Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Formation, Self-assembly and Transformation of a Transient Selenotungstate Building Block into Clusters, Chains and Macrocycles

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Materials and Physical Measurements

All reagents were purchased commercially from *Sigma Aldrich* or *Alfa Aesar* and used without further purification. HPLC grade solvents were purchased from *Fisher Scientific* and used as received.

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Single Crystal X-Ray Diffraction was performed on an *Oxford Diffraction Gemini A Ultra* diffractometer equipped with an *ATLAS* CCD detector ($\lambda(\mathrm{Mo}_{K\alpha}) = 0.71073$ Å). Single crystals of **1-5** were mounted in oil on a glass capillary prior to dataset collection. All measurements were performed at 150(2) K. Absorption effects were corrected for *via* an analytical method using a multifaceted crystal model[1] and data reduction was performed using the *CrysAlisPro* software package.

All structures were solved by direct methods and structural refinement was carried out using SHELX-97 by means of a full matrix least squares on F^2 method,[2] performed within the WinGX software suite.[3] Selected details of the data collection and structural refinement of compounds **1-5** can be found within Tables S1 and S2 and full details are available in the corresponding CIF files. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC 975306-975310) and may be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

Note that in most instances, the major components of each cluster anion were well defined with full occupancy in all non-hydrogen atoms. In rare cases, W atoms were found to be disordered over two positions and were modelled and refined within a given occupancy. Solvent and metal complex cation molecules in solvent areas were refined initially with flexible occupancies which were then later fixed to partial values in the final stage of the refinements. These treatments are reasonable for such large structures, in which solvent areas are highly disordered. Furthermore, due to the weakness of crystal diffraction intensities for these large structures and instrument restrictions, ideal absorption corrections could not be applied to these heavy-metal based moieties. Some unit occupancy sites of light atoms were therefore only refined isotropically, otherwise they were found to be 'non-positive defined'.

Elemental Analysis for metal content was performed *via* ICP-OES with thanks to the Zentralabteilung für Chemische Analysen, Forschungszentrum Jülich and Prof. Paul Kögerler (*RWTH Aachen University*). **Microanalysis** to determine carbon and nitrogen content was performed by the microanalysis service within the School of Chemistry, University of Glasgow on an *EA 1110 CHN CE-440* elemental analyser.

Thermogravimetric Analysis (TGA) was performed on a *TA Instruments Q500* thermogravimetric analyser at a heating rate of 10 $^{\circ}$C min^{-1} in a platinum pan. All measurements were conducted under a constant stream of nitrogen.

Fourier Transform Infrared Spectroscopy (FT-IR) was performed on a *Shimadzu FTIR 8400s* spectrometer fitted with a *golden gate* ATR attachment. Characteristic bands are reported in cm^{-1}, intensities denoted as: s = strong, m = medium, w = weak and b = broad.

Electrospray Ionisation Mass Spectrometry (ESI-MS) was performed on a Waters Synapt-G2 HDMS spectrometer operating in sensitivity mode, equipped with a quadropole and time of flight (Q/ToF) module for MS analysis. All samples were prepared by dissolving in 50:50 H2O:MeCN (HPLC grade) to a concentration of *ca.* 1 x 10^{-5} M and injected directly at a flow rate of 5 µL min^{-1} using a *Harvard* syringe pump. All spectra were collected in negative ion mode and analysed using the *Waters* MassLynx v4.1 software.

For all measurements the following parameters were employed: capillary voltage: 2.2 kV; sample cone voltage: 50 V; extraction cone voltage: 4 V; source temperature: 80 ˚C; desolvation temperature: 140 ˚C; cone gas flow: 15 L h^{-1} (N_2); desolvation gas flow: 750 L h^{-1} (N_2).

Density Functional Theory (DFT) Calculations All quantum chemical calculations were performed at the density functional theory (DFT) level. Accurate single-point energies were then calculated using the B3LYP[4-6] method as implemented by the TURBOMOLE V6.3.1 package.[7,8] For these calculations, the TZVP basis set was used on all atoms. To allow for solvation effects, the conductor-like screening model (COSMO) method was used with the dielectric constant corresponding to water ($\varepsilon_r = 78.5$).[9,10] The ionic radii of the atoms, which define the dimensions of the cavity surrounding the molecule, are chosen to be (in Å) 2.2 for W, 1.7 for O, 2.2 for Se, 1.3 for H and 2.1 for P. A reference to a recent review on *ab initio* calculations on polyoxometalates is provided.[11]

The electronic structure of a fully oxidized polyoxometalate has doubly occupied orbitals (HOMO) formally delocalized over the oxo ligands and perfectly separated from the unoccupied set of d-metal orbitals (LUMO). The new structures presented here share this classic electronic structure though, despite this, further study is needed. For instance, $[P_2W_{12}O_{46}]^{14-}$ is isolated as the di-protonated species $[H_2P_2W_{12}O_{46}]^{12-}$ and, as such, an analysis of the possible protonation sites would be beneficial in a more detailed future study. Our preliminary results are presented here in Figures 4, S4 and Table S4.

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Experimental

Synthesis of $(C_5H_{14}NO_2)_7Na_6[Mn_4Se_6W_{24}O_{94}Cl(H_2O)_6]\cdot37H_2O$ (1): $Na_2WO_4\cdot2H_2O$ (1.20 g, 3.64 mmol), Na_2SeO_3 (0.20 g, 1.16 mmol) and N-Methyldiethanolamine (2.0 ml, 17.42 mmol) were dissolved with stirring in 20 ml H_2O. After the pH of the mixture was adjusted to 4.0 by 37% HCl, $MnCl_2\cdot4H_2O$ (0.15 g, 0.76 mmol) was added. The resulting solution was subsequently stirred for 5 minutes before filtration and the collected filtrate was left for evaporation at room temperature. Orange-yellow needle-shaped crystals of **1** were obtained within one week. Yield: 0.21 g, (17 %, based on tungsten). IR (in cm^{-1}): 3363.9 (b), 1635.7 (w), 1464.0 (m), 1402.3(w), 1070.5 (m), 936.5 (m), 892.1 (w), 832.3 (s), 742.6 (s), 705.9 (s), 641.4 (s). Elemental analysis, *calc.* for $C_{35}H_{184}ClMn_4N_7Na_6O_{151}Se_6W_{24}$: C 5.01, N 1.17, Na 1.64, Mn 2.62, W 52.5 %; Found C 5.32, N 1.25, Na 1.58, Mn 2.51 W 51.9 %. TGA water loss from 20 to 250°C, calculated (found) %: 9.2 (9.2)

Synthesis of {$(NH_4)_{11}Na_4[Mn_3Se_6W_{24}O_{94}Cl(H_2O)_2]\cdot26H_2O$}$_n$ (2): $Na_2WO_4\cdot2H_2O$ (2.00 g, 6.06 mmol), Na_2SeO_3 (0.30 g, 1.73 mmol) and NH_4Cl (1.00 g, 18.70 mmol) were dissolved with stirring in 30 ml H_2O. After the pH of the mixture was adjusted to 4.6 by 37% HCl, $MnSO_4\cdot H_2O$ (0.08 g, 0.47 mmol) was added. The resulting solution was stirred for 5 minutes before filtration and the collected filtrate was left for evaporation at room temperature. Yellow block crystals of **2** were obtained within two weeks. Yield: 0.22 g, (11 %, based on tungsten). IR (in cm^{-1}): 3414.1 (b), 3181.7 (b), 3028.3 (b), 2835.5 (b), 1622.2 (m), 1413.9 (s), 936.5 (m), 837.1 (s), 743.6 (s), 641.4 (s). Elemental analysis, *calc*. for $ClH_{100}Mn_3N_{11}Na_4O_{122}Se_6W_{24}$: N 2.09, Na 1.25, Mn 2.23, W 59.7 %; Found N 2.45, Na 1.24, Mn 1.12, W 59.1 %; TGA water loss from 20 to 200°C, calculated (found) %: 6.8 (6.8).

Synthesis of $(NH_4)_6Na_{18}[Se_6W_{39}O_{141}(H_2O)_3]\cdot60H_2O$ (3): $Na_2WO_4\cdot2H_2O$ (4.0 g, 12.13 mmol), Na_2SeO_3 (0.4 g, 2.31 mmol) and NH_4NO_3 (0.15 g, 1.87 mmol) were dissolved with stirring in 40 ml H_2O. The pH of the solution was then adjusted to 4.0 by 70% HNO_3 and maintained at this value for 5 minutes. The solution was subsequently filtered and the filtrate was collected in a 100 ml conical flask and allowed to stand at 4 °C. Large colourless needle-shaped crystals of **3** were collected after two days. Yield: 0.72 g, (19.7 %, based on tungsten). IR (in cm^{-1}): 3406.4 (b), 3207.7 (b), 3039.0 (b), 1626.1 (m), 1421.6 (m), 938.4 (m), 839.1 (s), 752.3 (s). Elemental analysis, *calc.* for $H_{150}N_6Na_{18}O_{204}Se_6W_{39}$: N 0.73, Na 3.58, W 62.0 %; Found N 0.59, Na 3.43, W 61.2 %. TGA water loss from 20 to 200°C, calculated (found) %: 9.8 (9.2). Note that NH_4NO_3 and HNO_3 may readily be substituted for NH_4Cl and HCl respectively in order to isolate **3**, though the yield of the reaction and crystallinity of the products is generally slightly poorer than the synthesis provided above.

Synthesis of $(NH_4)_{12}Pd_5[PdSe_6W_{39}O_{141}(H_2O)_5]\cdot38H_2O$ (4): $Na_2WO_4\cdot2H_2O$ (3.00 g, 9.10 mmol), Na_2SeO_3 (0.30 g, 1.73 mmol) and NH_4NO_3 (0.50 g, 6.25 mmol) were dissolved with stirring in 40 ml H_2O. The pH of the solution was then adjusted to 4.0 by 70% HNO_3 and maintained at this value for 30 minutes. $Pd(NO_3)_2\cdot H_2O$ (0.08 g, 0.32 mmol) was then added and the resulting solution was then stirred for a further 5 minutes, filtered and allowed to stand at room temperature. Pale yellow block crystals of **4** were obtained within one day. Yield: 0.46 g (16 % based on W). IR (in cm^{-1}): 3435.3 (b), 3204.8 (b), 1617.4 (m), 1413.9 (m), 1296.2 (w), 945.1 (m), 878.6 (m), 815.9 (s), 734.9 (s). Elemental analysis, *calc.* for $H_{128}N_8O_{191}Pd_8Se_6W_{39}$: N 1.46, W 62.2 %. Found N 1.88, W 61.5 %. TGA water loss from 20 to 180°C, calculated (found) %: 6.7 (6.8).

Synthesis of $Li_{24}Na_8[Se_8W_{48}O_{176}].70H_2O$* (5): To 16 mL of H_2O was added, in order, LiCl (2.16 g, 50.95 mmol), $LiCH_3CO_2\cdot2H_2O$ (1.66 g, 25.16 mmol), $(NH_4)_6Na_{18}[Se_6W_{39}O_{141}(H_2O)_3]\cdot70H_2O$ **(3)** (1.5 g, 0.13 mmol) and $CuCl_2\cdot2H_2O$ (0.043 g, 0.25 mmol). The pH was then adjusted to 5.5 by the addition of CH_3COOH and the reaction then stirred for a further 45 minutes before the resulting mixture was then filtered and allowed to stand at room temperature. A small crop of colourless cubic crystals of **5** could be separated from the bulk precipitate after 5-6 months.

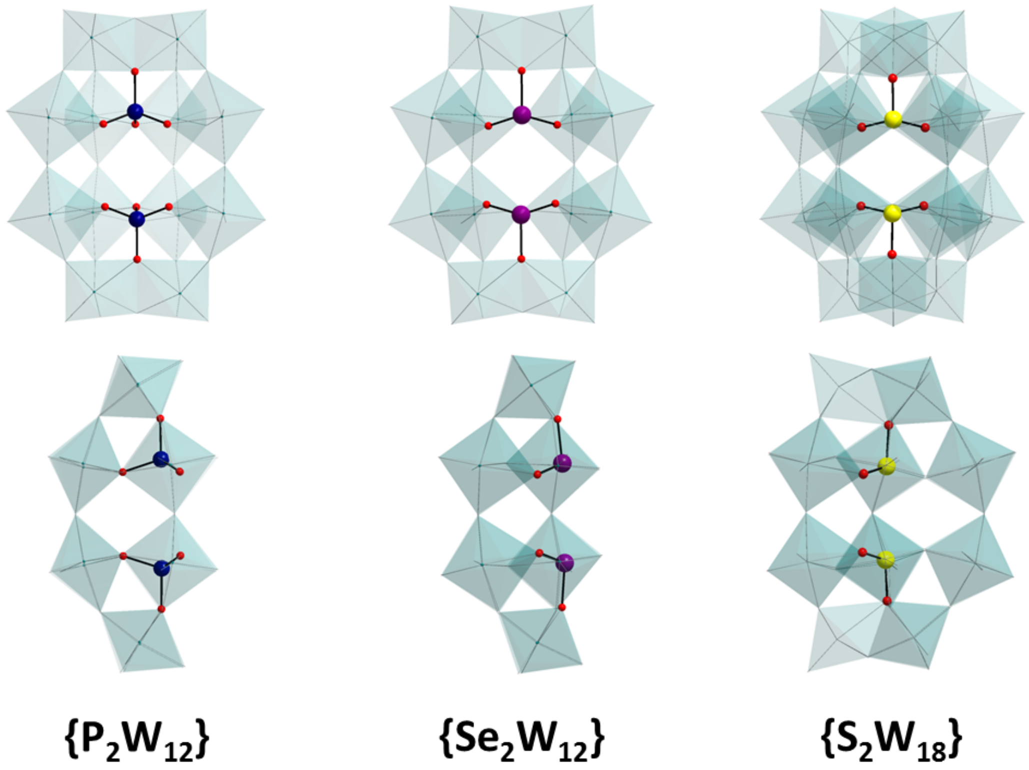
*The formula of **5** presented here is crystallographically derived, in which the anion $[Se_8W_{48}O_{176}]^{32-}$ is well-defined with estimated total numbers of Li^+ and Na^+ cations and additional solvent water molecules. Detailed analysis was impeded by the poor reproducibility, lengthy crystallisation times and low yields encountered in our initial explorations of this system. Given this, we do not attempt to provide a full characterisation at this point and will instead seek to do so in a following publication at a later date.

Table S1: Crystallographic Details

	1	**2**	**3**
Formula	$C_{35}H_{184}ClMn_4N_7Na_6O_{151}Se_6W_{24}$	$ClH_{100}Mn_3N_{11}Na_4O_{122}Se_6W_{24}$	$H_{150}N_6Na_{18}O_{204}Se_6W_{39}$
M_r (g mol^{-1})	8398.90	7384.98	11556.51
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$C2/c$	$P2_1/n$
a (Å)	15.8262(4)	34.2145(6)	22.8802(4)
b (Å)	14.0296(3)	17.0782(2)	38.7610(8)
c (Å)	33.2787(8)	25.5489(5)	24.4831(4)
α (°)	90	90	90
β (°)	91.992(2)	123.828(3)	96.610(2)
γ (°)	90	90	90
V (Å^3)	7384.6(3)	12401.5(5)	21568.7(7)
Z	2	4	4
T (K)	150(2)	150(2)	150(2)
F(000)	7628	13076	20448
$\rho_{\text{calcd.}}$ (g cm^{-3})	3.777	3.956	3.559
μ(Mo$_{K\alpha}$) (mm^{-1})	20.585	24.368	21.865
Rflns. (measd.)	68310	50642	176117
Rflns. (uniq.)	14497 ($R_{\text{int}} = 0.109$)	12184 ($R_{\text{int}} = 0.048$)	42335 ($R_{\text{int}} = 0.100$)
No. params.	853	768	2424
R_1 (I > 2σ(I))	0.0426	0.0323	0.0505
wR_2 (all)	0.1128	0.0795	0.1186
Goodness of Fit	0.969	1.069	1.032

Table S2: Crystallographic Details (cont'd)

	4	**5**
Chemical Formula	$H_{134}N_{12}O_{184}Pd_6Se_6W_{39}$	$H_{140}Li_{24}Na_8O_{246}Se_8W_{48}$
M_r (g mol^{-1})	11529.11	13884.07
Crystal System	Orthorhombic	Monoclinic
Space Group	*Cmcm*	*C*2/*m*
a (Å)	30.1962(6)	37.7155(19)
b (Å)	35.7662(6)	26.0468(19)
c (Å)	21.6486(4)	14.0820(7)
α (°)	90	90
β (°)	90	97.632(6)
γ (°)	90	90
V (Å^3)	23380.6(7)	13711.2(14)
Z	4	2
T (K)	150(2)	150(2)
F(000)	20224	12184
$\rho_{\text{calcd.}}$ (g cm^{-3})	3.275	3.363
μ(Mo$_{K\alpha}$) (mm^{-1})	20.573	21.220
Rflns. (measd.)	95297	111086
Rflns. (uniq.)	11646 ($R_{\text{int}} = 0.107$)	13795 ($R_{\text{int}} = 0.152$)
No. params.	614	672
R_1 (I > 2σ(I))	0.0628	0.0582
wR_2 (all)	0.1799	0.1564
Goodness of Fit	1.037	1.019



$\{P_2W_{12}\}$ $\{Se_2W_{12}\}$ $\{S_2W_{18}\}$

Figure S1: A comparison of the $\{Se_2W_{12}\}$ building block present in compounds **1-5** (centre) with the analogous $\{P_2W_{12}\}$ species, which can be isolated for use as a secondary building unit,[12] (shown left) and the fully condensed 'Trojan horse' $\{S_2W_{18}\}$ cluster,[13] the geometry of which may in fact be considered as an isomeric parent structure of the hexalacunary $\{Se_2W_{12}\}$ unit, related by a 180° rotation of the two $\{W_3\}$ capping triads (shown right). It is also notable that the bonding in the cluster framework also changes on moving from a tetrahedral (PO_4^{3-}) template to a pyramidal (SeO_3^{2-}/SO_3^{2-}) template. This can be seen in the 'belt-region' $\{WO_6\}$ polyhedra on the leading edge of the framework, which are edge-sharing with the $\{WO_6\}$ units on the back face of the cage in the $\{Se_2W_{12}\}$ species, but corner-sharing in the $\{P_2W_{12}\}$ species. This leads to a noticeable 'puckering' on the lacunary face of the cluster which may have an impact on the relative reactivity of each hexalacunary unit, something which future work will hope to address.

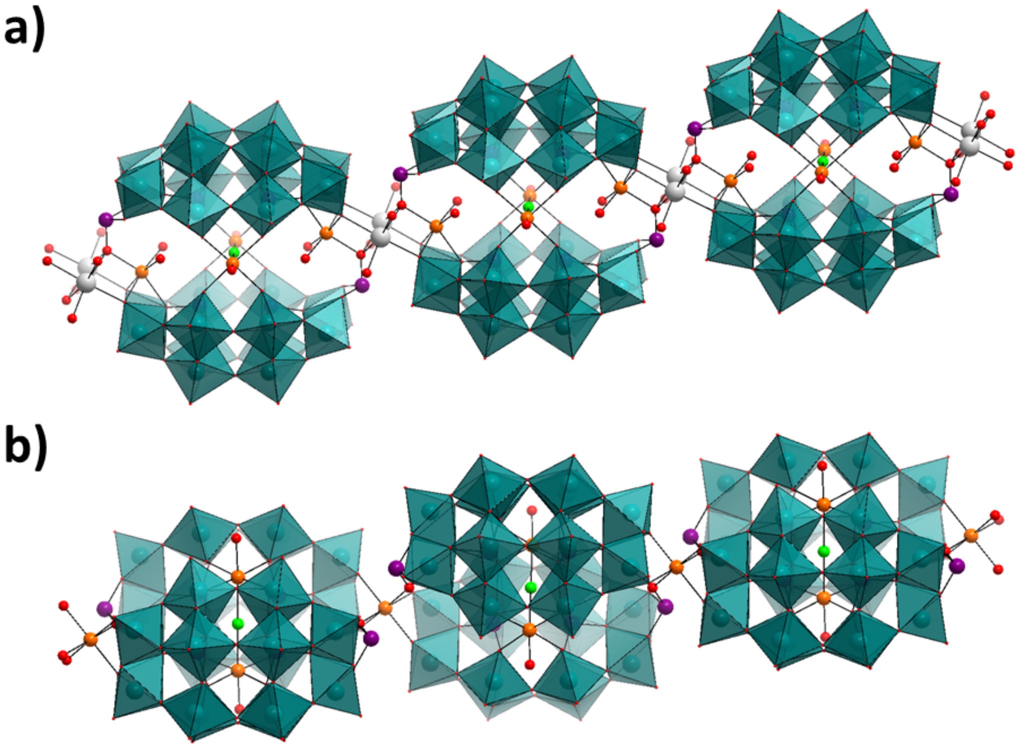


Figure S2: Comparison of the extended structures observed in compounds **1** and **2** in which: a) the discrete, dimeric $\{Mn_4Se_6W_{24}\}$ units in **1** are linked into a chain-like structure by the coordination of two addition Na^+ ions, which form a linking μ_4-oxo group via the Mn-O-Se bridge at the top and bottom of each cluster, and; b) the 'genuine' 1D-chain structure of **2**, in which the repeating $\{Mn_3Se_6W_{24}\}$ units are linked by a shared pendant Mn atom. Unlike in **1**, the chain of $\{Mn_3Se_6W_{24}\}$ units in **2** is twisted, with each cluster related to the next via a 110° rotation through its long axis.

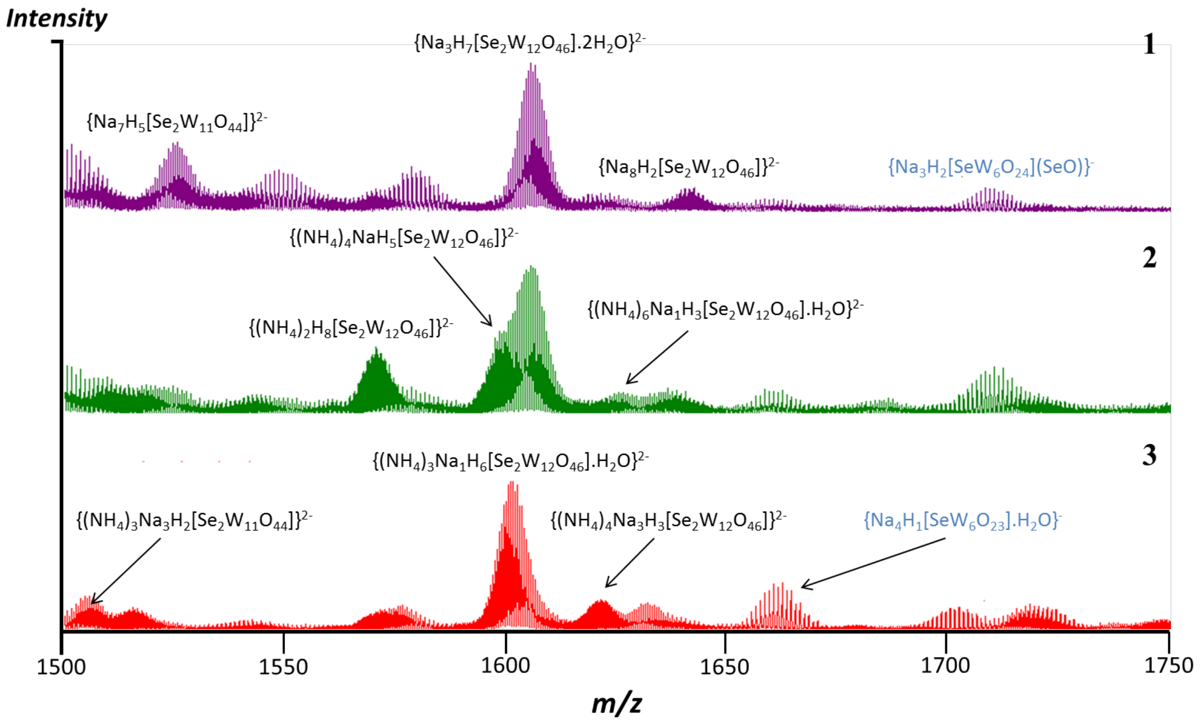


Figure S3: Comparison of the ESI-MS spectra of compounds **1-3** in the region 1500-1750 *m/z*. Intensity is relative, normalised to the highest intensity peak shown at *ca.* 1605 *m/z*. Full peak assignments are given below (Table S3).

Table S3: Selected mass spectrometry peak assignments for compounds **1-3**

	m/z (obs)	***z***	**Assignment**	**m/z (calc)**
Compound **1**	1525.5	2	{Na$_7$H$_5$[Se$_2$W$_{11}$O$_{44}$]}$^{2-}$	1525.5
	1548.5	1	{Na$_7$[SeW$_5$O$_{21}$].3H$_2$O	1548.5
	1605.5	2	{Na$_3$H$_7$[Se$_2$W$_{12}$O$_{46}$].2H$_2$O}$^{2-}$	1605.5
	1642.5	2	{Na$_8$H$_2$[Se$_2$W$_{12}$O$_{46}$]}$^{2-}$	1642.5
	1660.5	1	{Na$_4$H$_1$[SeW$_6$O$_{23}$].H$_2$O}$^{-}$	1660.5
	1710.5	1	{Na$_2$H$_3$[SeW$_6$O$_{24}$](SeO)}$^{-}$	1710.4
Compound **2**	1571.6	2	{(NH$_4$)$_2$H$_8$[Se$_2$W$_{12}$O$_{46}$]}$^{2-}$	1571.6
	1599.5	2	{(NH$_4$)$_4$NaH$_5$[Se$_2$W$_{12}$O$_{46}$]}$^{2-}$	1599.6
	1605.5	2	{Na$_3$H$_7$[Se$_2$W$_{12}$O$_{46}$].2H$_2$O}$^{2-}$	1605.5
	1625.6	2	{(NH$_4$)$_6$Na$_1$H$_3$[Se$_2$W$_{12}$O$_{46}$].H$_2$O}$^{2-}$	1625.6
	1636.6	2	{(NH$_4$)$_6$Na$_2$H$_2$[Se$_2$W$_{12}$O$_{46}$].H$_2$O}$^{2-}$	1636.6
	1660.5	1	{Na$_4$H$_1$[SeW$_6$O$_{23}$].H$_2$O}$^{-}$	1660.5
	1710.5	1	{Na$_2$H$_3$[SeW$_6$O$_{24}$](SeO)}$^{-}$	1710.4
Compound **3**	1505.6	2	{(NH$_4$)$_3$Na$_3$H$_2$[Se$_2$W$_{11}$O$_{44}$]}$^{2-}$	1505.1
	1515.6	2	{(NH$_4$)$_2$Na$_3$H$_4$[Se$_2$W$_{11}$O$_{44}$].2H$_2$O}$^{2-}$	1515.1
	1576.6	2	{Na$_2$H$_8$[Se$_2$W$_{12}$O$_{46}$]}$^{2-}$	1576.5
	1601.1	2	{(NH$_4$)$_2$Na$_1$H$_7$[Se$_2$W$_{12}$O$_{46}$].2H$_2$O}$^{2-}$	1600.6
	1621.5	2	{(NH$_4$)$_4$Na$_3$H$_3$[Se$_2$W$_{12}$O$_{46}$]}$^{2-}$	1621.6
	1632.1	2	{(NH$_4$)$_4$Na$_4$H$_2$[Se$_2$W$_{12}$O$_{46}$]}$^{2-}$	1632.6
	1660.5	1	{Na$_4$H$_1$[SeW$_6$O$_{23}$].H$_2$O}$^{-}$	1660.5
	1702.5	1	{(NH$_4$)$_4$Na$_2$H$_1$[SeW$_6$O$_{24}$].H$_2$O}$^{-}$	1702.6

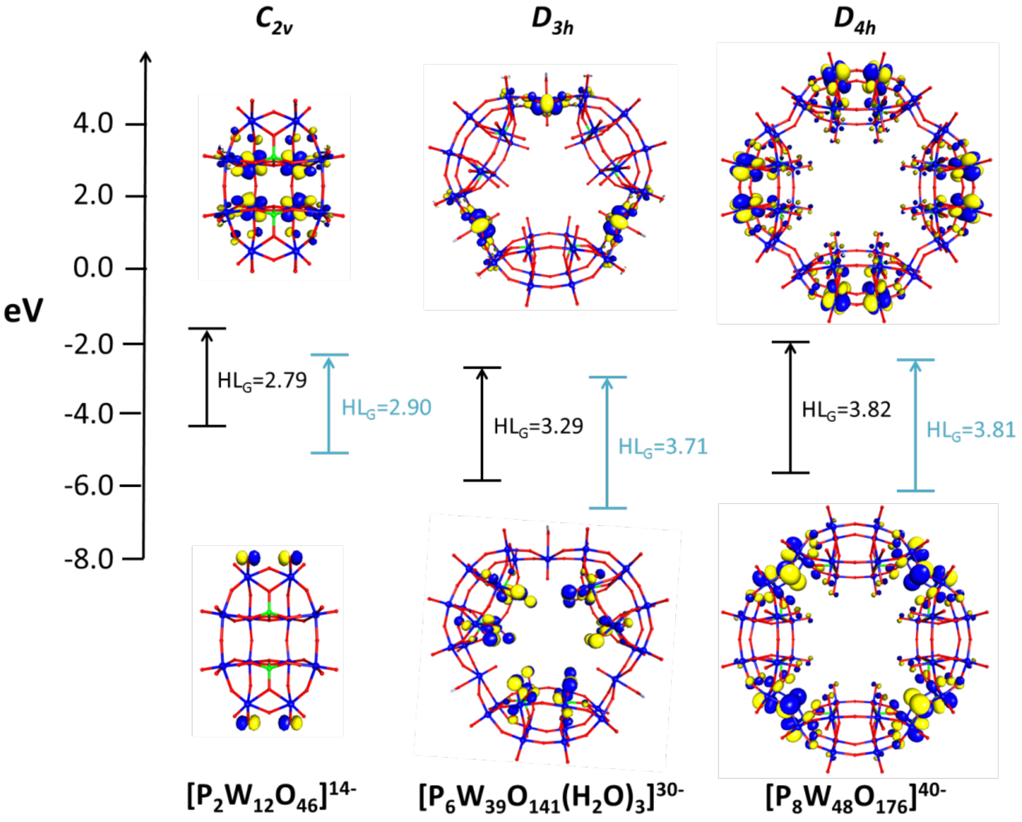


Figure S4: Comparison of the frontier molecular orbitals of the $[P_2W_{12}O_{46}]^{14-}$, $[P_6W_{39}O_{141}(H_2O)_3]^{30-}$ and $[P_8W_{48}O_{176}]^{40-}$ anions showing the positions of the HOMO and LUMO states and the corresponding HOMO-LUMO gap (shown in black). The HOMO-LUMO gap for the analogous Se-templated cluster ($\{Se_2W_{12}\}$, **3** and **5** respectively) is shown in blue (see Fig. 4 in manuscript). The similar energies of the $\{X_8W_{48}\}$ wheels in particular lend us to believe that their relative stabilities may be similar.

Table S4: Electronic parameters (in eV) for the clusters computed in Figures 4 and S4.

		q/m	HOMO	LUMO	ΔE_{H-L}
$[Se_2W_{12}O_{46}]^{12-}$	C_{2v}	1.00	-5.06	-2.16	2.90
$[Se_6W_{39}O_{141}(H_2O)_3]^{24-}$	D_{3h}	0.62	-5.92	-2.21	3.71
$[Se_8W_{48}O_{176}]^{32-}$	D_{4h}	0.67	-6.36	-2.53	3.82
$[P_2W_{12}O_{46}]^{14-}$	C_{2v}	1.17	-4.41	-1.62	2.79
$[P_6W_{39}O_{141}(H_2O)_3]^{30-}$	D_{3h}	0.77	-5.81	-2.52	3.29
$[P_8W_{48}O_{176}]^{40-}$	D_{4h}	0.83	-5.81	-1.97	3.83

* The q/m parameter is obtained by explicitly considering the overall negative charge, *q*, and the number of metal atoms, *m*, present in a structure. $\Delta E_{H-L} = E_{LUMO} - E_{HOMO}$

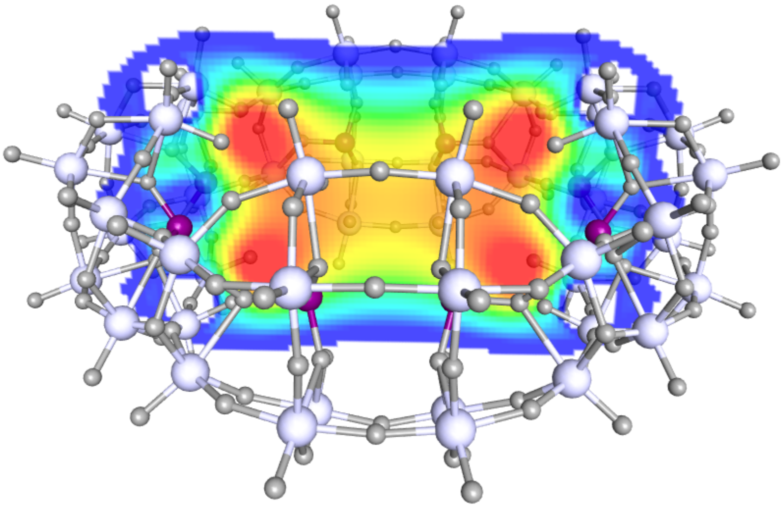


Figure S5: Computed molecular electrostatic potential (MEP) for **5** shown in cross-section through the $\{W_{48}\}$ ring. The most nucleophilic regions can be identified as those shown in red whilst the least nucleophilic regions are mapped in blue. As expected, the MEP for **5** is comparable to the phosphorous-templated analogue $[P_8W_{48}O_{184}]^{40-}$ (see Fig. 14 in reference 11 for example).

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