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New trimeric polyoxotungstate aggregates based on $[P_2W_{12}O_{48}]^{14-}$ building blocks†

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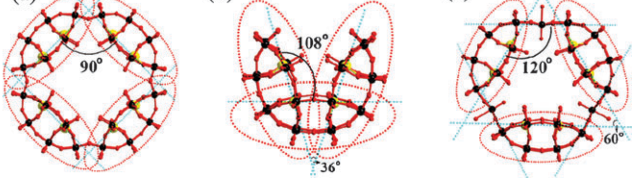
The first $\{P_2W_{12}\}$-based trimeric polyoxotungstates encapsulating various "guest" transition-metal and alkali-metal ions have been reported, exhibiting potentially aqua-ligand-induced capability of "trapping" metal ions.

The building block approach to nanoscale polynuclear transition-metal aggregates is currently a major focus of research in the area of nanosized materials, as is their potential application in catalysis, photochemistry, magnetism and electrochemistry.[1] Polyoxometalates (POMs), as a typical class of metal–oxo clusters with O-enriched surfaces, represent one of the excellent inorganic polydentate ligands to coordinate with transition-metal or rare-earth metal ions, leading to compounds with diverse nuclearities and structural features combined with interesting catalytic, electrochemical and magnetic properties.[2–4] In this field, highly lacunary POMs might be the best candidates to incorporate more metal centers into giant inorganic aggregates. A typical example is $[P_2W_{12}O_{48}]^{14-}$ (abbreviated as $\{P_2W_{12}\}$), a hexavacant derivative of the Dawson anion (Scheme S1, ESI†).[5] The polyoxoanion $\{P_2W_{12}\}$ is easily assembled into crown-type $\{P_8W_{48}\}$,[5] which exhibits strong reactivity on its inner surface with various electrophilic metal ions and provides an effective "reactor" for the assembly of high-nuclear metal aggregates.[6] The groups of Müller, Kortz, Mialane and Pope have reported a series of novel species: $\{V_{12}\}$ aggregate,[6a] $\{Cu_{20}\}$ cluster,[6b] $\{Cu_{20}\text{-azide}\}$ cluster[6c] and Ln-containing anions based on the crown $\{P_8W_{48}\}$ tetramer.[6d] Further, the organoruthenium groups have also been "grafted" on the crown $\{P_8W_{48}\}$ unit.[6e] All the above examples suggest that the basic building blocks $\{P_2W_{12}\}$ possess high activity to combine metal ions. This fact has also been confirmed by Gouzerh, Pope and others with $\{Fe_8\}$,[7a] $\{Fe_9\}$,[7b] $\{Fe_{27}\}$[7b] and $\{Ce_4\}$[7c] aggregates based on $\{P_2W_{12}\}$ units. Thus, the design and synthesis of new $\{P_2W_{12}\}$-based polyoxoanions should present a promising route for assembling new polynuclear metal aggregates with desirable functionalities and developing new structural models for the research of host–guest chemistry. However, only tetrameric $\{P_8W_{48}\}$[5,6] and dimeric $\{P_4W_{24}\}$[8] clusters based on $\{P_2W_{12}\}$ subunits have hitherto been reported. In these aggregates, the angles between two adjacent $\{P_2W_{12}\}$ units are 90 and 36°, respectively (see Scheme 1). If such angles in new $\{P_2W_{12}\}$-based POMs are different from 36 or 90°, the tension induced by the unreasonable W–O–W linkers must be overcome or avoided so as to realize the assembly. Therefore, the synthesis of new $\{P_2W_{12}\}$-based aggregates with various linking angles between the subunits is still a great challenge. Herein, we report a series of unprecedented $\{P_2W_{12}\}$-based trimeric polyoxoanions encapsulating various transition-metal ions and alkali-metal ions, $K_4Na_{15}[K_3\subset\{Mn(H_2O)_4\}_2\{WO_2(H_2O)_2\}_2\{WO(H_2O)\}_3(P_2W_{12}O_{48})_3]\cdot xH_2O$ ($x \approx 77$) (**1**, $K_4Na_{15}[\mathbf{1a}]\cdot xH_2O$), $K_3Na_7Li_{5.5}Ni_{0.25}[Na_3\subset\{Ni_{3.5}(H_2O)_{13}\}\{WO_2(H_2O)_2\}_2\{WO(H_2O)\}_3(P_2W_{12}O_{48})_3]\cdot xH_2O$ ($x \approx 64$) (**2**, $K_3Na_7Li_{5.5}Ni_{0.25}[\mathbf{2a}]\cdot xH_2O$) and $K_6Na_{11}[Na_3\subset\{Cu_3(H_2O)_9\}\{WO_2(H_2O)_2\}_2\{WO(H_2O)\}_3(P_2W_{12}O_{48})_3]\cdot xH_2O$ ($x \approx 47$) (**3**, $K_6Na_{11}[\mathbf{3a}]\cdot xH_2O$).

Compounds **1–3** were isolated from acidic aqueous solutions of freshly prepared $K_{12}[H_2P_2W_{12}O_{48}]\cdot 24H_2O$, $Na_2WO_4\cdot 2H_2O$ and transition-metal salts ($MnCl_2$ for **1**, $NiCl_2$ for **2** and $CuCl_2$ for **3**). Compounds **1–3** crystallize in the triclinic space group $P\bar{1}$. Single-crystal X-ray diffraction analyses confirm that all three compounds contain a trimeric crown-type cluster $[P_6W_{39}O_{147}(H_2O)_3]^{30-}$ (abbreviated as $\{P_6W_{39}\}$) (Fig. 1), representing the first $\{P_2W_{12}\}$-based trimeric aggregate in the POM chemistry (Fig. 1(a)). This $\{P_6W_{39}\}$ unit consists of three $\{P_2W_{12}\}$ subunits linked by three $\{WO(H_2O)\}$ fragments in a corner-sharing mode (Scheme S1b, ESI†). As shown in Fig. 1, the external diameter of this crown is *ca.* 19.4 Å and the thickness is about 10.0 Å. This aggregate contains a pumpkin-like inner cavity with shortest and longest diameters of *ca.* 8.3 Å and *ca.* 10.5 Å, respectively. It is worth mentioning that the angles between two $\{P_2W_{12}\}$ subunits are about 60° in this crown-type $\{P_6W_{39}\}$, however, the potential tensions



Scheme 1 Schematic view of $\{P_2W_{12}\}$-based crown- and half-crown-type POMs. (a) Tetrameric $\{P_8W_{48}\}$ displaying an angle of 90° between two adjacent $\{P_2W_{12}\}$ units. (b) Dimeric $\{P_4W_{24}\}$ displaying an angle of 36° between two $\{P_2W_{12}\}$ units; it also contains three structurally recognizable $\{P_2W_{12}\}$ units with angles of 108° between them. (c) Trimeric $\{P_3W_{39}\}$ displaying an angle of 60° between two $\{P_2W_{12}\}$ units and 120° between $\{P_2W_{12}\}$ and $\{WO(H_2O)\}$ linkers.

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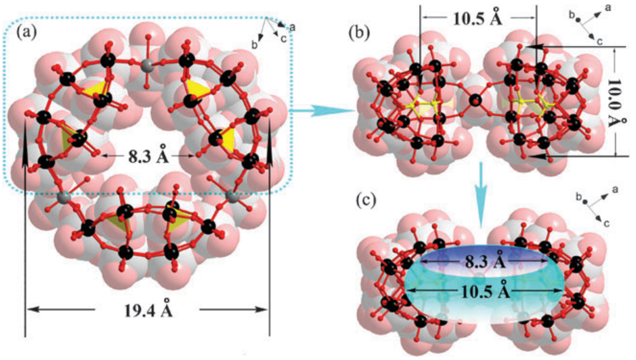

Fig. 1 Structure of the crown-type shell in polyoxoanion **1a–3a**. (a) View of the external and inner diameter of the crown; (b) view of the thickness of the crown; (c) schematic view of the inner cavity shape and size of the crown.

among $\{P_2W_{12}\}$ subunits are avoided by three $\{WO(H_2O)\}$ linkers (Scheme 1).‡§

In compound **1**, the crown $\{P_6W_{39}\}$ "host" combines two W^{VI} and two Mn^{II} "guests" (Fig. 2(b)) on its four vacant sites of the shell. The remaining two vacant sites are occupied by two potassium cations (Fig. S1 and S2, ESI†). Two guest W^{VI} centers are hexa-coordinated with four O atoms and two terminal water molecules. The bond lengths of W–O are in the range of 1.72(3)–2.37(2) Å and the bond angles of O–W–O 75.6(11)–172.4(1)°. The two Mn^{II} centers also exhibit the six-coordination environment with two O atoms and four water molecule ligands. Further, three potassium cations are encapsulated into the inner cavity of $\{P_6W_{39}\}$ (Fig. 2b and S3, ESI†). K1 and K2 sites are in a nine-coordination environment and K5 is octa-coordinated with eight O atoms on the inner surface of $\{P_6W_{39}\}$. In the packing arrangement, all the planes of these anions are parallel with each other, which are further connected by potassium and sodium cations into a three-dimensional (3-D) framework (Fig. S4, ESI†). Around 77 lattice water molecules reside in the interspaces of the crystal structure and are coordinated with alkali-metal cations or H-bonded to the surface O atoms of the **1a**.

In compound **2**, the six vacant sites on the $\{P_6W_{39}\}$ shell are occupied by two W^{VI} and four Ni^{II} guest ions, as shown in Fig. 2(c). However, all these metal centers except Ni5 position possess site-occupancy disorder (Fig. S5, ESI†), resulting actually in two W^{VI} and 3.5 Ni^{II} guest ions in the structure. Further, three sodium cations are enclosed into the inner cavity of the $\{P_6W_{39}\}$ unit (Fig. 2c and S6, ESI†). The Na1 position is disordered into two parts and both parts are coordinated by seven O atoms from the $\{P_6W_{39}\}$ unit and two aqua ligands on the Ni^{II} centers (Fig. S6a and S6b, ESI†). Na2 and Na3 sites exhibit the similar coordination geometry and are surrounded by seven inner surface O atoms of the $\{P_6W_{39}\}$ unit, two aqua ligands on the Ni^{II} centers and a lattice water molecule (Fig. S6c and S6d, ESI†). It is noteworthy that such two metal-encapsulated POMs are connected together *via* two equivalent Ni–O–W bridges with $d_{Ni–O}$ = 2.336(17) Å and $d_{W–O}$ = 1.7997(11) Å, leading to a giant dimeric cluster (Fig. S7, ESI†). In addition, such a dimeric cluster occupies one unit cell. In the packing arrangement, these dimeric clusters are arranged in the same direction and connected by the counter cations into a 3-D framework (Fig. S8, ESI†). About 64 lattice water molecules are located in the interspaces of the crystal structure.

In compound **3**, the six vacant sites on the $\{P_6W_{39}\}$ unit were all occupied by two W^{VI} and four Cu^{II} guest ions, as shown in Fig. 2(d). However, all these metal centers except the W40 site have site-occupancy disorder (Fig. S9, ESI†), resulting in actually two W^{VI} and 2.75 Cu^{II} guest ions in the structure. Noticeably, there is an extra Cu6 ion capping the top of the crown POMs and connecting with Cu2, Cu4 and W40 centers *via* the Cu–O_{aqua}–Cu and Cu–O–W bridges, resulting in a half-sealed POM capsule. Further, three sodium cations are sealed in the inner cavity of the half-sealed capsule. In the unit cell, two adjacent POMs are linked together by four Cu–O–W bridges into a giant dimeric cluster with $d_{Cu6–O133}$ = 2.05(3) Å, $d_{Cu4–O39}$ = 2.376(18) Å and $d_{W22–O133}$ = 1.73(2) Å, $d_{W15–O39}$ = 1.795(9) Å (Fig. S11, ESI†). In the packing arrangement, these dimeric clusters are arranged in the same mode and connected by the counter cations into a 3-D framework (see Fig. S12, ESI†). About 47 lattice water molecules exist in the interspaces of the crystal structure.

Based on the structural analyses of **1a–3a**, it is found that the $\{P_6W_{39}\}$ shell possesses the potentially adjustable capability of combining "guest" transition-metal ions, which is closely related to the positions of aqua ligands on three $\{WO(H_2O)\}$ linkers. When the aqua ligand sticks out of the shell, for example the O3W in **1a** (Fig. 2(b)), both vacant sites near the $\{WO(H_2O)\}$ linker are occupied by "guest" transition-metal ions (Mn^{2+}). Nevertheless, if the water ligand points into the shell (such as O1W and O2W in **1a**), only one vacant site near $\{WO(H_2O)\}$ linkers is occupied by "guest" transition-metal ion (W^{6+}). This intriguing structural feature is also observed in polyoxoanions **2a** and **3a** (Fig. 2). Since the bond length of W–O_{aqua} (*ca.* 2.25 Å) is longer than that of W=O (*ca.* 1.75 Å) on the $\{WO(H_2O)\}$ linkers, these sterically hindered aqua ligands seem to influence the combination between "guest" transition-metal ions and the vacant site on the "host" crown shell. To our knowledge, such an aqua-ligand-induced capability of "trapping" guest metal ions is

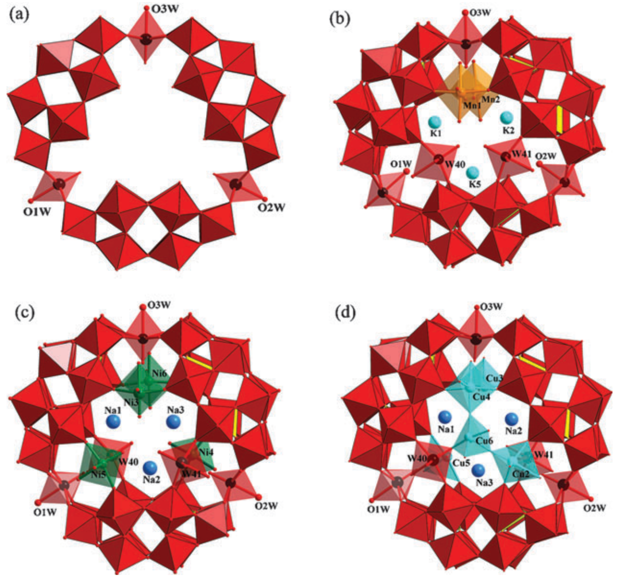

Fig. 2 Polyhedral representation of (a) $\{P_6W_{39}\}$ unit and its aqua-ligand-induced capability of combining metal ions, exemplified by the structures of (b) **1a**, (c) **2a**, (d) **3a**.

observed for the first time in the POM chemistry. Furthermore, the relatively open polyoxoanion **1a** has a large inner cavity, in which three potassium cations are encapsulated whereas the relatively close anions **2a** and **3a** can only contain three sodium ions in their inner cavity.

The electrochemical behaviors of compounds **1–3** and their electrocatalytic properties for nitrate were studied (Fig. S16–S19, ESI†). The cyclic voltammetric behavior for **1** in pH 4 (0.4 M $CH_3COONa–CH_3COOH$) buffer solution exhibits four reduction peaks in the potential range of +1.3 to −1.2 V and the mean peak potentials are 0.634, −0.029, −0.767 and −0.997 V (*vs.* Ag/AgCl), respectively (Fig. S16a, ESI†). The first two reduction waves located at 0.634 and −0.029 V and one single oxidation process (0.919 V) are attributed to the redox processes of the Mn^{II} centers.[9] The peaks at −0.767 and −0.997 V are ascribed to the reduction process of W^{VI} centers.[10] Compound **1** displays electrocatalytic activity to reduce nitrate (Fig. S16b, ESI†). On addition of modest amounts of nitrate, the two reduction peak currents of W increased while the corresponding oxidation peak currents dramatically decreased, suggesting that nitrate was reduced by the two reduced POM species. In comparison, no reduction of nitrate took place on the GC electrode in the absence of **1**.

In conclusion, three unprecedented $\{P_2W_{12}\}$-based trimeric crown POMs encapsulating various transition-metal ions and alkali-metal ions have been successfully synthesized, representing a new family of nanoscale inorganic POMs. The synthesis of these crown POMs may offer an interesting model for the preparation of new high-nuclear metal clusters with desirable electronic, optical and magnetic functionalities. This research is currently going on in our group.

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Notes and references

‡ *Synthesis* of **1**: Freshly prepared $K_{12}[H_2P_2W_{12}O_{48}]\cdot 24H_2O$ (1.5 g, 0.38 mmol) was dissolved in 50 mL of a pH 4.0 (0.4 M $CH_3COONa–CH_3COOH$) buffer solution. Then, 8 mL of 1 M $MnCl_2$ aqueous solution (8 mmol) and 0.125 g of $Na_2WO_4\cdot 2H_2O$ (0.38 mmol) were added with vigorous stirring and further stirred for 6 h. The resulting solution was filtered and the filtrate kept at room temperature for slow evaporation. Yellow block crystals of **1** were isolated after three weeks (yield 41% based on P). Anal. Found (%): K, 1.97; Na, 2.91; Mn, 0.76; P, 1.25; W, 59.9. Calc.: K, 2.19; Na, 2.75; Mn, 0.88; P, 1.48; W, 60.2. IR (KBr pellet): $\tilde{\nu}$ = 1143(m), 1089(m), 1021(w), 990(w), 929(s), 792(s), 688(s) and 463(w) cm^{-1}; **2**: Freshly prepared $K_{12}[H_2P_2W_{12}O_{48}]\cdot 24H_2O$ (1.5 g, 0.38 mmol) was dissolved in 75 mL of distilled water. Then 8 mL of 1 M $NiCl_2$ aqueous solution (8 mmol) and 0.125 g of $Na_2WO_4\cdot 2H_2O$ (0.38 mmol) were added with vigorous stirring and the pH value of the mixture was carefully adjusted to 2.50 with 4 M HCl solution. After 12 h stirring, the solution was filtered. Then, 0.5 mL of 1 M LiCl solution was added. The filtrate was kept at room temperature for slow evaporation. Green block crystals of **2** were isolated after two weeks (yield 33% based on P). Anal. Found (%): K, 0.87; Na, 2.01; Li, 0.32; Ni, 1.88; P, 1.33; W, 61.1. Calc.: K, 0.96; Na, 1.88; Li, 0.31; Ni, 1.80; P, 1.52; W, 61.5. IR (KBr pellet): $\tilde{\nu}$ = 1144(m), 1083(m), 1021(w), 990(w), 922(s), 868(s), 714(s), 688(s) and 464(w) cm^{-1}; **3**: The preparation of **3** is quite similar to that of **2**, except that no LiCl solution was used during the synthesis. Blue block crystals of **3** were isolated after two weeks (yield 45% based on P). Anal. Found (%): K, 1.75; Na, 2.81; Cu, 1.65; P, 1.37; W, 62.3. Calc.: K, 1.96; Na, 2.68; Cu, 1.59; P, 1.55; W, 62.7. IR (KBr pellet): $\tilde{\nu}$ = 1144(m), 1085(m), 1022(w), 992(w), 931(s), 869(s), 708(s) and 464(w) cm^{-1}.

§ *Crystal data* for **1**: $H_{184}K_7Mn_2Na_{15}O_{243}P_6W_{41}$, M = 12 525.57, triclinic, space group $P\bar{1}$, a = 19.481(4), b = 22.414(5), c = 29.869(6) Å, α = 70.31(3), β = 72.36(3), γ = 71.26(3)°, V = 11 348(4) $Å^3$, Z = 2, $F(000)$ = 11 200, D_c = 3.666 g cm^{-3}, R_1 (wR_2) = 0.0697 (0.1592) and S = 0.982 for 39 733 reflections with $I > 2\sigma(I)$; **2**: $H_{168}K_3Li_{5.5}Na_{10}Ni_{3.75}O_{235}P_6W_{41}$, M = 12 258.55, triclinic, space group $P\bar{1}$, a = 19.187(4), b = 20.947(4), c = 28.482(6) Å, α = 75.34(3), β = 79.86(3), γ = 73.54(3)°, V = 10 553(4) $Å^3$, Z = 2, $F(000)$ = 10 921, D_c = 3.858 g cm^{-3}, R_1 (wR_2) = 0.0759 (0.1630) and S = 0.999 for 35 547 reflections with $I > 2\sigma(I)$; **3**: $H_{126}Cu_3K_6Na_{14}O_{214}P_6W_{41}$, M = 12 021.76, triclinic, space group $P\bar{1}$, a = 19.186(4), b = 21.040(4), c = 26.248(5) Å, α = 76.76(3), β = 82.43(3), γ = 73.42(3)°, V = 9860(3) $Å^3$, Z = 2, $F(000)$ = 10 634, D_c = 4.049 g cm^{-3}, R_1 (wR_2) = 0.0778 (0.1714) and S = 1.034 for 32 034 reflections with $I > 2\sigma(I)$. CCDC 669274–669276. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718374g

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