Supplementary information for

Rearrangement of {α-P_2W_{15}} to {PW_6} Moieties during the Synthesis of a Series of Novel Polyoxometalates

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Contents

1) Instrumentation and Materials

Single Crystal X-Ray Diffraction: Single crystal datasets and unit cells were collected at 150(2) K on the following instruments: Oxford Diffraction Gemini Ultra S (λ (CuKα) = 1.5405 Å) equipped with a graphite monochromator and ATLAS CCD detector or a Bruker Apex II Quasar diffractometer equipped with a graphite monochromator (λ (MoKα) = 0.71Å) at 150(2)K. Data reduction was performed using the CrysAlis software package and structure solution and refinement was carried out using SHELXS-97[1] and SHELXL-97 [2] *via* WinGX[3]. Corrections for incident and diffracted beam absorption effects were applied using analytical numeric absorption correction using a multifaceted crystal model.[4]

UV-Vis spectroscopy: UV-Vis spectra were collected using a JASCO V-670 spectrometer.

Thermogravimetric Analysis (TGA): Thermogravimetric analysis was performed on a TA Instruments Q 500 Thermogravimetric Analyzer under air flow at a typical heating rate of 10 °C min^{-1}.

Flame Atomic Absorption Spectrometry (FAAS): FAAS was performed at the Environmental Chemistry Section, Department of Chemistry, University of Glasgow on a Perkin-Elmer 1100B Atomic Absorption Spectrophotometer for W, Co and Mn and a Sherwood M410 Flame photometer for Na and Li.

Fourier-transform infrared (FT-IR) spectroscopy: The compound was either prepared as a KBr pellet and the FT-IR spectrum was collected in transmission mode using a JASCO FT-IR 4100 spectrometer. Wavenumbers (ν) are given in cm^{-1}.

ESI-MS (electrospray ionization mass spectrometry): Measurements were performed using a *Waters Synapt-G2* spectrometer. The instrument was operated in negative mode and with an electrospray source regularly calibrated using 2μg/L NaI solution in 1:1 2-propanol/H_2O from Waters Q-ToF Qualification Standard Kit. The sample was dissolved in 1:1 mixture of HPLC grade deionized water and HPLC grade acetonitrile and injected into the spectrometer at a flow rate of 5 μL· min^{-1}. Data analysis was performed on the *Waters MassLynx v4.1* software.

2) Synthesis

All chemicals were purchased from Sigma Aldrich Chemical Company Ltd. and used without further purification. $K_{12}[\alpha\text{-}P_2W_{18}O_{62}]\cdot 14H_2O$[5] and $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$[6] were synthesised according literature procedures and used without further purification.

Compound 1: $Na_9Li_{14}[Co_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 55H_2O$

In a 50mL conical flask 0.290 g of $CoCl_2.6H_2O$ (1.22 mmol) was dissolved in 7 mL of 4 M $LiCl_{(aq)}$, then 0.080 g of Na_3PO_4 (0.49 mmol) was added and stirred for 5 minutes. The pH is adjusted to 6.5* by addition of 0.5 M LiOH and 0.1 M HCl solutions drop-wise with manual stirring. When the pH was stable, 3.00 g (0.68 mmol) of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ was added slowly. After complete addition the mixture was stirred for 10 minutes. The very dense pale brown mixture was centrifuged at 4400 rpm for 5 minutes. After this time the intense brownish-red solution was decanted into a 25 mL beaker and left overnight at 4°C. The next day the mother liquor was decanted and the precipitate re-dissolved in 2 M $LiCl_{(aq)}$. Long thin pink needle-shaped crystals formed within one week from the mother liquor. Yield: 50 mg (1.9 %, $4.3\cdot 10^{-3}$ mmol) based on $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$. Note that most of the $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ (>2 g) added initially does not participate in the reaction due to poor solubility causing a poor yield as a result. IR (KBr, cm-1): 3419, 2032, 1619, 1100, 1049, 952, 876, 836, 729, 596, 518, 448, 402; TGA weight loss from compound, $Na_9Li_{14}[Co_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 55H_2O$ (25 - 300°C), observed 9.26% calcd: 9.30% ; Elemental Analysis for $Na_9Li_{14}[Co_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 55H_2O$ (10665.58 $g\cdot mol^{-1}$) calcd. (%) W 62.0, Co 3.32, Li 0.91, Na 1.94, found: W 65.3, Co 2.97, Li 0.98, Na 2.14. Other type of crystals (pink plates) also appeared at the same time corresponding to $\{Co_4(\alpha\text{-}P_2W_{15}O_{56})_2\}$ (see Figure S5). In most cases this is the major product. This type of molecule has been reported previously in the literature.[7]

*If the pH was adjusted to any value higher than 7.50 another type of crystal (long dark pink needles) appeared as well in the crystallisation step. These correspond to a $\{Co_9(\alpha\text{-}P_2W_{15}O_{56})_3\}$ compound already reported in the literature.[8]

Compound 2: $Na_{11}Li_{12}[Mn_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 58H_2O$

In a 50mL conical flask 0.210 g of $MnCl_2.4H_2O$ (1.06 mmol) was dissolved in 7 mL of 4 M $LiCl_{(aq)}$, after that, 0.080 g of Na_3PO_4 (0.49 mmol) were added and stirred for 5 minutes. Then the pH was adjusted to 6.5-7.0* by addition of 0.5 M LiOH and 0.1 M HCl solutions drop-wise stirring manually. When the pH was stable, 3.00 g (0.68mmol) of $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ were added slowly. After complete addition the mixture was stirred for 10 minutes. The very dense bright orange liquid was transferred into a centrifuge tube and it was centrifuged at 4400 rpm for 5 minutes. After this time the intense orange solution was decanted into a 25 mL beaker and left overnight at 4°C. The next day the mother liquor was decanted and the precipitate was re-dissolved in 2 M LiCl. Long thin orange needle-shaped crystals formed over a period of between 10 days to three months. Yield: 50 mg (1.2 %, $4.33\cdot 10^{-3}$ mmol) based on $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$. Note that most of the $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]\cdot 24H_2O$ (>2 g) added initially does not participate in the reaction due to poor solubility causing a poor yield as a result. IR (KBr, cm^{-1}): 3398, 2056, 1614, 1088, 1045, 969, 929, 876, 831, 786, 715, 597, 562, 522, 467; TGA weight loss for the compound $Na_{11}Li_{12}[Mn_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 58H_2O$, (25 - 300°C) observed: 9.72%, calc'd: 9.74%; Elemental Analysis calcd. (%) for $Na_{11}Li_{12}[Mn_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 58H_2O$ (10727.75 $g\cdot mol^{-1}$) W 61.69, Mn 3.07, Li 0.77, Na 2.36, found: W 61.3, Mn 3.22, Li 0.78, Na 2.41. Other type of crystals (orange plates) also appeared at the same time corresponding to $\{Mn_4(\alpha\text{-}P_2W_{15}O_{56})_2\}$ (see Figure S5). In most cases this is the major product. This type of molecule has been reported previously in the literature.[7]

*Occasionally if the pH was adjusted to any value higher than 7.50 crystals (long dark orange needles) of Compound **3** appeared as well in the crystallisation step.

3) Graphic Representation of the Compounds

Compound 1: $[Co_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]^{23-}$

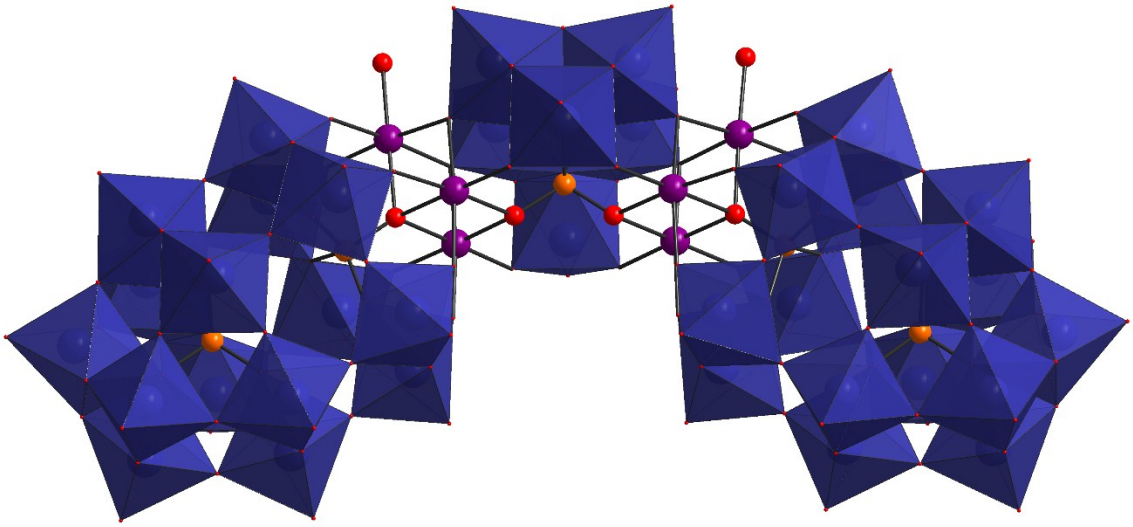


Figure S1. Polyhedral and ball-and-stick representation of Compound **1**: Co V-Shaped sandwich. W: indigo polyhedra, P: orange spheres, Co: purple spheres, O: red spheres. Counter ions have been omitted for clarity.

Compound 2: $[Mn_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]^{23-}$

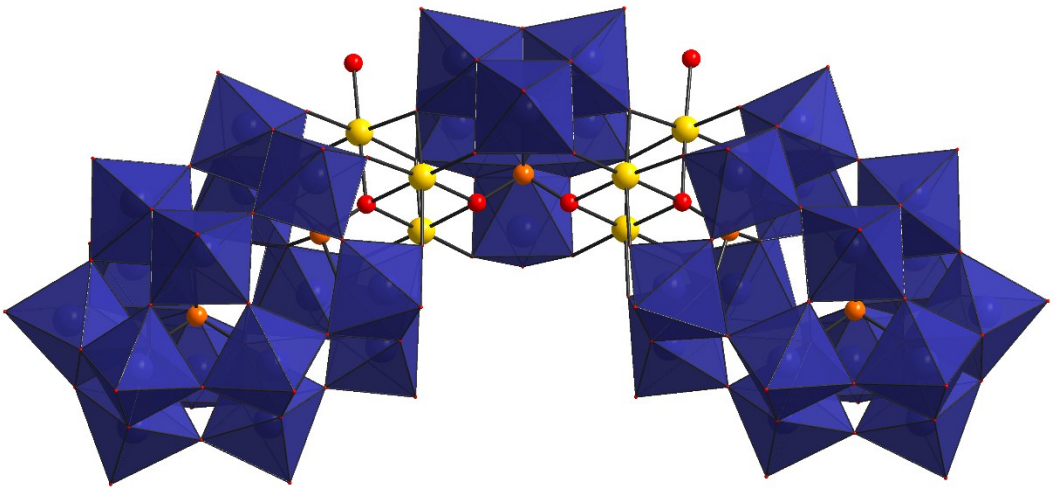


Figure S2. Polyhedral and ball-and-stick representation of Compound **2**: Mn V-Shaped sandwich. W: indigo polyhedra, P: orange spheres, Mn: yellow spheres, O: red spheres. Counter ions have been omitted for clarity.

Compound 3: $[Mn_9(\alpha\text{-}P_2W_{15}O_{56})_3(PO_3)_2(OH)_5(H_2O)_6]^{25-}$

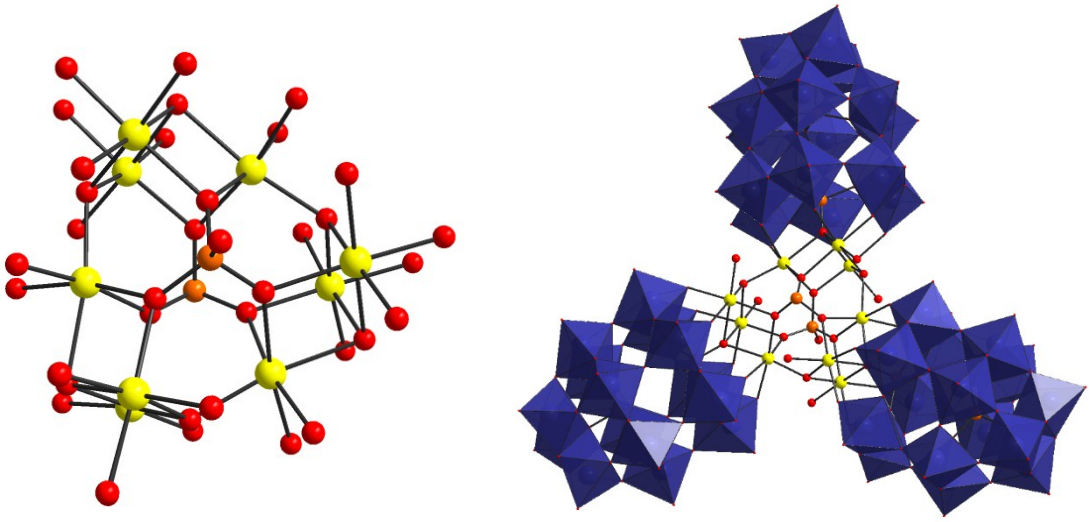


Figure S4. Left: Ball-and-stick representation of the core of Compound **3**: Right: Compound **3**. W: indigo polyhedra, P: orange spheres, Mn: yellow spheres, O: red spheres. Counter ions have been omitted for clarity.

4) Crystallographic Data

Compound 1: $Na_9Li_{14}[Co_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 55H_2O$

Identification code	**Compound 1** (CL3-20)	
CCDC code	CCDC 1430716	
Empirical formula	$Co_6\ H_{136}\ Li_{14}\ Na_9\ O_{206}\ P_5\ W_{36}$	
Formula weight	10666.01	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 14.5199(4) Å	α = 94.512(2)°.
	b = 25.6135(7) Å	β = 99.078(2)°.
	c = 27.6975(8) Å	γ = 93.145(2)°.
Volume	10116.6(5) $Å^3$	
Z	2	
Density (calculated)	3.501 Mg/m^3	
Absorption coefficient	21.019 mm^{-1}	
F(000)	9432	
Crystal size	0.280 x 0.080 x 0.040 mm^3	
Theta range for data collection	2.872 to 25.682°.	
Index ranges	-17<=h<=17, -31<=k<=31, -33<=l<=33	
Reflections collected	156837	
Independent reflections	38352 [R(int) = 0.1050]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Analytical	
Max. and min. transmission	0.4864 and 0.0668	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	38352 / 0 / 1918	
Goodness-of-fit on F2	0.801	
Final R indices [I>2sigma(I)]	R1 = 0.0492, wR2 = 0.1069	
R indices (all data)	R1 = 0.1339, wR2 = 0.1212	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.25 and -2.05 $e.Å^{-3}$	

Compound 2: $Na_{11}Li_{12}[Mn_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 58H_2O$

Identification code	**Compound 2** (CL3-81-2)	
CCDC code	CCDC 1430717	
Empirical formula	$H_{120}\ Li_{12}\ Mn_6\ Na_{11}\ O_{198}\ P_5\ W_{36}$	
Formula weight	10728.21	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 14.0471(2) Å	α= 87.466(2)°.
	b = 21.9582(4) Å	β= 88.627(2)°.
	c = 30.7558(4) Å	γ = 86.131(2)°.
Volume	9453.6(3) $Å^3$	
Z	2	
Density (calculated)	3.769 Mg/m^3	
Absorption coefficient	22.374 mm^{-1}	
F(000)	9500	
Crystal size	0.390 x 0.170 x 0.040 mm^3	
Theta range for data collection	2.956 to 25.682°.	
Index ranges	-17<=h<=17, -26<=k<=26, -37<=l<=37	
Reflections collected	144711	
Independent reflections	35819 [R(int) = 0.0764]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	35819 / 2 / 2126	
Goodness-of-fit on F^2	0.963	
Final R indices [I>2sigma(I)]	R1 = 0.0614, wR2 = 0.1616	
R indices (all data)	R1 = 0.1203, wR2 = 0.1774	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.584 and -3.004 $e.Å^{-3}$	

Compound 3: $Na_5Li_{20}[W_{45}Mn_9P_8O_{174}(OH)_5(H_2O)_6]\cdot 60H_2O$

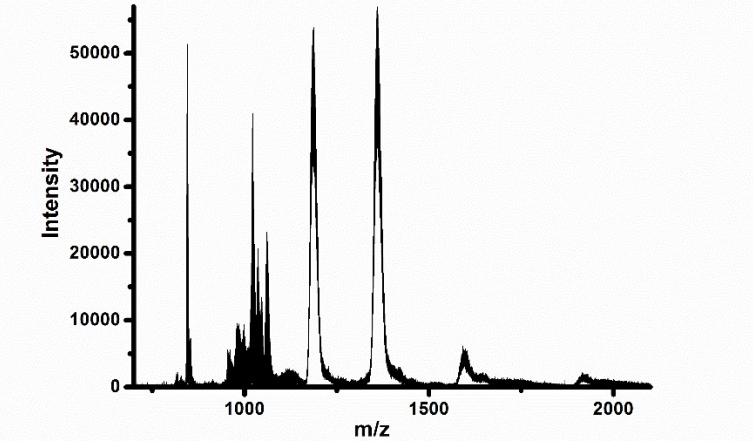
Identification code	**Compound 3** (MM19pH75)	
CCDC code	CCDC 1430718	
Empirical formula	$H_{137}\ Li_{20}\ Mn_9\ Na_5\ O_{245}\ P_8\ W_{45}$	
Formula weight	13327.32	
Temperature	150(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.0535(8) Å	α = 74.118(5)°.
	b = 29.6184(16) Å	β = 81.242(4)°.
	c = 31.8218(16) Å	γ = 89.716(4)°.
Volume	12582.0(12) $Å^3$	
Z	2	
Density (calculated)	3.518 Mg/m^3	
Absorption coefficient	41.986 mm^{-1}	
F(000)	11774	
Crystal size	0.31 x 0.06 x 0.04 mm^3	
Theta range for data collection	3.04 to 54.23°.	
Index ranges	$-14 \le h \le 14$, $-30 \le k \le 30$, $-33 \le l \le 33$	
Reflections collected	123054	
Independent reflections	29908 [R(int) = 0.2018]	
Completeness to theta = 54.23°	97.4 %	
Absorption correction	Analytical	
Max. and min. transmission	0.2845 and 0.0270	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	29908 / 0 / 2064	
Goodness-of-fit on F^2	0.882	
Final R indices [I>2sigma(I)]	R1 = 0.0886, wR2 = 0.2096	
R indices (all data)	R1 = 0.1857, wR2 = 0.2476	
Extinction coefficient	none	
Largest diff. peak and hole	1.72 and -1.51 $e.Å^{-3}$	

5) ESI-MS (Electrospray Ionization Mass Spectrometry)

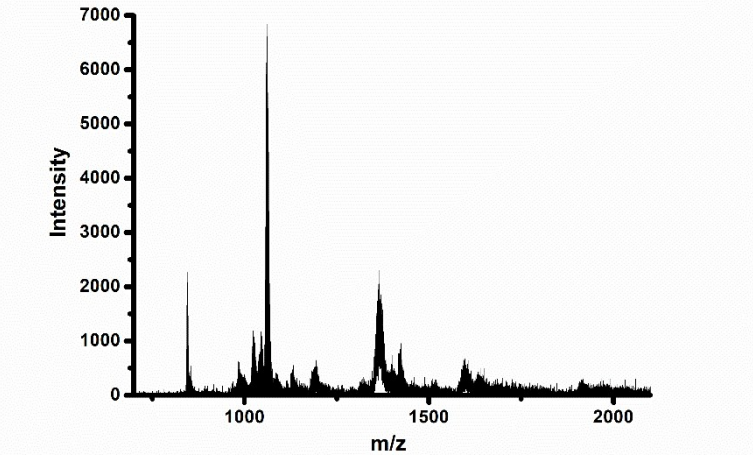
Compound 1: $Na_9Li_{14}[Co_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{565})_2(H_2O)_2]\cdot 55H_2O$

m/z (Obs)	z	Assignment	m/z (Calc)
845.4	-5	$Na_1Li_1H_5[Co_3P_2W_{15}O_{59}(H_2O)_3]\cdot 11H_2O$	845.4
1186.8	-8	$Na_2Li_2H_{11}[Co_6(P_2W_{15}O_{56})_2(PW_6O_{26})(H_2O)_2]\cdot 3H_2O$	1186.9
1359.8	-7	$Na_3Li_2H_{11}[Co_6(P_2W_{15}O_{56})_2(PW_6O_{26})(H_2O)_2]\cdot 3H_2O$	1359.7
1595.5	-6	$Na_3Li_2H_{12}[Co_6(P_2W_{15}O_{56})_2(PW_6O_{26})(H_2O)_2]\cdot 6H_2O$	1595.5

Table S1. Assignments of the major peaks for the ESI-MS analysis of Compound **1** collected over 10 minutes



Graph. S1. ESI-MS spectrum of Compound **1** freshly dissolved in 1:1 H_2O:MeCN collected over 10 min.

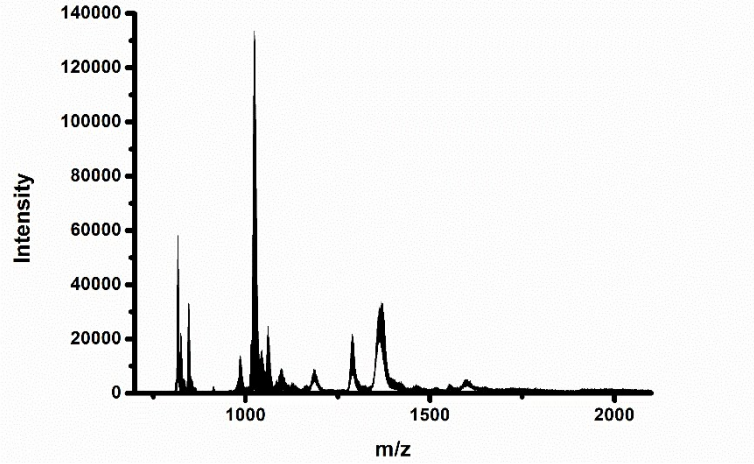


Graph. S2 ESI-MS spectrum of Compound **1** dissolved in 1:1 H_2O:MeCN collected over 10 min after 1 month in solution.

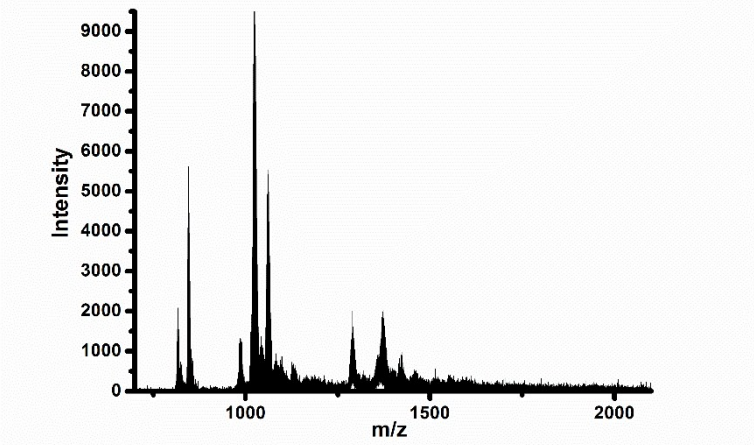
Compound 2: $Na_{11}Li_{12}[Mn_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 58H_2O$

m/z (Obs)	z	Assignment	m/z (Calc)
817.0	-5	$Li_4H_3[Mn_3P_2W_{15}O_{59}(H_2O)_3]\cdot 4H_2O$	817.0
846.6	-5	$Na_1Li_1H_5[Mn_3P_2W_{15}O_{59}(H_2O)_3]\cdot 12H_2O$	846.6
1024.5	-4	$Li_3H_5[Mn_3P_2W_{15}O_{59}(H_2O)_3]\cdot 5H_2O$	1024.5
1025.5	-4	$Na_1Li_3H_4[Mn_3P_2W_{15}O_{59}(H_2O)_3]\cdot 4H_2O$	1025.5
1187.2	-8	$Li_{14}H[Mn_6(P_2W_{15}O_{56})_2(PW_6O_{26})(H_2O)_2]\cdot 3H_2O$	1187.3
1363.5	-7	$Na_2Li_{11}H_3[Mn_6(P_2W_{15}O_{56})_2(PW_6O_{26})(H_2O)_2]\cdot 4H_2O$	1363.5
1598.2	-6	$Na_4Li_{11}H_1[Mn_6(P_2W_{15}O_{56})_2(PW_6O_{26})(H_2O)_2]\cdot 4H_2O$	1598.0
1599.9	-6	$Na_5Li_{12}[Mn_6(P_2W_{15}O_{56})_2(PW_6O_{26})(H_2O)_2]\cdot 3H_2O$	1599.9

Table S2. Assignments of the major peaks for the ESI-MS analysis of Compound **2**.



Graph. S3. ESI-MS spectrum of Compound **2** freshly dissolved in 1:1 H_2O:MeCN collected over 10 min.



Graph. S4. ESI-MS spectrum of Compound **2** dissolved in 1:1 H_2O:MeCN collected over 10 min after 1 month in solution.

To evaluate the stability of the cluster longer term, the ESI-MS analysis was performed on the cluster after immediate dissolution in 1:1 H_2O:MeCN and again after 1 month. We observe that the overall intensity of the samples is decreased with time and that the ratio of intact cluster:fragmented species decreases over time. To exemplify this we show how the total ion count (TIC) of the most intense signals for the fragmented $\{M_3P_2W_{15}O_{59}(H_2O)_3\}$ species and intact clusters ($Na_1Li_1H_5[Co_3P_2W_{15}O_{59}(H_2O)_3]\cdot 11H_2O$ at *m/z* 845.4 and $Na_3Li_2H_{11}[Co_6(P_2W_{15}O_{56})_2(PW_6O_{26})(H_2O)_2]\cdot 3H_2O$ at 1359.8 *m/z* for compound **1**, and $Li_3H_5[Mn_3P_2W_{15}O_{59}(H_2O)_3]\cdot 5H_2O$ at *m/z* 1024.5 and $Na_2Li_{11}H_3[Mn_6(P_2W_{15}O_{56})_2$-$(PW_6O_{26})(H_2O)_2]\cdot 4H_2O$ at *m/z* 1363.5 for compound **2**) change over time (see Tables S3 and S4 below).

Time	TIC of signal at *m/z* 845.4 $Na_1Li_1H_5[Co_3P_2W_{15}O_{59}(H_2O)_3]\cdot 11H_2O$	TIC of signal at *m/z* 1359.8 $Na_3Li_2H_{11}[Co_6(P_2W_{15}O_{56})_2(PW_6O_{26})(H_2O)_2]\cdot 3H_2O$	Ratio
0 d	4.39 e^4	5.61 e^4	1.28
28 d	2.28 e^3	2.28 e^3	1

Table S3. Change in the total ion count of the most intense signals for the intact cluster and most common fragmented species of Compound **1**.

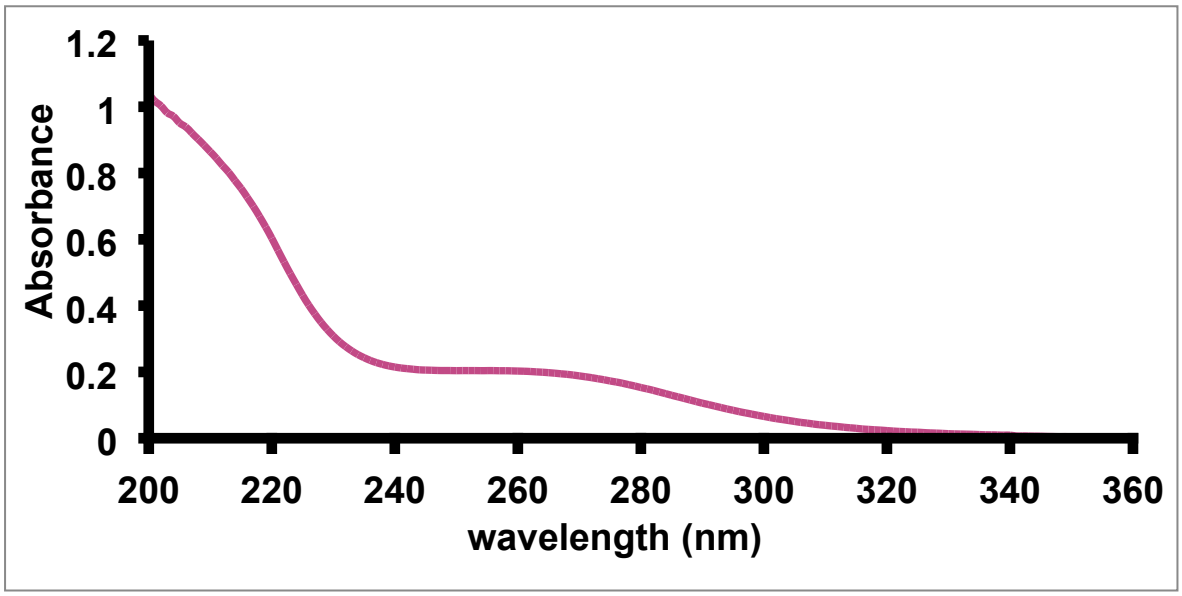
Time	TIC of signal at *m/z* 1024.5 $Li_3H_5[Mn_3P_2W_{15}O_{59}(H_2O)_3]\cdot 5H_2O$	TIC of signal at *m/z* 1363.5 $Na_2Li_{11}H_3[Mn_6(P_2W_{15}O_{56})_2(PW_6O_{26})(H_2O)_2]\cdot 4H_2O$	Ratio
0 d	1.30 e^5	3.35 e^4	0.26
28 d	9.55 e^3	1.08 e^3	0.11

Table S4. Change in the total ion count of the most intense signals for the intact cluster and most common fragmented species of Compound **2**.

Alongside the decrease in ratio of intact cluster:$\{M_3P_2W_{15}O_{59}(H_2O)_3\}$ over time, an increase in the intensity of the signals presenting in *m/z* range 1050-1250 for both spectra is also observed. As yet we have not been able to assign a fragment formula to any of these signals. These results show that while the cluster does remain intact in solution for a month, there is noticeable decomposition of the cluster into smaller fragments.

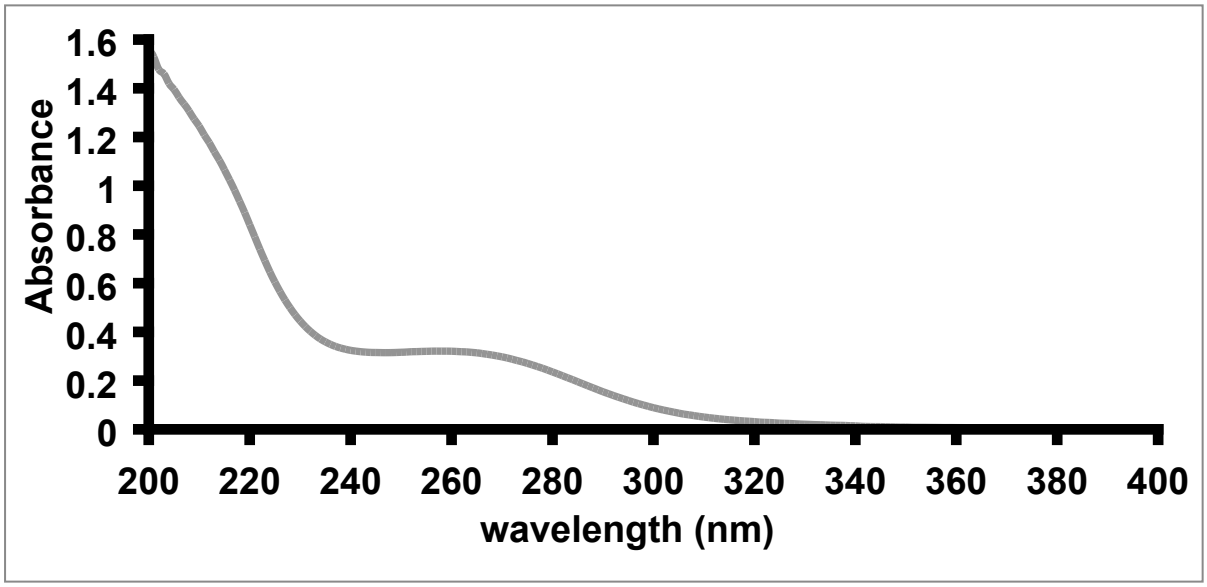
6) UV-vis spectra

Compound 1: $Na_9Li_{14}[Co_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 55H_2O$



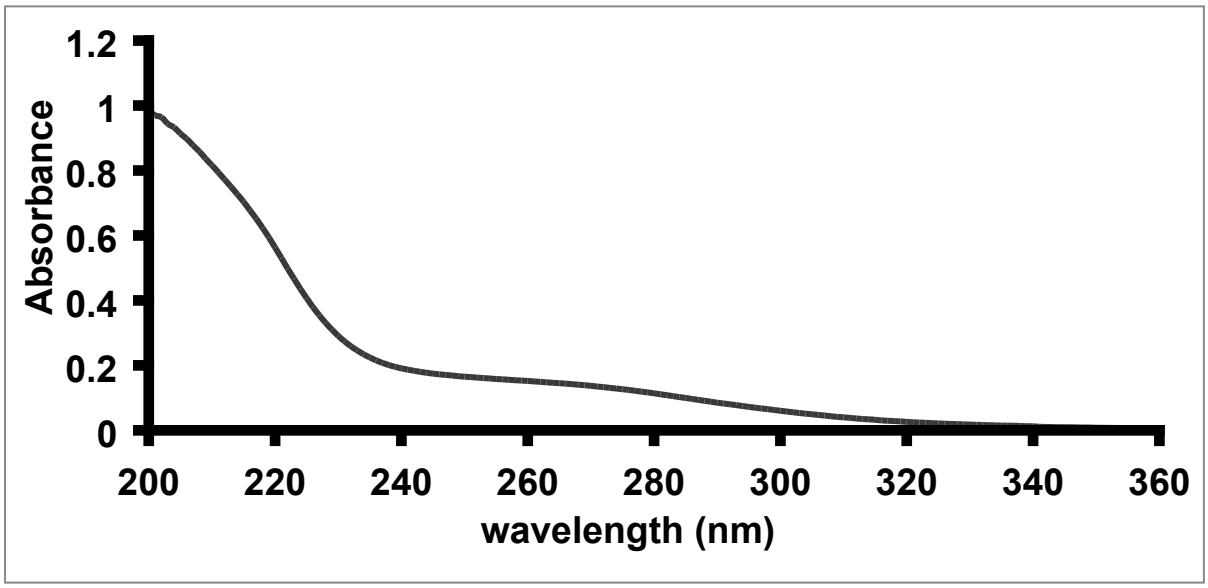
Graph S5. UV-vis spectra of Compound **1** (using water as a solvent).

Compound 2: $Na_{11}Li_{12}[Mn_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 58H_2O$



Graph S6. UV-vis spectra of Compound **2** (using water as a solvent).

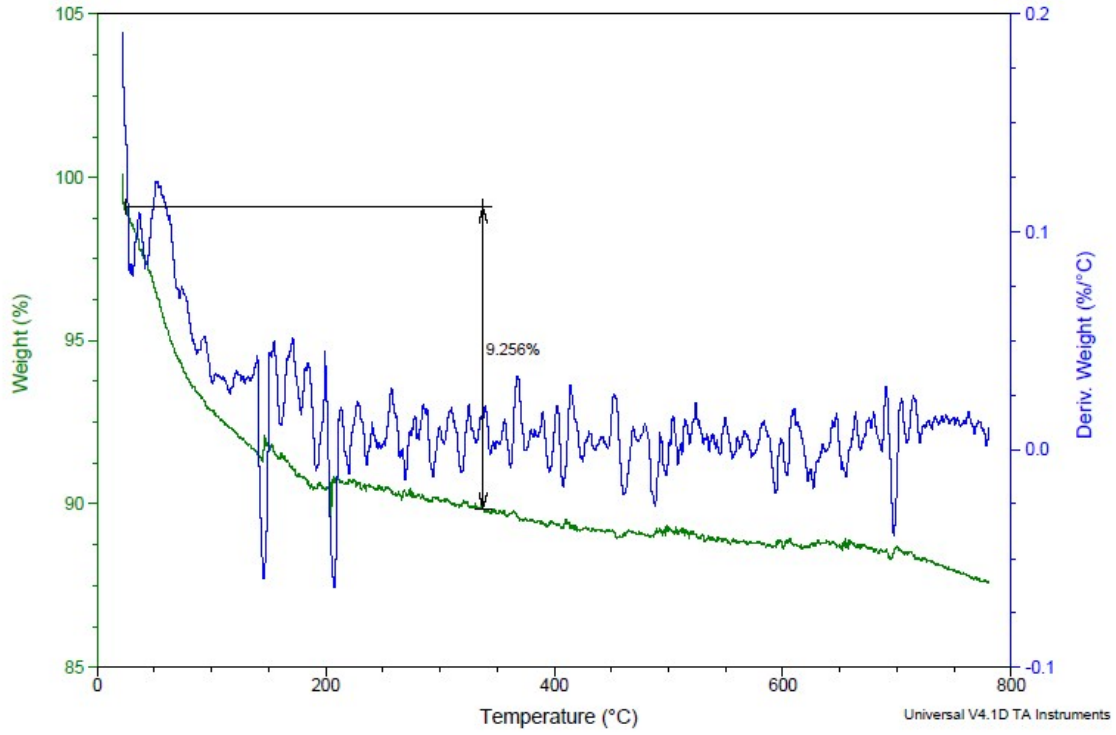
Compound 3: $Na_5Li_{20}[Mn_9(\alpha\text{-}P_2W_{15}O_{56})_3(PO_3)_2(OH)_5(H_2O)_6]\cdot 60H_2O$



Graph S7. UV-vis spectra of Compound **3** (using water as a solvent).

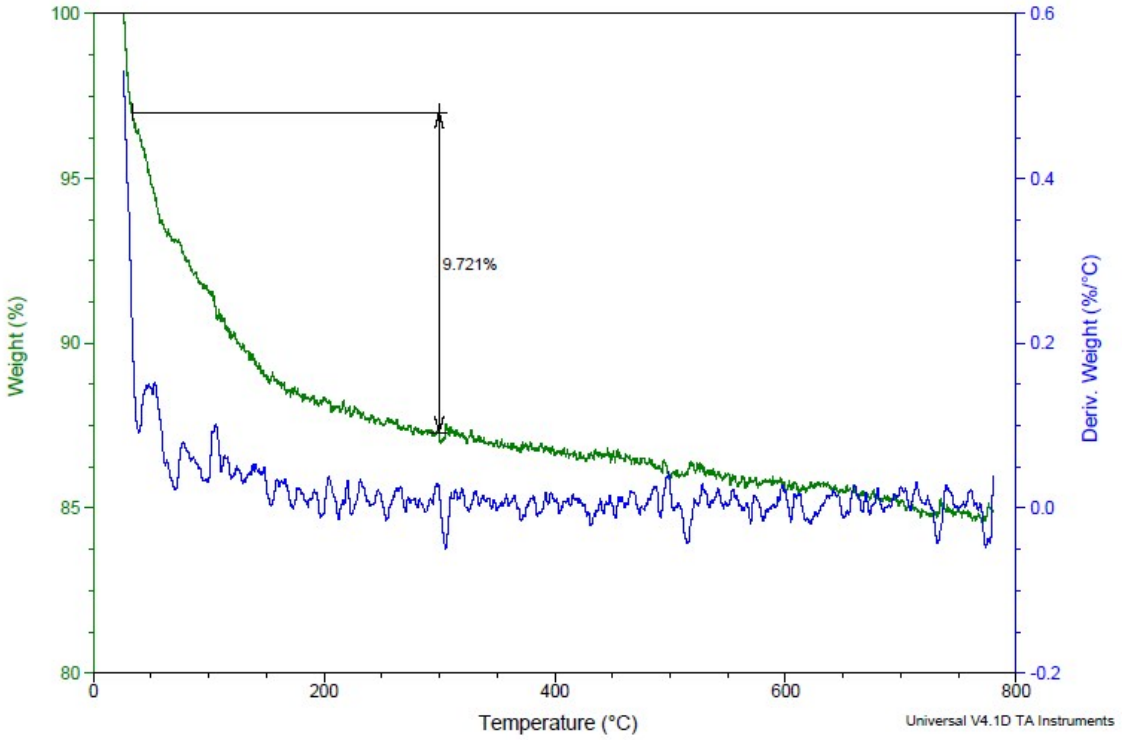
7) TGA analysis

Compound 1: $Na_9Li_{14}[Co_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 55H_2O$



Graph S8. TGA analysis for Compound **1**.

Compound 2: $Na_{11}Li_{12}[Mn_6(PW_6O_{26})(\alpha\text{-}P_2W_{15}O_{56})_2(H_2O)_2]\cdot 58H_2O$



Graph S9. TGA analysis for Compound **2**.

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