Heteropolyoxometalates (HPOMs) and lacunar HPOMs are the most explored subset of polyoxometalates (POMs) which contain heteroanion templates.[1–4] Lacunar HPOMs are particularly important since they can be used as building blocks to construct much larger structures of nanoscale dimensions. Most of the previous reports on lacunar HPOMs are based upon “conventional” heteroanion templates (e.g. SiO$_4^{4-}$, PO$_4^{3-}$, SO$_3^{2-}$, AsO$_3^{3-}$) which are redox-inactive. However HPOMs with anion templates that have the possibility of themselves being redox active have been far less explored.[3] During the past few years we have been targeting HPOMs with redox active heteroanions (e.g. SO$_3^{2-}$) in an effort to engineer clusters with intrinsically more diverse structures and redox active properties.[5–8] However a general building block strategy based upon lacunar HPOMs with non-conventional anions has not been developed.

Herein we report a strategy of constructing a “layered” molecular assembly in constructing a new family of Te$^{IV}$-containing HPOM building blocks which consist of a [W$_6$] top unit and one, two, and three layers of [TeW$_6$] base units in [Te$_2$W$_{15}$O$_{54}$]$^{10-}$, [Te$_2$W$_{15}$O$_{75}$]$^{12-}$, and [Te$_3$W$_{21}$O$_{75}$]$^{12-}$, respectively. Further, the principal axis of the TeO$_3$- unit and one, two, and three layers of {TeW$_6$} base units in [Te$_2$W$_{15}$O$_{54}$]$^{10-}$, [Te$_2$W$_{15}$O$_{75}$]$^{12-}$, and [Te$_3$W$_{21}$O$_{75}$]$^{12-}$, respectively.

In this work, the self-assembly of the three lacunary HPOM building blocks mentioned above yielded three polyanion types: [Pd$_3$(Te$_2$W$_9$O$_{33}$)$_2$]$^{5-}$ (1a) in the form of Na$_2$K$_8$[Pd$_3$(Te$_2$W$_9$O$_{33}$)$_2$]:51H$_2$O (1); [(WO$_4$)$_2$(Te$_2$W$_{15}$O$_{54}$)$_2$]$^{12-}$ in the two isomeric forms 2a and 2a’ which can be formulated as (C$_5$H$_8$N)$_2$Na$_8$[(WO$_4$)$_2$(Te$_2$W$_{15}$O$_{54}$)$_2$]:57H$_2$O (2) and (C$_5$H$_8$N)$_2$Na$_8$[(WO$_4$)$_2$(Te$_2$W$_{15}$O$_{54}$)$_2$]:77H$_2$O (2’); [Te$_2$W$_{15}$O$_{75}$]$^{12-}$ (3a) in the form of (C$_5$H$_8$N)$_2$Na$_8$[Te$_2$W$_{15}$O$_{75}$]:25H$_2$O (3). In addition to the structural studies, these clusters have also been explored using electrospray ionization mass spectrometry and cyclic voltammetry confirming stability and revealing interesting electronic properties.

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Compound 1 was synthesized by a simple one-pot reaction of Na$_3$WO$_4$, Te$_2$O$_3$, Pd(NO$_3$)$_2$·H$_2$O in a weakly acidic aqueous solution at 95°C. The X-ray crystal structure analysis of 1 reveals three square-coordinated Pd$^{II}$ ions are sandwiched between two B$_2$-[Te$_2$W$_{15}$O$_{54}$] subunits (Figure 2). The average Pd$^{II}$–O bond lengths are 1.999(19) Å which is in agreement with the literature.[9] Compound 1 together with those previously reported examples[10–12] confirmed the one-layered building block [Te$_2$W$_{15}$O$_{54}$]$^{10-}$ could be easily obtained in the presence of transition metal ions. To find new “pure” Te-containing HPOM building blocks, we then conducted similar one-pot reaction of only Na$_3$WO$_4$·2H$_2$O, Na$_2$TeO$_3$, and H$_2$O with a pH value of 4.6 in the presence of dimethylammonium (DMA) at room temperature, from which the high nuclearity [Te$_3$W$_{21}$O$_{75}$]$^{12-}$ compound 2 was isolated. X-ray crystal structure analysis of 2 reveals a topologically $D_{12h}$-symmetric [(WO$_4$)$_2$(Te$_2$W$_{15}$O$_{54}$)$_2$]$^{32-}$ cluster anion 2a (Figure 3 left). From Figure 3 (left) it can be seen that the cluster anion 2a,
[Te₆W₃O₂₄]₁²⁻, is tetrameric and consists of four [Te₂W₁₅O₅₄] subunits linked by four [WO₆] ([W₆] ) groups, giving the anion a cyclic structure. Each [W₆] linker joins two [Te₂W₁₅O₅₄] subunits by sharing two cis-oxygen atoms while each [Te₂W₁₅O₅₄] subunit consists of a [W₆] top and two layers of [TeW₆O₂₁] pieces that are composed of a [W₆] planar ring templated by a pyramidal [TeO₃] group. The two [TeW₆O₂₁] layers in each [TeW₆O₂₁] subunit of compound 2 are connected together by corner-sharing oxygen ligands. It is very interesting to note that the [TeO₃] template in the first layer has the same orientation to that in the second layer and the oxo ligands in both templates are eclipsed, which distinguishes these [Te₂W₁₅O₅₄] subunits from all other traditional lacunary HPOM building blocks, for example, [P,W₁₅] etc. derived from the Dawson parents. Further, since it is well known that nature of the charge balancing cations can have a profound effect on the self-assembly of POMs-based architectures, we explored the use of larger Cs⁺ and Na⁺ and crystalized water molecules while the latter is filled by disordered Cs⁺ and Na⁺ cations (Figure S2). Therefore it can be suggested that the planar middle cavity of 2 is deformed to reduce the steric hindrance which results in its structural re-arrangement, giving transformation from planar 2a to a saddle-shaped 2a′ (Figure 3). Building on the cation-controlled structures of 2 and 2′, we also attempted to utilize smaller Li⁺ cations in this reaction system which resulted in the formation of compound 3 containing the anion [Te₃W₂₃O₇₄]₁²⁻ (3a; Figure 4). However, it should be pointed out during our experimental exploration we found that Li⁺ is not essential to form compound 3 and we were able to devise a synthetic route that did not require Li⁺. Compared with the two-layered [Te₂W₁₅O₅₄] subunit contained in clusters 2a and 2a′, anion 3a has a three-layered structure with one more layer [TeW₆O₂₁] added to [Te₂W₁₅O₅₄] (Figure 4). The [TeO₃] templates in each layer of 3a oriented toward the same direction and all oxo ligands are eclipsed, the same as that in anion 2a and 2a′.

ESI-MS was utilized to explore the solution behavior of these compounds. The mass spectra of compound 1 in a mixture of deionized water and acetonitrile (5%; 95%) shows that the whole cluster [Pd₃(TeW₉O₃₃)] is present and all the main peaks can be assigned to its different charge/cation states (Figure S3 and Table S1). Further, the mass spectra of compounds 2 and 2′ are very similar: for each peak with the same charge, the m/z value of compound 2 is 58–70 mass units bigger than that of 2′ (Figure 5). Considering that both clusters 2 and 2′ have the same gross structure, the key difference lies with different species and numbers of cations, and crystalized water molecules. Both 2 and 2′ are observed as

![Figure 3. Structural representation of the anions (Te₆W₃O₂₄)₁²⁻ = ([WO₆]([Te₆W₃O₂₄])₁²⁻) found as isomeric 2a (left) and 2a′ (right).](image)

![Figure 4. Side view (left) and bottom view (right) of [Te₆W₃O₂₄]₁²⁻. Light purple octahedron: [WO₆]; green spheres: Te; light purple spheres: O.](image)

![Figure 5. Negative-ion mode ESI of compound 2 (dark gray) and 2′ (light gray) in mixed H₂O/MeCN solvent (5%;95%). All the peaks shown in each spectrum relate to different states of the same basic parent cluster [Te₆W₃O₂₄]₁²⁻, which are observed as either a monomer or a dimer in the gas phase.](image)
an assembly of related clusters with differing numbers of cations and water molecules existing either as a [Teₜ,W₆O₂₄] monomer or as a [Teₜ,W₄O₂₅] dimer; for example, the monomer can be assigned as [H₉₋₆(CH₃)₄N⁺][Na₄₋₅(NH₄)⁺(H₂O)₇₋₆](Teₜ,W₄O₂₅)⁺ and the dimer as [H₅₋₄(CH₃)₂N⁺][Na₂₋₃(NH₄)⁺(H₂O)₄₋₃](Teₜ,W₄O₂₅)₂⁺. Similarly, the monomer of 2a can be assigned as [H₉₋₆(CH₃)₄N⁺][Na₄₋₅(Ca₄Na₄)(H₂O)₃₋₄](Teₜ,W₄O₂₅)⁺ and the dimer as [H₅₋₄(CH₃)₂N⁺][Na₂₋₃(NH₄)⁺(H₂O)₃₋₄](Teₜ,W₄O₂₅)₂⁺ (see Tables S2 and S3).

It should be noted from the mass spectrum of anion 2a' that the number of the inorganic cations (one Cs⁺ and two Na⁺) occupying the middle cavity of 2a are double in all the dimer peaks compared to that in all the monomer peaks (Table S3), indicating that these inorganic cations are mainly responsible for the structural difference between polyanion 2a and 2a'. The assignments of polyanion 2a and 2a' were made possible due to their high charge, with assignments made via charge deconvolution. The ESI study of compound 3 in H₂O/MeCN solvent (5:95%) showed that the expected [Te₂,W₁₂O₄₈]₄⁺ cluster anion is present and all the main peaks can be assigned to different charge/cation states associated with the molecular species. The negative mode mass spectrum of compound 3 shows that there are four main peaks. Also all the peaks can be assigned as a three-layered dimer [Te₂,W₁₂O₄₈]₂⁺ (Table S4). This is a good indication that compound 3 can retain its structural integrity in solution, and shows the possibility that it might be an excellent precursor for functionalization.

It is well known that many HPOMs are highly redox-active, thus cyclic voltammetry experiments were performed to examine the redox properties of compounds 2, 2', and 3 in 0.1 M NaH₂PO₄/Na₂HPO₄ buffer solution, and these compounds display a range of different behaviors (Figures 6, S5 and S6). Between +0.257 to −0.700 V (vs. Ag/AgCl) all the compounds show waves associated with the reduction of tungstate centres. For compound 1, only one quasi-reversible couple is observed with \( E_{1/2} \) value located at −0.178 V because of the redox process of PdV⁺ ions (Figure S5). The oxidation peak at +0.810 V and the reduction peak at +0.200 V are related, which can be assigned to the redox process between PdV⁺ and PdV⁺⁺ couple.3 Surprisingly, all the other spectra of the multi-layered clusters contain an oxidation peak at +0.500 V which can be assigned as the oxidation of TeIV+, and it does not shift by varying scan rates. However, the redox processes of tungstate showed many differences between compound 2 and 3 (Figures S7 and S11). Although in both cases, four quasi-reversible couples can be observed, the first wave is significantly positively shifted in compound 2 (\( E_{1/2} = +0.137 \) V in 2 vs. +0.104 V in 3), while the other three peaks shifted towards the opposite direction (Figure 6). Furthermore, the topological isomers 2 and 2' showed different redox behaviors with only two quasi-reversible waves appeared under the similar condition for compound 2', in which the first wave negatively moved around 220 mV (\( E_{1/2} = −0.085 \) V).

In summary, we have discovered a new family of “layered” tungstatotellurite compounds showing unique layered structures built from a series of untraditional TeIV-containing POM building blocks, i.e., [Teₜ,W₉O₃₃]₈⁻, [Teₜ,W₉O₃₅]₆⁻, and [Teₜ,W₉O₃₅]₄⁻. The possibility to access “layered” clusters opens the door to more extended systems (e.g. for layers beyond 3 as depicted in Figure 1) and also the linking of the units allows the generation of nanostructured clusters whose gross conformation is cation controlled as demonstrated by compounds 2 and 3 [Te₁₆,W₁₆O₇₆]. In future work we will investigate the dynamic cation-mediated conformational switching of the nanoscale [Teₜ,W₉O₃₅]₈⁻ cluster, as well as exploring the development of photo- and electro-chemical properties of these and related clusters that exploit the incorporation of the Te heteroatom.

**Experimental Section**

Synthesis of 1: Na₅W₉O₃₄·2H₂O (1.00 g, 3.03 mmol) was dissolved in boiling water (40 mL), and a solution of TeO₂ (0.10 g, 0.63 mmol) in 2.5M KOH solution (2 mL) was added dropwise to the tungstate solution. The pH of this mixture was adjusted to 7.0 by addition of 70% nitric acid, and the mixture was heated at 95°C for 25 min. Pd(NO₃)₂·H₂O (0.08 g, 0.43 mmol) was added to the solution, during which the pH was kept around 5.4 by adding 2.5M KOH. The solution was kept at 95°C under stirring for more than 30 min, cooled, filtered and left to evaporate slowly. Dark red-brown block crystals of 1 appeared after two weeks. Yield: 0.17 g (16% based on W). IR (KBr disk): \( \nu = 3449, 1623, 954, 793, 743 \) cm⁻¹. Elemental analysis calculated for C₂₃,Na₂,K₄,W₉O₃₅·Pd·Te·W₉O₃₅ (%): C 5.03, Pd 5.13, W 53.2; found: C 5.12, Pd 5.17, W 53.0.

Synthesis of 2: Na₅W₉O₃₄·2H₂O (1.70 g, 5.15 mmol), Na₅TeO₅ (0.13 g, 0.58 mmol) and dimethylaminochloride (0.7 g, 8.58 mmol) were dissolved in water (30 mL). The pH was first adjusted to 6.0 by addition of 50% acetic acid and then further to 4.6 by 37% HCl. Then the solution was filtered and left to evaporate slowly. Colorless block crystals of 2 appeared after three weeks. Yield: 0.26 g (17% based on W). IR (KBr disk): \( \nu = 3408, 3147, 2784, 2558, 1623, 1464, 1019, 966, 788, 713 \) cm⁻¹. Elemental analysis calculated for C₈₉,H₈₀N₁₅O₁₅Te₉W₉O₃₅ (%): C 2.46, H 1.44, N 1.43, Na 1.61, W 63.35; found: C 2.83, H 1.21, N 1.47, Na 1.68, W 63.3.

Synthesis of 2: The procedure is exactly the same as that for preparing 2 but before filtration for crystallization, CsCl (0.22 g, 1.31 mmol) was added in and then the solution was filtered and left to

**Figure 6.** Cyclic voltammograms of compounds 1, 2, 2', and 3 in 0.1 M NaH₂PO₄/Na₂HPO₄ buffer solution. The scan rate was 100 mVs⁻¹, the working electrode was glassy carbon (3 mm), and the reference electrode was Ag/AgCl.
evaporate slowly. Colorless block crystals of 2′ appeared within one week. Yield: 0.32 g (22%). IR (KBr disk): ν = 3423, 3147, 2785, 2538, 1631, 1464, 1019, 962, 789, 714 cm⁻¹. Elementary analysis, calculated for C_{138}H_{266}N_{19}Na_{13}O_{281}Te_{8}W_{64}, M W = 18571.91 gmol⁻¹; colorless needle-shaped crystal: 0.35 × 0.06 × 0.02 mm³. Tetragonal, space group P4_{2}2_{1}2₁, a = 16.9647(7), c = 13.8221(10) Å, V = 3978.0(4) Å³, Z = 2, ρ = 4.591 g cm⁻³, λ(MoKα) = 0.71073 mm⁻¹, 16060 reflections measured, 37874 unique (R_{int} = 0.0634) which were used in all calculations. Final R₁ = 0.0450 and wR₂ = 0.0792 (all data). Crystal data and structure refinements for 2: C_{16}H_{114}N_{8}Na_{4}O_{100}Te_{3}W_{21}, M W = 19152.04 gmol⁻¹; colorless block crystal: 0.31 × 0.08 × 0.05 mm³. Monoclinic, space group C2/c, a = 3.51788(6), b = 38.8304(4), c = 30.7129(6) Å, β = 123.352(3), V = 35044.5(10) Å³, Z = 4, ρ = 3.572 g cm⁻³, λ(MoKα) = 0.71073 mm⁻¹, 226131 reflections measured, 60631 unique (R_{int} = 0.0579) which were used in all calculations. Final R₁ = 0.0515 and wR₂ = 0.1345 (all data). Crystal data and structure refinements for 3: C_{38}H_{266}N_{19}Na_{13}O_{281}Te_{8}W_{64}, M W = 3654.47 gmol⁻¹; colorless block crystal: 0.21 × 0.04 × 0.03 mm³. Monoclinic, space group C2/c, a = 16.9647(7), b = 15.0229(2), c = 54.3205(16) Å, β = 95.0512(1), V = 67162.3(2) Å³, Z = 8, ρ = 3.957 g cm⁻³, λ(MoKα) = 0.71073 mm⁻¹, 15483 reflections measured, 37874 unique (R_{int} = 0.0573) which were used in all calculations. Final R₁ = 0.0647 and wR₂ = 0.1780 (all data).

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- cluster compounds
- cyclic voltammetry
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