A novel type of heteropolyoxoanion precursors $\{[Ca(H_2O)]_6[P_4M_6O_{34}]_2\}^{12-}$ ($M = W^{VI}, Mo^{VI}$) constructed by two $[P_4M_6O_{34}]^{12-}$ subunits *via* a rare hexa-calcium cluster†

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A novel type of heteropolyoxoanion (HPOA) precursors $\{[Ca(H_2O)]_6[P_4M_6O_{34}]_2\}^{12-}$ [$M = W^{VI}$ (1), Mo^{VI} (2)] has been synthesized and structurally characterized, which represents the rare membership of the HPOA family constituted by two early-transition-metal clusters ($[P_4M_6O_{34}]^{12-}$) and a main-group metal cluster of high nuclearity ($[Ca_6]^{12+}$).

The continuous search and synthesis of novel polyoxometalates (POMs) with unique structures and properties are dominantly driven by their fascinating structural and compositional diversities and manifold potential applications in catalysis, medicine, biology, and material science.[1] Under this context, many novel transition-metal/lanthanide/organometal substituted POMs bearing benign properties have been successfully isolated by different synthetic approaches.[2] Furthermore, the exploration and discovery of novel heteropolyoxoanion (HPOA) precursors are still a longstanding research goal although it remains a great challenge from the viewpoint of rational design for synthetic chemists engaged in POM chemistry hitherto. Recently, some achievements in this respect have been made from persisting efforts. For example, in 1997, Bösing *et al.* reported the synthetic strategies for preparing the trivacant β-Keggin HPOA $[B\text{-}\beta\text{-}SbW_9O_{33}]^{9-}$ and its several large aggregates.[3] In 2001, Kortz *et al.* obtained a large chair-configuration HPOA $[As_6W_{65}O_{217}(H_2O)_7]^{26-}$ built by four inner $[B\text{-}\beta\text{-}AsW_9O_{33}]^{9-}$ and two outer $[B\text{-}\alpha\text{-}AsW_9O_{33}]^{9-}$ fragments by eleven corner-sharing WO_6 octahedra.[4] In 2006, Hervé *et al.* isolated an *S*-shaped HPOA $\alpha\text{-}[\{[K(H_2O)_2](\mu\text{-}H_2O)[Li(H_2O)_2]\}_2Si_4W_{36}O_{126}(H_2O)_4]^{16-}$ by the step-by-step assembly of trivacant tungstosilicates.[5] Kortz's group discovered the divacant decatungstogermanate HPOA $[\gamma\text{-}GeW_{10}O_{36}]^{8-}$.[6] Most of the newly reported HPOAs are often derived from lacunary Keggin HOPA fragments, however, to date, there is no systematic investigation with the aim of searching and exploiting novel HPOA species with structural types different from classical Keggin, Dawson and Anderson types. As we know, the P–W/Mo–O system can form Keggin ($PM_{12}O_{40}$),[7] Dawson ($P_2M_{18}O_{62}$),[7b,8] and Strandberg ($P_2M_5O_{23}$) types,[9] and their lacunary species[8,10] under appropriate conditions. Their common feature is that the P/M atomic ratio is very small. Therefore, we believe that the phosphotungstate HPOA species with the larger P/M atomic ratio should also exist if reaction conditions are appropriate. Since 2007, we concentrated on the systematic study and exploration of the P–W/Mo–O system based on the simple materials of $Na_2WO_4\cdot 2H_2O/Na_2MoO_4\cdot 2H_2O$, $Na_2HPO_4\cdot 12H_2O$ and H_2O in the presence of $CaCl_2$. As expected, a novel type of HPOA precursor $\{[Ca(H_2O)]_6[P_4M_6O_{34}]_2\}^{12-}$ [$M = W^{VI}$ (**1**), Mo^{VI} (**2**)] constructed by two $[P_4M_6O_{34}]^{12-}$ subunits *via* a rare hexa-calcium cluster was finally discovered (Fig. 1,S1†). To our knowledge, they represent the uncommon HPOA precursors built up from two early transition-metal clusters ($[P_4M_6O_{34}]^{12-}$) and a main-group metal cluster of high nuclearity ($[Ca_6]^{12+}$).

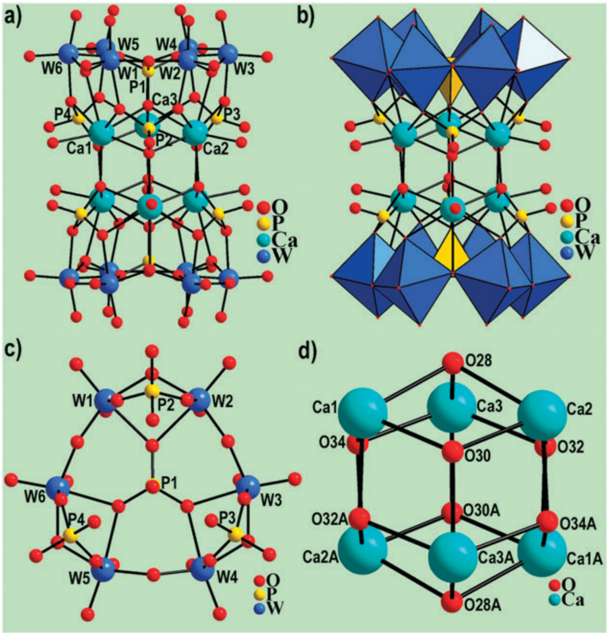

Fig. 1 (a) Ball-and-stick representation of **1** with selected labelling scheme. (b) Combined polyhedral/ball-and-stick representation of **1**. (c) The unique $[P_4W_6O_{34}]^{12-}$ subunit with selected labelling scheme in **1**. (d) The hexa-calcium octahedral cluster sandwiched by two unique $[P_4W_6O_{34}]^{12-}$ subunits. Atoms with "A" in their labels are symmetrically generated (A: $1 - x, -y, 1 - z$).

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† Electronic supplementary information (ESI) available: Discussion on the influences of the pH value on the stability of **1** and **2** in the aqueous solution, electrochemical properties and related figures. CCDC 713573 & 713574 for **1** and **2**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b822368h

The ammonium-sodium salts $(NH_4)_{10}Na_2\{[Ca(H_2O)]_6[P_4W_6O_{34}]_2\}\cdot 14H_2O$ (**1a**) and $(NH_4)_4Na_8\{[Ca(H_2O)]_6[P_4Mo_6O_{34}]_2\}\cdot 36\ H_2O$ (**2a**) of **1** and **2** were easily prepared by a mixture of $Na_2WO_4\cdot 2H_2O/Na_2MoO_4\cdot 2H_2O$, $Na_2HPO_4\cdot 12H_2O$, $CaCl_2$ and NH_4Cl in the acidic aqueous medium at ambient temperature.‡ X-ray single-crystal structural analyses indicate that **1** and **2** contain an unusual HPOA $\{[Ca(H_2O)]_6[P_4M_6O_{34}]_2\}^{12-}$ although both crystallize in two different crystal systems and space groups (monoclinic, $P2_1/n$ for **1**, triclinic, $P\bar{1}$ for **2**) resulting from the influence of the distribution of the charge compensation cations and lattice water molecules.§ Typically, only the crystal structure of **1** is discussed in detail here. **1** consists of a centrosymmetrical dimer $\{[Ca(H_2O)]_6[P_4W_6O_{34}]_2\}^{12-}$ (Fig. 1a, 1b). A crystallographically imposed C_2 axis passes through the inversion center (1/2, 0, 1/2). The centrosymmetrical dimeric moiety $\{[Ca(H_2O)]_6[P_4W_6O_{34}]_2\}^{12-}$ is established by two subunits $[P_4W_6O_{34}]^{12-}$ (Fig. 1c) linked by a rare hexa-calcium octahedral cluster $[Ca_6]^{12+}$ (Fig. 1d,S2†) *via* eighteen μ_3-O and two μ_4-O atoms from two $[P_4W_6O_{34}]^{12-}$ subunits and it can also be viewed as a novel sandwich structural type where a hexa-calcium cluster $[Ca_6]^{12+}$ is sandwiched by two subunits $[P_4W_6O_{34}]^{12-}$, which is evidently different from the classical sandwich type constituted by two trivacant Keggin/Dawson fragments and a transition-metal cluster.[11] Notably, the most interesting feature in **1** is that the subunit $[P_4W_6O_{34}]^{12-}$ is for the first time discovered, which is completely different from those reported HPOAs $[(H_3O)_2NaMo_6P_4O_{24}(OH)_7]^{2-}$,[12a] $[RPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (R = OH, CH_3, C_2H_5, H),[12b] $[CH_3AsMo_6O_{21}(H_2O)_6]^{2-}$,[12c] and $[Se^{IV}S_3{}^{VI}Mo_6O_{33}]^{8-}$.[12d] In the subunit $[P_4W_6O_{34}]^{12-}$, six nearly coplanar corner- and edge-sharing WO_6 octahedra [W–O: 1.709(5)–2.350(4) Å] are interconnected together by a central PO_4 tetrahedron [P–O: 1.513(4)–1.554(5) Å] through three μ_3-O atoms forming a six-numbered W_6 ring fashion with a P center, and then three outward PO_4 tetrahedra [P–O: 1.499(5)–1.562(5) Å] graft to three groups of edge-sharing W_2O_{10} dimers *via* six μ_3-O atoms respectively, furthermore, three PO_4 tetrahedra are all situated on the same side of a six-numbered W_6 ring plane (Fig. 1c). It should be noted that the corner- and edge-sharing M_6 ring fashion in **1** and **2** is very analogous to the Mo_6 ring in $[Se^{IV}S_3{}^{VI}\ Mo_6O_{33}]^{8-}$ reported by Robl and Haake.[12d] In the hexa-calcium cluster $[Ca_6]^{12+}$, each Ca^{2+} ion adopts an eight-coordinate hexagonal bipyramid geometry with Ca–O distances of 2.359(4)–2.848(5) Å, and six Ca^{2+} ions are arranged in a distorted octahedral geometry with neighboring Ca–Ca distances of 3.898(3)–4.073(3) Å and connected by eight μ_4-O atoms from eight PO_4 tetrahedra (Fig. 1d). To our knowledge, no such hexa-nuclear alkaline-earth metal cluster is reported albeit a similar hexa-nuclear rare-earth metal cluster has been observed in a POM-supported hydroxo/oxo cluster $[\{Yb_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_6(H_2O)_6\}(\alpha\text{-}P_2W_{15}O_{56})_2]^{14-}$.[13] In addition, if six grafting PO_4 tetrahedra can be viewed as the components of the hexa-calcium cluster $[Ca_6]^{12+}$, the resulting calcium phosphate cluster $\{Ca_6(H_2O)_6P_6O_{26}\}$ is also reported first by us (Fig. S2†).

Most intriguingly, each HPOA $\{[Ca(H_2O)]_6[P_4M_6O_{34}]_2\}^{12-}$ has twenty-four terminal oxygen atoms on twelve MO_6 octahedra and six terminal oxygen atoms on six outward PO_4 tetrahedra, which provides a precondition that the $\{[Ca(H_2O)]_6[P_4M_6O_{34}]_2\}^{12-}$ HPOA can function as an inorganic polydentate functional ligand in molecular and crystal engineering. Thus, the synthetic and structural chemistry of **1** and **2** guarantees that both probably have potential applications in three promising fields: (a) the easily accessible synthetic approach and the presence of rich and highly active surface oxygen atoms decide that the HPOA $\{[Ca(H_2O)]_6[P_4M_6O_{34}]_2\}^{12-}$ will be able to act as a very useful reaction material in the rationally designed synthesis of a large number of POM-based transition-metal/lanthanide/organometal derivatives; (b) according to the coordination features of Ca^{2+} ions, the hexa-calcium cluster should be substituted by lanthanide clusters generating novel magnetic and fluorescent materials; (c) as we know, the Ca^{2+} ion is an indispensable element in organisms, therefore, the occurrence of the $[Ca_6]^{12+}$ cluster in **1** and **2** will result in extensive exploration in biological and bioinorganic fields. The related work is under intensive progress in our laboratory.

^{31}P NMR spectra of **1a** and **2a** exhibit two peaks at 2.55, 0.93 ppm and 3.45, 0.32 ppm with their approximate intensity ratio of 3:1, respectively (The peak at 0 ppm is the signal of ^{31}P in the external 85% H_3PO_4) (Fig. 2), proving that the $\{[Ca(H_2O)]_6\ [P_4M_6O_{34}]_2\}^{12-}$ HPOA is still retained in aqueous solution. Furthermore, the ^{183}W NMR spectrum of **1a** displays the expected one peak at −166.7 ppm, being fully consistent with the structure of **1a**, which further proves the retainability of $\{[Ca(H_2O)]_6[P_4W_6O_{34}]_2\}^{12-}$ HPOA in aqueous solution (Fig. 3). In order to investigate the aging of the solution of **1a** and **2a**, the *in situ* UV spectroscopic measurements were performed in the aqueous system (Fig. S3,S4†). The systematic results reveal that the aqueous solution of **1** (5×10^{-5} mol L^{-1}) can stably exist about eight days at ambient temperature while the aqueous solution of **2**

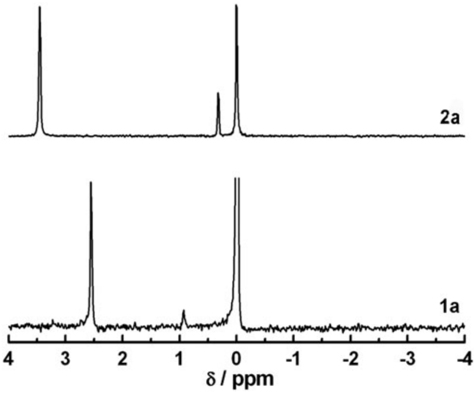

Fig. 2 ^{31}P NMR spectra of **1a** and **2a** in aqueous solution (20% D_2O). Chemical shifts are given with respect to the external 85% H_3PO_4 for ^{31}P.

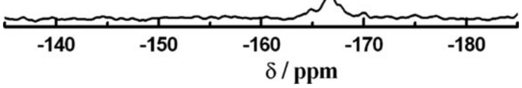

Fig. 3 ^{183}W NMR spectrum of **1a** recorded on a CH-100 NMR system with Na_2WO_4 saturated in D_2O as the external standard at room temperature.

can be stable for about six days. It is well known that the HPOAs are commonly sensitive to the pH value of the studied media. The influences of the pH value on the stability of **1** and **2** in aqueous solution have also been elaborately probed by means of UV spectra (Fig. S5–7†) and cyclic voltammetric measurements (Fig. S13–16†). Scrutinizing the variable processes adjusted using HCl or NaOH solution allows us to ascertain that **1** and **2** are stable in the pH ranges 4.5–9.0 and 4.8–9.3, respectively (Details are given in the ESI†). Moreover, the slow evolution of cyclic voltammetries of **1** and **2** at different pH conditions can also give a complementary proof of the stability in the larger pH ranges for **1** and **2**, which is in good agreement with the results of *in situ* UV spectra. In addition, Fig. S17 and S18† show the cyclic voltammetric behaviors of **1** and **2** in 0.5 M Na_2SO_4 aqueous solution, respectively, and the not well-defined redox waves, which are ascribed to the redox processes of the W^{VI} and Mo^{VI} atoms in $\{[Ca(H_2O)]_6[P_4M_6O_{34}]_2\}^{12-}$ anions, can be clearly observed. In addition, below 230 mV s^{-1}, the peak currents are proportional to the scan rates, indicating that the redox processes of **1** and **2** are surface-controlled (Fig. S19–S20†).[14]

In summary, a novel type of HPOA precursors $\{[Ca(H_2O)]_6[P_4M_6O_{34}]_2\}^{12-}$ [M = W^{VI} (**1**), Mo^{VI} (**2**)] has been synthesized and structurally characterized. As far as we know, both represent the rare membership of the HPOA family constituted by two early-transition-metal clusters ($\{[P_4M_6O_{34}]_2\}^{12-}$) and a main-group metal cluster of high nuclearity ($[Ca_6]^{12+}$). Examination of UV spectra and cyclic voltammograms indicate that both **1** and **2** can stably exist in the larger pH ranges in aqueous solution. Notably, **1** and **2** are promising available reaction precursors in the preparation chemistry of POM-based materials with novel magnetic or fluorescent properties. Moreover, their biological activity will be evaluated. The systematic insight into this area is under intensive investigation in our laboratory. We believe that some interesting results will be obtained in due time.

Notes and references

‡ Syntheses of **1a** and **2a**. **1a**: $Na_2WO_4{\cdot}2H_2O$ (10.00 g, 30.32 mmol), $Na_2HPO_4{\cdot}12H_2O$ (5.37 g, 14.99 mmol) and $CaCl_2$ (1.66 g, 14.96 mmol) were dissolved in water (100 mL) under stirring. After dissolution, the pH value was adjusted to 6.50 by adding 0.1 M HCl dropwise. The solution was kept at 80–90 °C for 0.5 h and then filtered. Finally, NH_4Cl (1.4 g, 26.17 mmol) was added and the solution was left to evaporate slowly at ambient temperature. After several days, colorless crystals of **1a** suitable for X-ray crystallography were obtained (Yield: *ca* 33% based on $Na_2WO_4{\cdot}2H_2O$). Elemental analysis (%) calcd for $(NH_4)_{10}Na_2\{[Ca(H_2O)]_6[P_4W_6O_{34}]_2\}{\cdot}14H_2O$: N 3.21, H 1.85, Na 1.05, Ca 5.50, P 5.67, W 50.49; found: N 3.01, H 2.03, Na 0.94, Ca 5.43, P 5.71, W 50.44. IR (KBr pellet): 3432(s), 3193(s), 1631(m), 1401(m), 1131(m), 1023(s), 941(s), 883(s), 702(s), 546(m), 447(w) cm^{-1} (Fig. S21†).

2a: $Na_2MoO_4{\cdot}2H_2O$ (6.73 g, 27.82 mmol), $Na_2HPO_4{\cdot}12H_2O$ (10.64 g, 29.71 mmol) and $CaCl_2$ (3.03 g, 27.30 mmol) were dissolved in water (70 mL) under stirring. After dissolution, the pH value was adjusted to 5.50 by adding 0.1 M HCl dropwise. The solution was kept at 80–90 °C for 0.5 h and then filtered. Finally, NH_4Cl (1.8 g, 33.65 mmol) was added and the solution was left to evaporate slowly at ambient temperature. After several days, colorless crystals of **2a** suitable for X-ray crystallography were obtained (Yield: *ca* 38% based on $Na_2MoO_4{\cdot}2H_2O$). Elemental analysis (%) calcd for $(NH_4)_4Na_8\{[Ca(H_2O)]_6[P_4Mo_6O_{34}]_2\}{\cdot}36H_2O$: N 1.50, H 2.69, Na 4.91, Ca 6.43, P 6.63, W 30.78; found: N 1.46, H 2.77, Na 4.82, Ca 6.39, P 6.68, W 30.83. IR (KBr pellet): 3456(s), 3226(s), 1639(m), 1401(m), 1131(m), 1113(s), 1047(s), 924(s), 891(s), 547(m), 439(w) cm^{-1} (Fig. S21†).

§ Crystal data for **1a** and **2a**: Crystal data: For **1a**, $H_{80}Ca_6N_{10}Na_2O_{88}P_8W_{12}$, M_r = 4369.16, monoclinic, space group $P2_1/n$, a = 13.773(7), b = 21.669(12), c = 16.636(9) Å, β = 106.860(6)°, V = 4752(4) $Å^3$, Z = 2, μ = 15.050 mm^{-1}, $F(000)$ = 4008, GOF = 1.032. Of 33957 total reflections collected, 8349 were unique (R_{int} = 0.0440). $R_1(wR_2)$ = 0.0330(0.0846) for 614 parameters and 6814 reflections [$I > 2\sigma(I)$]. For **2a**, $H_{100}Ca_6Mo_{12}N_4Na_8\,O_{110}P_8$, M_r = 3740.28, triclinic, space group $P\bar{1}$, a = 13.427(2), b = 13.814(2), c = 16.790(2) Å, α = 76.641(2), β = 66.753(2), γ = 62.278(2)°, V = 2528.7(6) $Å^3$, Z = 1, μ = 2.043 mm^{-1}, $F(000)$ = 1840, GOF = 1.081. Of 12938 total reflections collected, 8831 were unique (R_{int} = 0.0155). $R_1(wR_2)$ = 0.0321(0.0891) for 667 parameters and 7979 reflections [$I > 2\sigma(I)$]. Intensity data were collected at 296(2) K on a Bruker Smart APEXII CCD diffractometer for **1a** and **2a** using graphite monochromated Mo Kα radiation (λ = 0.71073 Å), respectively. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program. Direct methods were used to solve the structure and refined by full-matrix least-squares on F^2 using the SHELXTL-97 program package. All non-hydrogen atoms were refined anisotropically.

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