

Supporting Information

Heteratom Controlled Kinetics of Switchable Polyoxometalate Frameworks

Johannes Thiel, Chris Ritchie, Carsten Streb, De-Liang Long and Leroy Cronin*
WestCHEM, Department of Chemistry, The University of Glasgow, Glasgow, G12 8QQ, U.K.

Email: L.Cronin@chem.gla.ac.uk

General Materials and Methods

The precursor material $K_8[GeW_{10}O_{36}] \cdot 6H_2O$ was prepared as described previously.^{S1} All other materials were purchased from Sigma Aldrich Chemicals and used without further purification.

Fourier-transform infrared (FT-IR) spectroscopy: Unless stated otherwise, the materials were prepared as KBr pellets and FT-IR spectra were collected in transmission mode using a JASCO FT-IR-410 spectrometer or a JASCO FT-IR 4100 spectrometer. Wavenumbers ($\tilde{\nu}$) are given in cm^{-1} ; intensities as denoted as vs = very strong, s = strong, m = medium, w = weak, b = broad.

Single Crystal X-Ray Diffraction: Single crystal datasets were collected at 150(2) K unless stated otherwise on a Oxford Diffraction Gemini Ultra S ($\lambda (Mo_{K\alpha}) = 0.71073 \text{ \AA}$ and $\lambda (Cu_{K\alpha}) = 1.5405 \text{ \AA}$) equipped with a graphite monochromator.

UV-Vis spectroscopy: UV-Vis spectra were collected using a Shimadzu PharmaSpec UV-1700 UV-Vis spectrophotometer in transmission mode using quartz cuvettes with 1.0 cm optical path length.

Microanalysis: Carbon, nitrogen and hydrogen content were determined by the microanalysis services within the Department of Chemistry, University of Glasgow using a EA 1110 CHNS, CE-440 Elemental Analyser.

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.

1. Synthesis of $(C_4H_{10}NO)_{40}[W_{72}Mn^{III}_{12}O_{268}Ge_7] \cdot 48H_2O \cdot 4(C_4H_9NO) (2_{ox})$.

Morpholine (9.0 g, 103 mmol) was added to 200ml of 1M aqueous NaCl solution and the pH was subsequently adjusted to 8.0 using 4.5 M H_2SO_4 . Fresh air dried $K_8[GeW_{10}O_{36}] \cdot 6H_2O^I$ (1.455 g 0.5 mmol) was added and the reaction mixture was stirred vigorously until the material was fully dissolved. $MnSO_4 \cdot H_2O$ (0.126 g, 0.75 mmol) was added as a solid, resulting in a bright yellow solution and the pH was adjusted to 7.80. $KMnO_4$ (24 mg, 0.15 mmol) was then added over a period of 10 minutes and the solution stirred for a further 5 minutes. At this point a deep brown solution was obtained which was

centrifuged to remove any insoluble material. Finally the pH of the solution was set to 7.75 with 4.5 M H₂SO₄. Tetrahedral diffraction quality crystals began to form after 2 weeks. Yield after 1 month: 370 mg, 16.0 μmol, 20.6 % based on W). Elemental analysis for (C₄H₁₀NO)₄₀[W₇₂Mn₁₂O₂₆₈Ge₇]₄₈H₂O₄(C₄H₉NO), C₁₇₆H₅₃₂Ge₇Mn₁₂N₄₄O₃₆₀W₇₂, MW = 23430 g/mol, calcd (found) : C 9.02, (9.01); H 2.29, (2.87); N 2.63, (2.71); W 56.49, (55.34); Mn 2.86, (2.81). (Mn and W were analyzed using atomic absorption spectroscopy). Characteristic IR bands (KBr, in cm⁻¹): 3437 (s), 2925 (w), 2853 (w), 1628 (m), 1591 (m), 1452 (m), 1384 (m), 1307 (w), 1102 (s), 1042 (s), 940 (m), 871 (m), 794 (s), 722 (m), 600 (w), 459 (m). UV/Vis (H₂O): λ_{max} = 475 nm.

2. Synthesis of (C₄H₁₀NO)₄₀H₁₂[W₇₂Mn^{II}₁₂O₂₆₈Ge₇]₄₈H₂O₅(C₆H₆O₆) (2_{red}).

Air dried 2_{ox} (20 mg; 0.87 μmol) was added to 5 ml MeOH in which it is completely insoluble. Ascorbic acid (10 mg; 56.8 μmol) was then added and dissolved over the course of a few minutes. Within 10 minutes, the reduction of Mn(III) to Mn(II) was completed with retention of the single crystals' integrity as indicated by the color change from brown to yellow and confirmed by single crystal diffraction studies. Elemental analysis for (C₄H₁₀NO)₄₀[H₁₂W₇₂Mn₁₂O₂₆₈Ge₇]₄₈H₂O₅(C₆H₆O₆), C₁₉₀H₅₃₈Ge₇Mn₁₂N₄₀O₃₈₆W₇₂, MW = 23965 g/mol, calcd (found) : C 9.52, (9.42); H 2.26, (2.14); N 2.34, (2.43); W 55.24, (53.30); Mn 2.75, (2.04). Characteristic IR bands (KBr, in cm⁻¹): 3436 (s), 2925 (w), 2852 (w), 2360 (m), 1618 (m), 1591 (m), 1453 (m), 1384 (m), 1308 (m), 1233 (m), 1102 (s), 1042 (s), 939 (s), 872 (s), 770 (s), 720 (s), 593 (w). UV/Vis (H₂O): λ_{max} = 371 nm.

3. Structural Description

Compound 2_{ox/red} is built from two types of Keggin unit hence the structure of this material can be described as an infinite array of 3- and 4-connected Keggin polyanions, where each 3-connected unit is surrounded by three neighbouring clusters in a trigonal planar fashion, and each 4-connected unit features four nearest neighbours located on the vertices of a distorted tetrahedron, see Fig. S1.

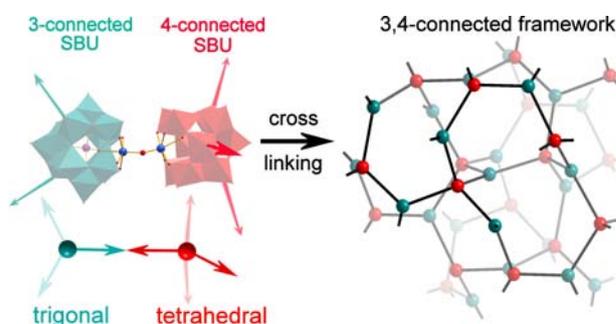


Figure S1. Rationalization of the POM-1 framework found in compound 1. The network is built from two types of lacunary Keggin clusters which act as either trigonal (green) or tetrahedral nodes (red). The polyhedral representation of the clusters (top left) more clearly shows how the secondary building units (SBUs) are linked into an infinite 3D framework based upon 3-connected and 4-connected clusters and the nodal connectivity is shown on the right.

Conceptually, the nodes of the framework can be described as an equal distribution of tetra-vacant {SiW₈O₃₆} (= W₈) and tri-vacant {SiW₉O₃₇} (= W₉) units which are cross-linked by [W-O-Mn] bridges which connect together the nodal units. Considering the statistical disorder of the W and Mn and the substitution pattern, this results in a formal assignment of 1.5 Mn and 1.5 W atoms to every trivacant cluster, with each tetravacant building block supporting 2 Mn and 2 W. Formally, the general framework description {W₇₂Mn₁₂} can thus be rationalized as {(MnW)_{3/2}W₉}₄{(MnW)_{4/2}W₈}₃.

4. Procedure for the kinetic experiments

4.1. Reduction of $1_{\text{ox}}/2_{\text{ox}}$

Compound $1_{\text{ox}}/2_{\text{ox}}$ (20 mg; 0.87 μmol) was carefully ground up and added to 50 ml of a methanolic phenylhydrazine solution (21.38 vol.-ppm). Samples of 3 ml were removed every 5 min. The suspended solid was removed from the samples by centrifugation and the phenylhydrazine concentration was determined using calibrated quantitative UV/VIS measurements.

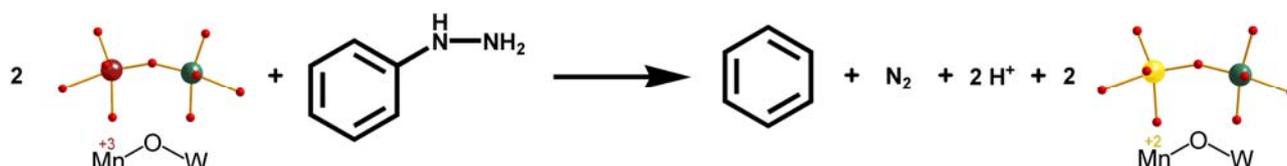


Figure S2: Schematic for the reduction of 1_{ox} and 2_{ox} with phenylhydrazine.

Table S1: Kinetic data for the reduction of 1_{ox} and 2_{ox} .

2_{ox}			1_{ox}		
t / min	c / vol.-ppm	$\Delta(y)$ / vol.-ppm	t / min	c / vol.-ppm	$\Delta(y)$ / vol.-ppm
0	21.381	0.091	0	21.381	0.091
5	21.134	0.091	5	21.195	0.091
10	20.806	0.090	10	20.983	0.091
15	20.478	0.090	15	20.737	0.090
20	20.274	0.089	20	20.59	0.090
25	20.155	0.089	25	20.38	0.090

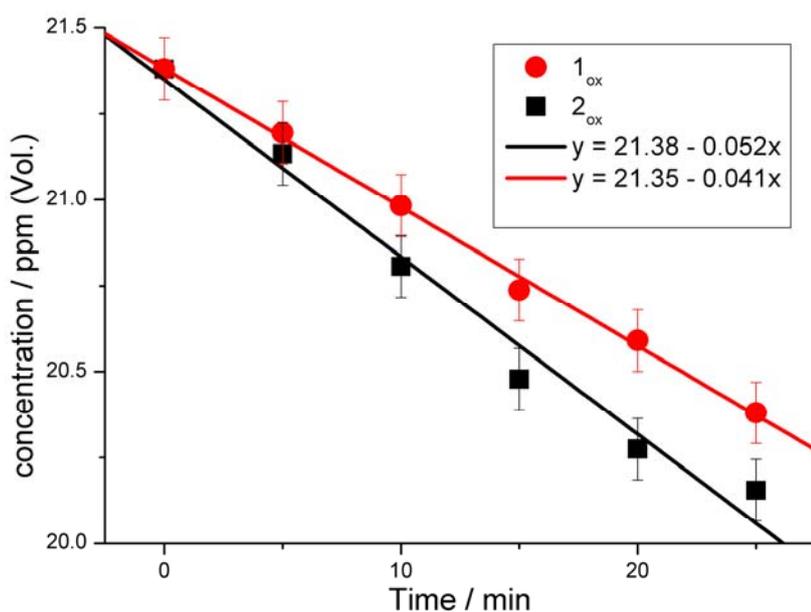


Figure S3: Graphical representation of the reduction kinetics of 1_{ox} and 2_{ox} , respectively.

4.2. Oxidation of $1_{\text{red}}/2_{\text{red}}$

Compound $1_{\text{red}}/2_{\text{red}}$ (20 mg; 0.87 μmol) was carefully ground up and added to 50 ml of a methanolic *p*-benzoquinone-solution (149 $\mu\text{mol/l}$). Samples of 3 ml were removed every 5 min. The suspended solid was removed from the samples by centrifugation and the *p*-benzoquinone-concentration was determined using calibrated quantitative UV/VIS measurements.

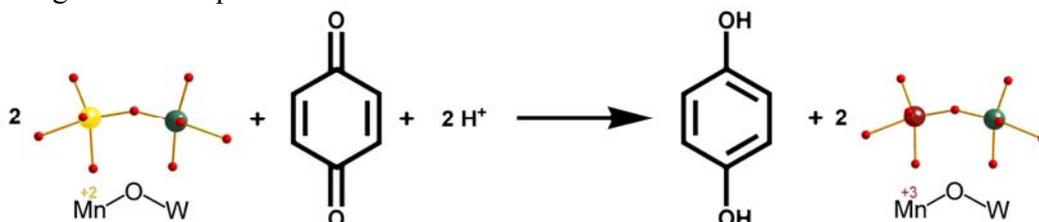


Figure S4: Schematic for the re-oxidation of 1_{ox} and 2_{ox} with *p*-benzoquinone.

Table S2: Kinetic data for the re-oxidation of 1_{red} and 2_{red}

2_{red}			1_{red}		
t / min	ln (c/c ₀)	Δ(y)	t / min	ln (c/c ₀)	Δ(y)
0	2.779	0.053	0	2.779	0.053
1	2.683	0.052	1	2.668	0.052
5	2.469	0.050	5	2.457	0.050
10	2.258	0.047	10	2.210	0.047
15	2.051	0.044	15	1.913	0.042
20	1.859	0.041	20	1.657	0.037
25	1.688	0.038	25	1.449	0.031

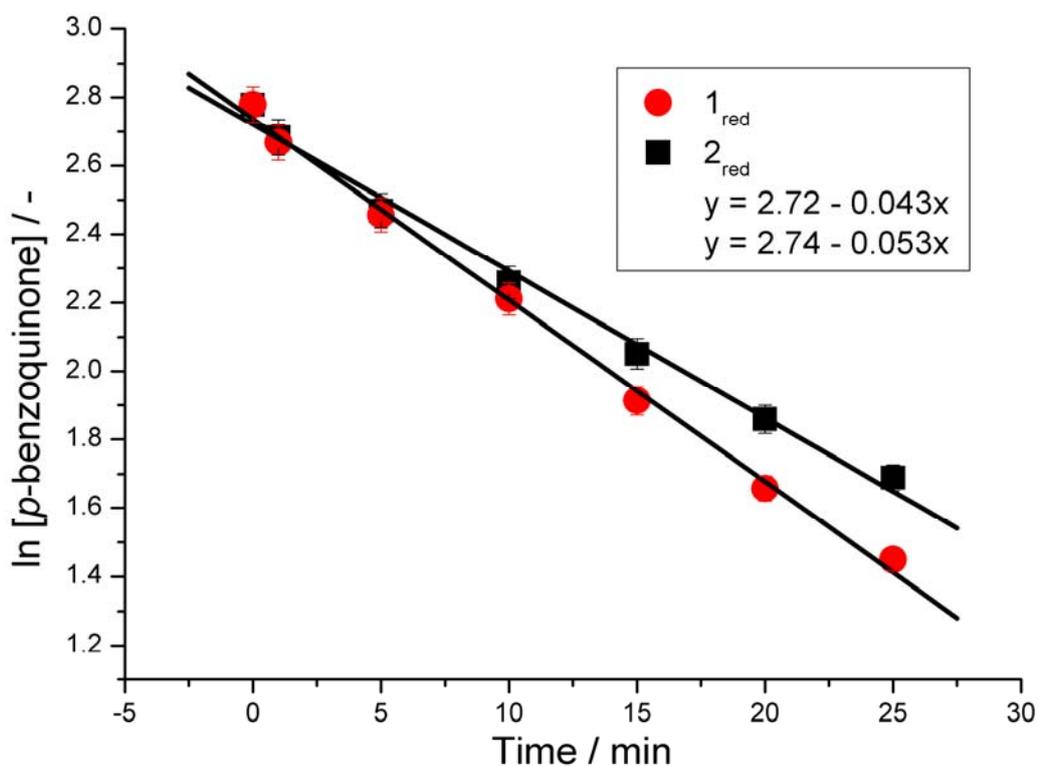


Figure S5: Graphical representation of the re-oxidation kinetics of 1_{red} and 2_{red} , respectively.

5. Redox titration of compound 2_{red} .

Compound 2_{red} : mass used = 20.40 mg

Oxidant = 0.01 M CeIV in 0.5 M of sulphuric acid solution

Theoretical amount of oxidant for 12 electron reduced species in mL: 10.66 mL

Experimental amount required: 10.48 mL

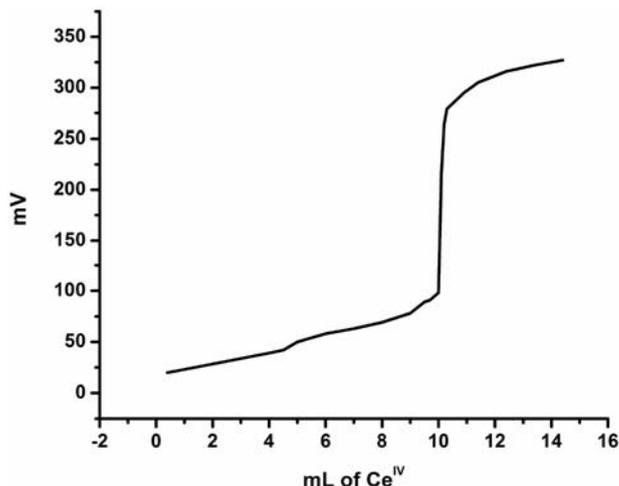


Figure S6: Graph of the redox titration of 2_{red} .

6. Crystallographic studies of $(\text{C}_4\text{H}_{10}\text{NO})_{40}[\text{W}_{72}\text{Mn}^{\text{III}}_{12}\text{O}_{268}\text{Ge}_7]\cdot 48\text{H}_2\text{O}\cdot 4(\text{C}_4\text{H}_9\text{NO})$ (2_{ox}) and $(\text{C}_4\text{H}_{10}\text{NO})_{40}\text{H}_{12}[\text{W}_{72}\text{Mn}^{\text{II}}_{12}\text{O}_{268}\text{Ge}_7]\cdot 48\text{H}_2\text{O}\cdot 5(\text{C}_6\text{H}_6\text{O}_6)$ (2_{red}).

Suitable single crystals were 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 Gemini Ultra diffractometer using $\text{MoK}\alpha$ radiation [$\lambda_{\text{MoK}\alpha} = 0.7103 \text{ \AA}$] for 2_{ox} and $\text{CuK}\alpha$ radiation [$\lambda_{\text{CuK}\alpha} = 1.5405 \text{ \AA}$] for 2_{red} . Structure solution and refinement were carried out with SHELXS-97^{S2} and SHELXL-97^{S3} via WinGX^{S4}. Corrections for incident and diffracted beam absorption effects were applied using analytical^{S5} methods.

Crystal data and structure refinement for $(\text{C}_4\text{H}_{10}\text{NO})_{40}[\text{W}_{72}\text{Mn}^{\text{III}}_{12}\text{O}_{268}\text{Ge}_7]\cdot 48\text{H}_2\text{O}\cdot 4(\text{C}_4\text{H}_9\text{NO})$ (2_{ox})
Mr = 23082.58 g mol⁻¹; tetrahedral shaped crystal: 0.18 × 0.16 × 0.16 mm³; T = 150(2) K. Cubic, space group $I-43d$, $a = b = c = 38.6584(15) \text{ \AA}$. $\alpha = \beta = \gamma = 90.00^\circ$. $V = 57774(4) \text{ \AA}^3$, $Z = 4$, $\rho = 2.654 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 14.966 \text{ mm}^{-1}$, $F(000) = 41744$, 8312 reflections measured of which 2112 are independent, 1087 refined parameters, $R1 = 0.0792$ and $wR2 = 0.1464$ (all data).

Crystal data and structure refinement for $(\text{C}_4\text{H}_{10}\text{NO})_{40}\text{H}_{12}[\text{W}_{72}\text{Mn}^{\text{II}}_{12}\text{O}_{268}\text{Ge}_7]\cdot 48\text{H}_2\text{O}\cdot 5(\text{C}_6\text{H}_6\text{O}_6)$ (2_{red})
Mr = 23094.68 g mol⁻¹; block crystal: 0.10 × 0.8 × 0.07 mm³; T = 150(2) K. Cubic, space group $I-43d$, $a = b = c = 39.2899(6) \text{ \AA}$. $\alpha = \beta = \gamma = 90.00^\circ$. $V = 60651.7(16) \text{ \AA}^3$, $Z = 4$, $\rho = 2.529 \text{ g cm}^{-3}$, $\mu(\text{Cu-K}\alpha) = 27.541 \text{ mm}^{-1}$, $F(000) = 41792$, 20967 reflections measured of which 4614 are independent, 240 refined parameters, $R1 = 0.1200$ and $wR2 = 0.3157$ (all data).

References:

(S1) Nsouli, N. H.; Bassil, B. S.; Dickman, M. H.; Kortz, U.; Keita, B.; Nadjjo, L. *Inorg. Chem.*, **2006**, *45*, 3858.

- (S2) Sheldrick, G. M. *Acta Crystallogr., Sect. A*, **1998**, *A46*, 467.
- (S3) Sheldrick, G. M. SHELXL-97. Program for Crystal structure analysis, University of Göttingen, Germany, 1997.
- (S4) Farrugia, L. J. *J. Appl. Cryst.*, **1999**, *32*, 837.
- (S5) Clark, R. C.; Reid, J. S. *Acta Cryst.*, **1995**, *A51*, 887.

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