SUPPLEMENTARY INFORMATION

Encapsulation of a $\{Cu_{16}\}\$ cluster containing four $[Cu_4O_4]$ cubanes within an isopolyoxometalate $\{W_{44}\}\$ cluster

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1. General Experimental Section

Thermogravimetric Analysis: TGA was carried out on compounds under nitrogen flow (50 mLmin⁻¹) with a *TA Instruments Q500 Thermogravimetric Analyser* at a heating rate of 10°Cmin⁻¹ up to 950°C, confirming the degree of hydration of these compounds.

Fourier-Transform Infrared (FT-IR) Spectroscopy: Infrared spectra ($4000 - 600 \text{ cm}^{-1}$) were recorded on a *Shimadzu FTIR 8400s* spectrometer fitted with a *Golden Gate* ATR attachment. Intensities denoted as: s = strong, m = medium, w = weak and b = broad.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES): A minimum of 10 mg of each compound was submitted to the *Institut für Festkörperforschung* in Jülich, Germany, for analysis. Samples were digested in a 1:1 mixture of HNO₃ and H₂O₂. A *TJA-IRIS-Advantage* spectrometer with echelle optics and CID semiconductor was used to observe across a wavelength range of 170 - 900 nm.

Microanalysis: Carbon, hydrogen and nitrogen contents were determined using an *EA 1110 CHNS, CE-440 Elemental Analyser*. 5 – 10 mg samples of the relevant compounds were submitted to the *Microanalytical Service* within the *School of Chemistry, University of Glasgow*. Carbon, hydrogen and nitrogen contents were analysed twice for each sample, with an average of the two readings presented herein.

Magnetic Analysis: Magnetic susceptibility measurements were carried out with a Quantum Design SQUID Magnetometer with an applied field of 1000 and 10000 G. The independence of the susceptibility value with respect to the applied field was checked at room temperature.

Cyclic Voltammograms (CV) Analysis: Cyclic voltammograms were recorded on a CH-600E electroanalytical system (CHI instruments, inc.). A standard three-electrode cell was used at room temperature, (20 ± 1) °C, including a glassy carbon working electrode (3 mm diam.), a Ag / AgCl / NaCl (sat.) reference electrode and a Pt mesh counter electrode. All the potentials are quoted relative to the reference electrode. The working electrode was polished sequentially with diamond suspensions of decreasing grain size (15 µm, 6 µm and 1 µm) on nylon pads and rinsed first with water and then with methanol after each polishing step. The analyte solutions were deareated with Ar for at least 10 min prior to obtaining the first voltammogram while an Ar blanket was maintained over the analyte solutions thereafter.

2. Synthesis and Experimental Section

Synthesis of $\{Na_4Cu_4[(H_2W_{11}O_{38})(CH_3COO)(OH)_3]\}_4 \cdot 88H_2O$:

Na₂WO₄·2H₂O (3.63 g, 11mmol) and Cu(Ac)₂·H₂O (0.8 g, 4 mmol) were dissolved in 10 ml hot H₂O (80°C) separately, and then Cu(Ac)₂ solution was added to Na₂WO₄ solution drop by drop on hot plate (80°C) with stirring at the same time. A large amount of yellow green solid was formed in the solution. After that the pH was adjusted to 3.2 by 6M hydrochloric acid, the solution became clear lime-green and was further stirred for about 3 minutes, then filtered and green block shaped single crystals suitable for X-ray diffraction were grown by slow Et₂O diffusion within one month. Yield: 1.45 g, (41.6 %, based on tungsten). IR: 3382 (w), 3071 (w), 1630.9 (m), 1524.8 (m), 1412.8 (m), 942.4 (s), 796 (s), 672.4 (s). Elemental analysis, calc. For C₈H₂₀₈O₂₆₀Na₁₆Cu₁₆W₄₄: C 0.69, H 1.5, Na 2.64, Cu 7.29, W 58.03 %; Found C 0.71, H 1.57, Na 2.55, Cu 7.28, W 57.52 %. TGA water loss from 25 to 160 °C, calculated (found) %: 11.4 (11.0).

Synthesis of $Na_6Cu_2[(H_2W_{11}O_{38})(CH_3COO)(OH)] \cdot 26H_2O$:

Na₂WO₄·2H₂O (4.00 g, 12.1 mmol) and Cu(Ac)₂·H₂O (0.8 g, 4 mmol) were dissolved in 10 ml hot H₂O (80°C) separately, and then Cu(Ac)₂ solution was added to Na₂WO₄ solution drop by drop on hot plate (80°C) with stirring at the same time. A large amount of yellow green solid was formed in the solution. When the pH was adjusted to 4 by 6M hydrochloric acid, the solution became clear blue and was stirred for further 3 minutes, then filtered and left for evaporation. Light green needle shaped crystals were obtained within one week. Yield: 2.4 g, (63.3 %, based on tungsten). IR: 3394 (w), 1627.9 (m), 1548.4 (m), 1445.8 (m), 925.5 (s), 798.3 (s), 725.9 (s). Elemental analysis, calc. For C₂H₅₅O₆₇Na₆Cu₂W₁₁: C 0.7, H 1.61, Na 4.01, Cu 3.7, W 58.81 %; Found C 0.71, H 1.56, Na 4.24, Cu 3.73, W 58.52 %. TGA water loss from 25 to 230 °C, calculated (found) %: 13.6 (13.0).

Synthesis studies

When the pH of this reaction was adjusted to 4, the solution began to become clear blue, from which a polyanion 1D chain structure 2 was obtained within one week. While if the acid was continually added to the clear blue solution to pH = 3.2, the colour became to lime-green. It is interesting that there are two stages in the crystallization process, firstly, a large amount of 2 was formed within 10 days and then 1 came out with very low yield after 2 months. The reason is the solubility of 1 is much higher than 2. In order to solve this problem, the diethyl ether diffusion method was used to reduce the solubility of 1 in aqua, and the chemical reagents in stoichiometry were added according to 1 to optimize the experiment. Finally, pure 1 was obtained in one month with the yield of 46 %. In this experiment, the kinds of copper salts and acids are also important factors. If CuCl₂ or Cu(NO₃)₂ was chosen instead of Cu(CH₃COO)₂, compound 1 cannot be obtained, which proves that acetate is an excellent bridging group in high-nuclearity Cu(II)-POM chemistry. But if CH₃COOH acid was used instead of HCl (increase the concentration of acetate), Cu(Ac)₂ was directly crystalized from the solution after one week, so in this experiment, the coordination among the reaction parameters (concentration, pH, cations, anions and the reagent ratio) is important to produce pure 1 with high yield.

3. Crystallographic Sections

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 Bruker Apex II Quasar diffractometer ($\lambda(Mo_{K\alpha}) = 0.71073$ Å). Corrections for incident and diffracted beam absorption effects were applied using either empirical or analytical methods respectively,^{1,2} while data reduction was performed using either the CrysAlisPro or Apex2 software as supplied by the manufacturers. Final structure solution and refinement were carried out with SHELXS-97 and SHELXL-97 (or later versions) *via* the WinGX software suite,^{3,4} with all structures solved by direct methods and refined using a full matrix least squares on F² method. Selected details of the data collection and structural refinement of each compound can be found in Table 1 and 2, and full details are available in the corresponding CIF files. The CIF

files were deposited at CCDC with the submission numbers: CCDC 1547065-1547066. There are a number of PLAT975 ALERT 2 A (residual density) issues appearing in the checkcif of compound 2. These residual densities are due to imperfect absorption correction of this heavy metal tungsten compound (mu = 22 cm^{-1}). There are many PLAT971 ALERT 2 A and PLAT972 ALERT 2 A (residual density) issues in the checkcif of compound 1. These high residual densities are due to unusual crystal twinning. Nevertheless, the gross connectivities are well established and show chemical structure of reasonable and meaningful bonding features that are consistent with polyoxometalate structures previously reported. From many datasets collected for 1, we found two unit cells for the same cluster structure. One is orthorhombic system with a=21.8487(8) b=40.9986(16) c=27.4044(10)Å V=24547.9(16)Å³ as reported here. The other is monoclinic system with a=40.8002(32)b=27.6591(20) c=21.8563(17)Å beta=92.827(5)° V=24634(3)Å³. Both systems had high residual densities at finishing stage. Noting the high similarity in all axes but significant difference in one angle, we recently have realized unusual twining in crystals of 1 and we are working on the structure of the monoclinic system by resolving the twinning issue towards a further publication.

(1) G. Sheldrick, ActaCrystallographica Section A, 1990, 46, 467-473.

(2) G. Sheldrick, ActaCrystallographica Section A, 2008, 64, 112-122.

(3) L. Farrugia, J. Appl. Crystallogr., 1999, 32, 837-838.

(4) R. C. Clark, J. S. Reid, ActaCrystallogr., Sect. A, 1995, 51, 887-897.

 Table S1. Crystal data and structure refinement for 1.

Identification code	1	
Empirical formula	$C_8H_{208}O_{260}Na_{16}Cu_{16}W_4$	4
Formula weight	13939.61	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pnna	
Unit cell dimensions	a = 21.8487(8) Å	$\alpha = 90^{\circ}$
	b = 40.9986(16) Å	$\beta = 90^{\circ}$
	c = 27.4044(10) Å	$\gamma = 90^{\circ}$
Volume	24547.9(16) Å ³	
Ζ	4	

Density (calculated)	3.772 Mg/m ³
Absorption coefficient	22.027 mm^{-1}
F (000)	24928
Crystal size	0.100 x 0.070 x 0.050 mm ³
Theta range for data collection	0.894 to 26°
Index ranges	-26<=h<=26, -46<=k<=50, -33<=l<=33
Reflections collected	194846
Independent reflections	24124 [$R(int) = 0.0786$]
Completeness to theta = 26.02°	99.9 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	24124 / 0 / 1288
Goodness-of-fit on F ²	1.185
Final R indices [I>2sigma(I)]	$R_1 = 0.0774, wR_2 = 0.1646$
R indices (all data)	$R_1 = 0.1079, wR_2 = 0.1840$
Largest diff. peak and hole	6.16 and -4.72 e.Å ⁻³

Table S2. Crystal data and structure refinement for 2.

Identification code	2	
Empirical formula	$C_2H_{55}O_{67}Na_6Cu_2W_{11}$	
Formula weight	3441.85	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_{1}/n$	
Unit cell dimensions	a = 25.2138(7) Å	$\alpha = 90^{\circ}$
	b = 21.9062(7) Å	$\beta = 117.608(3)^{\circ}$
	c = 26.2394(7) Å	$\gamma = 90^{\circ}$
Volume	12842.8(7) Å ³	
Ζ	8	
Density (calculated)	3.560 Mg/m^3	
Absorption coefficient	20.425 mm^{-1}	
F (000)	12352	
Crystal size	0.190 x 0.130 x 0.080 mm ³	
Theta range for data collection	2.788 to 26.000°	
Index ranges	-31<=h<=31, -27<=k<=27, -32<=l<=32	
Reflections collected	106086	
Independent reflections	25202 [<i>R</i> (int) = 0.0703]	

Completeness to theta = 25.242° Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F² Final R indices [I>2sigma(I)] R indices (all data) Extinction coefficient Largest diff. peak and hole 99.8 % Analytical 0.239 and 0.096 Full-matrix least-squares on F^2 25202 / 0 / 1641 1.042 $R_1 = 0.0438, wR_2 = 0.0853$ $R_1 = 0.0693, wR_2 = 0.0965$ n/a 3.18 and -2.79 e.Å⁻³



Figure S1. Representation of the polyanion cluster of **1** assembled from four building blocks $\{Cu_4W_{11}\}$ in idealized D_{2d} symmetry. The dash lines show the points where links are extended to neighboring building blocks. The $\{W_{11}\}$ building units are shown as teal polyhedron, Cu as blue sphere, O and C as rose and grey sticks.



Figure S2. Representation of the cubane-like $[Cu_4O_4]$ unit. Angles Cu1 - O2 - Cu2 (91.67°), Cu1 - O1 - Cu2 (110.15°), Cu1 - O2 - Cu1# (105.6°), Cu2 - O1 - Cu2# (93.64°) and Cu1 - O2# - Cu2# (78.61°). The unit for bond length is Å. # stands for the symmetric operation (x, 1.5-y. 0.5-z); W is shown as teal sphere, Cu as blue sphere, O as rose sphere and C as grey sphere.

4. Thermogravimetric Analysis (TGA)

TGA measurement of **1** showed water loss from 25 to 160 °C, calculated (found): 11.4 (10) %.



Figure S3. Thermo gravimetric analysis of compound 1.



TGA measurement of **2** showed water loss from 25 to 230 °C, calculated (found): 13.6 (13) %.

Figure S4. Thermo gravimetric analysis of compound 2.

5. Mass spectrometric Analysis (MS)

Electrospray Ionisation Mass Spectrometry (ESI-MS) was performed on a Waters Synapt-G2 HDMS spectrometer operating in resolution mode, equipped with a quadropole and time of flight (Q/ToF) module for MS analysis. All samples were prepared by dissolving in 2 : 1 H2O : MeCN (HPLC grade) to a concentration of *ca*. 1 x 10⁻⁵ M and injected directly at a flow rate of 10 μ L 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: 2.75 kV; sample cone voltage: 10 V; extraction cone voltage: 4 V; source temperature: 80 °C; desolvation temperature: 180 °C; cone gas flow: 15 L h⁻¹ (N₂); desolvation gas flow: 750 L h⁻¹ (N₂).



Figure S5. Negative mode mass spectrum of 1 in the m/z range of 1390-1570 showing the major envelopes labelled 2- and 10- corresponding to hypothesised intermediate units and intact molecular clusters.

<i>m/z</i> (obs)*	z	Assignment	<i>m/z</i> (calc)
1408.6	3-	[NaCu ₂ (H ₂ W ₁₁ O ₃₈)(H ₂ O) ₈₀] ³⁻	1408.7
1443.0	2-	[Na ₄ Cu ₂ (W ₁₁ O ₃₈)(H ₂ O) ₂] ²⁻	1443.6
1452.6	2-	[Na ₄ Cu ₂ (W ₁₁ O ₃₈)(H ₂ O) ₃] ²⁻	1452.6
1470.5	2-	[Na ₄ Cu ₂ (W ₁₁ O ₃₈)(H ₂ O) ₅] ²⁻	1470.6
1483.7	2-	[Na ₂ Cu ₄ (W ₁₁ O ₃₈)(OH) ₂] ²⁻	1483.5
1501.8	2-	[Na ₂ Cu ₄ (W ₁₁ O ₃₈)(OH) ₂ (H ₂ O) ₂] ²⁻	1501.5
1510.4	2-	[Na ₂ Cu ₄ (W ₁₁ O ₃₈)(OH) ₂ (H ₂ O) ₃] ²⁻	1510.5
1518.8	2-	[Na ₂ Cu ₄ (W ₁₁ O ₃₈)(OH) ₂ (H ₂ O) ₄] ²⁻	1519.5
1528.2	2-	[Na ₂ Cu ₄ (W ₁₁ O ₃₈)(OH) ₂ (H ₂ O) ₅] ²⁻	1528.5
1537.2	2-	[Na ₂ Cu ₄ (W ₁₁ O ₃₈)(OH) ₂ (H ₂ O) ₆] ²⁻	1537.5
1546.9	2-	[Na ₂ Cu ₄ (W ₁₁ O ₃₈)(OH) ₂ (H ₂ O) ₇] ²⁻	1546.5
1564.5	2-	[Na ₂ Cu ₄ (W ₁₁ O ₃₈)(OH) ₂ (H ₂ O) ₉] ²⁻	1564.5

Table S3: Selected mass spectrometry peak assignments for compound 1 in the range 1390-1570 m/z

*Significant discrepancy (>0.5) between observed and calculated m/z values arises as a result of the difficulty in unambiguously assigning the centroid of overlapping isotopic envelopes, particularly in cases where the resolution of the peak is poor. In these cases, an m/z value is assigned based on the most intense peak found at near the centre of an estimated Gaussian distribution, which may not always represent the true value. The flexible number and type of cations and solvent molecules contribute relatively little to the molecular mass but do give rise to broadening of the peak envelopes defined by the cluster. This is a common issue in the accurate mass spectrometric assignment of high nuclearity POM species.



Figure S6. Negative mode mass spectrum of 2 in the m/z range of 680-1020 showing the major envelopes labelled 3- and 4- corresponding to the hypothesised intermediate units.

m/z (obs)	Z	Assignment	<i>m/z</i> (calc)
677	4-	[Na ₄ (W ₁₁ O ₃₇)] ⁴⁻	677.3
681.4	4-	[Na ₄ (H ₂ W ₁₁ O ₃₈)] ⁴⁻	681.8
685.8	4-	[Na ₄ (H ₂ W ₁₁ O ₃₈)(H ₂ O)] ⁴⁻	686.3
690.7	4-	[Cu ₂ (H ₂ W ₁₁ O ₃₈)] ⁴⁻	690.8
695.3	4-	[Cu ₂ (H ₂ W ₁₁ O ₃₈)(H ₂ O)] ⁴⁻	695.3
747.8	4-	[Na ₂ Cu ₂ (H ₂ W ₁₁ O ₃₈)(OH)(CH ₃ COO)(H ₂ O) ₆] ⁴⁻	748.3
752.5	4-	[Na ₂ Cu ₂ (H ₂ W ₁₁ O ₃₈)(OH)(CH ₃ COO)(H ₂ O) ₇] ⁴⁻	752.8
757.6	4-	[Na ₂ Cu ₂ (H ₂ W ₁₁ O ₃₈)(OH)(CH ₃ COO)(H ₂ O) ₈] ⁴⁻	757.3
762.3	4-	[Na ₂ Cu ₂ (H ₂ W ₁₁ O ₃₈)(OH)(CH ₃ COO)(H ₂ O) ₉] ⁴⁻	761.8
766.8	4-	[Na ₂ Cu ₂ (H ₂ W ₁₁ O ₃₈)(OH)(CH ₃ COO)(H ₂ O) ₁₀] ⁴⁻	766.3
771.4	4-	[Na ₂ Cu ₂ (H ₂ W ₁₁ O ₃₈)(OH)(CH ₃ COO)(H ₂ O) ₁₁] ⁴⁻	770.8
992.9	3-	[Na ₃ Cu ₂ (H ₂ W ₁₁ O ₃₈)(OH)(CH ₃ COO)(H ₂ O) ₄] ³⁻	993.1
998.7	3-	[Na ₃ Cu ₂ (H ₂ W ₁₁ O ₃₈)(OH)(CH ₃ COO)(H ₂ O) ₅] ³⁻	999.1
1005.0	3-	[Na ₃ Cu ₂ (H ₂ W ₁₁ O ₃₈)(OH)(CH ₃ COO)(H ₂ O) ₆] ³⁻	1005.1
1011.0	3-	[Na ₃ Cu ₂ (H ₂ W ₁₁ O ₃₈)(OH)(CH ₃ COO)(H ₂ O) ₇] ³⁻	1011.1
1017.5	3-	[Na ₃ Cu ₂ (H ₂ W ₁₁ O ₃₈)(OH)(CH ₃ COO)(H ₂ O) ₈] ³⁻	1017.1

Table S4: Selected mass spectrometry peak assignments for compound 2 in the range 680-1020 m/z.

6. Cyclic Voltammograms Analysis (CV)



Figure S7. Cyclic voltammograms of a solution of **1** (2 x 10^{-4} mol L⁻¹) in NaCH₃COO/H⁺ buffer solution (0.5 M, pH = 4.4). The initial potential was the open circuit potential and the scan rate was 5 mV s⁻¹. The working and counter electrodes were glassy carbon and Pt mesh respectively.



Figure S8. Cyclic voltammograms of a solution of **2** (2 x 10^{-4} mol L⁻¹) in NaCH₃COO/H⁺ buffer solution (0.5 M, pH = 4.4). The initial potential was the open circuit potential and the scan rate was 5 mV s⁻¹. The working and counter electrodes were glassy carbon and Pt mesh respectively.