(o-H<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-AsO<sub>3</sub>)<sub>4</sub>P<sub>4</sub>W<sub>24</sub>O<sub>85</sub>]<sup>14-</sup>  $((o-NH_2-C_6H_6-AsO)_4P_4W_{24}O_{92})$ , by the condensation reaction of o-aminophenylarsonic and  $P_2W_{12}$  in acidic media. The polyanion (o-NH2-C6H6-AsO)4P4W24O92 was further reacted with divalent transition metal ions Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>. The introduction of the divalent transition metal ions in the reaction mixture resulted in V-shaped one-dimensional (1D) coordination polymeric polyanions  $[\{M(H_2O)_4\}P_4W_{24}O_{92}(C_6H_6AsNO)_2]^{14-}$   $(M = Mn^{2+}, Co^{2+},$  $Ni^{2+}$ ) (M(o-NH<sub>2</sub>-C<sub>6</sub>H<sub>6</sub>-AsO)<sub>2</sub>P<sub>4</sub>W<sub>24</sub>), where a similar type of structure was first observed by Kortz group (vide infra). Each monomeric unit of (o-NH<sub>2</sub>-C<sub>6</sub>H<sub>6</sub>-AsO)<sub>4</sub>P<sub>4</sub>W<sub>24</sub>O<sub>92</sub> consists of P<sub>2</sub>W<sub>12</sub>, comprising two PW<sub>4</sub>O<sub>21</sub> belts capped with two W<sub>2</sub>O<sub>10</sub> units linked through oxygen atoms. The transition metal complex M(o-NH2-C6H6-AsO)2P4W24 exhibits dimeric anionic assembly and coordinates one oxygen atom from the upper PW<sub>4</sub>O<sub>21</sub> belt of each P<sub>2</sub>W<sub>12</sub>L subunits.

#### 3.3 Trimeric structures

In 2008, Wang and coworkers were able to isolate three trimeric polyoxotungstates upon the reaction of 3d metal ions with  $P_2W_{12}$  at different pH,  $[K_3\subset\{Mn(H_2O)_4\}_2\{WO_2(H_2O)_2\}_2\{WO(H_2O)\}_3(P_2W_{12}O_{48})_3]^{19^-}$   $(Mn_2(P_2W_{12})_3W_5)$  (Fig. 6),  $K_3Na_7Li_{5.5}Ni_{0.25}$   $[Na_3\subset\{Ni_{3.5}(H_2O)_{13}\}\{WO_2(H_2O)_2\}_2\{WO(H_2O)\}_3(P_2W_{12}O_{48})_3]^{164}H_2O$   $(Ni_{3.5}(P_2W_{12})_3W_5)$ , and  $[Na_3\subset\{Cu_3(H_2O)_9\}\{WO_2(H_2O)_2\}_2\{WO(H_2O)\}_3(P_2W_{12}O_{48})_3]^{17^-}$   $(Cu_3(P_2W_{12})_3W_5)$ . These polyanions were prepared by reaction of the corresponding transition metal salts  $(Mn^{2^+}, Ni^{2^+}, and Cu^{2^+})$  with  $P_2W_{12}$  and  $Na_2WO_4$  in aqueous acidic solutions. The polyanion  $Mn_2(P_2W_{12})_3W_5$  was obtained in a pH 4.0 solution, whereas the other two polyanions  $Ni_{3.5}(P_2W_{12})_3W_5$  and  $Cu_3(P_2W_{12})_3W_5$  were obtained in the pH

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Fig. 6 Combined polyhedral/ball-and-stick representation of  $[K_3\subset \{Mn(H_2O)_4\}_2\{WO_2(H_2O)_2\}_2\{WO(H_2O)\}_3\{P_2W_{12}O_{48}\}_3]^{19}$ . Color code:  $WO_6$  octahedra (green),  $PO_4$  tetrahedra (pink), Mn (teal), O (red). 71

range 1.5–2.5.<sup>71</sup> As based on the formula, the Ni-containing polyanion appears to be a mixture of at least two species.

Yao et al. suggested that the pH plays an important role in forming these P<sub>2</sub>W<sub>12</sub>-based heteropolytungstates.<sup>72</sup> Upon further decreasing the pH to 1.0, they were able to isolate two new compounds,  $[Na_3 \subset \{Co(H_2O)_4\}_6 \{WO(H_2O)\}_3 (P_2W_{12}O_{48})_3]^{15-}$  $[Na_3 \subset \{Ni(H_2O)_4\}_6 \{WO(H_2O)\}_3$  $(Co_6(P_2W_{12})_3W_3),$ and  $(P_2W_{12}O_{48})_3^{15-}$   $(Ni_6(P_2W_{12})_3W_3)^{72}$  It is worth mentioning that all the vacant sites in  $Co_6(P_2W_{12})_3W_3$  and  $Ni_6(P_2W_{12})_3W_3$  are occupied by the 3d metal ions. Therefore, it is observed that a lower pH facilitates the combination of more transition metal atoms encapsulated within the  $\{(P_2W_{12})_3W_3\}$  shell. All these polyanions have crown-type structures, comprising three P<sub>2</sub>W<sub>12</sub> subunits linked by three {WO(H<sub>2</sub>O)} fragments in a corner-sharing arrangement, resulting in the trimeric cluster  $[P_6W_{39}O_{147}(H_2O)_3]^{30-}$  (abbreviated as  $P_6W_{39}$ ). In such crownshaped polyanions, the three W atoms in the hinges are all in a hexa-coordinated environment, with all transition metal atoms also fully coordinated. The six vacant sites on the polyanion  $Mn_2(P_2W_{12})_3\{WO_2(H_2O)_2\}\{WO(H_2O)\}_3$  are occupied by two WVI atoms, two Mn2+ ions, and two potassium counter cations, respectively. For the polyanion Ni<sub>3.5</sub>(P<sub>2</sub>W<sub>12</sub>)<sub>3</sub>{WO<sub>2</sub>  $(H_2O)_2$ { $WO(H_2O)$ }<sub>3</sub>, two W<sup>VI</sup> and four Ni<sup>2+</sup> atoms fill up the six vacant sites of the P<sub>6</sub>W<sub>39</sub> shell, with all the Ni<sup>2+</sup> centers fully occupied, except the Ni5 position which exhibits a crystallographic site-occupancy disorder with a Na atom, resulting in a total of two  $W^{VI}$  and 3.5  $Ni^{2+}$  ions being incorporated in the structure. In a similar sense, for the polyanion  $Cu_3(P_2W_{12})_3$  $\{WO_2(H_2O)_2\}_2\{WO(H_2O)\}_3$ , two W<sup>VI</sup> and four Cu<sup>2+</sup> guest atoms occupy the six vacant sites of the P6W39 unit. However, all these metal sites, except W40, also have site-occupancy disorder, resulting in two WVI and 2.75 Cu2+ atoms as guests in

More recently, Wang and coworkers have reported mixed 3d/4f metal ion-based  $P_6W_{39}$  structures,  $[K_3\subset \{GdMn(H_2O)_{10}\} \{HMnGd_2(tart)O_2(H_2O)_{15}\}\{P_6W_{42}O_{151}(H_2O)_7\}]^{11-}$  ( $\{MnGd\}(HMnGd)(HMnG$ 

 $Gd_2P_6W_{42}$ <sub>∞</sub>) and  $[K_3\subset \{GdCo(H_2O)_{11}\}_2\{P_6W_{41}O_{148}(H_2O)_7\}]^{13-}$  $(CoGdP_6W_{41})_{\infty}$ , with organic guests (tartrate (CH<sub>3</sub>)<sub>2</sub>NH·HCl respectively).<sup>73</sup> According to the authors, the introduction of such secondary organic ligands stabilizes the lanthanide atoms and/or reduces the reactivity of the lanthanide atoms with the polyanions. The crown-shaped  $P_6W_{39}$  is formed by the encapsulation of transition metal and lanthanide atoms inside the cavity of the polyanion. The polyanion  $(MnGd)(HMnGd_2P_6W_{42})_{\infty}$  forms two-dimensional porous frameworks through the Gd and Mn linkers, whereas the polyanion (CoGdP<sub>6</sub>W<sub>41</sub>)<sub>∞</sub> forms a one-dimensional chain linked through Gd ions, which exhibit a square-antiprismatic geometrical environment. These are the first POM structures comprising mixed lanthanide and transition metal atoms. Wang, Niu, and coworkers have isolated a trimeric assembly of P<sub>2</sub>W<sub>12</sub> units joined by Cr-atoms,  $[H_{23}(Cr(H_2O)_2)_3(H_2P_2W_{12}O_{48})_3]^{4-}$  $(Cr_3(P_2W_{12})_3)^{74}$  The structure bears similarity with a trimeric  $\{P_6W_{39}\}$  unit, except that Cr has replaced the W-atoms.

#### 3.4 Tetrameric structures

Following Gouzerh's report of the metastable polyanion  $Fe_9(OAc)_7P_2W_{12}$  (section 3.1, vide supra), which was isolated as a lithium-potassium salt,58 subsequent heating of this polyanion in aqueous sodium acetate solution transformed it into different compounds, which were successively isolated as sodium-potassium salts, such as Na<sub>16</sub>K<sub>12</sub>[H<sub>56</sub>P<sub>8</sub>W<sub>48</sub>Fe<sub>28</sub>O<sub>248</sub>]  $(\textbf{Fe}_{28}\textbf{P}_{8}\textbf{W}_{48}) \text{ and } \textbf{Na}_{16}\textbf{K}_{10} [\textbf{H}_{55}\textbf{P}_{8}\textbf{W}_{49}\textbf{Fe}_{27}\textbf{O}_{248}] \left(\textbf{Fe}_{27}\textbf{P}_{8}\textbf{W}_{49}\right)^{.58} \text{ The}$ polyanion Fe28P8W48 was characterized by electrochemistry and magnetic measurements and by determination of the unit cell parameters. Subsequently, the formula of the polyanion Fe<sub>27</sub>P<sub>8</sub>W<sub>49</sub> was proposed on the basis of an X-ray diffraction study. Godin et al. hinted at other novel compounds' formation by lowering either the pH or the  $Fe^{3+}$ :  $P_2W_{12}$  ratio. However, IR spectroscopy and chemical analysis were insufficient to determine the composition and purity of these species. The polyanion Fe<sub>27</sub>P<sub>8</sub>W<sub>49</sub> comprises four {P<sub>2</sub>W<sub>12</sub>Fe<sub>6</sub>} units, each bridged through Fe-O-Fe linkages to an {Fe4O6} cluster core. The linkage is through pairs of three Fe-O-Fe bridges involving the three outer iron atoms. According to crystallographic refinement, the polyanion Fe<sub>27</sub>P<sub>8</sub>W<sub>49</sub> seems to have 25% W and 75% Fe occupancy, suggesting a mixture of polyanions. The polyanion exhibits antiferromagnetic coupling between the Fe<sup>3+</sup> centers (Fig. 7).

Wang and coworkers have reported the 3d transition metal  $(Co^{2^+}, Ni^{2^+})$  modified  $\{P_8W_{49}\}$  polyanions  $\{[Co(H_2O)_2Cl][Co(H_2O)_3]_2[Co(H_2O)_5]_{1.5}[Co(H_2O)_3H_4P_8W_{49}O_{187}(H_2O)]\}^{26^-}$  ( $[Co(H_2O)_3]_2[Co(H_2O)_3]_{1.5}P_8W_{49}$ ) and  $\{[Ni(H_2O)_3]_2[Ni(H_2O)_3]_{1.5}P_8W_{49}O_{187}(H_2O)]\}^{30^-}$  ( $[Ni(H_2O)_3]_2[Ni(H_2O)_3]_{1.5}P_8W_{49}$ ), respectively, by the reaction of  $P_2W_{12}$  with the respective transition metal salt. $^{75}$  The transformation from  $P_2W_{12}$  to  $P_8W_{49}$  happens during the reaction performed in an aqueous acidic medium. The structural arrangements of  $Co^{2^+}$  and  $Ni^{2^+}$  in  $[Co(H_2O)_2][Co(H_2O)_3]_2[Co(H_2O)_5]_{1.5}P_8W_{49}$  and  $[Ni(H_2O)_3]_2[Ni(H_2O)_3]_{1.5}P_8W_{49}$  are different from that of several other  $Mn^{2^+}$  complexes reported by Cronin's and Proust's groups (see section 5). $^{21,76,77}$ 

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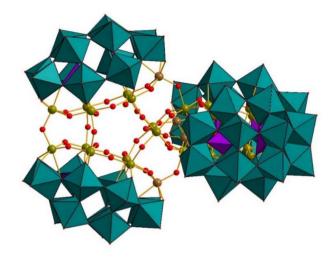


Fig. 7 Combined polyhedral/ball-and-stick representation of  $[H_{55}P_8W_{49}Fe_{27}O_{248}]^{27-}$ . Color code:  $WO_6$  octahedra (green),  $PO_4$  tetrahedra (pink), O (red), Fe (green-yellow), Fe/W (brown). <sup>58</sup>

In 2014, Niu and coworkers reported the gigantic  $Nb_{28}$  cluster encapsulated in a hexa-lacunary  $\{P_2W_{12}\}$  precursor,  $[\{Nb_4O_6(OH)_4\}\{Nb_6P_2W_{12}O_{61}\}_4]^{36-}$   $((Nb_4O_6)(Nb_6P_2W_{12})_4)^{.78}$  This polyanion was formed directly by controlling the reaction parameters (e.g., pH, concentration, temperature) and isolated as a sodium salt. The salt was characterized by single-crystal X-ray diffraction, IR spectroscopy, and elemental analysis. The structure of  $(Nb_4O_6)(Nb_6P_2W_{12})_4$  reveals that the polyanion comprises two  $[P_4W_{24}Nb_{12}O_{122}]^{20-}$  dimeric units, rotated  $180^\circ$  with respect to each other and connected by four Nb-O-Nb bridges, resulting in an adamantane-type  $\{Nb_4O_6\}$  core.

Very recently, Zhang and coworkers have reported the formation of  $Na_{24}[Mn_8(H_2O)_{32}P_8W_{48}O_{184}]\cdot 58H_2O$ ,  $K_4Na_{16}H_4[Co_8(H_2O)_{32}P_8W_{48}O_{184}]\cdot 76H_2O$ , and  $Na_{20}H_4[Ni_8(H_2O)_{32}P_8W_{48}O_{184}]\cdot 72H_2O$   $(\textbf{M}_8\textbf{P}_8\textbf{W}_{48},~M=Mn^{2+},~Co^{2+},~Ni^{2+})$  by reaction of the respective divalent metal ion with the hexavalent  $\textbf{P}_2\textbf{W}_{12}$  at room temperature in aqueous solution. The direct reaction of the metal ions with  $\textbf{P}_8\textbf{W}_{48}$  was not successful.

#### 3.5 Hexameric structures

In 2015, Niu, Wang, and coworkers reported a hexameric  $\{Nb_6P_2W_{12}\}$ -based Mn<sub>15</sub>-oxo  $[H_{123}Nb_{36}P_{12}W_{72}Mn_{12}^{III}Mn_{3}^{II}NaO_{424}]^{10-}$  ( $Mn_{15}(Nb_{6}P_{2}W_{12})_{6}$ ), with single-molecule magnet (SMM) properties.80 The polyanion structure consists of three main parts: six peroxo-free {Nb<sub>6</sub>P<sub>2</sub>W<sub>12</sub>} units, four {Mn<sub>3</sub><sup>III</sup>} trinuclear cores, and four {Mn<sup>II</sup>} hinges. The {Mn<sub>3</sub><sup>III</sup>} unit is made of three mutually cornerbridged {MnIIIO6} octahedra (Fig. 8). Two of the Mn···Mn distances in the trinuclear {Mn<sub>3</sub><sup>III</sup>} unit are observed to be identical and slightly longer or shorter than the third Mn···Mn distance, having an overall shape of an equivalent isosceles triangle. Each {Mn<sub>3</sub><sup>III</sup>} unit is surrounded by three Wells-Dawson {Nb<sub>6</sub>P<sub>2</sub>W<sub>12</sub>} units and six Mn-O-Nb bridges. Further, each {MnII} hinge shows crystallographic positional disorder of  $\mathrm{Mn}^{2+}$  and  $\mathrm{Na}^{+}$  (0.75:0.25), being coordinated by three  $\mu_2$ -oxo

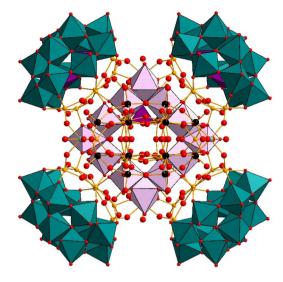


Fig. 8 Combined polyhedral/ball-and-stick representation of  $[H_{123}Nb_{36}P_{12}W_{72}Mn_{11}^{11}Mn_{3}^{11}NaO_{424}]^{10^{-}}$ . Color code: WO<sub>6</sub> octahedra (green), W (black), Nb (yellow), MnO<sub>6</sub> octahedra (light pink), PO<sub>4</sub> tetrahedra (pink), O (red), Na (turquoise).<sup>80</sup>

groups and four-terminal oxygen atoms (water molecules), thus leading to a distorted octahedral geometry. Therefore, the authors suggest that the disordered metal centre should be formulated as  $[Mn_{0.75}^{II}Na_{0.25}(H_2O)_4]^{1.75+}$ .

In 2016, Mizuno and coworkers isolated a giant hexameric manganese-substituted ring-shaped polyanion,  $[\{\gamma - P_2 W_{12} O_{48} M n_4 (acac)_2 (OAc)\}_6]^{42-}$  (acac = acetylacetonate, OAc = acetate)  $\{P_2W_{12}O_{48}Mn_4\}_6$  by reaction of the hexavacant lacunary P<sub>2</sub>W<sub>12</sub> precursor with Mn(acac)<sub>3</sub> in organic medium. 81 The polyanion {P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>Mn<sub>4</sub>}<sub>6</sub> is composed of six manganese-substituted monomeric {P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>Mn<sub>4</sub>} units, overall resulting in a cyclic, hexameric structure. Each {P2W12Mn4} monomeric unit consists of two types of Mn-coordinated ligands acetyl acetonate (acac) and acetate, respectively, so the polyanion has two different active sites. Interestingly, the hexameric polyatransforms to the tetrameric polyanion,  $[\{\gamma - P_2W_{12}O_{48}Mn_4(H_2O)_6\}_4(H_2O)_4]^{24-} \{P_2W_{12}O_{48}Mn_4\}_4$  in the absence of the organic ligands capping the manganese ions.

Following the report of Mizuno's 2016 work, Yamaguchi and coworkers in 2019 have reported the synthesis of the tetra-n-buty-lammonium (TBA) salts of a series of new isostructural divalent transition metal substituted polyanion family, (TBA $_5$ [ $\gamma$ -P $_2$ W $_1$ 2O $_4$ 4M $_2$ (OAc)(CH $_3$ CONH) $_2$ ]· $_1$ H $_2$ O· $_2$ CH $_3$ CN;  $M = Mn^{2+}$ , Co $_2$ +, Ni $_2$ +, Cu $_2$ +, or Zn $_2$ +; OAc = acetate) ( $\gamma$ -P $_2$ W $_1$ 2O $_4$ 4M $_2$ (OAc)) including unique edge-shared bis (square-pyramidal) {O $_2$ M( $\mu_3$ -O) $_2$ ( $\mu$ -OAc)MO $_2$ } core. The metal ions occupy the vacant belt positions of the  $\gamma$ -P $_2$ W $_1$ 2 precursor, whereas the two acetamide (CH $_3$ CONH $_2$ ) groups stabilize the  $\gamma$ -P $_2$ W $_1$ 2 unit.  $^{82}$ 

## 3.6 Rearrangement of $[H_2P_2W_{12}O_{48}]^{12-}$ in acidic medium

Lanthanide-containing POMs are interesting due to potentially attractive photoluminescence, Lewis acid catalysis, electro-

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chemistry, and magnetic properties. Due to the larger size and resulting higher coordination number of lanthanide ions as compared to d-block metal ions, they cannot be fully incorporated into the vacant sites of lacunary POMs and hence tend to link two or more polyanions, as observed in one of the largest polyanions,  $[As_{12}^{III}Ce_{16}^{III}(H_2O)_{36}W_{148}O_{524}]^{76-}$  ( $W_{148}$ ), reported by Pope and coworkers.<sup>83</sup>

In 2000, Pope's group reported the polyanion  $[Ce_4(OH_2)_9(OH)_2(\alpha_1,\alpha_1\text{-}P_2W_{16}O_{59})_2]^{14-}$   $(Ce_4(\alpha_1\alpha_1\text{-}P_2W_{16})_2)$  in which the  $P_2W_{12}$  precursor picks up extra tungsten atoms and then incorporates four cerium(III) ions. The polyanion  $Ce_4(\alpha_1\alpha_1\text{-}P_2W_{16})_2$  exhibits a dimeric structure with  $C_{2v}$  symmetry, comprising two  $\{\alpha_1,\alpha_1\text{-}P_2W_{16}O_{59}\}$  (abbreviated as  $P_2W_{16}$ ) units connected via a central core of four cerium atoms. There are two structural types of cerium in this polyanion, the first one has 10-coordination and the other has 9-coordination. The  $^{31}P$  and  $^{183}W$  NMR studies in aqueous solution suggested that the polyanion is stable in solution.

In 2003, Kortz reported the lanthanum-substituted polyanion  $[\{La(CH_3COO)(H_2O)_2(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{16-}$   $(La(OAc)\text{-}(\alpha_2\text{-}P_2W_{17})_2)$ , which was synthesized by reaction of La³+ ions with the hexalacunary polyanion  $P_2W_{12}$ .  $^{84}$  It was observed that  $P_2W_{12}$  rearranges quickly in an aqueous, acidic medium to the monolacunary  $\left[\alpha_1\text{-}P_2W_{17}O_{61}\right]^{10-}$  which in turn rearranges to  $\left[\alpha_2\text{-}P_2W_{17}O_{61}\right]^{10-}$ . The polyanion  $La(OAc)\text{-}(\alpha_2\text{-}P_2W_{17})_2$  is composed of two  $\left[\alpha_2\text{-}P_2W_{17}O_{61}\right]^{10-}$  fragments connected by two lanthanum acetato dimers  $(La_2(CH_3COO)_2(H_2O)_4)^{4+}$ , resulting in a head-on, transoid dimer with  $C_{2h}$  symmetry. Each La³+ atom exhibits a nine-coordinatied geometry.  $^{61}$  The monolacunary Wells–Dawson ion  $\left[\alpha_2\text{-}P_2W_{17}O_{61}\right]^{10-}$  is known to react with lanthanide ions to form Pope's "head-on dimers" or Francesconi's "side-on dimers".  $^{61,85}$ 

The Enbo Wang group has shown considerable interest in synthesizing metal–organic frameworks containing the Wells–Dawson ion. In 2008, they reported three transition metal-containing Wells–Dawson-based assemblies, using the  $P_2W_{12}$  anion as a reagent,  $K_4Na_{10}[\alpha_1\text{-Cu}P_2W_{17}O_{60}(OH)]_2\cdot58H_2O$  ( $Cu_2P_4W_{34}$ ),  $Na_2[H_2en][H_2hn]_{0.5}[Cu(en)_2]_{4.5}[\alpha_1\text{-Cu}P_2W_{17}O_{60}(OH)]_2\cdot43H_2O$  (Cu (en)\_2\alpha\_1\cdot CuP\_2W\_{17}\rangle\_0, and  $Na_3[H_2hn]_{2.5}[P_2W_{17}O_{60}Cu(OH)_2]\cdot14H_2O$  ((H\_2hn(CuP\_2W\_{17})\_2)\_\infty, where en = 1,2-ethylenediamine; hn = 1,6-hexamethylene diamine). The Cu\_2P\_4W\_{34} polyanion consists of two \alpha\_1\cdot P\_2W\_{17} units with the vacant \alpha\_1 (belt) position being occupied by a Cu^{2+} atom and the two Wells–Dawson units are connected by two W-OH-Cu groups resulting in a dimeric [\alpha\_1\cdot CuP\_2W\_{17}O\_{60}(OH)]\_2^{14-} (Cu\_2P\_4W\_{34}) assembly.

The  $(Cu(en)_2\alpha_1\text{-}CuP_2W_{17})_{\infty}$  constitutes the first 2-D organic–inorganic hybrid network based on such double-Dawson-type polyanion (DDTP) building blocks and (Cu  $(en)_2)^{2+}$  bridging units, representing a large polyoxotungstate building block for the construction of extended organic–inorganic hybrid materials. Subsequently,  $\{(H_2hn)(CuP_2W_{17})_2\}_{\infty}$  possesses a 3-D hybrid supramolecular framework with 1-D channels that are constructed from the half-unit of the 'DDTP' and 'hn' cations. A magnetic study of  $(Cu(en)_2\alpha_1\text{-}CuP_2W_{17})_{\infty}$  indicated weak antiferromagnetic interactions and that the two types of  $Cu^{2+}$  centers are well separated.

All the above examples consist of mono-Cu2+ substituted Wells-Dawson-type polyanions. Further exploration by the Wang group focused on feasible synthetic routes by adjusting the composition of Wells-Dawson polyanions to capture more transition metal ions. Subsequently, they reported a 1-D inorganic polymer formed by the reaction of P<sub>2</sub>W<sub>12</sub> with Mn<sup>2+</sup>  $Na_8H_2L(H_2enMe)_4[Mn(H_2O)_2]$  $(W_4Mn_4O_{12})$  $(P_2W_{14}O_{54})_2$ ]·17H<sub>2</sub>O,  $\{W_4Mn_4(MnP_2W_{14})_2\}_{\infty}$  (L = pyromellitic dianhydride PMDA).87 The structure of this compound consists of two tetravacant Dawson moieties  $[P_2W_{14}O_{54}]^{14-}(P_2W_{14})$ sandwiching an eight-metal cluster with W-O-W(Mn) and P-O- $W_{(Mn)}$  connecting modes. The metal centers in this eightmetal cluster form an almost regular cubane-like (W4Mn4) cluster. The solid-state network is completed by multi-Mn<sup>2+</sup>substituted DDTP and Mn2+ linkers with idealized C2 symmetry, which is further connected into a 3-D supramolecular network via extensive hydrogen-bonding interactions.

In 2013, Yang and coworkers reported three lanthanide derivatives of  $P_8W_{48}$ ,  $\{[Ln_2(\mu\text{-OH})_4(H_2\text{O})x]_2(H_{24}P_8W_{48}O_{184})\}^{12-}$  (Ln = Nd, Sm, Tb) ( $Ln_4P_8W_{48}$ ), and a manganese derivative, [K ( $H_2\text{O})_2$ ] $_4$ [K $_4$ ( $\mu\text{-H}_2\text{O})_8$ ] $_2$ [K( $H_2\text{O}$ )] $_8$ {[Mn $_8$ ( $H_2\text{O}$ ) $_1$ 6]( $H_4P_8W_{48}O_{184}$ )} ( $K_8Mn_8P_8W_{48}$ ), starting from  $P_2W_{12}$  as precursor and working under hydrothermal conditions. So The cavities of  $P_8W_{48}$  in  $Ln_4P_8W_{48}$  are occupied by lanthanide ions bridged by hydroxyl groups, and the 8 lanthanide ions have a 50% occupancy each. The  $K_8Mn_8P_8W_{48}$  polyanion is formed by incorporating eight Mn<sup>2+</sup> atoms inside the eight vacant sites within the cavity of the cyclic  $P_8W_{48}$ . These  $Mn^{2+}$  atoms are observed to be disordered over eight positions with  $K^+$  atoms. The compounds were characterized by single-crystal XRD, FTIR, elemental analysis, thermogravimetry, and powder XRD.

In 2020, Abramov and coworkers reported the dimeric triniobium-substituted  $P_2W_{15}$  polyanion,  $[\mathit{cis}\text{-}(P_2W_{15}Nb_3O_{61})_2]^{14-}$   $(P_2W_{15}Nb_3)$ , and two phases of the disordered derivative  $[\mathit{trans}\text{-}(P_2W_{14.7}Nb_{3.3}O_{61})_2]^{14.6-}$  using  $P_2W_{12}$  as a precursor. <sup>90</sup> The main structural unit consists of the dimeric  $[(P_2W_{16}Nb_4O_{60})_2(\mu\text{-}O)_2]^{n-}$  archetype anion based on two Wells–Dawson-type subunits, connected by two Nb–O–Nb bridges. Interestingly, out of the 12 niobium positions, only four are fully occupied. The addition of  $Me_2NH_2Cl$  to the reaction media yields a mixture of triclinic and orthorhombic crystal-

line phases. The dimeric units are comprised of two Dawson anions connected via Nb-O-Nb bridges. In 2020, Kortz and coworkers reported the gigantic, macrocyclic 48-Fe<sup>III</sup>-96-tungsto- $[Fe_{48}(OH)_{76}(H_2O)_{16}(HP_2W_{12}O_{48})_8]^{36-}$ 

16-phosphate, (Fe<sub>48</sub>(P<sub>2</sub>W<sub>12</sub>)<sub>8</sub>), which was prepared by reaction of P<sub>2</sub>W<sub>12</sub> and 22-iron(III)-containing coordination  $[Fe_{22}O_{14}(OH)_3(O_2CMe)_{21}(mda)_6]\cdot(ClO_4)_2$ (mdaH<sub>2</sub> N-methyldiethanolamine) and isolated as a potassium salt,  $K_{36}[Fe_{48}(OH)_{76}(H_2O)_{16}(HP_2W_{12}O_{48})_8]$ . 91 The crystal structure of Fe48(P2W12)8 revealed that there are eight equivalent {Fe<sub>6</sub>P<sub>2</sub>W<sub>12</sub>} Dawson-type subunits linked to each other via Fe-O-Fe/W bonds, resulting in a cyclic assembly with idealized  $D_2$ point group symmetry and a cavity of ca. 24 Å  $\times$  13 Å. Magnetic studies indicated that the 48 Fe<sup>3+</sup> centers in Fe<sub>48</sub>(P<sub>2</sub>W<sub>12</sub>)<sub>8</sub> share several exchange pathways. The averaged exchange coupling constant was estimated to be  $J_{av} = -7.07$  K. The electrochemical study of Fe48(P2W12)8 exhibited redox transitions, suggesting the electroactivity of the  $\mathrm{Fe}^{\mathrm{3+}}$  and  $\mathrm{W}^{\mathrm{VI}}$  ionic states.

# 4. Metal complexes of $[H_6P_4W_{24}O_{94}]^{18-}$

**Dalton Transactions** 

Kortz and co-workers first showed that the super-lacunary Preyssler-Jeannin-Pope ion  $[H_2P_4W_{24}O_{94}]^{22-}$   $(P_4W_{24})$  can react with electrophiles. The dimethyltin-containing hybrid organic-inorganic polyanion  $[\{Sn(CH_3)_2\}_4(H_2P_4W_{24}O_{92})_2]^{28-}$  $({Sn(CH_3)_2}_4(P_4W_{24})_2)$  (Fig. 9) was prepared by reaction of  $(CH_3)_2SnCl_2$  with  $P_4W_{24}$  in an aqueous, acidic medium at ambient temperature and isolated as a potassium salt.<sup>44</sup> The polyanion comprises two P4W24 units linked through four dimethyltin groups, leading to a structure with  $D_{2d}$  point group symmetry. The two P4W24 units of the polyanion {Sn (CH<sub>3</sub>)<sub>2</sub>}<sub>4</sub>(P<sub>4</sub>W<sub>24</sub>)<sub>2</sub> are oriented orthogonally to each other and held together by four dimethyltin groups. Room temperature <sup>119</sup>Sn [ $\delta$  (ppm) = -243.2 ppm], <sup>31</sup>P [ $\delta$  (ppm) = -7.1, -8.7 ppm],  $^{13}$ C [ $\delta$  (ppm) = 8.6 ppm], and  $^{1}$ H [ $\delta$  (ppm) = 0.7 ppm] NMR studies in aqueous medium proved the integrity of the solidstate structure in solution.

The continued study of Kortz and coworkers of the lacunary precursor P<sub>4</sub>W<sub>24</sub> has produced interesting new compounds with interesting physical and chemical properties. Kortz and coworkers studied the interaction of phosphotungstates with actinide ions, especially uranyl, as these complexes can potentially have rich structural, magnetic, and electrochemical properties. In 2008, the uranyl-peroxo-containing 36-tungsto-8phosphate  $[Li(H_2O)K_4(H_2O)_3\{(UO_2)_4(O_2)_4(H_2O)_2\}_2(PO_3OH)_2P_6$  $W_{36}O_{136}]^{25-}$  (Li(UO<sub>2</sub>)<sub>4</sub>(O<sub>2</sub>)<sub>4</sub>(PO<sub>3</sub>OH)<sub>2</sub>P<sub>6</sub>W<sub>36</sub>) (Fig. 10) was synthesized and structurally characterized using P4W24 as precursor. 92 The structure comprises three P2W12 units encapsulating two independent, neutral [(UO<sub>2</sub>)(O<sub>2</sub>)]<sub>4</sub> units in the central cavity, resulting in a U-shaped (P2W12)3 assembly. Notably, the resulting polyanion could not be isolated using P2W12 as a reagent instead of P<sub>4</sub>W<sub>24</sub>. Notably, from the single-crystal X-ray diffraction data, a lithium atom embedded in the structure was observed, which is rare in polyoxotungstate chemistry,

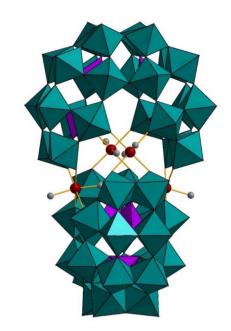


Fig. 9 Combined polyhedral/ball-and-stick representation of [{Sn  $(CH_3)_2$ <sub>4</sub> $(H_2P_4W_24O_{92})_2$ <sup>28-</sup>. Color code: WO<sub>6</sub> octahedra (green), PO<sub>4</sub> tetrahedra (pink), C (grey), Sn (red). No hydrogen atoms are shown for clarity.44

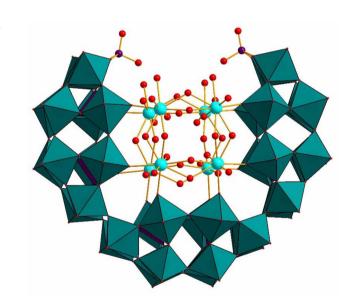


Fig. 10 Combined polyhedral/ball-and-stick representation of [Li(H2O)  $K_4(H_2O)_3\{(UO_2)_4(O_2)_4(H_2O)_2\}_2(PO_3OH)_2P_6W_{36}O_{136}]^{25-}$ . Color code:  $WO_6$ octahedra (green), PO<sub>4</sub> tetrahedra (pink), U (turquoise), P (pink), O (red).92

given that the high electron density of the W atoms generally tends to obscure such a low electron-dense atom. The coordination of the central uranium-peroxo unit  $\{(UO_2)_4(O_2)_4(H_2O)_2\}_2$ comprises eight uranyl-peroxo units subdivided in two [(UO2)  $(O_2)$ <sub>4</sub> squares, the  $\eta^2$ -peroxo ions being bound side-on to each

pair of uranium atoms. The room temperature <sup>31</sup>P NMR spectrum of the polyanion in water was fully consistent with its solid-state structure.

A mixed-valent vanadium derivative  $[Rb_3 \subset \{V^VV_3^{IV}O_7(H_2O)_6\}_2$  $\left\{H_6P_6W_{39}O_{147}(H_2O)_3\right\}]^{15-}\left((\boldsymbol{V^VV_3^{IV}O_7})_2(P_6W_{39})\right) \text{ (Fig. 11) was also}$ reported by Kortz and coworkers. 93 This polyanion was synthesized by the reaction of vanadium(IV) and vanadium(V) with P<sub>4</sub>W<sub>24</sub> in an acidic aqueous medium (pH 3.2-3.7). A mixed rubidium/potassium salt was isolated and characterized by single-crystal XRD, elemental analysis, TGA, IR, and 31P NMR spectroscopy. The polyanion is composed of three P2W12 subunits, which form a macrocyclic template of P<sub>6</sub>W<sub>39</sub>, capped by two mixed-valent  $\{(V^{V}=O)(V^{IV}=O)_3(\mu_2-O)_3(H_2O)_6\}^{3+} \{(V^{V}V_3^{IV})\}$ groups. Each {VVV<sub>3</sub><sup>IV</sup>} cap comprises three octahedrally-coordinated VIV atoms and one tetrahedrally-coordinated VV atom. Each of the P<sub>2</sub>W<sub>12</sub> units is linked through {WO(H<sub>2</sub>O)} groups to form a cyclic P<sub>6</sub>W<sub>39</sub> assembly in this polyanion. The connectivity mode of the  $P_2W_{12}$  units in this polyanion resembles what Wang and coworkers had seen previously.<sup>58</sup> In the polyanion  $(V^{V}V_{3}^{IV}O_{7})_{2}P_{6}W_{39}$ , the tetrahedral  $V^{V}=O$  oxo group of each {VVV3V} cap is bridged by three VIVO6 octahedra, which occupy the hexavacant positions in the P<sub>6</sub>W<sub>39</sub> unit. Notably, the terminal oxo-ligands of both the  $V^{IV}$  and  $V^{V}$ metal centers are directed towards the interior of the polyanion. The solid-state structure of the polyanion  $(V^{V}V_{3}^{IV}O_{7})_{2}P_{6}W_{39}$  was maintained in solution, as confirmed by <sup>31</sup>P NMR. The same type of connectivity and geometry of vanadium(ıv/v) has been observed before for Müller's/Pope's mixed-valent vanadium-containing polyanion [K<sub>8</sub>C{V<sub>4</sub><sup>V</sup>V<sub>2</sub><sup>IV</sup>O<sub>12</sub>  $(H_2O)_2\}_2\{P_8W_{48}O_{184}\}]^{24-} \quad ((V_4^VV_2^{IV}O_{12})_2P_8W_{48}) \quad (\textit{vide infra},$ section 6).94

# 5. Metal complexes of $[H_7P_8W_{48}O_{184}]^{33-}$

Since the pioneering discovery of the Cu2+-containing polya- $[Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$  $(Cu_{20}ClP_8W_{48})$ (Fig. 12) in 2005, the chemistry of P<sub>8</sub>W<sub>48</sub> has continued to inspire chemists to study this unique cyclic, multilacunary polyanion. Since then, numerous compounds have been reported using the wheel-shaped P8W48 polyanion as a precursor, which includes distinct anionic species as well as zeolitic frameworks.95

The first transition metal-containing P8W48 polyanion, Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub>, was synthesized by Kortz and coworkers by reacting Cu2+ ions with P8W48 in an aqueous medium, and the product was fully characterized by IR, <sup>31</sup>P NMR, single-crystal X-ray diffraction and magnetic studies.<sup>96</sup> The 20-copper-oxo cluster in Cu20ClP8W48 comprises three structurally unique types of copper(II) atoms with respect to their coordination geometry, namely octahedral, square-pyramidal, and squareplanar, with a central chloride ion acting as a template. The copper ions are connected by \( \mu\_3\)-hydroxo-ligands, resulting in a highly symmetrical, cage-like copper-hydroxo cluster assembly,  $\{Cu_{20}(OH)_{24}\}^{16+}$ . In order to study the variation of the magnetic properties of the cluster in the presence of different halide ions, Mal et al. prepared derivatives of Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub>, with the central chloride guest being replaced by a bromide and an iodide ion,  $[Cu_{20}Br(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$  $(Cu_{20}BrP_8W_{48})$  $[Cu_{20}I(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$  $(Cu_{20}IP_8W_{48}).^{97}$ 

DFT calculations were performed on the Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub> polyanion in order to obtain additional information on the pro-

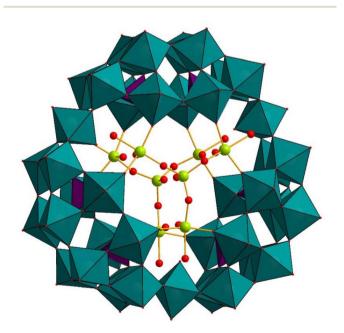


Fig. 11 Combined polyhedral/ball-and-stick representation  $[Rb_3 \subset \{V^V V_3^{V} O_7 (H_2 O)_6\}_2 \{H_6 P_6 W_{39} O_{147} (H_2 O)_3\}]^{15-}$ . Color code: WO<sub>6</sub> octahedra (green), PO<sub>4</sub> tetrahedra (pink), O (red), V (yellow). 93

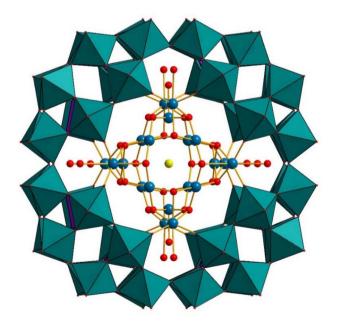


Fig. 12 Combined polyhedral/ball-and-stick representation of [Cu<sub>20</sub>X  $(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$  (X = Cl, Br, I). Color code: WO<sub>6</sub> octahedra (green), PO<sub>4</sub> tetrahedra (pink), O (red), Cu (blue), X (yellow). 96

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perties of the anionic guest inside the cavity created by the 20-copper-hydroxo cage, related to its electronic structure and energies of encapsulation.98 The DFT calculations indicated the central halide ion to be extremely stable inside the polyanion cavity and cannot be released even at higher temperatures, without the destruction of the POM framework. Magnetic measurements showed that the Cu<sup>2+</sup> atoms in all halide-derivatives are antiferromagnetically coupled, leading to an overall diamagnetic ground state.97

The solution stability of the polyanion Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub> was investigated by electrochemical studies at varying pH. 98 It was observed that the resolution of the reduction wave for Cu<sup>2+</sup> to Cu<sup>0</sup> through Cu<sup>+</sup> was much better at pH 5.0, than compared with measurements performed at lower or higher pH values. It was also observed that all 20 Cu<sup>2+</sup> centers within the polyanionic complex remain electroactive, as observed using controlled potential coulometry measurements and strong electrocatalytic reduction behavior towards NO<sub>x</sub>. 98,99

Scanning tunneling microscopic (STM) and scanning tunneling spectroscopic (STS) studies were performed on a highly oriented pyrolytic graphite (HOPG) surface at room temperature to visualize the 20-copper cluster. 100 STS measurements were done especially to better understand the STM results of Cu20ClP8W48, such as the Cu...Cu distances and the orientation of the polyanion after deposition. The STM and STS images show a regular assembly of the polyanions and the regularly separated single copper atoms in the organic matrix. Several types of polyanion arrangements were observed by STM measurements on the HOPG surface, ostensibly due to the different concentration levels of Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub>.

Most POMs exhibit hydrophilicity accompanied by high solubility of the corresponding salt in polar solvents, mainly due to a substantial negative charge and oxo/hydroxo/aqua ligands on the surface. Based on such a notion, Kortz and coworkers investigated several solution properties of the Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub> polyanion, for example, the investigation of supramolecular interaction resulting in "blackberry-type" structures, where the highly soluble homogeneous electrolytes tend to self-assemble into single layer, spherical, vesical-like structures in dilute solution. 101,102 Earlier reports of such studies were limited to polyoxomolybdate structures, 103-106 until Liu, Kortz, and coworkers showed that polyoxotungstates could also form "blackberry-type" arrangements. Such phenomena were mainly studied by dynamic light scattering (DLS), static light scattering (SLS), and zeta potential measurements. 103-106 The DLS studies showed that a slow supramolecular assembly formation in an aqueous Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub> solution starts spontaneously on the 11<sup>th</sup> day of the experiment, accompanied by continuous growth until 40 days before finally becoming stable. 101,102 Further studies using SLS indicated that the "blackberry-type" structure solution is relatively stable over prolonged periods, as evidenced by no change in scattering intensity for a month-old solution. It should be noted that the "blackberry-type" structure for Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub> only forms at 50 °C. DLS and SLS also provide important information regarding the mechanism of formation

The individual such "blackberry-type" structures. Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub> polyanions first overcome the high kinetic energy barrier, 107-110 and then slowly nucleate together, quickly forming a "blackberry-type" structure with an average radius of 38 nm. It was also observed that the counter cations play a major role in forming the blackberry solution. 111

The Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub> polyanion was also investigated for the fabrication of organized thin films by the Langmuir-Blodgett (LB) technique. The polyanions can be introduced into organic-inorganic hybrid films using different LB techniques, resulting well-defined lavered structures. Dimethyldioctadecylammonium bromide (DODA) observed to react with Cu20ClP8W48 to form a surfactant-encapsulated Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub>, which was characterized by different analytical techniques, such as NMR, FT-IR, TGA, powder X-ray diffraction (XRD), and elemental analysis. XRD studies indicated that two different types of DODA-Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub> structures are present (DODA/Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub> and DODA-Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub>) based on the diameter and thickness of the layer spacing. The two types of LB films were successfully fabricated onto the substrate by using different deposition methods. It was also observed that Cu20ClP8W48 exhibits different packing modes in the two LB films, depending on the deposition strategy used. 112,113 Further studies on Cu20ClP8W48 include electrocatalytic reduction of NO<sub>x</sub>. 98 The polyanion Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub> has also been shown to be a very efficient heterogeneous catalyst for the solvent-free aerobic oxidation of n-hexadecane. 114 In such a study, Cu20ClP8W48 was first supported on 3-aminopropyltriethoxysilane (apts)-modified SBA-15 and then subsequently used for the aerobic oxidation of n-hexadecane, showing an exceptionally high turnover frequency (TOF) of 20 000 h<sup>-1</sup> and resistance to CS<sub>2</sub> poisoning. The efficiency of the polyanion catalyst was observed to increase dramatically upon immobilization on mesoporous support due to a large increase in the surface area, which enhanced the oxidation of n-hexadecane into ketones and alcohols. Moreover, it was found that the supported catalyst can be reused at least five times, retaining almost the same catalytic activity as the fresh catalyst.

Mialane and coworkers have been exploring POMs containing azido ligands since 2003. 115 The azido ligands can act as connectors between the 3d metal centers embedded in a POM unit and also act as intermolecular linkers between different POM subunits, leading to high-nuclearity POM complexes. Pichon et al. have shown that azido groups can also function as ligands in P8W48 by preparing the large azido-POM  $\begin{array}{ll} \left[P_8W_{48}O_{184}Cu_{20}(N_3)_6(OH)_{18}\right]^{24-} \left(Cu_{20}(N_3)_6P_8W_{48}\right).^{116} \text{ The polyanion } Cu_{20}(N_3)_6P_8W_{48} \quad \text{has two} \quad \left\{Cu_5(OH)_4\right\}^{6+} \quad \text{and} \quad \text{two} \end{array}$  $\{Cu_5(OH)_2(\mu_{1,1,3,3}-N_3)\}^{7+}$  subunits encapsulated in the crownshaped P8W48.

In each of the four subunits  $\{Cu_5(OH)_4\}^{6+}$  $\{Cu_5(OH)_2(\mu_{1,1,3,3}-N_3)\}^{7+}$ , the five  $Cu^{2+}$  atoms form a square pyramid with two µ3-hydroxo ligands connecting the apical Cu<sup>2+</sup> center to the four basal copper atoms. Interestingly, in each {Cu5(OH)4}6+ fragment, the apical copper atom has an axially distorted coordination geometry, and the four remain-

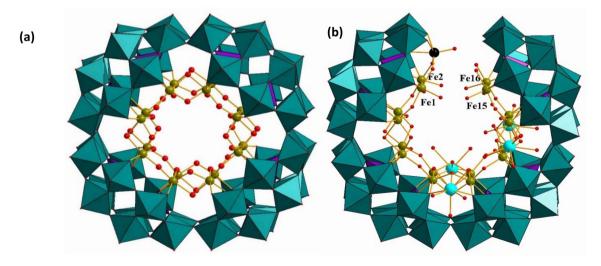
ing Cu centers exhibit a distorted trigonal-bipyramidal geometry. Moreover, the  $\{Cu_5(OH)_4\}^{6+}$  fragments in  $Cu_{20}(N_3)_6P_8W_{48}$ are crystallographically disordered between the hydroxo and azido ligands connecting the Cu2+ atoms. Hence, the polyanion is a mixture of species containing two different  $\{Cu_5(OH)_4\}^{6+}$  subunits.

Kortz, Müller, and coworkers have synthesized the 16-Fe<sup>3+</sup> containing polyanion  $[P_8W_{48}O_{184}Fe_{16}(OH)_{28}(H_2O)_4]^{20-}$  $(Fe_{16}P_8W_{48})$  (Fig. 13a), which was prepared independently.<sup>117</sup> The polyanion contains a cationic 16-iron(III)-hydroxo nanocluster  $\{Fe_{16}(OH)_{28}(H_2O)_4\}^{20+}$  in the cavity of the crown-shaped  $P_8W_{48}$ . The  ${\rm \{Fe_{16}(OH)_{28}(H_2O)_4\}^{20+}}$  cluster comprises eight pairs of structurally equivalent, edge-shared {Fe2O12} octahedra, which are connected to each other via corners. Notably, the binding mode of the 16 Fe<sup>3+</sup> centers in Fe<sub>16</sub>P<sub>8</sub>W<sub>48</sub> differs from the 20 Cu2+ centers in Cu20ClP8W48. In Fe16P8W48, each of the 16 equivalent Fe<sup>3+</sup> centers is connected to P<sub>8</sub>W<sub>48</sub> by Fe-O(W) and a Fe-O(P) bonds, resulting in a tight anchoring of the 16-iron-hydroxo core,  $\{Fe_{16}(OH)_{28}(H_2O)_4\}^{20+}$ , to the wheelshaped POM host. In Cu<sub>20</sub>ClP<sub>8</sub>W<sub>48</sub>, only eight of the 20 Cu<sup>2+</sup> ions form two Cu-O(W) bonds each and hence are bound to the P<sub>8</sub>W<sub>48</sub> host. On the other hand, the eight phosphate hetero groups of P8W48 are not directly bonded to the cationic  $\{Cu_{20}(OH)_{24}\}^{16+}$  cluster. Nevertheless,  $Cu_{20}CIP_8W_{48}$  is quite stable in solution. In fact, Fe<sub>16</sub>P<sub>8</sub>W<sub>48</sub> is structurally more closely related to Mialane's Cu20-azide derivative,  $Cu_{20}(N_3)_6P_8W_{48}$ . <sup>116</sup> In  $Cu_{20}(N_3)_6P_8W_{48}$ , 16 of the 20  $Cu^{2+}$  ions are connected to the inner cavity of  $P_8W_{48}$  in the same fashion as the Fe3+ centers in Fe16P8W48. The sites of the remaining four unique Jahn-Teller distorted Cu2+ atoms in Cu<sub>20</sub>(N<sub>3</sub>)<sub>6</sub>P<sub>8</sub>W<sub>48</sub> are observed to remain empty in Fe<sub>16</sub>P<sub>8</sub>W<sub>48</sub>. Kortz and coworkers further investigated the Fe<sub>16</sub>P<sub>8</sub>W<sub>48</sub> polyanion toward incorporating lanthanide ions in the remaining vacancies. They successfully prepared an unprecedented, horseshoe-shaped 16-iron(III)-containing  $\left[Fe_{16}O_{2}(OH)_{23}(H_{2}O)_{9}P_{8}W_{49}O_{189}Ln_{4}(H_{2}O)_{19}\right]^{11-} \ (Ln \ = \ Eu, \ Gd)$  $(Fe_{16}Ln_4P_8W_{49})$  (Fig. 13b) with a central  $[Fe_{16}(OH)_{28}(H_2O)_4]^{20+}$ guest. These Fe<sub>16</sub>Ln<sub>4</sub>P<sub>8</sub>W<sub>49</sub> polyanions can be called open derivatives of  $Fe_{16}P_8W_{48}$ , where the  $P_8W_{48}$  template wheel does not remain intact and is cut open. The {Fe<sub>16</sub>} ring in Fe<sub>16</sub>Ln<sub>4</sub>P<sub>8</sub>W<sub>49</sub> is cleaved between four Fe atoms (Fe1/Fe2 on one side and Fe15/Fe16 on the other). Interestingly, an extra tungsten atom is incorporated into the P8W48 framework, resulting in an open  $\{P_8W_{49}\}$  unit. The extra W atom occupies the cap of the P2W12 Wells-Dawson fragment and is connected to the novel open  $P_8W_{48}$  fragment through one  $\mu_4$ -oxo and two  $\mu_2$ -oxo bridges.

Kortz and coworkers have also reported Co2+, Mn2+, Ni2+, and V<sup>V</sup>-containing derivatives based on the P<sub>8</sub>W<sub>48</sub> wheel. For the Mn and Ni derivatives, the tungsten-oxo wheel has accumulated two extra tungsten atoms, resulting in the unpreunit.120 cedented  $P_8W_{50}$ All four compounds,  $K_{12}Li_{16}Co_{2}[Co_{4}(H_{2}O)_{16}P_{8}W_{48}O_{184}]$  ( $Co_{4}P_{8}W_{48}$ ), <sup>121</sup> (Fig. 14a)  $K_{12}Li_{10}Mn_3[Mn_4(H_2O)_{16}(P_8W_{48}O_{184})(WO_2(H_2O)_2)_2]$  $(\mathbf{Mn_4P_8W_{50}})^{121}$   $K_{14}Li_8Ni_3[Ni_4(H_2O)_{16}(P_8W_{48}O_{184})(WO_2(H_2O)_2)_2]$  $(Ni_4P_8W_{50})$  (Fig. 14b), <sup>121</sup> and  $K_{20}Li_{16}[(VO_2)_4(P_8W_{48}O_{184})]$  $((VO_2)_4P_8W_{48})$ , <sup>121</sup> were synthesized and characterized by singlecrystal XRD, FTIR, elemental analysis, electrochemistry, magnetic susceptibility, and EPR techniques.

The Co<sub>4</sub>P<sub>8</sub>W<sub>48</sub> and (VO<sub>2</sub>)<sub>4</sub>P<sub>8</sub>W<sub>48</sub> were prepared by reacting Co<sup>2+</sup> and VO<sup>2+</sup> with P<sub>8</sub>W<sub>48</sub> in aqueous solution, respectively. Bassil et al. have isolated the manganese(II) derivative Mn<sub>4</sub>P<sub>8</sub>W<sub>50</sub> and its nickel(II) analogue Ni<sub>4</sub>P<sub>8</sub>W<sub>50</sub>, using similar synthetic procedures but in the presence of small amounts of H<sub>2</sub>O<sub>2</sub>. 121

The solid-state structure of Co<sub>4</sub>P<sub>8</sub>W<sub>48</sub> consists of four Co<sup>2+</sup> atoms coordinated to the hinge-oxygens at the inner rim of P<sub>8</sub>W<sub>48</sub>. As perceived from the structures of similar transition



polyhedral/ball-and-stick  $[P_8W_{48}O_{184}Fe_{16}(OH)_{28}(H_2O)_4]^{20-}$ Fig. 13 Combined (a) (h) representations  $[Fe_{16}O_2(OH)_{23}(H_2O)_9P_8W_{49}O_{189}Ln_4(H_2O)_{19}]^{11} - (Ln = Eu, Gd). \ Color \ code: WO_6 \ octahedra \ (green), PO_4 \ tetrahedra \ (pink), O \ (red), Fe \ (green), Ln \ (tur-local tetrahedra \ (pink), O \ (red), Fe \ (pink), Cn \ (pink),$ quoise), W (black). 118,119

**Dalton Transactions** Perspective

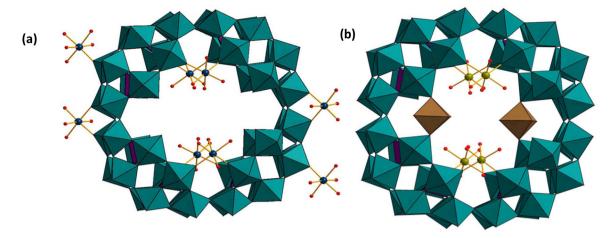


Fig. 14 (a) Combined polyhedral/ball-and-stick representations of (a)  $[Co_4(H_2O)_{16}P_8W_{48}O_{184}]^{32-}$  and (b)  $[Ni_4(H_2O)_{16}(P_8W_{48}O_{184})(WO_2(H_2O)_2)_2]^{28-}$ . Color code: WO<sub>6</sub> octahedra (green and brown), PO<sub>4</sub> tetrahedra (pink), O (red), Co (deep blue), Ni (green). The brown WO<sub>6</sub> octahedra have an occupancy of 50% each. 121

metal derivatives of  $P_8W_{48}$ ,  $^{71,72}$  the terminal W-O oxygen atoms are observed to point towards the center of the polyanion. Interestingly, in Co<sub>4</sub>P<sub>8</sub>W<sub>48</sub> only half of the eight equivalent hinge sites are occupied by the four Co<sup>2+</sup> atoms that are coordinated in a cis fashion to two oxo(W) ligands from two adjacent P2W12 subunits. Aqua ligands occupy the remaining four terminal coordination sites. In addition to the four inner Co<sup>2+</sup> ions, two outer Co<sup>2+</sup> ions were found in Co<sub>4</sub>P<sub>8</sub>W<sub>48</sub>, linking adjacent polyanions and forming a one-dimensional chain in the solid state. Magnetic studies indicated that the two types of Co<sup>2+</sup> centers are non-interacting with each other.

Cronin and coworkers have reported a cobalt(II) salt of a cobalt(II)-containing  $P_8W_{48}$  assembly  $\{Co_4[Co_6(P_8W_{48}O_{184})]\}_{\infty}$  $(Co_4(Co_6P_8W_{48})_{\infty})$  with six internal and four external  $Co^{2+}$  ions bridging neighboring polyanions, resulting in a 1D chain or 3D network, respectively. 122 Kortz's group reported the tetracobalt(11)-containing polyanion Co<sub>4</sub>P<sub>8</sub>W<sub>48</sub> (which crystallized with two extra cobalt(II) counter cations). The coordination of two pairs of Co2+ ions in diagonally related positions of  $Co_4P_8W_{48}$  led to a subtle distortion of the  $P_8W_{48}$  assembly, as reflected by a difference of ca. 1.6 Å between the polyanion diameter of opposite W centers where the Co<sup>2+</sup> ions are bound and the diameter of opposite W centers perpendicular to the previous one. Wang, Su, and coworkers have synthesized three  $\text{Co}^{2+}$  linked derivatives of  $P_8W_{48}$ ,  $\text{Na}_8\text{Li}_8\text{Co}_5[\text{Co}_{5.5}(\text{H}_2\text{O})_{19}]$  $P_8W_{48}O_{184}$ ]-60H<sub>2</sub>O (Co<sub>5</sub>(Co<sub>5.5</sub>P<sub>8</sub>W<sub>48</sub>)<sub>∞</sub>), K<sub>2</sub>Na<sub>4</sub>Li<sub>11</sub>Co<sub>5</sub>[Co<sub>7</sub>(H<sub>2</sub>O)<sub>28</sub> P<sub>8</sub>W<sub>48</sub>O<sub>184</sub>Cl·59H<sub>2</sub>O  $(Co_5(Co_7P_8W_{48})_{\infty}),$ and K<sub>2</sub>Na<sub>4</sub>LiCo<sub>11</sub>  $[Co_8(H_2O)_{32}P_8W_{48}O_{184}](CH_3COO)_4Cl\cdot47H_2O \quad (Co_{11}(Co_8P_8W_{48})_{\infty}),$ which were characterized by FTIR, thermogravimetric analysis, elemental analysis, and magnetic measurements. 123 In  $Co_5\{Co_{5.5}P_8W_{48}\}_{\infty}$  and  $Co_5\{Co_7P_8W_{48}\}_{\infty}$ , four external cobalt(II) ions are observed to link adjacent polyanions, resulting in twodimensional networks, while  $Co_{11}\{Co_8P_8W_{48}\}_{\infty}$  is observed to form three-dimensional networks.  $Co_{11}\{Co_8P_8W_{48}\}_{\infty}$  exhibits the largest cobalt(II) containing P<sub>8</sub>W<sub>48</sub> to date when counterions are also considered.

Kortz's group reported the polyanions Mn<sub>4</sub>P<sub>8</sub>W<sub>50</sub> and Ni<sub>4</sub>P<sub>8</sub>W<sub>50</sub> with four Mn<sup>2+</sup>/Ni<sup>2+</sup> ions bound in the cavity of  $P_8W_{48}$  as the  $Co^{2+}$  ions in  $Co_4P_8W_{48}$ , and two additional  $\{WO_6\}$ octahedral units disordered over the four equivalent positions perpendicular to the plane of the Mn2+/Ni2+ ions, resulting in a polyanion with  $C_{2h}$  point group symmetry. The "extra" tungsten centers in Mn<sub>4</sub>P<sub>8</sub>W<sub>50</sub> and Ni<sub>4</sub>P<sub>8</sub>W<sub>50</sub> are coordinated to oxygens of the P<sub>8</sub>W<sub>48</sub> wheel just like the Mn<sup>2+</sup>/Ni<sup>2+</sup> ions, but in a trans-related fashion. The average M-O(W) distance for the Mn2+ centers in Mn4P8W50 and for the Ni2+ centers in  $Ni_4P_8W_{50}$  is 2.13(2) Å and 2.02(2) Å, respectively. The average  $\mathrm{Mn}^{2+}$ -O(aqua) bond in  $\mathrm{Mn_4P_8W_{50}}$  and the  $\mathrm{Ni}^{2+}$ -O(aqua) bond in  $Ni_4P_8W_{50}$  are 2.20(2) and 2.06(2) Å, respectively.

Cronin and coworkers, as well as Proust and coworkers, have reported Mn-based P8W48 derivatives, which differ in the number and location of the Mn<sup>2+</sup> ions and their network arrays. The Cronin group reported an open framework nanocube-based,  $[Mn_8(H_2O)_{48}P_8W_{48}O_{184}]^{24-}$   $(\{Mn_8(H_2O)_{48}P_8W_{48}\}_{\infty})$  and a multidiframework  $[Mn_{14}(H_2O)_{30}P_8W_{48}O_{184}]^{12-}$  $(\{Mn_{14}P_8W_{48}\}_{\infty})$  polyanion. 21,76 Each  $P_8W_{48}$  fragment is linked by Mn-O-W coordination bonds, which form a higher-order packing arrangement. Proust and coworkers have reported two new  $Mn^{II}$  derivatives of  $P_8W_{48}$ :  $[Mn_8(H_2O)_{26}(P_8W_{48}O_{184})]^{24-}$  $(Mn_8(H_2O)_{26}P_8W_{48})$  $[Mn_6(H_2O)_{22}(P_8W_{48}O_{184})$ and  $\{WO_2(H_2O)_2\}_{1.5}^{25-}$  $(Mn_6\{WO_2(H_2O)_2\}_{1.5}P_8W_{48})^{.77}$ Mn<sub>8</sub>(H<sub>2</sub>O)<sub>26</sub>P<sub>8</sub>W<sub>48</sub>, six Mn<sup>2+</sup> centers are observed to be located inside the P8W48 cavity, while two other Mn2+ centers are coordinated to the outer rim of P<sub>8</sub>W<sub>48</sub>. The internal six Mn<sup>2+</sup> ions are distributed among the eight hinges between the {P2W12} subunits. Four of the sites are fully occupied by the four Mn<sup>2+</sup>, which is the orthogonal plain to the main  $\{P_8W_{48}\}$ , and the remaining two Mn<sup>2+</sup> centers are disordered over the four other positions, which resembles the Co<sup>2+</sup> complex reported by the Cronin group.  $^{122}$  In  $Mn_6\{WO_2(H_2O)_2\}_{1.5}P_8W_{48}$ , four  $Mn^{2+}$  centers are located inside the P8W48 cavity, while two other Mn2+ centers are coordinated to the outer rim of  $P_8W_{48}$ , as in the former structure.

Müller and coworkers have also studied the interaction of P<sub>8</sub>W<sub>48</sub> with VO<sup>2+</sup> and Mo<sup>VI</sup> in acetate buffer. They have successfully isolated the mixed-valent vanadium(IV/V) containing poly- $[P_8W_{48}O_{184}\{V_4^VV_2^{IV}O_{12}(H_2O)_{12}\}_2]^{32-}$  $((V_4^V V_2^{IV})_2 P_8 W_{48})$ (Fig. 15a), 94 and the mixed-valent molybdenum(v/vI)  $[\{P_8W_{48}O_{184}\}\{Mo^{VI}O_2\}_4\{(H_2O)(O=)Mo^V(\mu_2-O)_2(O=)Mo^V(\mu_2-H_2O)\}]$ the first examples of mixed-valent complexes incorporated in  $P_8W_{48}$ . <sup>124</sup> In  $(V_4^VV_2^{IV})_2P_8W_{48}$ , two  $\{V_4^VV_2^{IV}O_{12}(H_2O)_2\}^{4+}$  units are observed to be trapped inside the cavity of the polyanion. The  $\{V_4^V V_2^{IV} O_{12}(H_2O)_2\}^{4+}$  unit consists of two octahedrally-coordinated V<sup>IV</sup> and four tetrahedrally-coordinated V<sup>V</sup> centers. The oxidation of V<sup>IV</sup> to V<sup>V</sup> occurs in situ due to air. Such type of oxidation has also been observed for (VO2)4P8W48, as reported by Kortz and coworkers. 121 Wu's and Bi's groups have reported the reduction of  $Au^{3+}$  in the presence of  $(V_4^V V_2^{IV})_2 P_8 W_{48}$ , acting as a stabilizing and reducing agent, forming the bamboo jointlike gold microstructure in aqueous medium at ambient temperature. 125

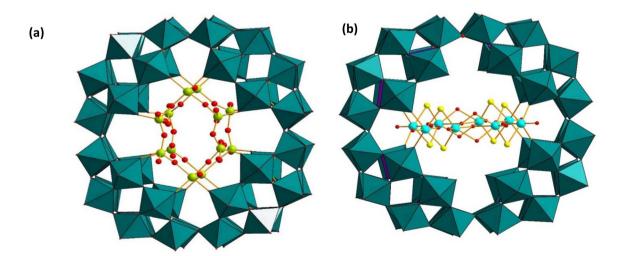
Mo4VIMo4VP8W48 was observed to consist of two neutral tetranuclear {Mo<sub>4</sub><sup>V</sup>O<sub>10</sub>(H<sub>2</sub>O)<sub>3</sub>} and four {Mo<sup>VI</sup>O<sub>2</sub>}<sup>2+</sup> units connected to the P<sub>8</sub>W<sub>48</sub> ring via Mo-O-W bonds. Furthermore, the {Mo<sub>4</sub><sup>V</sup>O<sub>10</sub>(H<sub>2</sub>O)<sub>3</sub>} unit contains two of the well-known diamagnetic  $\{Mo_2^VO_4\}^{2^+}$ -type units. The four trapped  $\{Mo^{VI}O_2\}^{2^+}$  units bind to two oxygen atoms of adjacent P2W12 units, resulting in tetrahedral coordination of the Mo atoms. The 31P and 183W NMR data fully support the solid-state structure.

Cadot and coworkers have reported molybdenum oxothiocation complexes with the cyclic  $P_8W_{48}$ . The reaction of the  $\left[\text{Mo}_2\text{S}_2\text{O}_2(\text{H}_2\text{O})_6\right]^{2^+}$  oxothiocation with  $P_8W_{48}$  in an aqueous acidic medium resulted in two new molybdenum oxothiocation based compounds:  $[K_4\{MO_4O_4S_4(H_2O)_3(OH)_2\}_2(WO_2)$  $(P_8W_{48}O_{184})]^{30-}$   $((Mo_4O_4S_4)_2(WO_2)P_8W_{48})$  and  $[\{Mo_4O_4S_4(H_2O)_3\}]^{30-}$  $(OH)_{2}_{1}(P_{8}W_{48}O_{184})^{36-}$   $((Mo_{4}O_{4}S_{4})_{2}P_{8}W_{48})$  (Fig. 15b). In  $(Mo_4O_4S_4)_2(WO_2)P_8W_{48}$ , the two disordered

(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>|<sup>2+</sup> oxothiomolybdenum clusters are observed to be grafted on both sides of the cyclic P<sub>8</sub>W<sub>48</sub> surface, resulting geometrical isomers where  ${\rm MO_4O_4S_4(H_2O)_3(OH)_2}^{2+}$  groups are arranged either in a perpendicular or parallel mode. The structure also comprises of a {WO<sub>2</sub>}<sup>2+</sup> group, which is disordered over four positions in  $P_8W_{48}$ . The polyanion  $(Mo_4O_4S_4)_2(WO_2)P_8W_{48}$  is closely related to the compound  $Mo_4^{VI}Mo_4^{V}P_8W_{48}$ , 124 where the oxocation  ${\rm Mo_2O_4}^{2+}$  exhibits a similar mode of connectivity as is usually observed for oxothio {Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>}-based polyanions. In  $\mathbf{Mo_4^{VI}Mo_4^{V}P_8W_{48}}$ , the neutral core  $[\mathbf{Mo_4^{V}O_{10}(H_2O)_3}]$  is observed to be formed by connections of two dinuclear units through a double oxo-bridge. In contrast, in the oxothio derivative (Mo<sub>4</sub>O<sub>4</sub>S<sub>4</sub>)<sub>2</sub>WP<sub>8</sub>W<sub>48</sub>, such connections are through a double hydroxo bridge. The polyanion (Mo<sub>4</sub>O<sub>4</sub>S<sub>4</sub>)<sub>2</sub>P<sub>8</sub>W<sub>48</sub> is observed to composed disordered be of the same two  $[Mo_4O_4S_4(OH)_2(H_2O)_3]^{2+}$ oxothiomolybdenum clusters but without the extra {WO<sub>2</sub>}<sup>2+</sup> group. Both compounds were characterized in the solid-state by XRD and solution by NMR.

Kortz and coworkers have further investigated the reactivity of the cyclic P8W48 with 4d transition metal ions in a buffer solution. Interaction of  $[Ru(p-cymene)Cl_2]_2$  with  $P_8W_{48}$  in lithium buffer solution at pH 6.0 resulted in the polyanion [{K  $(H_2O)_3\{Ru(p\text{-cymene})(H_2O)\}_4P_8W_{49}O_{186}(H_2O)_2]^{27}$   $(Ru_4P_8W_{49})$ (Fig. 16). 127 The structure of the polyanion Ru<sub>4</sub>P<sub>8</sub>W<sub>49</sub> reveals that it has four  $\{Ru(p\text{-cymene})(H_2O)\}^{2+}$  groups covalently attached to the inner rim of the cyclic P8W48 unit, resulting in a structure with  $C_i$  symmetry. Each organoruthenium group is bound to P<sub>8</sub>W<sub>48</sub> via two Ru-O(W) bonds involving belt oxygens of each of two adjacent, hexalacunary P2W12 building blocks and the extra tungsten atom, resulting in Ru<sub>4</sub>P<sub>8</sub>W<sub>49</sub>, which has been observed previously for other related polyanions. 121

Pope and coworkers have investigated the interaction of the P<sub>8</sub>W<sub>48</sub> ion with early lanthanide metal ions. They have synthesized and structurally characterized a family of four new



 $[P_8W_{48}O_{184}\{V_4^VV_2^{IV}O_{12}(H_2O)_{12}\}_2]^{32-}.$ Fig. 15 Combined polyhedral/ball-and-stick representations (a)  $[\{MO_4O_4S_4(H_2O)_3(OH)_2\}_2(P_8W_{48}O_{184})]^{36-}$ . Color code:  $WO_6$  octahedra (green), PO<sub>4</sub> tetrahedra (pink), Mo (turquoise), V (green), S (yellow), O

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(b) (a)

 $\textbf{Fig. 16} \quad \text{Combined polyhedral/ball-and-stick representation of } [\{K(H_2O)\}_3\{Ru(\textit{p}-\text{cymene})(H_2O)\}_4P_8W_{49}O_{186}(H_2O)_2]^{27-}. \ \ (a) \quad \text{Front-view, (b) side-view.}$ Color code: WO<sub>6</sub> octahedra (green), PO<sub>4</sub> tetrahedra (pink), Ru (sky blue), O (red), C (grey), H (white). 127

lanthanide-substituted polyoxotungstates,  $[K \subset P_8W_{48}]$  $O_{184}(H_4W_4O_{12})_2Ln_2(H_2O)_{10}]^{25-}$   $(Ln_2(W_4O_{12})_2P_8W_{48})$  (Ln = La, Ce, Pr, Nd) (Fig. 17) and all polyanions were characterized by infrared spectroscopy, <sup>31</sup>P NMR, and X-ray crystallography. <sup>128</sup> The structural elucidation of the polyanions reveals that the

Fig. 17 Combined polyhedral/ball-and-stick representation  $[\mathsf{K} \subset \mathsf{P_8W_{48}O_{184}}(\mathsf{H_4W_4O_{12}})_2\mathsf{Ln_2}(\mathsf{H_2O})_{10}]^{25-}. \ \ \mathsf{Color} \ \ \mathsf{code} \colon \ \mathsf{WO_6} \ \ \mathsf{octahedra}$ (green and brown), PO<sub>4</sub> tetrahedra (pink), O (red), Ce (turquoise), K (grey).128

central cavity of P<sub>8</sub>W<sub>48</sub> is occupied by two additional {W<sub>4</sub>O<sub>12</sub>} groups, along with four lanthanides and two potassium ions, each with an occupancy of 50%. Therefore, the polyoxotungstate shell comprises two P2W16 and two P2W12 subunits, with equivalent ones facing each other.

In 2015, Kögerler and coworkers reported the reactivity of the main group element Sn<sup>2+</sup> with P<sub>8</sub>W<sub>48</sub> in aqueous solution and isolated the  $\text{Sn}^{2^+}$ -containing  $\left[K_{4.5} \subset (\text{ClSn})_8 P_8 W_{48} O_{184}\right]^{17.5-}$ ((ClSn)<sub>8</sub>P<sub>8</sub>W<sub>48</sub>) (Fig. 18). 129 Interestingly, a color change from bright-orange (reduction of WVI to WV) to brown and then to dark-green (air oxidation of WV to WVI) was observed during the reaction. In the polyanion (ClSn)<sub>8</sub>P<sub>8</sub>W<sub>48</sub>, all eight Sn<sup>2+</sup> atoms are incorporated in the central cavity of P8W48, occupying the eight equivalent vacant hinge-positions of the P8W48 moiety. The rate of evaporation of the reaction solution, temperature, and concentration of Sn2+ play a crucial role in the formation of this polyanion. The structure of (CISn)<sub>8</sub>P<sub>8</sub>W<sub>48</sub> comprises eight {ClSn} groups, with each Sn<sup>2+</sup> atom in a trigonalpyramidal coordination geometry and the chloride ligand of {ClSn} pointing towards the center of the P8W48 cavity. The bond distance of Sn-Cl in (ClSn)<sub>8</sub>P<sub>8</sub>W<sub>48</sub> is 2.515(6) Å, which is comparable with Cs[SnCl<sub>3</sub>] (2.523 Å) and [SnCl<sub>2</sub>(H<sub>2</sub>O)]·H<sub>2</sub>O (2.595 Å). Similarly, the Sn-O bond is in good agreement with the Sn-O bond lengths in [SnCl<sub>2</sub>(H<sub>2</sub>O)]·H<sub>2</sub>O (2.169 Å) and other Sn<sup>2+</sup>-containing polyoxotungstates. 130

Recently, Kögerler and coworkers have reported aromatic organoarsenate-functionalized  $P_8W_{48}$ ,  $[(RAs^VO)_4P_8^VW_{48}^{VI}O_{184}]^{32-}$  $[R = C_6H_5 \text{ or } p\text{-}(H_2N)C_6H_4]$  ((RAsO)<sub>4</sub>P<sub>8</sub>W<sub>48</sub>,  $R = C_6H_5 \text{ or } p\text{-}(H_2N)$ C<sub>6</sub>H<sub>4</sub>).<sup>131</sup> Recrystallization of the K<sup>+</sup>/Li<sup>+</sup>/dimethylammonium salt of  $((p-(H_2N)C_6H_4AsO)_4P_8W_{48})$  from 4 M LiCl solution was

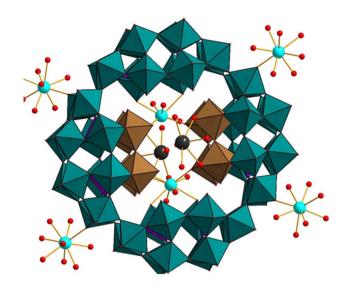


Fig. 18 Combined polyhedral/ball-and-stick representation  $[K_{4.5} \subset (ClSn)_8 P_8 W_{48} O_{184}]^{17.5-}$ . Color code: WO<sub>6</sub> octahedra (green), PO<sub>4</sub> tetrahedra (pink), O (red), Sn (brown), K (grey), Cl (green). 129

observed to yield a further functionalized product,  $[(H_3NC_6H_4AsO)_3P_8W_{48}O_{184}H_x\{WO_2(H_2O)_2\}_{0.4}]^{(30.2-x)-}$ , revealing dissociation of the organoarsonate groups in slightly acidic aqueous solution followed by their rearrangement within the inner polyanion cavity. 131

In 2018, Khashab and coworkers isolated two main group 3 metal-substituted P<sub>8</sub>W<sub>48</sub> in aqueous acidic solution, {[Na  $(NO_3)(H_2O)_{14}[Al_{16}(OH)_{24}(H_2O)_{8}(P_8W_{48}O_{184})]^{16-}$  $(Al_{16}P_8W_{48})$ Ga analogue  $[Ga_{16}(OH)_{32}(P_8W_{48}O_{184})]^{24-}$  $(Ga_{16}P_8W_{48})$ . The connectivity of  $Al^{3+}/Ga^{3+}$  in  $Al_{16}P_8W_{48}$  and Ga<sub>16</sub>P<sub>8</sub>W<sub>48</sub> is similar to that of Fe<sub>16</sub>P<sub>8</sub>W<sub>48</sub> reported by Kortz and coworkers (Fig. 13a). The incorporated "{Al<sub>16</sub>} ring" comprises eight pairs of structurally equivalent, edge-shared AlO<sub>6</sub> octahedra that are interconnected via corners. The degree of protonation is different in the cationic aluminum-hydroxo core {Al<sub>16</sub>(OH)<sub>24</sub>(H<sub>2</sub>O)<sub>8</sub>}<sup>24+</sup> compared to the isostructural Ga<sup>3+</sup> analogue  $\{Ga_{16}(OH)_{32}\}^{16+}$ . This is due to different reaction pH (pH 4.0 for  $Al_{16}P_8W_{48}$  vs. pH 5.0 for  $Ga_{16}P_8W_{48}$ ). The bond distances of AlIII-O, GaIII-O, and FeIII-O fall in the range of 1.796 (10)-2.044(9), 1.896(5)-2.068(5), and 1.895(12)-2.153(12) Å, respectively, and the corresponding Al-O-Al, Ga-O-Ga, and Fe-O-Fe angles are similar within the respective range of 92.7  $(4)^{\circ}-148.0(5)^{\circ}$ ,  $96.4(2)^{\circ}-143.9(3)^{\circ}$ , and  $94.2(5)^{\circ}-139.6(7)^{\circ}$ , respectively.

In 2019, Wang and coworkers introduced selenium into the cavity of P8W48 and isolated a mixed potassium-lithium salt,  $K_{26}Li_{6}[(SeO)_{4}P_{8}W_{48}O_{184}]\cdot 98H_{2}O (Se_{4}P_{8}W_{48})^{133}$  Four  $[SeO_{3}]^{2-}$ ions were grafted in the cavity of the crown-shaped P<sub>8</sub>W<sub>48</sub>, like for Co<sub>4</sub>P<sub>8</sub>W<sub>48</sub>, resulting in a structure with D<sub>2h</sub> point group symmetry.

Sokolov and coworkers reported the incorporation of  $\{NbO\}^{3+}$  units into the cyclic  $P_8W_{48}$  ion *via* reaction with the Nb-O<sub>x</sub> reagent in different ratios (4:1, 8:1, and 16:1) and different concentrations. They have isolated mixed salts of

different compounds with differing numbers of coordinated {NbO(H<sub>2</sub>O)}<sup>3+</sup> groups, disordered over the eight equivalent binding sites. The formulas suggest that the compounds are likely mixtures of two or more polyanions: K25.7Li5(NH4)5  $[(HP_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_{3.3}]\cdot 73H_2O$  $((NbO(C_2O_4)$  $(H_2O)_{3.3}P_8W_{48},$  $K_{30.8}Li_{3.5}(NH_4)_3[(P_8W_{48}O_{184})(NbO(C_2O_4)$  $(H_2O)_{1.7}$ ]  $\cdot 74.5H_2O$   $((NbO(C_2O_4)(H_2O))_{1.7}P_8W_{48})$ ,  $K_{21.6}Li_5(NH_4)_8$  $H_{6.8}[(P_8W_{48}O_{184})(NbO(H_2O))_{4.4}(C2O_4)_{1.5}]\cdot 66H_2O ((NbO(C_2O_4)_{1.5})\cdot 66H_2O)$  $(H_2O)_{4.4}P_8W_{48},$  $K_{24.4}Li_5(NH_4)_{5.5}[(HP_8W_{48}O_{184})(NbO(C_2O_4)$  $(H_2O)_{3.1}$ :59 $H_2O$   $((NbO(C_2O_4)(H_2O))_{3.1}P_8W_{48})$ ,  $K_{26.7}Li_4(NH_4)_{5.5}$  $H_{2.6}[(P_8W_{48}O_{184})(NbO(H_2O))_{3.8}(C_2O_4)_{2.5}]\cdot 55.5H_2O$  $(C_2O_4)_{2.5}(H_2O))_{3.8}P_8W_{48}$ . 134

Duval and coworkers have introduced the uranyl cation into the cavity of the cyclic P<sub>8</sub>W<sub>48</sub> polyanion, resulting in the salt  $K_{11.3}Li_{8.1}Na_{22}[(UO_2)_{7.2}(HCOO)_{7.8}(P_8W_{48}O_{184})Cl_8]\cdot 89H_2O$  ((UO<sub>2</sub>)<sub>7.2</sub>  $(HCOO)_{7.2}P_8W_{48})$  (Fig. 17). This is the first time that actinide elements were incorporated in the cavity of  $P_8W_{48}$ . The structure of (UO2)7.2(HCOO)7.2P8W48 revealed that the 7.2 uranyl cations are disordered over eight positions, suggesting the presence of mixtures of two or more polyanions in the material. 126 Interestingly, Kortz and coworkers first introduced the peroxouranium containing wheel-shaped P8W48, resulting in peroxouranium complex  $K_{18}Li_{22}[(UO_2)_8(O_2)_8(P_8W_{48}O_{184})]\cdot 133H_2O$  $((UO_2)_4(O_2)_4P_8W_{48})^{136}$  The polyanion  $((UO_2)_4(O_2)_4P_8W_{48})$  consists of four peroxo groups, and each one is connected to two uranium cations. The  $\{(UO_2)_4(O_2)_4\}$  unit comprises neutral four uranyl atoms and four peroxo groups, connecting to each other by side-on peroxo bridges, which is similar to previously reported  $(\text{Li}(\text{UO}_2)_4(\text{O}_2)_4(\text{PO}_3\text{OH})_2\text{P}_6\text{W}_{36})$  by the same group. <sup>92</sup>

In 2019, Ibrahim et al. reported an isopoly tetratungstenoxo cluster incorporated inside the rim of P8W48 along with six internal and four external  $Mn^{2+}$  ions, resulting in [( $P_8W_{48}O_{184}$ )  $(W_4O_{16})K_{10}Li_4Mn_{10}Na(H_2O)_{50}Cl_2]^{15-}$   $(Mn_{10}W_4P_8W_{48})^{137}$  The Mn-O bond lengths are in the range of 2.087-2.315 Å, while Mn-Cl is 2.365 Å. The oxidation states of the Mn ions were checked by bond valence sum analysis, 138-140 and all were shown to be Mn<sup>2+</sup>. The outer Mn<sup>2+</sup> ions assist the formation of a 3D network through intermolecular Mn-O(W) bonding together with potassium ions. Interestingly, the origin of the one Na<sup>+</sup> ion in the compound is ambiguous.

Kögerler and coworkers studied the isomerization of the four  $\{\alpha P_2W_{12}O_{48}\}$  units comprising the  $P_8W_{48}$  wheel in the presence of Cu<sup>2+</sup> ions in 0.66 M acetate buffer at pH 5.2. They able isolate  $K_7Li_2Na_{27}$  [αγαγ- $P_8W_{48}O_{184}$  {Cu to  $(H_2O)_{2}$   $\cdot 78H_2O$   $(Cu_2-\alpha\gamma\alpha\gamma-P_8W_{48})$ ,  $K_{7.5}Na_{17}Cu_{2.425}(WO_2)_{1.325}$  $[\gamma\gamma\gamma\gamma-P_8W_{48}O_{184}\{Cu(H_2O)_{0.5}\}_4]\cdot102H_2O\ (Cu_4-\gamma\gamma\gamma\gamma-P_8W_{48}),\ and$  $K_7Li_2Na_{19.5}Cu_{1.75}(WO_2)[\alpha\gamma\gamma\gamma-P_8W_{48}O_{184}\{Cu(H_2O)\}_3]\cdot72H_2O$  $(Cu_3-αγγγ-P_8W_{48})$ . The molar ratio of  $Cu^{2+}$  to  $P_8W_{48}$ , temperature, and reaction time played a crucial role when trying to prepare the three compounds. The synthesis of Kortz's  $\text{Cu}_{20}\text{P}_8\text{W}_{48},^{78}$  and Mialane's  $\text{Cu}_{20}(\text{N}_3)_6\text{P}_8\text{W}_{48}$   $^{90}$  took 1 h and 15 min, respectively, at 80 °C, whereas Cu<sub>2</sub>-αγαγ-P<sub>8</sub>W<sub>48</sub> was isolated after 2 h reaction time at 95 °C, in order to transform two  $P_2W_{12}$  units from  $\alpha$  to  $\gamma$  in the  $P_8W_{48}$  wheel. According to the authors, Li<sup>+</sup> ions also play a crucial role in such isomeric transformation.

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In the same year, Suzuki, Yamaguchi, and coworkers synthesized a series of P8W48 ions with eight incorporated 3d metal ions from mixed organic solvent. The products were isolated as tetra-n-butylammonium (TBA) salts, TBA<sub>14</sub>H<sub>2</sub>-[{M<sub>2</sub><sup>II</sup>  $(OH_2)_2$ { $_2$ { $M^{II}(OH_2)_2$ }{ $_4$  $P_8W_{48}O_{176}(OCH_3)_8$ } $\cdot nH_2O\cdot mCH_3CN$ , where  $M^{II} = Mn$ , Co, Ni, Cu, Zn  $(M_8P_8W_{48}O_{176})^{142}$  Edge-shared bis pyramidal) metal-aqua sites  $\{(\mu-O)_2(M-OH_2)\}$ (square  $(\mu_3 O)_2 (M-OH_2)(\mu-O)_2$  were incorporated in the cavity of  $P_8 W_{48}$ . Interestingly, a new type of  $\alpha, \gamma, \alpha, \gamma$ -type  $P_8W_{48}$  was observed after the reaction with the 3d metal ions, with two of the four  $\alpha$ -P<sub>2</sub>W<sub>12</sub> units having been transformed to  $\gamma$ -P<sub>2</sub>W<sub>12</sub>. The Co<sup>2+</sup> ions are disordered over two of the four P2W12 units. However, with increased methanol concentration in the reaction, the Co2+ ions fully occupied each of the four P2W12 units. The Mn<sup>2+</sup> and Ni<sup>2+</sup>-containing P<sub>8</sub>W<sub>48</sub> polyanions exhibit the first examples of edge-shared bis(square pyramidal)manganeseaqua and nickel-aqua complexes. The M-O axial bond length increased for the metal ion M from left to right in the periodic table. For example, in the Mn<sup>2+</sup> derivative Mn<sub>8</sub>P<sub>8</sub>W<sub>48</sub>O<sub>176</sub>, the axial Mn-O bond lengths of 2.17-2.22 Å (Mn3-O13, Mn3-O60, Mn4-O14, Mn4-O59) were similar to the equatorial bond lengths of 2.10-2.24 Å (Mn3-O3, Mn3-O4, Mn3-O39, Mn3-O42; Mn4-O5, Mn4-O6, Mn4-O40, Mn4-O41). On the other hand, for the Co<sup>2+</sup> and Ni<sup>2+</sup> derivatives, the axial bonds (2.13-2.18 Å) are longer than the equatorial ones (1.99-2.07 Å). As expected, for the Cu<sup>2+</sup> derivative, the Cu-O axial bonds (2.22-2.27 Å) are much longer than the equatorial bonds (1.98-2.08 Å). For the Mn<sup>2+</sup> and Co<sup>2+</sup> derivatives, a decrease in magnetic susceptibility was observed upon cooling, implying antiferromagnetic interactions between the 3d metal ions. However, ferromagnetic interactions were observed for the Ni<sup>2+</sup> and Cu<sup>2+</sup> derivatives. The same authors have also reported two high-nuclear manganese derivatives of P8W48, (C24PH20)17  $H_{37}[Mn_{18}P_8W_{48}O_{214}]\cdot 16H_2O\cdot 4CH_3CN$   $(Mn_{18}P_8W_{48}O_{214})$  and  $(C_{16}H_{36}N)_{12}H_{16}[Mn_{20}P_8W_{48}O_{216}]\cdot 4C_2H_3N\cdot C_2Cl_2H_4 \quad (\textbf{Mn}_{\textbf{20}}P_8W_{\textbf{48}})$  $O_{216}$ ). The  $Mn_{18}P_8W_{48}O_{214}$  polyanion is a mixed-valent species with 18  $Mn^{2+/3+}$  ions in the cavity of  $P_8W_{48.}$  Bond valence sum calculations revealed the presence of 8 Mn<sup>2+</sup> and 10  $Mn^{3^{\scriptscriptstyle +}}$  ions. The four  $P_2W_{12}$  units isomerized from  $\alpha\text{-}$  to  $\gamma$ -type in situ in the presence of the transition metal ions, which was observed previously. 98,138 The Mn<sub>20</sub>P<sub>8</sub>W<sub>48</sub>O<sub>216</sub> polyanion was obtained by reacting P8W48 with 20 equivalents of Mn(OAc)<sub>3</sub> in acetonitrile medium. This polyanion was also found to be mixed-valent as per bond valence sum calculations, showing the presence of 12 Mn<sup>3+</sup> and 8 Mn<sup>4+</sup> ions. All 20 Mn ions are bound in the cavity of  $P_8W_{48}$  and all four units of  $P_2W_{12}$  remained as  $\alpha$ -type. The connectivity of the Mn ions in  $Mn_{20}P_8W_{48}O_{216}$  is different from  $Mn_{18}P_8W_{48}O_{214}$ . In the former, four  $Mn^{3+}$  ions are bound to each  $\alpha$ - $P_2W_{12}$  unit, and four Mn ions are bound at the hinges of the four α-P<sub>2</sub>W<sub>12</sub> units Eight Mn ions of oxidation state either +3 or +4 are bound to the vacant sites within the cavity of the cyclic P8W48, which are disordered over eight positions together with K<sup>+</sup> ions.88 Two Mn ions occupy the middle part of opposing P2W12 units, and four Mn ions are at the hinges of the four P<sub>2</sub>W<sub>12</sub> units. Very recently, Suzuki, Yamaguchi, and coworkers

have reported a series of multi-nuclear copper(II)-containing P<sub>8</sub>W<sub>48</sub> derivatives, which were synthesized in organic solvent. The four compounds reported were TBA<sub>11</sub>H<sub>13</sub>[Cu<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>P<sub>8</sub>W<sub>48</sub>O<sub>176</sub>(OCH<sub>3</sub>)<sub>8</sub>]·28H<sub>2</sub>O·3CH<sub>3</sub>NO<sub>2</sub>  $(Cu_4P_8W_{48})$ ,  $TBA_{14}H_2[Cu_8(H_2O)_{12}P_8W_{48}O_{176}(OCH_3)_8] \cdot 24H_2O \cdot CH_3CN$  $(Cu_8P_8W_{48})$ ,  $TBA_{14}H_2[Cu_{12}(H_2O)_{16}P_8W_{48}O_{184}]\cdot 4H_2O$   $(Cu_{12}P_8W_{48})$ ,  $TBA_{16}H_{8} \\ [Cu_{16}(OH)_{16}(H_{2}O)_{4}P_{8}W_{48}O_{184}] \\ \cdot 12H_{2}O \cdot C_{3}H_{6}O$ (Cu<sub>16</sub>P<sub>8</sub>W<sub>48</sub>), respectively. 144 Interestingly, the authors were able to obtain the high nuclearity polyanions from the reaction of low nuclearity polyanions with copper(II) salt, for example,  $Cu_8P_8W_{48}$  from  $Cu_4P_8W_{48}$ ,  $Cu_{12}P_8W_{48}$  from  $Cu_8P_8W_{48}$ , and Cu<sub>16</sub>P<sub>8</sub>W<sub>48</sub> from Cu<sub>12</sub>P<sub>8</sub>W<sub>48</sub>, respectively. Moreover, in the case of Cu<sub>4</sub>P<sub>8</sub>W<sub>48</sub> and Cu<sub>8</sub>P<sub>8</sub>W<sub>48</sub>, two P<sub>2</sub>W<sub>12</sub> units with copper ions connected transformed from  $\alpha$  to  $\gamma$ -type isomers by 60° rotation of the central {PO<sub>4</sub>} hetero groups. The reactive sites of the remaining two  $\{\alpha - P_2 W_{12}\}$  units are occupied by methoxy groups. This result was similar to the previously reported cobalt-containing P8W48 work by the same group where eight cobalt(II) ions were introduced without affecting the presence of the methoxy groups, 145 suggesting that they act as a protecting organic ligands being essential for metal incorporation inside the cavity of P8W48 without disorder. In Cu12P8W48 and  $Cu_{16}P_8W_{48}$  comprising the same  $\gamma, \gamma, \gamma, \gamma$ -type  $P_8W_{48}$  framework, the copper(II) coordination geometry differs from each other. The arrangements and connectivity of the copper(II) ions in these structures are also different from the  $Cu_{20}P_8W_{48}$  polyanion.94 Very recently, the same group has demonstrated the  $H_2$ -based reduction of copper(II) ions in the cavity of  $P_8W_{48}$ , resulting in a catalyst which is active for the catalytic hydrogenation of several organic substrates, such as alkenes, alkynes, as well as carbonyl- and nitro-containing compounds. 146

In 2019, Cronin and coworkers reported that P<sub>8</sub>W<sub>48</sub> selfassembled into inorganic frameworks in the presence of silver ions, enabling interaction with the POM wheel and linking them together. It was observed that P8W48 was highly reactive towards silver ions, resulting in the formation of fragments as the compounds  $\text{Li}_{8}\text{K}_{9.5}\text{Ag}_{21}[\text{H}_{16}\text{P}_{10}\text{W}_{66}\text{O}_{251}]_{0.5}$  $[H_{14}P_9W_{63}O_{235}]\cdot 0.5Cl_2\cdot 50H_2O$  $(Ag_{21}P_9W_{63}O_{235}),$  $Li_8K_{13}Ag_{13}$  $[H_{12}P_8W_{51}O_{196}]\cdot 50H_2O$  $(Ag_{13}P_8W_{51}O_{196}),$  $\text{Li}_{10}\text{K}_{12}\text{Ag}_{4}[\text{H}_{14}\text{P}_{8}\text{W}_{48}\text{O}_{184}]\cdot 170\text{H}_{2}\text{O} \quad (\text{Ag}_{4}\text{P}_{8}\text{W}_{48}\text{O}_{148}), \text{ respect-}$ ively.  $^{147}$  The species  $Ag_{21}P_9W_{63}O_{235}$  revealed two cocrystallized P<sub>8</sub>W<sub>48</sub> units connected by 10 Ag<sup>+</sup> ions, forming a "POMzite" framework. In  $Ag_{13}P_8W_{51}O_{196}$ , the  $P_8W_{48}$  units are linked forming a framework with 9 Ag<sup>+</sup> ions per formula unit. Further tuning of the reaction conditions yields  $Ag_4P_8W_{48}O_{148}$ , where 4 Ag<sup>+</sup> ions are linked to P<sub>8</sub>W<sub>48</sub>, resulting in a cubic array, and surprisingly, no Ag<sup>+</sup> ions were detected in the cavity of P<sub>8</sub>W<sub>48</sub>. Very recently, Suzuki, Yamaguchi, and coworkers have reported within cluster  $(Ag_{30})$ P<sub>8</sub>W<sub>48</sub>, TBA<sub>17</sub>H  $[Ag_{30}(P_8W_{48}O_{184})]\cdot 10DMF\cdot 30H_2O$   $(Ag_{30}P_8W_{48})$ , which was synthesized from a {Ag<sub>16</sub>} cluster-containing P<sub>8</sub>W<sub>48</sub> derivative. 145 The Ag<sub>30</sub>P<sub>8</sub>W<sub>48</sub> nanocluster possesses an additional 14 silver atoms that were introduced into the Ag<sub>16</sub> cavity, resulting in an Ag<sub>30</sub> nanocluster with distorted body-centered-cubic atom arrangements inside the P8W48 polyanion, revealed by single crystal X-ray crystallography. The Ag<sub>30</sub>P<sub>8</sub>W<sub>48</sub> exhibits high and

Table 1 Structural characteristics and component building blocks of tungstophosphate-based compounds

No alones are connected by four \$\frac{1}{2}\$ catums, one \$\frac{1}{2}\$ by \$\frac{1}{2}\$ \text{interpolate} \$\frac{1}{2}\$ in	Sl. no.	Formula	Abbreviation	Brief description	Ref
K- Fe (OH-)P, W <sub>1</sub> -Mo,O <sub>1</sub>     PsP <sub>1</sub> -W <sub>1</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are coupled by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are coupled by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are coupled by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are coupled by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are coupled by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are coupled by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are coupled by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are coupled by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by five Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by file Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by file mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by file Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by file Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by file Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub> ] are filled up by file Mo <sup>2</sup>   CuP <sub>W</sub> -Mo <sub>0</sub> , O <sub>2</sub>   All six-vacant positions of [P <sub>2</sub> W <sub>2</sub>	1	$\text{Li}_{5.5}\text{K}_3\text{H}_{3.5}[P_2\text{W}_{12}(\text{NbO}_2)_6\text{O}_{56}]\cdot\text{H}_2\text{O}$	P <sub>2</sub> W <sub>12</sub> (Nb-O <sub>2</sub> ) <sub>6</sub>	Nb atoms are connected by four $\eta^2$ -O atoms, one $\eta^4$ -bridging O atom (cap sites or triply-bridging O atom on belt	53
Eq. (a, Te(GIL) <sub>2</sub> P,W <sub>1</sub> ,Mo <sub>2</sub> O <sub>6</sub> ) and Eq. (a, Cu(GIL) <sub>2</sub> P,W <sub>1</sub> ,Mo <sub>2</sub> O <sub>6</sub> )   Cu,W <sub>2</sub> Mo <sub>5</sub>	2	$K_7[Fe(OH_2)P_2W_{12}Mo_5O_{61}]$	FeP <sub>2</sub> W <sub>12</sub>	All six-vacant positions of $\{P_2W_{12}\}$ are filled up by five $Mo^{VI}$ ions in the belt and one cap position and one cap position	54
Fig.   Ca(10H2)P, W12M0,Oa]   Oc. CaP, W12M0, Oc.	3	$K_7[\alpha_1\text{-Fe}(OH_2)P_2W_{13}Mo_4O_{61}] \text{ and } K_8[\alpha_2\text{-Cu}(OH_2)\text{-}P_2W_{13}Mo_4O_{61}]$		Four Mo <sup>6+</sup> , one Fe <sup>3+</sup> /Cu <sup>2+</sup> ion, and one extra tungsten atom fill the six vacancies of $\{P_2W_{12}\}$ , generating a $\{P_2W_{13}\}$	54
Li <sub>2</sub> K <sub>4</sub>  H <sub>1</sub> P <sub>2</sub> W <sub>1</sub> P <sub>2</sub> C <sub>2</sub> O <sub>20</sub>  34H <sub>2</sub> O   Fe <sub>3</sub> (OA)-P <sub>2</sub> W <sub>1</sub>   Fe <sub>3</sub> P <sub>3</sub> W <sub>2</sub>   Fe <sub>3</sub> D <sub>4</sub> W <sub>3</sub>   Fe <sub>3</sub> D <sub>4</sub>	1	$K_{8}[\alpha_{2}\text{-Cu}(OH_{2})P_{2}W_{12}Mo_{5}O_{61}]$	$\alpha_2\text{-CuP}_2W_{12}Mo_5$	The vacant positions of $\{P_2W_{12}\}$ are occupied by five $Mo^{VI}$ ions in the two belts and a cap and a $Cu^{2^+}$ ion in the other	54
K,Na   [H <sub>1</sub> -P,W <sub>1</sub> -Pe <sub>0</sub> O <sub>1-m</sub> ] 34H <sub>2</sub> O   Fe <sub>p</sub> P,W <sub>2</sub>   Fe <sub>0</sub> O <sub>1-m</sub> ] 34H <sub>2</sub> O   M. Fe <sub>p</sub> P,W <sub>2</sub>   M. Fe <sub>p</sub> P		$Li_{2}K_{4}[H_{4}P_{2}W_{12}Fe_{9}O_{56}(OAc)_{7}]\cdot 34H_{2}O$	Fe <sub>9</sub> (OAc) <sub>7</sub> P <sub>2</sub> W <sub>12</sub>	The six vacancies of $\{P_2W_{12}\}$ are occupied by $Fe^{3+}$ ions, forming a $\{P_2W_{12}Fe_6\}$ unit to which three additional $Fe^{3+}$	58
K <sub>1</sub> [[M[H <sub>1</sub> O <sub>1</sub> ] <sub>0</sub> [H <sub>1</sub> P <sub>1</sub> W <sub>2</sub> P <sub>1</sub> S <sub>2</sub> O <sub>1</sub> O <sub>2</sub> ]] 30H <sub>2</sub> O (M = Co <sup>31</sup> , Mn <sup>31</sup> , Ni <sup>32</sup> )   M <sub>2</sub> S <sub>2</sub> P <sub>1</sub> W <sub>2</sub> <sub>2</sub> M = Co <sup>31</sup> , Mn <sup>31</sup> , Ni <sup>32</sup>   Six and significant and six help and six help are positions and eight Fe <sup>32</sup> emains in the better positions. Two such [Fe <sub>2</sub> P <sub>2</sub> W <sub>3</sub> ] units are bridged by Co <sup>31</sup> , Ni <sup>32</sup> , or Mn <sup>32</sup> isons. Two such [Fe <sub>2</sub> P <sub>2</sub> W <sub>3</sub> V <sub>3</sub> ] units are bridged by Co <sup>32</sup> , Ni <sup>32</sup> , or Mn <sup>32</sup> isons. Two such [Fe <sub>2</sub> P <sub>2</sub> W <sub>3</sub> V <sub>3</sub> ] units are bridged by Co <sup>32</sup> , Ni <sup>32</sup> , or Mn <sup>32</sup> isons. Two such [Fe <sub>2</sub> P <sub>2</sub> W <sub>3</sub> V <sub>3</sub> ] units are bridged by Co <sup>32</sup> , Ni <sup>32</sup> , or Mn <sup>32</sup> isons. Two such [Fe <sub>2</sub> P <sub>2</sub> W <sub>3</sub> V <sub>3</sub> ] units faced by Co <sup>32</sup> isons are bound in the vector positions of two [Fe <sub>2</sub> W <sub>3</sub> V <sub>3</sub> ] and the fixed by Co <sup>32</sup> , Ni <sup>32</sup> , or Mn <sup>32</sup> isons. The dimerical via Ni-O-Nb bridges and the six vaccant sites of the law of the control of	,	$\rm K_6Na_{10}[H_{12}P_4W_{28}Fe_8O_{120}]\cdot 34H_2O$	$\mathrm{Fe_8P_4W_{28}}$	Dimeric clusters with four extra tungsten atoms in the cap	59
Ky8a <sub>1</sub>    (WyCo <sub>2</sub> O <sub>3</sub> (HyO <sub>2</sub> )  (P <sub>2</sub> W <sub>11</sub> O <sub>3</sub> O <sub>2</sub> )  2)-48H <sub>2</sub> O   P <sub>2</sub> W <sub>12</sub> Nb <sub>3</sub> (NbO <sub>2</sub> )  <sub>2</sub>   <sub>2</sub>   The dimeric structure consists or two (P <sub>2</sub> W <sub>12</sub> ) units stude via four W-W-W bonds and two W <sup>3</sup> and Cod <sup>2</sup> atoms are bound in the vacant positions. Six Blatoms occurred to the six by the sum of the vacant positions. Six Blatoms occurred to the vacant positions. The well-blatoms occurred to the vacant positions. Six Blatoms occurred to the vacant positions. The well-blatoms occurred to the vacant positions. Th	,	$K_{12}[\{M(H_2O)_4\}_2\{H_{12}P_4W_{28}Fe_8O_{120}\}]\cdot 30H_2O\ (M=Co^{2+},\ Mn^{2+},\ Ni^{2+})$		Two $\{P_2W_{12}\}$ units with four extra tungsten atoms in the cap positions and eight $F^{3^+}$ atoms in the belt positions. Two such $\{Fe_4P_2W_{14}\}$ units are bridged by $C^{2^+}$ , $Ni^{2^+}$ , or	59
K,Na, H <sub>4</sub> P <sub>2</sub> W <sub>12</sub> Nb <sub>2</sub> O <sub>23</sub>  NDO <sub>23</sub>   <sub>2</sub> 148H <sub>2</sub> O   P <sub>2</sub> W <sub>12</sub> Nb <sub>3</sub> (NO <sub>23</sub>   <sub>2</sub>   <sub>2</sub>   Six Nb atoms occup; two cap and four best sites of the lacunary (P <sub>2</sub> W <sub>2</sub> ) Society (P <sub>2</sub> W <sub>2</sub> ) Soc		$K_3Na_{17}[\{W_2Co_2O_8(H_2O)_2\}(P_2W_{12}O_{46})_2]\cdot 30H_2O$	$W_2Co_2O_8(P_2W_{12})_2$	The dimeric structure consists of two $\{P_2W_{12}\}$ units fused $\emph{via}$ four W–O–W bonds and two $W^{VI}$ and $Co^{2+}$ atoms are	62
0 K; H <sub>13</sub> (Nb <sub>0</sub> (O <sub>2</sub> ) <sub>µ</sub> P <sub>2</sub> W <sub>1</sub> O <sub>2</sub> D <sub>3</sub> ) 31H <sub>2</sub> O	)	$K_4Na_4[H_6P_2W_{12}Nb_4O_{59}(NbO_2)_2]_2\cdot 48H_2O$	$\{P_2W_{12}Nb_4(NbO_2)_2\}_2$	Six Nb atoms occupy two cap and four belt sites of the lacunary $\{P_2W_{12}\}$ precursor. Two such $\{P_2W_{12}Nb_4(NbO_2)_2\}$	63
1 (NH <sub>4</sub> )n <sub>E</sub> [H <sub>4</sub> (P <sub>2</sub> W <sub>1</sub> NN <sub>5</sub> -O <sub>6</sub> (H <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> (ND <sub>5</sub> O <sub>4</sub> (OH <sub>6</sub> O <sub>3</sub> ) <sub>3</sub> ) Ph <sub>2</sub> O <sub>4</sub> (OC (P <sub>2</sub> W <sub>12</sub> ) <sub>3</sub> ND <sub>5</sub> (P <sub>2</sub> W <sub>2</sub> O <sub>3</sub> ) Ph <sub>3</sub> O <sub>4</sub> (OC occ encapsulated by two (Nb <sub>2</sub> P <sub>2</sub> W <sub>2</sub> O <sub>3</sub> ) <sup>3</sup> mits (without any Nb-perxos groups).  KH <sub>3</sub> [(CH <sub>4</sub> ) <sub>3</sub> NH <sub>3</sub> ] <sub>4</sub> [(Ph <sub>3</sub> N <sub>5</sub> C <sub>4</sub> H <sub>4</sub> AsO <sub>3</sub> ) <sub>4</sub> P <sub>4</sub> W <sub>2</sub> O <sub>6</sub> O <sub>8</sub> ; Ph <sub>3</sub> O <sub>5</sub> O <sub>6</sub> (Ph <sub>3</sub> O <sub>4</sub> C <sub>4</sub> H <sub>4</sub> AsO <sub>3</sub> ) <sub>4</sub> P <sub>4</sub> W <sub>2</sub> O <sub>6</sub> O <sub>8</sub> ; Ph <sub>3</sub> O <sub>5</sub> O <sub>6</sub> (Ph <sub>3</sub> O <sub>4</sub> ) <sub>4</sub> (H <sub>4</sub> O <sub>4</sub> ) <sub>4</sub> [(CH <sub>3</sub> )NH <sub>3</sub> D <sub>4</sub> (H <sub>4</sub> O <sub>4</sub> )] <sub>4</sub> [(CH <sub>4</sub> )NH <sub>3</sub> D <sub>4</sub> (CH <sub>4</sub> O <sub>4</sub> )] <sub>4</sub> (Ph <sub>3</sub> N <sub>5</sub> O <sub>6</sub> B <sub>4</sub> ) Ph <sub>3</sub> O <sub>5</sub> D <sub>4</sub> (CH <sub>4</sub> O <sub>4</sub> ) Ph <sub>3</sub> O <sub>5</sub> D <sub>4</sub> P <sub>4</sub> W <sub>2</sub> O <sub>6</sub> D <sub>5</sub> P <sub>5</sub> W <sub>2</sub> O <sub>6</sub> D <sub>6</sub> P <sub>5</sub> W <sub>2</sub> D <sub>6</sub> D <sub>6</sub> P <sub>6</sub> W <sub>2</sub> D <sub>6</sub> P <sub>6</sub> W <sub>2</sub> D <sub>6</sub> D <sub>6</sub> P <sub>6</sub> W <sub>2</sub> D <sub>6</sub> D <sub>6</sub> P <sub>6</sub> W <sub>2</sub> D <sub>6</sub> P <sub>6</sub> W <sub>2</sub> D <sub>6</sub> P <sub>6</sub> W <sub>2</sub> D <sub>6</sub> D <sub>6</sub> P <sub>6</sub> W <sub>2</sub> D <sub>6</sub> D <sub>6</sub> P <sub>6</sub> W <sub>2</sub> D <sub>6</sub> P <sub>6</sub> W <sub>2</sub> D <sub>6</sub> D <sub>6</sub> P <sub>6</sub> W <sub>2</sub> D	0	$K_7[H_{13}{Nb_6(O_2)_4P_2W_{12}O_{57}}_2]\cdot 31H_2O$	$\{P_2W_{12}Nb_6(O_2)_4\}_2$	The Wells–Dawson dimer consists of two $\{P_2W_{12}\}$ units linked by two Nb–O–Nb bridges and the six vacant sites of	67
2. K <sub>1,2</sub> L <sub>2</sub> ([CH <sub>2</sub> ) <sub>2</sub> )RH <sub>2</sub> L <sub>2</sub> ([PNO <sub>2</sub> )P <sub>2</sub> V <sub>1,2</sub> O <sub>2</sub> ] PH <sub>2</sub> O (X = P, n = 35 and X = A <sub>8</sub> , n = 40)  3. KLi <sub>3</sub> ([CH <sub>3</sub> )RN <sub>3</sub> ] <sub>3</sub> ([O+1 <sub>3</sub> N-C <sub>4</sub> L <sub>4</sub> ASO))P <sub>2</sub> V <sub>3</sub> V <sub>2</sub> O <sub>2</sub> ] PH <sub>3</sub> O <sub>2</sub> O <sub>3</sub>  P <sub>3</sub> N <sub>3</sub> O <sub>3</sub>  P <sub>3</sub> N <sub>3</sub> O <sub>3</sub> O <sub></sub>	1	$(NH_4)_{16}[H_{14}\{P_2W_{12}Nb_7O_{63}(H_2O)_2\}_4\{Nb_4O_4(OH)_6\}]\cdot 16H_2O$	$\{(P_2W_{12})Nb_7\}_4Nb_4$	This polyanion comprises an adamantine-like $\{Nb_4O_6\}$ core encapsulated by two $[Nb_6P_2W_{12}O_{61}]^{10-}$ units (without any	67
3 KLi, [(CH <sub>3</sub> ),NH <sub>3</sub> ,Jn([O+H <sub>3</sub> N-C <sub>6</sub> H <sub>3</sub> ASO),P,W <sub>2</sub> O <sub>3</sub> D),PW <sub>3</sub> O <sub>4</sub> D,PW <sub>3</sub> D,O <sub>4</sub> D, MH <sub>3</sub> CH <sub>4</sub> ASO),PW <sub>3</sub> D <sub>4</sub> D, MH <sub>3</sub> CH <sub>4</sub> ASO),PW <sub>3</sub> D <sub>4</sub> D, MH <sub>3</sub> CH <sub>4</sub> ASO),PW <sub>3</sub> D <sub>4</sub> D, MH <sub>3</sub> CH <sub>4</sub> ASO),PW <sub>3</sub> D <sub>4</sub> D, MH <sub>3</sub> CH <sub>4</sub> ASO),PW <sub>3</sub> D <sub>4</sub> D, MH <sub>3</sub> CH <sub>4</sub> ASO),PW <sub>3</sub> D <sub>4</sub> D, MH <sub>3</sub> CH <sub>4</sub> ASO),PW <sub>3</sub> D <sub>4</sub> D, MH <sub>3</sub> CH <sub>4</sub> ASO),PW <sub>3</sub> D <sub>4</sub> D, MH <sub>3</sub> CH <sub>4</sub> ASO),PW <sub>3</sub> D <sub>4</sub> D, MH <sub>3</sub> CH <sub>4</sub> DO <sub>5</sub> D, MH <sub>3</sub> CH <sub>4</sub> ASO),PW <sub>3</sub> D <sub>4</sub> D <sub>4</sub> D, MH <sub>3</sub> CH <sub>4</sub> DO <sub>5</sub> D, MH <sub>3</sub> CH <sub>4</sub> DO <sub></sub>	2		$PhXOP_4W_{24}, X = P, As$	The structure consists of a {P <sub>4</sub> W <sub>24</sub> O <sub>29</sub> } unit capped by two	68
<ul> <li>4 K,Na15[K,C[Mn[H,O]]<sub>2</sub>]-{WO<sub>2</sub>(H<sub>2</sub>O]<sub>2</sub>]-{WO</li> <li>(H<sub>2</sub>O)]<sub>3</sub>(PW<sub>2</sub>O<sub>4</sub><sub>3</sub>)<sub>4</sub>]-7H<sub>2</sub>O</li> <li>5 K<sub>3</sub>Na<sub>2</sub>Li<sub>3</sub>,3iN<sub>10.25</sub>[Na<sub>3</sub>C{Ni<sub>3.3</sub>(H<sub>2</sub>O<sub>13</sub>}{WO<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-2(WO</li> <li>(H<sub>2</sub>O)]<sub>3</sub>(P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>)<sub>3</sub> 64H<sub>2</sub>O</li> <li>6 K<sub>6</sub>Na<sub>11</sub>[Na<sub>3</sub>C{CO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]-2(WO</li> <li>(H<sub>2</sub>O)]<sub>3</sub>(P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>)<sub>3</sub> 47H<sub>2</sub>O</li> <li>(H<sub>2</sub>O)]<sub>3</sub>(P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>)<sub>3</sub> 47H<sub>2</sub>O</li> <li>(H<sub>2</sub>O)]<sub>3</sub>(P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>)<sub>3</sub> 47H<sub>2</sub>O</li> <li>(H<sub>2</sub>O)]<sub>3</sub>(P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>)<sub>3</sub> 47H<sub>2</sub>O</li> <li>(H<sub>2</sub>O)]<sub>3</sub>(P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>)<sub>3</sub> 47H<sub>2</sub>O</li> <li>(H<sub>2</sub>O)]<sub>3</sub>(P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>)<sub>3</sub> 47H<sub>2</sub>O</li> <li>(M<sub>2</sub>O)<sub>2</sub>(P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>)<sub>3</sub> 4WO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>)<sub>2</sub>(WO</li> <li>(H<sub>2</sub>O)<sub>3</sub>(P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>)<sub>3</sub> 4WO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>)<sub>3</sub>(P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>)<sub>3</sub> 110H<sub>2</sub>O</li> <li>(M<sub>2</sub>O)<sub>13</sub>(P<sub>2</sub>W<sub>12</sub>O<sub>13</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O))<sub>3</sub>(P<sub>2</sub>W<sub>12</sub>O<sub>48</sub>)<sub>3</sub> 110H<sub>2</sub>O</li> <li>(M<sub>2</sub>O)<sub>13</sub>(M<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>(H<sub>2</sub>O)<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>O<sub>4</sub>O<sub>3</sub>)<sub>3</sub>(WO<sub>4</sub>O<sub>4</sub>O<sub>3</sub>O<sub>4</sub>O<sub>4</sub>O<sub>4</sub>O<sub>4</sub>O<sub>4</sub>O<sub>4</sub>O<sub>4</sub>O<sub>4</sub>O<sub>4</sub>O<sub>4</sub></li></ul>	3	$\begin{split} & K \dot{L} i_3 [(CH_3)_2 N H_2]_{10} [(o \cdot H_2 N \cdot C_6 H_4 A S O_3)_4 P_4 W_{24} O_{85}] \cdot 17 H_2 O \cdot Li C I, \\ & K H L i_2 [(CH_3)_2 N H_2]_6 [M n (H_2 O)_4]_2 [\{M n (H_2 O)_4\} (o \cdot H_2 N \cdot C_6 H_4 - A S O)_2 P_4 W_{24} O_{92}] \cdot 25 H_2 O \cdot 0.2 K C I \cdot 0.4 Li C I, K_{1.5} Li_2 [(CH_3)_2 N H_2]_{6.5} [C O (H_2 O)_4]_2 [\{C O (H_2 O)_4\} (o \cdot H_2 N \cdot C_6 H_4 \cdot A S O)_2 P_4 W_{24} O_{92}] \cdot 24 H_2 O \cdot 0.5 Li C I, \\ & and K_{1.5} Li_2 [(CH_3)_2 N H_2]_{6.5} [N i (H_2 O)_4]_2 [\{N i (H_2 O)_4\} (o \cdot H_2 N \cdot C_6 H_4 \cdot M_2 N \cdot M_2$	$(o-NH_2-C_6H_6-AsO)_2P_4W_{24}$ (M =	The introduction of divalent transition metal ions ( $Mn^{2+}$ , $Co^{2+}$ , $Ni^{2+}$ ) in the reaction mixture containing ( $\textbf{o}\text{-NH}_2\text{-}$ $C_6H_6\text{-AsO}$ ) $_4P_4W_{24}O_{92}$ resulted in 1D coordination polymers $[\{M(H_2O)_4\}P_4W_{24}O_{92}(C_6H_6AsNO)_2]^{14-}$ ( $M=Mn^{2+}$ , $Co^{2+}$ ,	69
<ul> <li>K,NAs,Lis,Z,Nio,Z,S(Na),C(Lis,Lig,O),13}{WO (H2O),2}{WO (H2O),3}{WO (H2O),3}</li></ul>	4	$K_4Na_{15}[K_3\subset\{Mn(H_2O)_4\}_2\{WO_2(H_2O)_2\}_2\{WO$		hinges forming a cyclic P <sub>6</sub> W <sub>39</sub> assembly which accommo-	71
6 K <sub>6</sub> N <sub>31</sub> [Na <sub>3</sub> C(Cu <sub>3</sub> (H <sub>2</sub> O <sub>3</sub> ) <sub>2</sub>  WO <sub>2</sub> (H <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ]z(WO (H <sub>2</sub> O) <sub>3</sub> ) <sub>3</sub> +7H <sub>2</sub> O (H <sub>2</sub> O) <sub>3</sub> ) <sub>3</sub> +7H <sub>3</sub> O (H <sub>2</sub> O) <sub>3</sub> ) <sub>3</sub> +7H <sub>3</sub> O (H <sub>2</sub> O) <sub>3</sub> (P <sub>2</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ]+7H <sub>3</sub> O (O <sub>6</sub> (P <sub>2</sub> W <sub>12</sub> ) <sub>3</sub> (WO(H <sub>2</sub> O) <sub>3</sub> ) <sub>3</sub> (P <sub>2</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ]+10H <sub>2</sub> O (O <sub>6</sub> (P <sub>2</sub> W <sub>12</sub> ) <sub>3</sub> (WO(H <sub>2</sub> O)) <sub>3</sub> (P <sub>3</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ]+10H <sub>2</sub> O (O <sub>6</sub> (P <sub>2</sub> W <sub>12</sub> ) <sub>3</sub> (WO(H <sub>2</sub> O)) <sub>3</sub> (P <sub>3</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ]+10H <sub>2</sub> O (O <sub>6</sub> (P <sub>2</sub> W <sub>12</sub> ) <sub>3</sub> (WO(H <sub>2</sub> O)) <sub>3</sub> (P <sub>3</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ]+10H <sub>2</sub> O (O <sub>6</sub> (P <sub>2</sub> W <sub>12</sub> ) <sub>3</sub> (WO(H <sub>2</sub> O)) <sub>3</sub> (P <sub>3</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ]+10H <sub>2</sub> O (O <sub>6</sub> (P <sub>2</sub> W <sub>12</sub> ) <sub>3</sub> (WO(H <sub>2</sub> O)) <sub>3</sub> (P <sub>3</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ]+10H <sub>2</sub> O (O <sub>6</sub> (P <sub>2</sub> W <sub>12</sub> ) <sub>3</sub> (WO(H <sub>2</sub> O)) <sub>3</sub> (P <sub>3</sub> W <sub>12</sub> O <sub>48</sub> ) <sub>3</sub> ) (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> ) <sub>3</sub> (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> ) (	5			Two $W^{VI}$ and four $Ni^{2+}$ ions are incorporated in the cyclic $P_6W_{39}$ host. One of the $Ni^{2+}$ ions is disordered with a Na	71
7 Na <sub>15</sub> [Na <sub>5</sub> C{O(H <sub>2</sub> O] <sub>3</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> ]-10H <sub>2</sub> O Na <sub>15</sub> [Na <sub>5</sub> C{Ni(H <sub>2</sub> O] <sub>3</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> ]-110H <sub>2</sub> O Ni <sub>6</sub> (P <sub>2</sub> W <sub>12</sub> ) <sub>3</sub> (WO(H <sub>2</sub> O)) <sub>3</sub> (P <sub>6</sub> W <sub>42</sub> O <sub>151</sub> (H <sub>2</sub> O) <sub>7</sub> ) <sub>5</sub> (P <sub>6</sub> W <sub>42</sub> O <sub>16</sub> (H <sub>1</sub> O) <sub>16</sub> (HMnGd <sub>2</sub> (tart)O <sub>2</sub> (H <sub>2</sub> O) <sub>15</sub> ) {(MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> ) <sub>3</sub> (WO(H <sub>2</sub> O)) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O) <sub>3</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O <sub>11</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O <sub>11</sub> assembly.  (MnGd)(HMnGd <sub>2</sub> P <sub>6</sub> W <sub>42</sub> O <sub>1</sub> assembly.	6			Two $W^{VI}$ and three $Cu^{2^+}$ ions are incorporated in the cyclic	71
The trimeric crown-shaped $P_kW_{30}$ encapsulates a $Mn^{2+}$ and $Q_s^{3+}$ ions in the cavity. In addition, a $Mn^{2+}$ and $Q_s^{3+}$ ion are present outside the polyanion, resulting in a two-dimensional solid-state framework.  Okayo $K_3Na_{10}[K_3C\{GdCo(H_2O)_{11}\}_2\{P_6W_{41}O_{148}(H_2O)_7\}]_{-43H_2O}$ (GdCoP <sub>6</sub> W <sub>41</sub> ) <sub>∞</sub> (Festivation of polyanions to a one-dimensional chain, where this Gd <sup>3+</sup> ion shows a square-antiprismatic coordination geometry. Trimeric, cyclic assembly of $\{P_2W_{12}\}$ units joined by three $C_1^{**}$ ions.  Na <sub>16</sub> K <sub>12</sub> [H <sub>56</sub> P <sub>8</sub> W <sub>48</sub> Fe <sub>28</sub> O <sub>248</sub> ]-20H <sub>2</sub> O  (Na <sub>16</sub> K <sub>12</sub> [H <sub>56</sub> P <sub>8</sub> W <sub>48</sub> Fe <sub>28</sub> O <sub>248</sub> ]-20H <sub>2</sub> O  (Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Fe <sub>27</sub> O <sub>248</sub> ]-20H <sub>2</sub> O  (Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Fe <sub>27</sub> O <sub>248</sub> ]-20H <sub>2</sub> O  (Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> )-1 <sub>27</sub> (Go(H <sub>2</sub> O) <sub>3</sub> ] <sub>2</sub> [Co(H <sub>2</sub> O) <sub>3</sub> ] <sub>3</sub> [Co(H <sub>2</sub> O)	7	$Na_{15}[Na_3 \subset \{Co(H_2O)_4\}_6\{WO(H_2O)\}_3(P_2W_{12}O_{48})_3]\cdot 109H_2O$ and	$Co_6(P_2W_{12})_3\{WO(H_2O)\}$ and	Six $\text{Co}^{2+}$ or $\text{Ni}^{2+}$ ions are incorporated in the cyclic $P_6W_{39}$	72
Fe <sub>28</sub> P <sub>8</sub> W <sub>48</sub> Fe <sub>28</sub> O <sub>248</sub> ]·20H <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Fe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Fe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>2</sub> O <sub>3</sub> ] <sub>2</sub> [{[Co(H <sub>2</sub> O) <sub>3</sub> ] <sub>1.5</sub> H <sub>3</sub> P <sub>8</sub> W <sub>49</sub> O <sub>187</sub> (H <sub>2</sub> O)]]·2NaCl·41.5H <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [N <sub>3</sub> O <sub>8</sub> (Nb <sub>4</sub> O <sub>8</sub> (Nb <sub>6</sub> P <sub>2</sub> W <sub>12</sub> ) <sub>3</sub> Na <sub>16</sub> K <sub>10</sub> [N <sub>3</sub> O <sub>8</sub> (Nb <sub>6</sub> P <sub>2</sub> W <sub>12</sub> O <sub>13</sub> ] <sub>3</sub> ]·10H <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [N <sub>3</sub> O <sub>8</sub> (O <sub>8</sub> O <sub>13</sub> ] <sub>3</sub> ]·10H <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Fe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Fe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Fe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Pe <sub>27</sub> O <sub>248</sub>	8	$K_3Na_8[K_3\subset \{GdMn(H_2O)_{10}\}\{HMnGd_2(tart)O_2(H_2O)_{15}\}$	$\{(MnGd)(HMnGd_2P_6W_{42})\}_{\infty}$	The trimeric crown-shaped $P_6W_{39}$ encapsulates a $Mn^{2+}$ and two $Gd^{3+}$ ions in the cavity. In addition, a $Mn^{2+}$ and $Gd^{3+}$ ion are present outside the polyanion, resulting in a two-	73
Trimeric, cyclic assembly of {P <sub>2</sub> W <sub>12</sub> } units joined by three Cr <sup>III</sup> ions.  Na <sub>16</sub> K <sub>12</sub> [H <sub>56</sub> P <sub>8</sub> W <sub>48</sub> Fe <sub>28</sub> O <sub>248</sub> ]·20H <sub>2</sub> O  Fe <sub>28</sub> P <sub>8</sub> W <sub>48</sub> Na <sub>16</sub> K <sub>12</sub> [H <sub>56</sub> P <sub>8</sub> W <sub>48</sub> Fe <sub>28</sub> O <sub>248</sub> ]·20H <sub>2</sub> O  Fe <sub>28</sub> P <sub>8</sub> W <sub>48</sub> Trimeric, cyclic assembly of {P <sub>2</sub> W <sub>12</sub> } units joined by three Cr <sup>III</sup> ions.  The tetrameric polyanion comprises four {P <sub>2</sub> W <sub>12</sub> Fe <sub>6</sub> } units, and each is bridged through Fe–O–Fe linkages to a {Fe <sub>4</sub> O <sub>6</sub> } cluster core. The linking is through pairs of three Fe–O–Fe bridges, which involve the three outer Fe atoms.  Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Fe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  Fe <sub>27</sub> P <sub>8</sub> W <sub>49</sub> K <sub>4</sub> Na <sub>22</sub> {[Co(H <sub>2</sub> O <sub>2</sub> ] <sub>2</sub> Cl][Co(H <sub>2</sub> O <sub>3</sub> ] <sub>2</sub> [Co(H <sub>2</sub> O) <sub>3</sub> ] <sub>1.5</sub> [Co  (H <sub>2</sub> O <sub>3</sub> ) <sub>4</sub> H <sub>4</sub> P <sub>8</sub> W <sub>49</sub> O <sub>187</sub> (H <sub>2</sub> O)]]·2NaCl·41.5H <sub>2</sub> O, and, Na <sub>30</sub> {[Ni (H <sub>2</sub> O) <sub>3</sub> ] <sub>2</sub> [Xi(H <sub>2</sub> O <sub>3</sub> ] <sub>3</sub> ] <sub>4</sub> Ki(H <sub>2</sub> O <sub>3</sub> ] <sub>3</sub> -1,5H <sub>3</sub> P <sub>8</sub> W <sub>49</sub> O <sub>187</sub> (H <sub>2</sub> O)]]·41.5H <sub>2</sub> O  (Nb <sub>4</sub> O <sub>6</sub> (Nb <sub>6</sub> P <sub>2</sub> W <sub>12</sub> )  (Nb <sub>4</sub> O <sub>6</sub> (Nb <sub>6</sub> O <sub>8</sub>	•	$K_{3}Na_{10}[K_{3}\subset \{GdCo(H_{2}O)_{11}\}_{2}\{P_{6}W_{41}O_{148}(H_{2}O)_{7}\}]\cdot 43H_{2}O$	$(GdCoP_6W_{41})_{\infty}$	The structure comprises a trimeric, crown-shaped $P_6W_{39}$ ion encapsulating two $\mathrm{Co}^{2+}$ and a $\mathrm{Gd}^{3+}$ ion as well as two $\mathrm{W}^{VI}$ atoms. The second $\mathrm{Gd}^{3+}$ ion is outside $P_6W_{39}$ , linking polyanions to a one-dimensional chain, where this $\mathrm{Gd}^{3+}$	73
The tetrameric polyanion comprises four {P <sub>2</sub> W <sub>12</sub> Fe <sub>6</sub> } units, and each is bridged through Fe–O–Fe linkages to a {Fe <sub>4</sub> O <sub>6</sub> } cluster core. The linking is through pairs of three Fe–O–Fe bridges, which involve the three outer Fe atoms.  2 Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Fe <sub>27</sub> O <sub>248</sub> ]·yH <sub>2</sub> O  3 K <sub>4</sub> Na <sub>22</sub> {[Co(H <sub>2</sub> O) <sub>3</sub> ] <sub>2</sub> [Co(H <sub>2</sub> O) <sub>3</sub> ] <sub>2</sub> [Co(H <sub>2</sub> O) <sub>5</sub> ] <sub>1.5</sub> [Co (H <sub>2</sub> O) <sub>3</sub> H <sub>4</sub> P <sub>8</sub> W <sub>49</sub> O <sub>187</sub> (H <sub>2</sub> O)]]·2NaCl·41.5H <sub>2</sub> O, and, Na <sub>30</sub> {[Ni (H <sub>2</sub> O) <sub>3</sub> ] <sub>2</sub> [Ni(H <sub>2</sub> O) <sub>3</sub> ] <sub>2</sub> [Ni(H <sub>2</sub> O) <sub>3</sub> ] <sub>2</sub> [-3H <sub>3</sub> P <sub>8</sub> W <sub>49</sub> O <sub>187</sub> (H <sub>2</sub> O)]]·41.5H <sub>2</sub> O  4 (NH <sub>4</sub> ) <sub>36</sub> [{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> ]·16H <sub>2</sub> O (Nb <sub>4</sub> O <sub>6</sub> (Nb <sub>6</sub> P <sub>2</sub> W <sub>12</sub> ) <sub>4</sub> The tetrameric polyanion comprises four {P <sub>2</sub> W <sub>12</sub> Fe <sub>6</sub> } units, and each is bridged through Fe–O–Fe linkages to a {Fe <sub>4</sub> O <sub>6</sub> } cluster core. The linking is through pairs of three Fe–O–Fe bridges, which involve the three outer Fe atoms.  Similar structure as Fe <sub>28</sub> P <sub>8</sub> W <sub>48</sub> with one of the sites having an occupancy of 25% W and 75% Fe.  The transformation of four {P <sub>2</sub> W <sub>12</sub> } ions to the cyclic P <sub>8</sub> W <sub>49</sub> happens in situ via self-condensation, performed in aqueous acidic medium in the presence of Co <sup>2+</sup> /Ni <sup>2+</sup> ions.  The extra W atom originates from partial decomposition of {P <sub>2</sub> W <sub>12</sub> }.	0	$K_{4}[H_{23}(Cr(H_{2}O)_{2})_{3}(H_{2}P_{2}W_{12}O_{48})_{3}]\cdot 34H_{2}O$	$Cr_3(P_2W_{12})_3$	Trimeric, cyclic assembly of {P <sub>2</sub> W <sub>12</sub> } units joined by three	74
2 Na <sub>16</sub> K <sub>10</sub> [H <sub>55</sub> P <sub>8</sub> W <sub>49</sub> Fe <sub>27</sub> O <sub>248</sub> ]yH <sub>2</sub> O Fe <sub>27</sub> P <sub>8</sub> W <sub>49</sub> Similar structure as Fe <sub>28</sub> P <sub>8</sub> W <sub>48</sub> with one of the sites having an occupancy of 25% W and 75% Fe.  3 K <sub>4</sub> Na <sub>22</sub> {[Co(H <sub>2</sub> O) <sub>2</sub> Cl][Co(H <sub>2</sub> O) <sub>3</sub> ] <sub>2</sub> [Co(H <sub>2</sub> O) <sub>5</sub> ] <sub>1.5</sub> [Co (H <sub>2</sub> O) <sub>3</sub> H <sub>4</sub> P <sub>8</sub> W <sub>49</sub> O <sub>187</sub> (H <sub>2</sub> O)]]·2NaCl·41.5H <sub>2</sub> O, and, Na <sub>30</sub> {[Ni (H <sub>2</sub> O) <sub>3</sub> ] <sub>2</sub> [Ni(H <sub>2</sub> O) <sub>3</sub> ] <sub>1.5</sub> H <sub>3</sub> P <sub>8</sub> W <sub>49</sub> O <sub>187</sub> (H <sub>2</sub> O)]]·41.5H <sub>2</sub> O  P <sub>8</sub> W <sub>49</sub> happens in situ via self-condensation, performed in aqueous acidic medium in the presence of Co <sup>2+</sup> /Ni <sup>2+</sup> ions. The extra W atom originates from partial decomposition of {P <sub>2</sub> W <sub>12</sub> }.  4 (NH <sub>4</sub> ) <sub>36</sub> [{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> } <sub>4</sub> ]·16H <sub>2</sub> O (Nb <sub>4</sub> O <sub>6</sub> (Nb <sub>6</sub> P <sub>2</sub> W <sub>12</sub> ) <sub>4</sub> The polyanion comprises a {Nb <sub>4</sub> O <sub>6</sub> } core which is sur-	1	$Na_{16}K_{12}[H_{56}P_8W_{48}Fe_{28}O_{248}]\cdot 20H_2O$	$Fe_{28}P_8W_{48}$	The tetrameric polyanion comprises four $\{P_2W_{12}Fe_6\}$ units, and each is bridged through Fe–O–Fe linkages to a $\{Fe_4O_6\}$ cluster core. The linking is through pairs of three Fe–O–Fe	55
3 $K_4Na_{22}\{[Co(H_2O)_3]_2[Co(H_2O)_3]_1.5[Co$ $Co_{5.5}P_8W_{49}$ , and $Ni_{3.5}P_8W_{49}$ The transformation of four $\{P_2W_{12}\}$ ions to the cyclic $(H_2O)_3H_4P_6W_{49}O_{187}(H_2O)]\}$ -2NaCl-41.5H <sub>2</sub> O, and, $Na_{30}\{[Ni(H_2O)_3]_1.5H_3P_8W_{49}O_{187}(H_2O)]\}$ -41.5H <sub>2</sub> O The transformation of four $\{P_2W_{12}\}$ ions to the cyclic $P_8W_{49}$ happens in situ via self-condensation, performed in aqueous acidic medium in the presence of $Co^{2+}/Ni^{2+}$ ions. The extra W atom originates from partial decomposition of $\{P_2W_{12}\}$ . The polyanion comprises a $\{Nb_4O_6\}$ core which is sur-	2	$Na_{16}K_{10}[H_{55}P_8W_{49}Fe_{27}O_{248}]yH_2O$	$Fe_{27}P_8W_{49}$	Similar structure as $Fe_{28}P_8W_{48}$ with one of the sites having	55
$4 (NH_4)_{36}[\{Nb_4O_6(OH)_4\}\{Nb_6P_2W_{12}O_{61}\}_4]$ The polyanion comprises a $\{Nb_4O_6\}$ core which is sur-	3	$(H_2O)_3H_4P_8W_{49}O_{187}(H_2O)]\}\cdot 2NaCl\cdot 41.5H_2O,\ and,\ Na_{30}\{[Ni$	$\text{Co}_{5.5}\text{P}_8\text{W}_{49}$ , and $\text{Ni}_{3.5}\text{P}_8\text{W}_{49}$	The transformation of four $\{P_2W_{12}\}$ ions to the cyclic $P_8W_{49}$ happens in situ via self-condensation, performed in aqueous acidic medium in the presence of $\operatorname{Co}^{2^+}/\operatorname{Ni}^{2^+}$ ions. The extra W atom originates from partial decomposition of	75
founded by four Mogravita units.	4	$(NH_4)_{36}[\{Nb_4O_6(OH)_4\}\{Nb_6P_2W_{12}O_{61}\}_4]\cdot 16H_2O$	$(Nb_4O_6)(Nb_6P_2W_{12})_4$		78

**Dalton Transactions** 

#### Table 1 (Contd.)

Sl. no.	Formula	Abbreviation	Brief description	Ref.
25	$Na_{24}[Mn_8(H_2O)_{32}P_8W_{48}O_{184}]\cdot58H_2O, \\ K_4Na_{16}H_4[Co_8(H_2O)_{32}P_8W_{48}O_{184}]\cdot76H_2O, and \\ Na_{20}H_4[Ni_8(H_2O)_{32}P_8W_{48}O_{184}]\cdot72H_2O$	$(\mathbf{M_8P_8W_{48}}, \mathbf{M} = \mathbf{Mn}, \mathbf{Co}, \mathbf{Ni})$	Eight divalent 3d metal ions are incorporated in the cyclic $P_8W_{48}$ host.	79
26	$\begin{array}{lll} & & & & & & & & & & & & \\ & & & & & & $	$Mn_{15}(Nb_6P_2W_{12})_6$	The structure consists of six $\{Nb_6P_2W_{12}\}$ units which are connected alternately by four $Mn^{2+}$ ions and four trinuclear $\{Mn_3^{III}\}$ moieties.	80
27	$[(n\text{-}\mathrm{C}_4\mathrm{H}_9)_4\mathrm{N}]_{20}\cdot 5\mathrm{H}_{21.5}[\{\gamma\text{-}\mathrm{P}_2\mathrm{W}_{12}\mathrm{O}_{48}\mathrm{Mn}_4(\mathrm{C}_5\mathrm{H}_7\mathrm{O}_2)_2(\mathrm{CH}_3\mathrm{CO}_2)\}_6]\cdot 35\mathrm{H}_2\mathrm{O}_{12}\mathrm{Mn}_4(\mathrm{C}_5\mathrm{H}_7\mathrm{O}_2)_2(\mathrm{CH}_3\mathrm{CO}_2)\}_6]\cdot 35\mathrm{H}_2\mathrm{O}_{12}\mathrm{Mn}_4(\mathrm{C}_5\mathrm{H}_7\mathrm{O}_2)_2(\mathrm{CH}_3\mathrm{CO}_2)\}_6]\cdot 35\mathrm{H}_2\mathrm{O}_{12}\mathrm{Mn}_4(\mathrm{C}_5\mathrm{H}_7\mathrm{O}_2)_2(\mathrm{CH}_3\mathrm{CO}_2)\}_6]\cdot 35\mathrm{H}_2\mathrm{O}_{12}\mathrm{Mn}_4(\mathrm{C}_5\mathrm{H}_7\mathrm{O}_2)_2(\mathrm{CH}_3\mathrm{CO}_2)\}_6]\cdot 35\mathrm{H}_2\mathrm{O}_{12}\mathrm{Mn}_4(\mathrm{C}_5\mathrm{H}_7\mathrm{O}_2)_2(\mathrm{CH}_3\mathrm{CO}_2)\}_6]\cdot 35\mathrm{H}_2\mathrm{O}_{12}\mathrm{Mn}_4(\mathrm{C}_5\mathrm{H}_7\mathrm{O}_2)_2(\mathrm{CH}_3\mathrm{CO}_2)\}_6]\cdot 35\mathrm{H}_2\mathrm{O}_{12}\mathrm{Mn}_4(\mathrm{C}_5\mathrm{H}_7\mathrm{O}_2)_2(\mathrm{CH}_3\mathrm{CO}_2)]_6]\cdot 35\mathrm{H}_2\mathrm{O}_{12}\mathrm{Mn}_4(\mathrm{C}_5\mathrm{H}_7\mathrm{O}_2)_2(\mathrm{CH}_3\mathrm{CO}_2)_2(\mathrm{CH}_3\mathrm{CO}_2)_3(\mathrm{CH}_3\mathrm{O}_2)_2(\mathrm{CH}_3\mathrm{CO}_2)_2(\mathrm{CH}_3\mathrm{CO}_2)_3(\mathrm{CH}_3\mathrm{CO}_2)_$	$\{P_2W_{12}O_{48}Mn_4\}_6$	The polyanion $P_2W_{12}$ reacts with Mn(acac), forming a hexameric polyanion in an organic medium. Two types of manganese coordination sites are present in each unit of manganese-substituted $\{P_2W_{12}\}$ , and each unit is connected to the other unit of manganese-substituted $P_2W_{12}$ unit.	81
28	$[(\textit{n-}\text{C}_4\text{H}_9)_4\text{N}]_{16.6}\text{H}_{7.4}[\{\gamma\text{-P}_2\text{W}_{12}\text{O}_{48}\text{Mn}_4(\text{H}_2\text{O})_6\}_4(\text{H}_2\text{O})_4]\text{:}8\text{H}_2\text{O}$	$\{P_{2}W_{12}O_{48}Mn_{4}\}_{4}$	The tetrameric polyanion forms after removing the organic capping in the manganese cation from the hexameric complex.	81
29	$\begin{split} &([(n\text{-}C_4H_9)_4N]_5[\gamma\text{-}P_2W_{12}O_{44}M_2(\text{OAc})(\text{CH}_3\text{CONH})_2]\cdot nH_2\text{O}\cdot m\text{CH}_3\text{CN};  M\\ &=Mn^{2^+}, \text{Co}^{2^+}, \text{Ni}^{2^+}, \text{Cu}^{2^+}, \text{or} \text{Zn}^{2^+}; \text{OAc}=\text{acetate}) \end{split}$	$\left(\gamma\text{-P}_2W_{12}O_{44}M_2\text{(OAc)}\right)$	The polyanion comprises a central edge-shared bis(square-pyramidal) $\{O_2M(\mu_3-O)_2(\mu-OAc)MO_2\}$ group bound to the belt area of $\{\gamma-P_2W_{12}\}$ and two acetamide (CH <sub>3</sub> CONH <sub>2</sub> ) groups are coordinated to the vacant cap positions.	82
30	$K_{12}H_2[Ce_4(OH_2)_9(OH)_2(\alpha_1,\alpha_1\text{-}P_2W_{16}O_{59})_2]\cdot 48H_2O$	$Ce_4(\alpha_1\alpha_1\text{-}P_2W_{16})_2$	groups are coordinated to the vacant cap positions. The polyanion has a dimeric structure composed of two $\{\alpha_1, \alpha_1 \cdot P_2 W_{16} O_{59}\}$ units connected by four cerium(           ions.	60
31	$K_{16}[\{La(CH_{3}COO)(H_{2}O)_{2}(\alpha_{2}\text{-}P_{2}W_{17}O_{61})\}_{2}]\cdot 36H_{2}O$	$La(OAc)(\alpha_2-P_2W_{17})_2$	The polyanion consists of two $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ units connected by two lanthanum acetate dimers $(\text{La}_2(\text{CH}_3\text{COO})_2(\text{H}_2\text{O})_4)^{4+}$ , resulting in a head-on transoid dimer. In an acidic medium, $\text{P}_2\text{W}_{12}$ quickly transforms into the monovacant $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}]^{10-}$ .	84
32	$K_4Na_{10}[\alpha_1\text{-}CuP_2W_{17}O_{60}(OH)]_2$ :~58 $H_2O$	$Cu_2P_4W_{34}$	The dimeric polyanion cluster is formed from two units each of $\alpha_1$ -{CuP <sub>2</sub> W <sub>17</sub> }, connected through the W-OH-Cu bonds resulting in the dimeric cluster.	86
33	$Na_{2}[H_{2}en][H_{2}hn]_{0.5}[Cu(en)_{2}]_{4.5}[\alpha_{1}\text{-}CuP_{2}W_{17}O_{60}(OH)]_{2}\cdot\sim43H_{2}O$	$\{\mathrm{Cu}(\mathrm{en})_{2}\mathrm{CuP}_{2}\mathrm{W}_{17}\}_{\infty}$	The dimeric polyanion assembly [a <sub>1</sub> -CuP <sub>2</sub> W <sub>17</sub> O <sub>60</sub> (OH)] <sub>2</sub> is linked to an extended network by {Cu(en) <sub>2</sub> } <sup>2+</sup> units.	86
34	$Na_{3}[H_{2}hn]_{2.5}[P_{2}W_{17}O_{60}Cu(OH)_{2}]\cdot \sim 14H_{2}O$	$\{(H_2hn)(CuP_2W_{17})_2\}_{\infty}$	The polyanion possesses a 3-D hybrid supramolecular framework with 1-D tunnels.	86
35	$Na_{8}H_{2}L(H_{2}enMe)_{4}[Mn(H_{2}O)_{2}(W_{4}Mn_{4}O_{12})(P_{2}W_{14}O_{54})_{2}]\cdot 17H_{2}O$	$\{W_4Mn_4(MnP_2W_{14})_2\}_{\infty}$	The 1-D inorganic polymer building blocks comprise multi $\mathrm{Mn^{2^+}}$ -substituted Wells–Dawson ions and $\mathrm{Mn^{2^+}}$ linkers with the idealized $C_2$ symmetry, further connected into a 3-D supramolecular network $via$ extensive hydrogenbonding interactions.	87
36	$\label{eq:K56} K_{56} {\rm Li}_{74} H_{14} [Mn_{40} P_{32} W_{224} O_{888}] {\it ca. } 680 \ {\rm H_2O}$	$\begin{array}{l} (P_8W_{48}) \\ (Mn_4P_2W_{14})_4(Mn_3P_2W_{15})_8 \end{array}$	The polyanion consists of $\{P_2W_{14}\}$ , $\{P_2W_{15}\}$ and $\{P_8W_{48}\}$ corner-sharing Wells-Dawson type units with no Mn <sup>2+</sup> ions found inside the cavity of $P_8W_{48}$ .	88
37	$\begin{split} &[K(H_2O)_2]_4[K_4(\mu\text{-}H_2O)_4(H_2O)_4]_2\{[Ln_2(\mu\text{-}OH)_4(H_2O)\\x]_2(H_{24}P_8W_{48}O_{184})\}\cdot yH_2O\ (Ln=Nd,Sm,Tb) \end{split}$	$Ln_4P_8W_{48}$	Eight lanthanide ions occupy the cavities of $P_8W_{48}$ , with each lanthanide ion being bridged through hydroxyl	89
38	$[K(H_2O)_2]_4[K_4(\mu\text{-}H_2O)_8]_2[K(H_2O)]_8\{[Mn_8(H_2O)_{16}](H_4P_8W_{48}O_{184})\}$	$K_8Mn_8P_8W_{48}$	groups and having a 50% occupancy in each position. Eight Mn <sup>2+</sup> and eight K <sup>+</sup> ions are incorporated in the cavity	89
39	$\left[ {\it cis}\text{-}(P_2W_{15}Nb_3O_{61})_2 \right]^{14-}$ and two phases of $\left[ {\it trans}\text{-}(P_2W_{14.7}Nb_{3.3}O_{61})_2 \right]^{14.6-}$	$P_2W_{15}Nb_3$	of $P_8W_{48}$ . $Nb^V$ ions are taken up by $P_2W_{12}$ in acidic media resulting in the dimer $[(P_2W_{15}Nb_3O_{61})_2]^{14-}$ and a mixture of derivatives with an average formula $[(P_2W_{14.7}Nb_{3.3}O_{61})_2]^{14.6-}$ , indicating the coexistence of species with different composition, such as $\{(P_2W_{15}Nb_3)_2\}$ (70%) and $\{(P_2W_{14}Nb_4)_2\}$ (30%).	90
40	$\left[Fe_{48}(OH)_{76}(H_2O)_{16}(HP_2W_{12}O_{48})_8\right]^{36-}$	$Fe_{48}(P_2W_{12})_8$	This structure contains 48 Fe <sup>3+</sup> ions surrounded by eight $P_2W_{12}$ ions, comprising eight equivalent $\{Fe_6P_2W_{12}\}$ subunits, linked to each other <i>via</i> Fe-O-Fe/W bonds.	91
41	$K_{17} \text{Li}_{11} [\{ \text{Sn}(\text{CH}_3)_2 \}_4 (\text{H}_2 \text{P}_4 \text{W}_{24} \text{O}_{92})_2 ] \cdot 51 \text{H}_2 \text{O}$	${Sn(CH_3)_2}_4(P_4W_{24})_2$	The structure consists of two $\mathbf{P_4W_{24}}$ units linked through four dimethyltin groups, resulting in a dimeric hybrid inorganic-organic polyanion cluster.	44
42	$\begin{array}{l} K_6 \text{Li}_{19} [\text{Li}\{H_2 O) \\ K_4 (H_2 O)_3 \{(\text{UO}_2)_4 (\text{O}_2)_4 (\text{H}_2 O)_2\}_2 (\text{PO}_3 \text{OH})_2 \text{P}_6 W_{36} \text{O}_{136}] \cdot 74 \text{H}_2 O \end{array}$	$Li(UO_2)_4(O_2)_4(PO_3OH)_2P_6W_{36}$	The structure consists of three $P_2W_{12}$ units encapsulating two independent, neutral symmetrical uranium-peroxo $[(UO_2)(O_2)]_4$ units in the central cavity, resulting in a	92
43	$K_{12}Rb_{3}[Rb_{3}C\{V^{V}V_{3}^{IV}O_{7}(H_{2}O)_{6}\}_{2}\{H_{6}P_{6}W_{39}O_{147}(H_{2}O)_{3}\}]\cdot 63H_{2}O$	$(V^{V}V_{3}^{IV}O_{7})_{2}P_{6}W_{39}$	U-shaped $\{P_2W_{12}\}_3$ assembly for the first time. The polyanion cluster is composed of three $\alpha$ - $\{P_2W_{12}\}$ subunits, which form a macrocyclic template of $P_6W_{39}$ , capped by two mixed-valent $\{(V^V=O)(V^{1V}=O)_3(\mu_2 O)_3(\mu_2 O)_6\}^{3^+}$ $\{(V^VV_3^{1V}\})$ groups.	93
44	$Na_{12}K_{8}H_{4}[K_{8}{\subset}\{V_{4}^{V}V_{2}^{IV}O_{12}(H_{2}O)_{2}\}_{2}\{P_{8}W_{48}O_{184}\}]\cdot80H_{2}O$	$\big(V_4^VV_2^{IV}O_{12}\big)_2P_8W_{48}$	( $\{V \ V_3^*\}$ ) groups.  In this polyanion, two $\{V_4^V V_2^{IV} O_{12}(H_2O)_2\}^{4+}$ units are observed to be trapped inside the cavity of $P_8W_{48}$ . The $\{V_4^V V_2^{IV} O_{12}(H_2O)_2\}^{4+}$ unit consists of two octahedral $V^{IV}$ and four tetrahedral $V^V$ centers. The oxidation of $V^{IV}$ to $V^V$ occurs due to air.	94
45	$K_{12} Li_{13} [Cu_{20} Cl(OH)_{24} (H_2 O)_{12} (P_8 W_{48} O_{184})] \cdot 22 H_2 O$	$\mathrm{Cu_{20}ClP_8W_{48}}$	This structure was the first example demonstrating that d-metal ions can be incorporated in the cavity of $P_8W_{48}$ . Here, twenty $Cu^{2+}$ ions are grafted in $P_8W_{48}$ , and the coordination geometry of $Cu^{2+}$ ranges from octahedral to square-pyramidal and square-planar, with a chloride ion encapsulated in the center of the structure.	96

# Perspective Table 1 (Contd.)

Sl. no.	Formula	Abbreviation	Brief description	Ref.
46	$\begin{array}{c} K_{12}Li_{13}[Cu_{20}Br(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]\cdot 60H_2O \ and \ K_{12}Li_{13}[Cu_{20}I\\ (OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]\cdot 50H_2O \end{array}$	$\text{Cu}_{20}\text{BrP}_8\text{W}_{48},$ and $\text{Cu}_{20}\text{IP}_8\text{W}_{48}$	Identical structure to $Cu_{20}ClP_8W_{48}$ but with bromide or iodide acting as the central template rather than instead of	97
47	$LiK_{14}Na_9[P_8W_{48}O_{184}Cu_{20}(N_3)_6(OH)_{18}]\cdot 60H_2O$	$Cu_{20}(N_3)_6P_8W_{48}$	chloride. The polyanion comprises two $\{Cu_5(OH)_4\}^{6+}$ and two $\{Cu_5(OH)_2(\mu_{1,1,3,3}-N_3)\}^{7+}$ units incorporated in the cavity of	116
48	${\rm Li_4K_{16}[P_8W_{48}O_{184}Fe_{16}(OH)_{28}(H_2O)_4]\cdot 66H_2O\cdot 2KCl}$	$\mathrm{Fe}_{16}\mathrm{P}_{8}\mathrm{W}_{48}$	$P_8W_{48}$ . The polyanion contains a cationic $\{Fe_{16}(OH)_{28}(H_2O)_4\}^{20+}$ cluster incorporated in the cavity of $P_8W_{48}$ . The 16-iron(III)-hydroxo core consists of eight pairs of structurally equivalent, edge-shared $\{Fe_2O_{12}\}$ units.	117
49	$\begin{split} &K_9LiNa[Fe_{16}O_2(OH)_{23}(H_2O)_9P_8W_{49}O_{189}Gd_4(H_2O)_{19}]\cdot 50H_2O \text{ and} \\ &K_{8.5}Na_{0.5}Li_{0.5}Eu_{0.5}[Fe_{16}O_2(OH)_{23}(H_2O)_9P_8W_{49}O_{189}Eu_4(H_2O)_{19}]\cdot 70H_2O \end{split}$	$Fe_{16}Ln_{4}P_{8}W_{49}\left(Ln=Gd^{3+},Eu^{3+}\right)$	The $Fe_{16}Ln_4P_8W_{49}$ (Ln = $Gd^{3+}$ , $Eu^{3+}$ ) polyanion can be described as a derivative of $Fe_{16}P_8W_{48}$ with four $Ln^{3+}$ ions grafted on the iron-oxo core and the $P_8W_{48}$ wheel is cleaved with an extra tungsten atom being bound right there.	118
50	$K_{12} Li_{16} Co_2 [Co_4 (H_2 O)_{16} P_8 W_{48} O_{184}] \cdot 60 H_2 O$	$Co_4P_8W_{48}$	The structure has four Co2+ ions bound at two opposite	121
51	$\begin{split} &K_{12} \text{Li}_{10} \text{Mn}_3 [\text{Mn}_4 (\text{H}_2 \text{O})_{16} (\text{P}_8 \text{W}_{48} \text{O}_{184}) (\text{WO}_2 (\text{H}_2 \text{O})_2)_2] \cdot 67 \text{H}_2 \text{O} \text{ and } \\ &K_{14} \text{Li}_8 \text{Ni}_3 [\text{Ni}_4 (\text{H}_2 \text{O})_{16} (\text{P}_8 \text{W}_{48} \text{O}_{184}) (\text{WO}_2 (\text{H}_2 \text{O})_{2)2}] \cdot 44 \text{H}_2 \text{O} \end{split}$	$Mn_4P_8W_{50}$ and $Ni_4P_8W_{50}$	hinge sites of $P_8W_{48}$ . This structure is identical to $Co_4P_8W_{48}$ , except that two additional $W^{VI}$ ions in the form of $\{WO_2(H_2O)_2\}$ groups are grafted in the cavity, one each at the two hinges which are not occupied by $M^{2+}$ $(M=Mn,Ni)$ ions, resulting in a cyclic $P_8W_{50}$ unit.	121
52 53	$\begin{split} &K_{20}\text{Li}_{16}[(VO_2)_4(P_8W_{48}O_{184})]\text{-}48H_2O\\ &K_{15}\text{Li}_5[\{Co_{10}(H_2O)_{34}(P_8W_{48}O_{184})\}]\text{-}54\ H_2O \end{split}$	$\begin{aligned} &(VO_2)_4 P_8 W_{48} \\ &\{Co_{10} (H_2 O)_{34} P_8 W_{48} \}_{\infty} \end{aligned}$	Four $V^V$ O groups are coordinated in the cavity of $P_8W_{48}$ . This polyanion structure is similar to that of $Co_4P_8W_{48}$ , except that an additional four external $Co^{2+}$ ions link adjacent polyanions resulting in 1D chains.	121 122
54	$K_8 \text{Li}_{12}[\{\text{Co}_{10}(\text{H}_2\text{O})_{44}(\text{P}_8\text{W}_{48}\text{O}_{184})\}] \cdot 60\text{H}_2\text{O}$	$\{Co_{10}(H_2O)_{44}P_8W_{48}\}_{\infty}$	Similar to Co <sub>4</sub> P <sub>8</sub> W <sub>48</sub> , except an additional four external Co <sup>2+</sup> ions link the adjacent polyanions, resulting in 3D networks.	122
55	$Na_8Li_8Co_5[Co_{5.5}(H_2O)_{19}P_8W_{48}O_{184}]\cdot 60H_2O$	$Co_{5}\{Co_{5.5}P_{8}W_{48}\}_{\infty}$	Five external Co <sup>2+</sup> ions are observed to link adjacent polyanions of Co <sub>5.5</sub> P <sub>8</sub> W <sub>48</sub> , resulting in two-dimensional chains.	123
56	$K_2Na_4Li_{11}Co_5[Co_7(H_2O)_{28}P_8W_{48}O_{184}]Cl\cdot 59H_2O$	$Co_{5}\{Co_{7}P_{8}W_{48}\}_{\infty}$	Co <sub>2</sub> P <sub>8</sub> W <sub>48</sub> is linked <i>via</i> 5 external Co <sup>2+</sup> ions are observed to link adjacent polyanions, resulting in two-dimensional chains.	123
57	$K_2Na_4LiCo_{11}[Co_8(H_2O)_{32}P_8W_{48}O_{184}](CH_3COO)_4Cl\cdot 47H_2O$	$Co_{11}\{Co_{8}P_{8}W_{48}\}_{\infty}$	$Co_8P_8W_{48}$ is linked <i>via</i> 11 external $Co^{2+}$ ions into a three-dimensional network.	123
58	$K_{18}Li_{6}[Mn_{8}(H_{2}O)_{48}P_{8}W_{48}O_{184}]\cdot 108H_{2}O$	$\{Mn_8(H_2O)_{48}P_8W_{48}\}_{\infty}$	The Mn <sub>8</sub> (H <sub>2</sub> O) <sub>48</sub> P <sub>8</sub> W <sub>48</sub> polyanion forms an open framework nanocube structure with each P <sub>8</sub> W <sub>48</sub> fragment linked by Mn-O-W coordination bonds, which forms the higher order packing arrangement.	21 and 76
59	$K_{12}[Mn_{14}(H_2O)_{30}P_8W_{48}O_{184}]\cdot 111H_2O$	$\{Mn_{14}P_8W_{48}\}_{\infty}$	A solid-state framework formed by $P_8W_{48}$ units linked by external $\mathrm{Mn}^{2^+}$ ions.	21 and 76
60	$K_{13} Li_{11} [Mn_8 (H_2 O)_{26} (P_8 W_{48} O_{184})] \cdot 60 H_2 O$	$Mn_8(H_2O)_{26}P_8W_{48}$	In this polyanion, six $Mn^{2+}$ ions are observed to be located inside the $P_8W_{48}$ cavity, while two other $Mn^{2+}$ ions are considered by the $Mn^{2+}$ ions are considered by the $Mn^{2+}$ in $Mn^{2+}$ ions are considered by the $Mn^{2+}$ in $Mn^{2+}$ ions are considered by the $Mn^{2+}$ in $Mn^$	77
61	$K_{12} Li_{13} [Mn_6 (H_2O)_{22} (P_8W_{48}O_{184}) \{WO_2 (H_2O)_2\}_{1.5}] \cdot 75H_2O$	$Mn_{6}\{WO_{2}(H_{2}O)_{2}\}_{1.5}P_{8}W_{48}$	ordinated to the outer rim of $P_8W_{48}$ . Four $Mn^{2^+}$ ions are located in the cavity of $P_8W_{48}$ , whereas two other $Mn^{2^+}$ centers are attached to the surface of the wheel. In addition, one or two $\{WO_2(H_2O)_2\}$ groups are	77
62	$\begin{array}{l} K_{10}Na_{14}[\{P_8W_{48}O_{184}\}\{Mo^{VI}O_2\}_4\{(H_2O)(O=)Mo^V(\mu_2\text{-}O)_2(O=)Mo^V(\mu_2\text{-}H_2O)(\mu_2\text{-}O)_2Mo^V(=O)(\mu_2\text{-}O)_2Mo^V(=O)(H_2O)\}_2]\cdot 80H_2O \end{array}$	$\mathbf{Mo_4^{VI}Mo_4^{V}P_8W_{48}}$	grafted in the cavity, leading to a mixture of products. Observed to consist of two unprecedented neutral tetranuclear $\{Mo_{10}^V(D_{10}(H_2O)_3\}$ and four $\{Mo^{VI}O_2\}^{2+}$ units connected to the $P_8W_{48}$ ring $via$ Mo–O–W bonds.	124
63	$K_{20} Li_6 H_4 [K_4 \{Mo_4O_4S_4(H_2O)_3(OH)_2\}_2 (WO_2) (P_8 W_{48}O_{184})] \cdot 95 H_2 O$	$(Mo_4O_4S_4)_2(WO_2)P_8W_{48}$	Two cationic [Mo <sub>4</sub> O <sub>4</sub> S <sub>4</sub> (OH) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ] <sup>2+</sup> groups are grafted on both sides of <b>P<sub>8</sub>W<sub>48</sub></b> . Different bonding modes of the oxothiomolybdenum groups result in two geometrical	126
64	$K_{26} Li_2 H_8 [\{Mo_4 O_4 S_4 (H_2 O)_3 (OH)_2\}_2 (P_8 W_{48} O_{184})] \cdot 90 H_2 O$	$(Mo_4O_4S_4)_2P_8W_{48} \\$	isomers. This polyanion is composed of the same two disordered $\{Mo_4O_4S_4\}$ oxothiomolybdenum clusters observed in $\{Mo_4O_4S_4\}_2(WO_2)P_8W_{48}$ but without the extra $\{WO_2\}^{2^+}$ group.	126
65	$K_{16} \text{Li}_{11} [\{K(H_2 O)\}_3 \{Ru(\textit{p-cymene})(H_2 O)\}_4 P_8 W_{49} O_{186}(H_2 O)_2] \cdot 87 H_2 O$	$Ru_4P_8W_{49}$	Four $\{Ru(p\text{-cymene})(H_2O)\}^{2^+}$ groups are covalently grafted to the cavity of $P_8W_{48}$ $\nu ia$ two $Ru$ – $O(W)$ bonds.	127
66	$Ln_4(H_2O)_{28}K_6Li_7[KCP_8W_{48}O_{184}(H_4W_4O_{12})_2Ln_2(H_2O)_{10}]\cdot 87H_2O$ (Ln = $L_1a^{3+}C_2a^{3+}P_7a^{3+}N_4d^{3+}$ )	$Ln_2(W_4O_{12})_2P_8W_{48}$	The cavity of $\mathbf{P_8W_{48}}$ was worked with boiles. The cavity of $\mathbf{P_8W_{48}}$ contains four lanthanide ions and two $\{\mathbf{W_4O_1}\}$ groups, along with two potassium ions.	128
67 68	$\begin{split} & \text{La}^{3^+}, \text{Ce}^{3^+}, \text{Pr}^{3^+}, \text{Nd}^{3^+}) \\ & \text{K}_{10}\text{Li}_{1.7.5}[\text{K}_{4.5}\text{C}(\text{ClSn})_8\text{P}_8\text{W}_{48}\text{O}_{184}] \cdot 50\text{H}_2\text{O} \\ & \text{K}_8\text{Li}_{1.7}[(\text{CH}_3)_2\text{NH}_2]_7[(\text{C}_6\text{H}_5\text{ASO})_4\text{P}_8\text{W}_{48}\text{O}_{184}] \cdot 130\text{H}_2\text{O}, \\ & \text{K}_{10.5}\text{Li}_{14}[(\text{CH}_3)_2\text{NH}_2]_{3.5}[(\text{H}_3\text{NC}_6\text{H}_4\text{ASO})_4\text{P}_8\text{W}_{48}\text{O}_{184}] \cdot 92\text{H}_2\text{O} \ [\text{R} = \text{C}_6\text{H}_5 \\ & \text{or} \ p \cdot (\text{H}_2\text{N})\text{C}_6\text{H}_4] \end{split}$	$(ClSn)_8P_8W_{48}$ $(RASO)_4P_8W_{48}, R = C_6H_5 \text{ or } p$ - $(H_2N)C_6H_4$	$\{W_4O_{12}\}$ groups, along with two potassium ions. Eight $\operatorname{Sn}^H$ Cl groups are incorporated in the cavity of $P_8W_{48}$ . Four $\{RAsO_3\}$ units are bound covalently to the cavity of $P_8W_{48}$ through As–O(W) bonds.	129 131

 $\big(H_{3}NC_{6}H_{4}AsO\big)_{3}P_{8}W_{48}\big(WO_{2}\big)_{0.4}$ 

 $Al_{16}P_8W_{48}$ 

 $K_{7.2} \text{Li}_{23-x} [(\text{H}_3 \text{NC}_6 \text{H}_4 \text{AsO})_3 \text{P}_8 \text{W}_{48} \text{O}_{184} \text{H}_x \{ \text{WO}_2 (\text{H}_2 \text{O})_2 \}_{0.4} ] \cdot n \text{H}_2 \text{O}$ 

 $K_8Na_3Li_5\{[Na(NO_3)(H_2O)]_4[Al_{16}(OH)_{24}(H_2O)_8(P_8W_{48}O_{184})]\}\cdot 66H_2O$ 

131

This compound has the  $(RAsO)_4P_8W_{48}$  structure, but in

addition 0.4 equivalents of tungsten atoms are incorporated in the cavity, which indicates the presence of a compound mixture. The polyanion contains a cationic  $\left\{Al_{16}(OH)_{24}(H_2O)_8\right\}^{24+}$  hydroxo-cluster inside the cavity of  $P_8W_{48}.$  The 16-alu-

minium-hydroxo unit comprises eight pairs of edge-shared

AlO<sub>6</sub> units connected *via* corners.

Table 1 (Contd.)

**Dalton Transactions** 

Sl. no.	Formula	Abbreviation	Brief description	Ref.
71	$K_{11}Li_9(NH_4)_4[Ga_{16}(OH)_{32}(P_8W_{48}O_{184})]\cdot 112H_2O$	$Ge_{16}P_8W_{48}$	The polyanion contains the cationic nanocluster $\{Ga_{16}(OH)_{32}\}^{16+}$ incorporated in the cavity of the crownshaped $P_8W_{48}$ . The 16-gallium-hydroxo core $\{Ga_{16}(OH)_{32}\}^{16+}$ comprises eight pairs of structurally equivalent, edge-shared $GaO_6$ units interconnected <i>via</i> corners,	132
72	$K_{26} \text{Li}_6 [(\text{SeO})_4 P_8 W_{48} O_{184}] \text{-} 98 \text{H}_2 O$	$\mathrm{Se_4P_8W_{48}}$	and all bridging oxygens are monoprotonated. The crown-shaped $P_8W_{48}$ polyanion has four $[SeO_3]^{2-}$ ions inside the cavity in such a way that each Se atom is located	133
73	$K_{25.7} Li_5 (NH_4)_5 [(HP_8W_{48}O_{184})(NbO(C_2O_4)(H_2O))_{3.3}] \cdot 73H_2O$	$[(NbO(C_2O_4)(H_2O))_{3.3}P_8W_{48}]$	inside the cavity perpendicular to the main plan of $P_8W_{48}$ . The $\{NbO(H_2O)\}^{3+}$ groups in the cavity of $P_8W_{48}$ have two different types of coordination environments.	134
74	$K_{30.8} \text{Li}_{3.5} (\text{NH}_4)_3 [(P_8 W_{48} O_{184}) (\text{NbO} (C_2 O_4) (\text{H}_2 O))_{1.7}] \cdot 74.5 \text{H}_2 O$	$[(NbO(C_2O_4)(H_2O))_{1.7}P_8W_{48}]$	The {NbO(H <sub>2</sub> O)} <sup>3+</sup> groups in the cavity of P <sub>8</sub> W <sub>48</sub> have two different types of coordination environments.	134
75	$K_{21.6} \text{Li}_5 (\text{NH}_4)_8 [(P_8 W_{48} O_{184}) (\text{NbO} (\text{C}_2 O_4)_{1.5} (\text{H}_2 O))_{4.4}] \cdot 66 \text{H}_2 O$	$[(NbO(C_2O_4)_{1.5}(H_2O))_{4.4}P_8W_{48}]$	The {NbO(H <sub>2</sub> O)} <sup>3+</sup> groups in the cavity of P <sub>8</sub> W <sub>48</sub> have two different types of coordination environments.	134
76	$K_{24.4} \text{Li}_5 (\text{NH}_4)_{5.5} [(\text{HP}_8 \text{W}_{48} \text{O}_{184}) (\text{NbO}(\text{C}_2 \text{O}_4) (\text{H}_2 \text{O}))_{3.1}] \cdot 59 \text{H}_2 \text{O}$	$[(NbO(C_2O_4)(H_2O))_{3.1}P_8W_{48}]$	The $\{NbO(H_2O)\}^{3+}$ groups in the cavity of $P_8W_{48}$ have two different types of coordination environments.	134
77	$K_{26.7} \text{Li}_4 (\text{NH}_4)_{5.5} H_{2.6} [(P_8 W_{48} O_{184}) (\text{NbO} (C_2 O_4)_{2.5} (H_2 O))_{3.8}] \cdot 55.5 H_2 O$	$[(NbO(C_2O_4)_{2.5}(H_2O))_{3.8}P_8W_{48}]$	The $\{NbO(H_2O)\}^{3+}$ groups in the cavity of $P_8W_{48}$ have two different types of coordination environments.	134
78	$K_{11.3} \text{Li}_{8.1} \text{Na}_{22} [(\text{UO}_2)_{7.2} (\text{HCOOH})_{7.8} (P_8 W_{48} \text{O}_{184}) \text{Cl}_8] \cdot 89 \text{H}_2 \text{O} \\$	$[(UO_2)_{7.2}(HCOO)_{7.2}P_8W_{48}]$	The 7.2 uranyl groups are disordered over eight positions,	135
79	$K_{18} \text{Li}_{22} [(\text{UO}_2)_8 (\text{O}_2)_8 (\text{P}_8 \text{W}_{48} \text{O}_{184})] \cdot 133 \text{H}_2 \text{O}$	(UO <sub>2</sub> ) <sub>4</sub> (O <sub>2</sub> ) <sub>4</sub> P <sub>8</sub> W <sub>48</sub>	suggesting a mixture of compounds.  The polyanion contains four peroxo groups connected to two uranium ions. The connectivity of each peroxo-group is similar to the previously reported polyanion (Li	136
80	$K_{3} Li_{8} Mn_{2} [ (P_{8} W_{48} O_{184}) (W_{4} O_{16}) K_{10} Li_{4} Mn_{10} Na (H_{2} O)_{50} Cl_{2} ] -62 H_{2} O$	$Mn_{10}W_4P_8W_{48}$	$\begin{array}{l} (UO_2)_4(O_2)_4(PO_3OH)_2P_6W_{36}). \\ \text{The cavity of $P_8W_{48}$ contains six $Mn^{2^+}$ ions and a tetratung-state unit $\{W_4O_{16}\}^{8^-}$, and four additional, external $Mn^{2^+}$ ions acting as linkers of the polyanions resulting in an } \end{array}$	137
81	$K_7 \text{Li}_2 \text{Na}_{27} [\alpha \gamma \alpha \gamma \text{-P}_8 W_{48} O_{184} \{\text{Cu}(\text{H}_2 \text{O})\}_2] \text{-}78 \text{H}_2 \text{O}$	$(Cu_2$ -αγαγ- $P_8W_{48})$	extended network.  The molar ratio of Cu <sup>2+</sup> and P <sub>8</sub> W <sub>48</sub> , temperature, and reaction time were crucial for obtaining this compound.	141
82	$K_{7.5}Na_{17}Cu_{2.425}(WO_2)_{1.325}[\gamma\gamma\gamma\gamma \cdot P_8W_{48}O_{184}\{Cu(H_2O)_{0.5}\}_4]\cdot 102H_2O$	$\left(\text{Cu}_4\text{-}\gamma\gamma\gamma\gamma\text{-P}_8\text{W}_{48}\right)$	The molar ratio of Cu <sup>2+</sup> and P <sub>8</sub> W <sub>48</sub> , temperature, and reac-	141
83	$\text{K}_7\text{Li}_2\text{Na}_{19.5}\text{Cu}_{1.75}(\text{WO}_2)\![\alpha\gamma\gamma\gamma\text{-P}_8\text{W}_{48}\text{O}_{184}\{\text{Cu}(\text{H}_2\text{O})\}_3]\cdot 72\text{H}_2\text{O}$	$(Cu_3$ - $\alpha\gamma\gamma\gamma$ - $P_8W_{48})$	tion time were crucial for obtaining this compound. The molar ratio of $\text{Cu}^{2+}$ and $P_8W_{48}$ , temperature, and reac-	141
84	$\begin{split} &[(n\text{-}\mathrm{C}_4\mathrm{H}_9)_4\mathrm{N}]_{14}\mathrm{H}_2[\{\mathrm{M}_2(\mathrm{OH}_2)_2\}_2\{\mathrm{M}\\ &(\mathrm{OH}_2)_2\}_4\mathrm{P}_8\mathrm{W}_{48}\mathrm{O}_{176}(\mathrm{OCH}_3)_8]\cdot n\mathrm{H}_2\mathrm{O}\cdot m\mathrm{CH}_3\mathrm{CN} \end{split}$	$\mathbf{M_8P_8W_{48}O_{176}}$ ( $\mathbf{M^{II}}$ = Mn, Co, Ni, Cu, Zn)	tion time were crucial for obtaining this compound. Reaction of divalent 3d metal ions with $\alpha$ - $P_2W_{12}$ resulted in a partial transformation to the $\gamma$ - $P_2W_{12}$ isomer, yielding a new type of $\alpha_1 \gamma_1 \alpha_2 \gamma$ -type $P_8W_{48}$ ring, and the incorporation	142
85	$\begin{array}{l} \text{Li}_{18}K_{9,5}Ag_{21}[H_{16}P_{10}W_{66}O_{251}]_{0.5}[H_{14}P_{9}W_{63}O_{235}]0.5Cl_{2}\cdot 50H_{2}O \text{ and} \\ \text{Li}_{8}K_{13}Ag_{13}[H_{12}P_{8}W_{51}O_{196}]\cdot 50H_{2}O \text{ and} \\ \text{Li}_{10}K_{12}Ag_{4}[H_{14}P_{8}W_{48}O_{184}]\cdot 170H_{2}O \end{array}$	$\begin{aligned} &Ag_{21}P_9W_{63}O_{235}, Ag_{13}P_8W_{51}O_{196}, \\ &Ag_4P_8W_{48}O_{148} \end{aligned}$	of eight metal ions M <sup>11</sup> .  Heating <b>P8W48</b> in the presence of Ag <sup>+</sup> ions at a high concentration (1:30). Ag <sub>13</sub> P <sub>8</sub> W <sub>51</sub> O <sub>196</sub> forms in a similar procedure with a lower concentration of silver ions (1:12) and at a lower temperature. The Ag <sub>4</sub> P <sub>8</sub> W <sub>48</sub> O <sub>148</sub> formed at even	147
86	$\begin{array}{l} (C_{24}PH_{20})_{17}H_{37}[Mn_{18}P_8W_{48}O_{214}]\cdot 16H_2O\cdot 4CH_3CN \ and \\ (C_{16}H_{36}N)_{12}H_{16}[Mn_{20}P_8W_{48}O_{216}]\cdot 4C_2H_3N\cdot C_2Cl_2H_4 \end{array}$	$\begin{aligned} &Mn_{18}P_{8}W_{48}O_{214},\\ &Mn_{20}P_{8}W_{48}O_{216} \end{aligned}$	lower concentration of silver ions at room temperature. The $\mathbf{Mn_{18}P_8W_{48}O_{214}}$ polyanion contains 18 Mn ions of oxidation state +2 or +3 in the cavity of $\mathbf{P_8W_{48}}$ and the four $\mathbf{P_2W_{12}}$ units were transformed from $\alpha$ - to $\gamma$ -isomer in the course of the reaction. In the $\mathbf{Mn_{20}P_8W_{48}O_{216}}$ ion, the 20 Mn ions have an oxidation state either +3 or +4 and are allowed at the inpact rips of $\mathbf{P_8W_{48}O_{216}}$	143
87	$\begin{split} & [(n\text{-}C_4H_9)_4N]_{11}H_{13}[Cu_4(H_2O)_4P_8W_{48}O_{176}(OCH_3)_8]\text{-}28H_2O\text{-}3CH_3NO_2,\\ & \text{and } [(n\text{-}C_4H_9)_4N]_{14}H_2,\\ & [Cu_8(H_2O)_{12}P_8W_{48}O_{176}(OCH_3)_8]\text{-}24H_2O\text{-}CH_3CN, \text{ and } [(n\text{-}C_4H_9)_4N]_{14}H_2[Cu_{12}(H_2O)_{16}P_8W_{48}O_{184}]\text{-}4H_2O, \text{ and } [(n\text{-}C_4H_9)_4N]_{16}H_8[Cu_{16}(OH)_{16}(H_2O)_4P_8W_{48}O_{184}]\text{-}12H_2O\text{-}C_3H_6O \end{split}$	$Cu_{4}P_{8}W_{48}, Cu_{8}P_{8}W_{48}, \\ Cu_{12}P_{8}W_{48}, Cu_{16}P_{8}W_{48}$	aligned at the inner rim of $P_8W_{48}$ . In $Cu_1P_8W_{48}$ and $Cu_8P_8W_{48}$ the two middle $P_2W_{12}$ units to which the copper( $\pi$ ) ions are connected, had transformed from from $\alpha$ - to $\gamma$ -isomer with a 60° rotation of the PO <sub>4</sub> hetero groups. In $Cu_{12}P_8W_{48}$ and $Cu_16P_8W_{48}$ the same $\gamma,\gamma,\gamma,\gamma$ -type $P_8W_{48}$ framework is present, but the copper coordination geometry differs from each other.	144
88	$\big[ \big[ (n\text{-}\mathrm{C}_4\mathrm{H}_9)_4\mathrm{N} \big]_{17} \mathrm{H} \big[ \mathrm{Ag}_{30} \big( \mathrm{P}_8\mathrm{W}_{48}\mathrm{O}_{184} \big) \big] \cdot 10\mathrm{DMF} \cdot 30\mathrm{H}_2\mathrm{O}$	$Ag_{30}P_8W_{48}$	This nanocluster material has exposed silver surfaces and interfaces with metal oxides, and it is highly stable despite the exposed silver surfaces, acting as a catalytically active sites for the selective reduction of organic substrates using	145
89	$\left(Bu_{4}N\right)_{16}H_{8}[Au_{8}Ag_{26}(P_{8}W_{48}O_{184})]$	$Au_8Ag_{26}P_8W_{48}$	$H_2$ under mild reaction conditions. The polyanion comprises $\{Au_6\}$ as well as $\{Ag_6Au\}$ clusters embedded in the control $E_0W$	148
90	$\begin{array}{l} (Me_2NH_2)_{13}K_7Na_2Li_{10}[\{As_3^{II}O_4(OH)_3\}_2(P_8W_{48}O_{184})]\cdot 32H_2O,\\ K_2_0Li_{12}[[Sb^{III}OH)_4(P_8W_{48}O_{184})]\cdot 52H_2O,\ and\\ (Me_2NH_2)_8K_6Na_5Li_5[[Sb^{III}OH)_8(P_8W_{48}O_{184})]\cdot 65H_2O \end{array}$	$\begin{aligned} &As_{10}P_8W_{48},Sb_4P_8W_{48},\\ &Sb_8P_8W_{48} \end{aligned}$	embedded in the cavity of $P_8W_{48}$ . Ten $As^{III}$ ions or four/eight $Sb^{III}$ ions are grafted in the cavity of $P_8W_{48}$ .	149
91		$\mathrm{Fe_8Ce_4P_8W_{48}}$	The polyanion comprises an $iron(iii)$ -cerium(iii)-phosphato moiety $\{Fe_8^{III}Ce_4^{III}O_2(OH)_{12}(H_2O)_8(PO_4)_2\}$ in the cavity of $P_8W_{48}$ .	150

selective catalytic activity towards reducing nitrobenzene and aromatic aldehydes under mild conditions. Very recently, Suzuki and coworkers have reported the mixed-metal silvergold derivative of  $P_8W_{48}$ , wherein a  $\left[Au_8Ag_{26}\right]$  cluster is

embedded within the  $P_8W_{48}$  core,  $(Bu_4N)_{16}H_8$   $[Au_8Ag_{26}(P_8W_{48}O_{184})]$   $(Au_8Ag_{26}P_8W_{48})^{.148}$  In the silver–gold cluster, six out of eight Au atoms form an octahedral  $\{Au_6\}$  assembly, while in another one Au atom replaces the Ag site at

the center of a hexagonal  $\{Ag_7\}$ , forming the  $\{Ag_6Au\}$  assembly. The 26 Ag atoms were thus observed to surround Au atoms to form the nano-cluster Au<sub>8</sub>Ag<sub>26</sub>P<sub>8</sub>W<sub>48</sub>.

Recently, Yang and coworkers were able to incorporate As III O3 and Sb III O3 in the cavity of P8W48, resulting in  $\left[ \{ As_5^{III}O_4(OH)_3 \}_2 (P_8W_{48}O_{184}) \right]^{32-} \qquad (\textbf{As_{10}P_8W_{48}}),$ [(Sb<sup>III</sup>OH)<sub>4</sub>  $(P_8W_{48}O_{184})^{32-}$   $(Sb_4P_8W_{48})$ , and  $[(Sb^{III}OH)_8(P_8W_{48}O_{184})]^{24-}$ (Sb<sub>8</sub>P<sub>8</sub>W<sub>48</sub>). 149 Very recently, the same group has reported the  $[Fe_8^{III}Ce_4^{III}O_2(OH)_{12}]$ 3d-4f iron(III)-cerium(III) derivative  $(H_2O)_8(PO_4)_2\{(P_8W_{48}O_{184})\}^{26-}$  (Fe<sub>8</sub>Ce<sub>4</sub>P<sub>8</sub>W<sub>48</sub>), comprising an  $\{Fe_8^{III}Ce_4^{III}O_2(OH)_{12}$ iron(III)-cerium(III)-phosphato moiety  $(H_2O)_8(PO_4)_2$  encapsulated in the  $P_8W_{48}$  cavity, resulting in a polyanion with idealized  $D_{2h}$  symmetry and it exhibited high sensitivity and specificity to detect ascorbic acid (Table 1).150 In Table 1, the structural characteristics and component building blocks of the compounds presented in this review are summarized.

## Summary and outlook

Over the years, many tungstophosphates have been synthesized and structurally characterized. This review focuses on the structural family  $P_2W_{12}$ ,  $P_4W_{24}$ , and  $P_8W_{48}$  and their interaction with metal ions during the last 20 years emphasizing synthetic and structural aspects. We have discussed the formation and stability of these polyanions in different reaction conditions, including pH, temperature, solvent, concentration, counterions, and ionic strength. Although P2W12, P4W24, and P<sub>8</sub>W<sub>48</sub> all contain the P<sub>2</sub>W<sub>12</sub> unit as a key building block, their stability and reactivity with metal ions is vastly different, and hence, unique products are observed. While the monomeric P2W12 is the least stable amongst the three in solution, the cyclic P<sub>8</sub>W<sub>48</sub> (comprising four P<sub>8</sub>W<sub>48</sub> units) is the most stable.

The reactivity, particularly the large, crown-shaped P<sub>8</sub>W<sub>48</sub> with transition metal ions, has been systematically developed only since 2005. All three derivatives, P8W48, P4W24, and  $P_2W_{12}$ , are multilacunary, containing six or more vacant sites, which in principle can accommodate multiple transition metal ions. The literature in this area has expanded dramatically in the last two decades, reflecting the synthesis and property studies of a wide variety of compounds.

Subsequently, we discussed the versatile nature of these three polyanions, and their chemistry with an emphasis on their reactivity towards d and f-block metal ions, including mixed d/f derivatives, leading to discrete monomeric, dimeric, trimeric, and tetrameric structures, or extended solid state frameworks. Furthermore, gaining extra tungsten atoms in situ (arising from trace decomposition of the parent polyanion) provides additional degrees of structural flexibility. Other interesting features of P<sub>2</sub>W<sub>12</sub>, P<sub>4</sub>W<sub>24</sub>, and P<sub>8</sub>W<sub>48</sub> are the multifunctional ways to accommodate high nuclearity transition metal oxo/hydroxo/aqua clusters according to their needs. Several novel and unexpected compounds have been isolated depending on the reaction conditions (e.g., type of transition metal, reaction temperature, solution pH, solvent, ionic

strength, ratio and concentration of reagents, and countercations), which are all important parameters in synthetic POM chemistry. Several compounds have shown attractive properties in homogeneous and heterogeneous catalysis, as well as in magnetic studies. Researchers are still searching for new materials based on P2W12, P4W24, and P8W48, which are yet to be explored and examined and can benefit their associated properties and potential applications.

## Data availability

This is a review paper and hence no new data is presented.

Only scientific publications that can be accessed via the usual academic routes have been cited.

## Conflicts of interest

The authors declare no competing conflicts of interest.

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