

## Supporting Information

### Self Assembly of a Nanosized, Saddle Shaped, Solution-Stable Polyoxometalate Anion Built from Pentagonal Building Blocks: $[\text{H}_{34}\text{W}_{119}\text{Se}_8\text{Fe}_2\text{O}_{420}]^{54-}$

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#### I Synthesis of compound

Reagents were purchased commercially and used without further purification. FTIR spectra were run on a JASCO FTIR 410 spectrometer and analyzed using JASCO software. The elements analysis is done by using Flame Atomic Absorption Spectroscopy: FAAS analysis was performed at the Environmental Chemistry Section, Department of Chemistry, The University of Glasgow on Perkin-Elmer 1100B and Perkin-Elmer A Analyst 400 Atomic Absorption Spectrophotometers.

#### Synthesis of $\text{K}_{44}\text{Na}_{10}[\text{H}_{34}\text{W}_{119}\text{Se}_8\text{Fe}_2\text{O}_{420}] \cdot 220\text{H}_2\text{O}$ **1**

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (4.5 g, 13.6 mmol) and  $\text{Na}_2\text{SeO}_3$  (0.40 g, 2.3 mmol) were dissolved in 60mL water. The pH value of the solution was adjusted to *ca.* 5.0 by 50% acetic acid, and then KCl (0.50 g, 6.7 mmol) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.25 g, 0.62mmol) were added in, the clear colourless solution turn to yellow cloudy mixture immediately. 37% HCl was added by dropwise to the mixture while stirring until it becomes clear yellowish-green solution. The final pH was kept at 1.7 for another five minutes. Slow evaporation of the solution results in the colourless crystal **1** forming in a month. Yield: 3.7% (0.15 g, 0.004 mmol)

I.R. (KBr disk):  $\nu/\text{cm}^{-1}$  3449, 2370.1, 1622.8, 1380.8, 966.2, 788.7, 505.2

Elemental analysis, calc. for  $\text{H}_{474}\text{Fe}_2\text{K}_{44}\text{Na}_{10}\text{O}_{640}\text{Se}_8\text{W}_{119}$ : W 62.1, Se 1.79, K 4.88, Na 0.65, Fe 0.32%; Found: W 61.9, Se 1.5, K 4.8, Na 0.6, Fe 0.2%

#### II Crystallographic studies of $\text{K}_{44}\text{Na}_{10}[\text{H}_{34}\text{W}_{119}\text{Se}_8\text{Fe}_2\text{O}_{420}] \cdot 220\text{H}_2\text{O}$ (**1**)

Suitable single crystal was selected and mounted onto the end of a thin glass fiber using Fomblin oil. X-ray diffraction intensity data were measured at 150(2) K on a Oxford Diffraction Xcalibur Gemini Ultra diffractometer using  $\text{CuK}\alpha$  radiation [ $\lambda = 1.54184 \text{ \AA}$ ]. Structure solution and refinement were carried out with SHELXS-97<sup>1</sup> and SHELXL-97<sup>2</sup> via WinGX<sup>3</sup>. Corrections for incident and diffracted beam absorption effects were applied using analytical<sup>4</sup> methods.

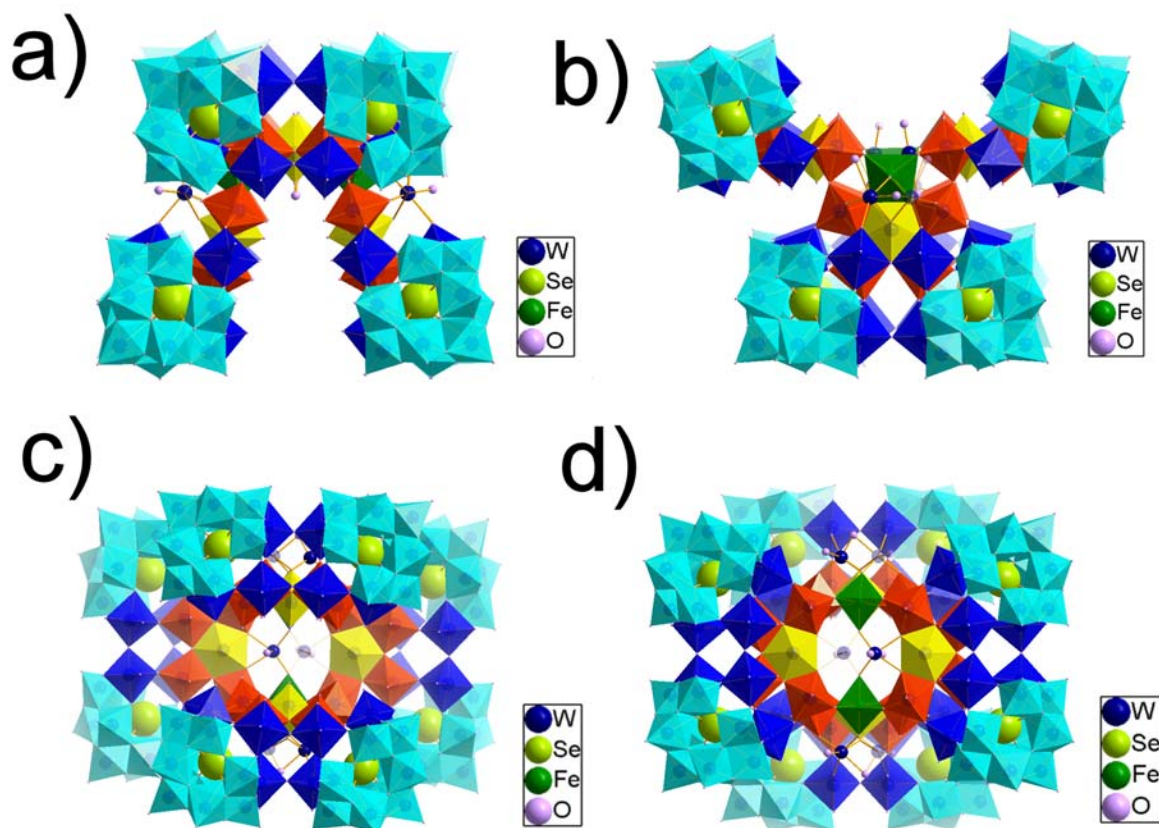
(1) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1998**, *A46*, 467.

(2) Sheldrick, G. M. SHELXL-97. Program for Crystal structure analysis, University of Göttingen, Germany, 1997.

(3) Farrugia, L. J. *J. Appl. Cryst.*, **1999**, *32*, 837.

(4) Clark, R. C.; Reid, J. S. *Acta Cryst.*, **1995**, *A51*, 887.

Crystal data and structure refinement for  $\text{K}_{44}\text{Na}_{10}[\text{H}_{34}\text{W}_{119}\text{Se}_8\text{Fe}_2\text{O}_{420}] \cdot 220\text{H}_2\text{O}$  (**1**)  $M_r = 35289.62 \text{ g mol}^{-1}$ ; block crystal:  $0.22 \times 0.18 \times 0.13 \text{ mm}^3$ ;  $T = 150(2) \text{ K}$ . Triclinic, space group  $P-1$ ,  $a = 24.8548(3)$ ,  $b = 33.1678(4)$ ,  $c = 40.1311(4) \text{ \AA}$ .  $\alpha = 94.990(2)^\circ$ ,  $\beta = 94.485(2)^\circ$ ,  $\gamma = 109.091(2)^\circ$ .  $V = 30944.7(6) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho = 3.787 \text{ cm}^{-3}$ ,  $\mu(\text{Cu-K}\alpha) = 44.367 \text{ mm}^{-1}$ ,  $F(000) = 31340$ , 289879 reflections measured, of which 101947 are independent ( $R_{\text{int}} = 0.0760$ ), 5848 refined parameters,  $R_1 = 0.0669$  and  $wR_2 = 0.1998$  (all data).



**Figure S2.1** Structure of the “saddle” shaped anionic cluster **1a**  $[\text{H}_{34}\text{W}_{119}\text{Se}_8\text{Fe}_2\text{O}_{420}]^{54-}$  in different orientations: (a) front-view, (b) side-view, (c) top-view, (d) bottom-view,

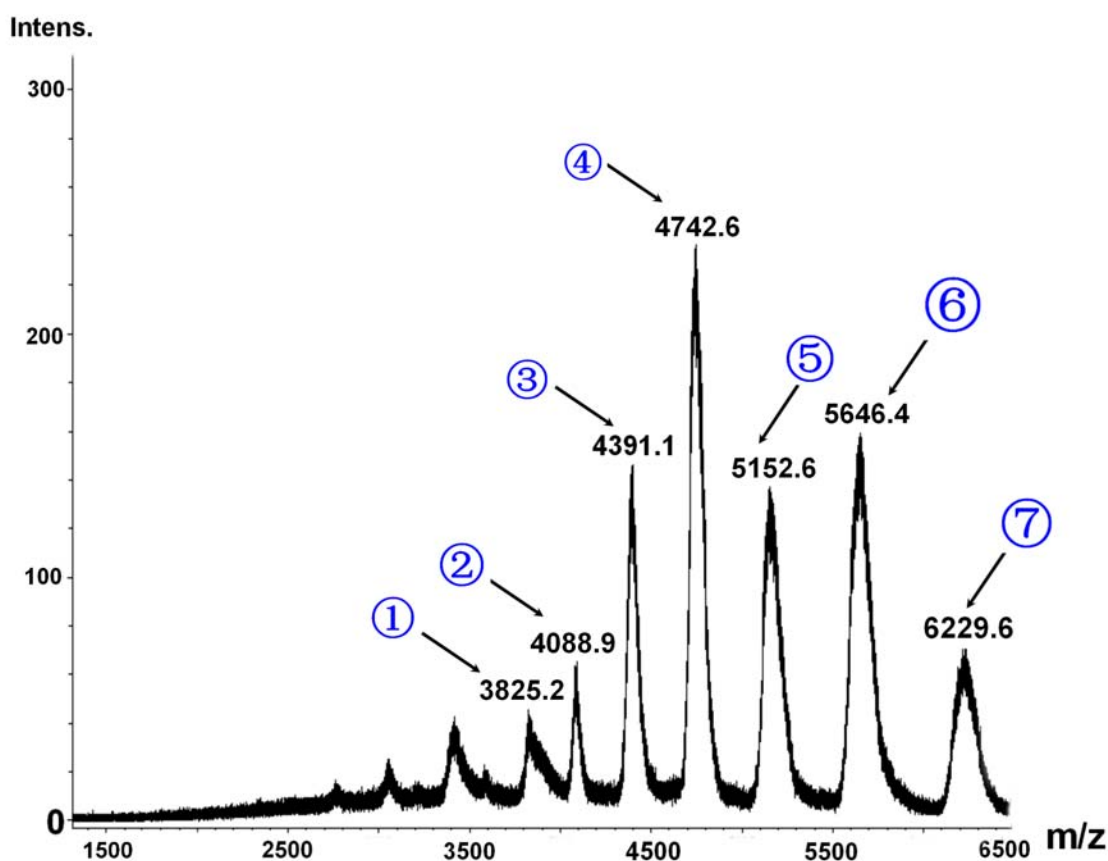
**Table S2.1** the BVS calculation result of the cluster **1a**.

Oxygen Code	Bond Valence	Protonation Degree	Oxygen Code	Bond Valence	Protonation Degree
O94	0.355	2	O260	0.385	2
O102	0.369	2	O359	0.366	2
O103	0.374	2	O360	1.046	1
O193	0.427	2	O401	0.400	2
O194	0.440	2	O409	0.457	2
O202	0.413	2	O413	0.267	2
O205	1.075	1	O414	0.247	2
O252	0.401	2	O417	0.250	2
O257	0.356	2	O418	0.237	2

Total 34 protons per clusters

### III Mass Spectrometric study of compounds

All MS data was collected using a micrOTOF<sub>Q</sub>, time-of-flight MS instrument supplied by Bruker Daltonics Ltd. The detector was a time-of-flight, micro-channel plate detector and all data was processed using the Bruker Daltonics Data Analysis 4.0 software, whilst simulated isotope patterns were investigated using Bruker Isotope Pattern software and Molecular Weight Calculator 6.45. All theoretical peak assignments were determined via comparison of the experimentally determined isotopic patterns for each peak, with simulated isotopic patterns. The following parameters were consistent for all ESI-MS scans given below. The calibration solution used was Agilent ES tuning mix solution, enabling calibration between approximately 100m/z and 6000m/z. Samples were introduced into the MS *via* direct injection at 180 $\mu$ L/hr. For all MS scans recorded the end-plate offset was set at -500V, funnel 1RF at 300Vpp, funnel 2 RF at 400Vpp, hexapole RF at 400Vpp, and active focus ON.



**Figure S3.1** The negative mode Mass Spectrum of compound **1**

The solutions of the systems investigated were prepared by making up a solution of **1** in water/acetonitrile (5%:95%) mixture solvent (1 mg/mL). The negative mode MS of compound **1** is shown in Figure S3.1

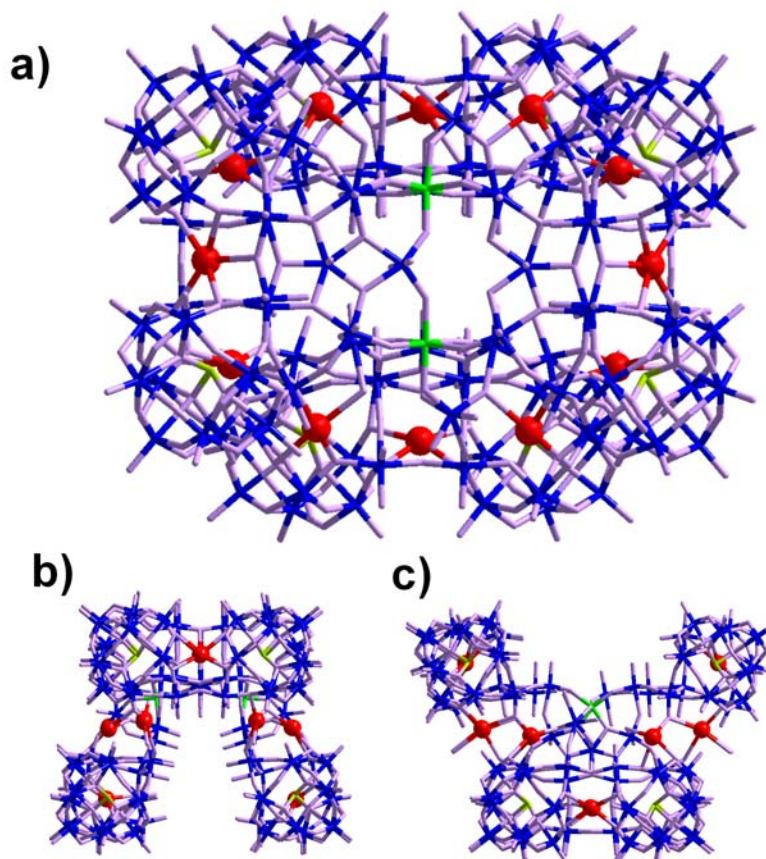
The cluster forms strong ionic interaction with the cations and brawny H-bond with solvent water because of the high negative charge ( $\sim 54$ ) and gigantic molecular weight (over 30000), which leads to that it is hard to observe the naked single cluster without any cation and solvent molecules intact. Also because the molecular weights are beyond the instrument resolution limit, it is hard to recognize the charge number of each peak. However, from the separations of peaks, we proposed all the seven main peaks are relevant and can be assigned as gradually charged anions which derived from the cluster **1a**, which represents the heaviest POM anions ever detected by ESI-MS, see Table S3.1. The clusters in solution can dimerize through H-bond and cation bridging interactions and all the peaks can be assigned

as a cluster with molecular mass located at the reasonable narrow range between 61203 to 62296 Da., which fit the theoretic calculated molecular mass range between 58857 (for  $\{H_{54}[H_{34}W_{119}Fe_2Se_8O_{420}]\}_2$ ) to 62971 Da. ( for  $\{K_{54}[H_{34}W_{119}Fe_2Se_8O_{420}]\}_2$ ). Meanwhile, as these peaks do not appear in the Gaussian distribution (for example the peak at 5152.6 is much lower than its two neighbors), it is also proposed that possible peak overlapping of multiple charged species exists. This kind of overlies also accounts for the impracticable assignment of the peaks by using direct method. For example, the peak at  $m/z$  5152.6 may contain the overlapping of two kinds of anions  $\{H_{30}K_9Na_9(H_{34}W_{119}Fe_2Se_8O_{420})(H_2O)_{53}\}^{6-}$  and  $\{H_{61}K_{18}Na_{17}(H_{34}W_{119}Fe_2Se_8O_{420})_2(H_2O)_{107}\}^{12-}$ . The comprehensive investigation of cluster **1a** behavior in solution is on the way.

**Table S3.1 Assignment of peaks in negative mode Mass spectrum of compound 1**

	Peak code	m/z	Charge	Molecular mass	Envelop Assignment*
dimeric species	1	3825.2	-16	61203	$\{H_{57}K_{16}Na_{19}(H_{34}W_{119}Fe_2Se_8O_{420})_2(H_2O)_{74}\}^{16-}$
	2	4088.9	-15	61333	$\{H_{57}K_{17}Na_{19}(H_{34}W_{119}Fe_2Se_8O_{420})_2(H_2O)_{79}\}^{15-}$
	3	4391.1	-14	61475	$\{H_{58}K_{17}Na_{19}(H_{34}W_{119}Fe_2Se_8O_{420})_2(H_2O)_{87}\}^{14-}$
	4	4742.6	-13	61653	$\{H_{61}K_{17}Na_{18}(H_{34}W_{119}Fe_2Se_8O_{420})_2(H_2O)_{98}\}^{13-}$
	5	5152.6	-12	61831	$\{H_{61}K_{18}Na_{17}(H_{34}W_{119}Fe_2Se_8O_{420})_2(H_2O)_{107}\}^{12-}$
	6	5646.4	-11	62110	$\{H_{60}K_{18}Na_{19}(H_{34}W_{119}Fe_2Se_8O_{420})_2(H_2O)_{120}\}^{11-}$
	7	6229.6	-10	62296	$\{H_{60}K_{18}Na_{20}(H_{34}W_{119}Fe_2Se_8O_{420})_2(H_2O)_{129}\}^{10-}$
Single cluster species	1	3825.2	-8	30602	$\{H_{29}K_8Na_9(H_{34}W_{119}Fe_2Se_8O_{420})(H_2O)_{34}\}^{8-}$
	3	4391.1	-7	30738	$\{H_{29}K_8Na_{10}(H_{34}W_{119}Fe_2Se_8O_{420})(H_2O)_{36}\}^{7-}$
	5	5152.6	-6	30916	$\{H_{30}K_9Na_9(H_{34}W_{119}Fe_2Se_8O_{420})(H_2O)_{53}\}^{6-}$
	7	6229.6	-5	31148	$\{H_{30}K_9Na_{10}(H_{34}W_{119}Fe_2Se_8O_{420})(H_2O)_{64}\}^{5-}$

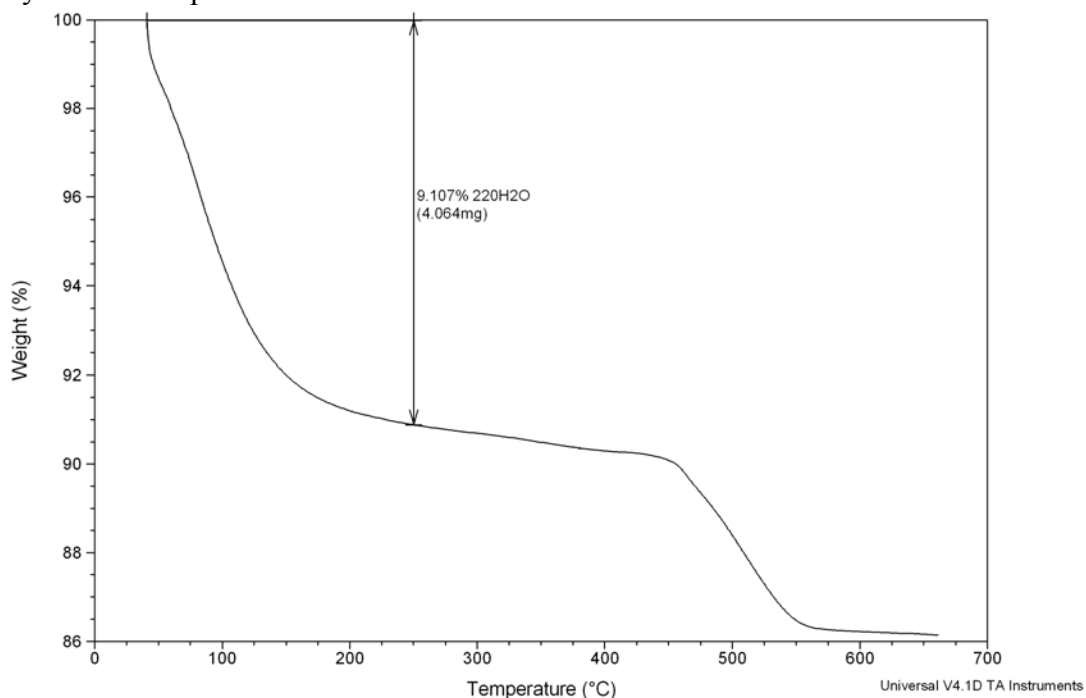
\* The envelopes encompass a range of different cation-anion compositions i.e. different combinations of  $H^+$ ,  $K^+$ ,  $Na^+$  and solvent molecules is possible, reflected by the broad  $m/z$  distribution in the peaks, however the assignment of the anion cluster is consistently linked via the charge-progression analysis.



**Figure S3.2** representation of K<sup>+</sup> cations in the cavity of **1a** [H<sub>34</sub>W<sub>119</sub>Se<sub>8</sub>Fe<sub>2</sub>O<sub>420</sub>]<sup>54-</sup> in different orientations: (a) top-view (b) front-view, (c) side- view. The cluster is shown in stick mode and the K<sup>+</sup> cations are shown in red ball.

#### IV Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed under N<sub>2</sub> atmosphere at a heating rate of 15 °C min<sup>-1</sup> on crystalline samples.



**Figure S4.1** Thermogravimetric analysis of **K<sub>44</sub>Na<sub>10</sub>[H<sub>34</sub>W<sub>119</sub>Se<sub>8</sub>Fe<sub>2</sub>O<sub>420</sub>]•220H<sub>2</sub>O**