

The Trinity of Polyoxometalates: Connecting {M₁₂} Keggin and {M₁₈} Dawson clusters to Triangles

Scott G. Mitchell,[†] Sumit Khanra,[†] Haralampos N. Miras, Thomas Boyd, De-Liang Long and Leroy Cronin*

WestCHEM, Department of Chemistry, University of Glasgow, Joseph Black Building, University Avenue, Glasgow, UK G12 8QQ. [†] These authors contributed equally to this publication.

E-mail: L.Cronin@chem.gla.ac.uk; Web : www.croninlab.com;

Fax: +44 141 330 4888; Tel: +44 141 330 6650

Supplementary Information

Experimental

Synthesis of Rb₁₁K₆[Rb \subset (GeW₁₀Mn₂O₃₈)₃] \cdot 39H₂O (**1**): K₈[γ -GeW₁₀O₃₆] \cdot 6H₂O (1.5 g, 0.5 mmol) was dissolved in 15 mL water and dropwise con. HNO₃ was added to adjust the pH around 3.8-4.0. In a separate flask Mn(OAc)₂ \cdot 4H₂O (0.2 g, 0.8 mmol) was dissolved in 5mL water and slowly added to the 15mL water solution containing K₈[γ -GeW₁₀O₃₆] \cdot 6H₂O. It was stirred for 10 minutes and the pH of the resulting solution was maintained at ~ 4.5. Then KMnO₄ (0.04 g, 0.2 mmol) was also dissolved in 5 mL water and was dropwise added to the previous solution. It was stirred for a further 10 minutes whereby the solution turned deep brown. RbCl (0.5g) was added to the resulting solution and stirred for a further 10 minutes. The solution was filtered and the clear pink filtrate was kept for crystallization. Well-formed pink rectangular crystals appeared in solution after one week. The crystalline product was filtered and dried in air. Yield: 0.203 g (33 % based on W). Characteristic IR-bands: 3388(b), 1619(s), 1097(s), 1063(w), 948(s), 897(s), 792(s), 490(s). Elemental analysis for the dehydrated material, Rb₁₂K₆O₁₁₄W₃₀Mn₆Ge₃, MW = 9146.8 gmol⁻¹ (solvated waters lost). Calculated values (found values in brackets): Mn: 3.60 (3.53), W: 60.30 (60.87), K 2.56(2.49). TGA water loss from 25 to 300°C, experimental (found): 6.23 (6.16 %).

Synthesis of Na₂₁K₂[K \subset (P₂W₁₆Co₂O₆₀)₃] \cdot 73H₂O (**2**): K₆[α -P₂W₁₈O₆₂] \cdot 14(H₂O) (10.38 g, 2.14 mmol) was dissolved in 40 mL H₂O and in a separate flask

tris(hydroxymethyl)aminomethane (6.05 g, 0.05 mmol) was dissolved in 25 mL water. When all solid products had been completely dissolved and both solutions were crisp and clear, the TRIS BASE solution was poured into the POM solution and allowed to stir for exactly 30 min. Meanwhile, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (6.75 g, 0.05 mmol) was dissolved in 50 mL of water. After the stirring period, the TM solution was added to the POM-TRIS solution to precipitate out a thick, deep purple precipitate which was allowed to stir for a further 5 min. The mixture was centrifuged in order to separate the precipitate which was subsequently dried overnight *in vacuo*. The weight of this crude product was 10.32 g. Recrystallization of the crude product was achieved by dissolving a 0.5 g sample in a hot aqueous 1M NaCl solution and adjusting to pH 7.0 with 1M HCl. Filtration was required to remove a small amount of undissolved crude material, resulting in a striking deep maroon-coloured solution. Well-formed dark red rectangular crystals appear in solution after 24 hours and were separated by Büchner filtration. Yield: 0.41 g (82 % based on W). Characteristic IR-bands: 3453(b), 1610(s), 1210(w), 1063(s), 944(s), 958(s), 878(s), 796(s), 739(s), 516(w). Elemental analysis for the dehydrated material, $\text{K}_3\text{Na}_{21}\text{O}_{180}\text{W}_{48}\text{Co}_6\text{P}_2$, MW = 12719.9 g mol^{-1} (solvated waters lost). Calculated values (found values in brackets): Co: 2.78 (3.02), W: 69.37 (69.5), K: 0.92 (0.64), Na: 3.80 (3.64) %. TGA water loss from 25 to 300°C, experimental (found): 10.28 (10.14 %).

Crystallographic data:

Crystal data for **1**: orthorhombic, *Cmcm*, $a = 24.3052(2)$ Å, $b = 34.8021(14)$ Å, $c = 18.1552(4)$ Å, $V = 15357.0(7)$ Å³, $Z = 4$, $T = 150$ K, $\rho_{\text{calcd}} = 4.268$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 27.475$ mm⁻¹, 48142 reflections measured, 7520 unique ($R_{\text{int}} = 0.0692$) which were used in all calculations. Final $R1 = 0.0477$ and $wR2 = 0.1137$ (all data).

Compound **2**: triclinic, *P*-1, $a = 17.2294(2)$ Å, $b = 25.6034(4)$ Å, $c = 28.8610(5)$ Å, $\alpha = 79.469(2)$, $\beta = 87.590(2)$, $\gamma = 83.489(2)$ °, $V = 12433.3(3)$ Å³, $Z = 2$, $T = 150$ K, $\rho_{\text{calcd}} = 3.782$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 22.729$ mm⁻¹, 118924 reflections measured, 38601 unique ($R_{\text{int}} = 0.0912$) which were used in all calculations; structure solution and refinement as done using WINGX.⁸ Final $R1 = 0.0630$ and $wR2 = 0.1543$ (all data).

Instrumentation:

Crystallographic data for both **1** and **2** was measured on an Oxford Diffraction Gemini Ultra with a CrysAlis CCD detector [$\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$]. Structure solution and refinement were performed by using SHELXTL *via* the CrysAlis software package. Atomic Absorption Data: Perkin-Elmer 1100B Atomic Absorption Spectrophotometer. K / Na Data: Corning Flame Photometer 410. TGA Data: TA Q500 instrument under a nitrogen atmosphere. The initial heating range was from room temperature to 300°C at 5.00° per min followed by a second range from 300° to 1000°C at 10.00° per min. Infrared spectra were recorded on samples dispersed in a KBr disk on a Jasco FT/IR-4100.

Electrochemistry.

Voltammograms were obtained using a Voltalab model GPZ 301 electro analysis system. The standard three-electrode arrangement was employed with a Pt mesh auxiliary electrode, 3 mm glassy carbon working electrode, and Ag/AgCl reference electrode. All potentials are quoted relative to the Ag/AgCl reference electrode. The glassy carbon working electrodes (diameter 3 mm) were polished with alumina (3 μm) on polishing pads, rinsed with distilled water and sonicated in H₂O and then acetone solution before each experiment. The cell was purged with Ar for at least 10 min before each experiment.

Electrochemistry Discussion

The redox behavior of the compounds **1** and **2** were studied in aqueous solution. Fig. S1 and Fig. S2 show the main characteristic peaks associated with W centered redox couples in the region -0.900 to +1.000 V of potential values vs. Ag/AgCl at a scan rate of 100 mV s⁻¹. The form of the diagram remained identical no matter the scanning potential direction indicating that the phenomena observed in one domain had a negligible influence on those in the other domain. At the aforementioned scan rate and scanning towards the negative region of potential values, the reduction of W centers for compound **1** occurs through two separated steps, with the corresponding $E_{1/2}$ peak potentials located respectively at -0.161 for the electrochemically irreversible process and at -0.395 V for the quasi reversible redox couple (*vs.* Ag/AgCl) while for compound **2** were observed

four quasi reversible redox processes located at $E_{1/2}$ peak potentials of -0.105, -0.260, -0.325 and -0.575 V respectively. In both cases, the observed redox couples revealed to be slightly shifted towards the region of positive potential values indicative of proton confined reduction processes. Additionally, it is well known for the electrochemical behavior of the majority of the polyoxometalates that the number and the characteristics of these W-waves depend on the pH and on the buffering strength of the electrolyte.¹⁻³ The cyclic voltammograms of both compounds at different scan rates are presented in Fig. S3 and S4 respectively. The peak currents were proportional to the square root of the scan rate, indicating that the redox processes are diffusion-controlled in the 50 – 400 mV/sec region of scan rate.

At the positive region of potential values two ill-defined irreversible oxidation peaks observed for compound **1** at +1.448 and +1.886. In agreement with expectations, there is no process attributable to any presence of Mn^{II} species. Various cases were described in the literature for the oxidation pathways of Mn centers within POMs, with a variety of situations, including important differences in potential locations⁴. The present preliminary results shows that, upon driving the potential to the solvent window the Mn⁴⁺ state is obtained with a peak potential located at +1.448 V, whilst a further oxidation process could potentially be attributed to the formation of Mn⁵⁺ state at +1.886 V (although this assignment is tentative due to the presence of the solvent window). Further studies on catalytic processes are under way and we will be reported shortly.

- (1) L. H. Bi, E.-B. Wang, J. Peng, R. D. Huang, L. Xu and C. W. Hu, *Inorg. Chem.*, 2000, **39**, 671.
- (2) I. M. Mbomekalle, B. Keita, L. Nadjo, P. Berthet, W. A. Neiwert, C. L. Hill, M. D. Ritorto and T. M. Anderson, *Dalton. Trans.*, 2003, 2646.
- (3) a) B. Keita, Y.W. Lu, L. Nadjo and R. Contant, *Eur. J. Inorg. Chem.*, 2000, 567; b) M. Sadakane, E. Steckhan, *Acta Chem. Scand.*, 1999, **53**, 837.
- (3) a) J. Liw, F. Ortega, P. Sethuraman, D. E. Katsoulis, C. E. Costello and M. T. Pope, *J. Chem. Soc. Dalton Trans.*, 1992, 1901; b) I. M. Mbomekalle, B. Keita, M. Nierlich, U. Kortz, P. Berthet and L. Nadjo, *Inorg. Chem.*, 2003, **42**, 5143; c) D. Jabbour, B. Keita, I. M. Mbomekalle, L. Nadjo and U. Kortz, *Eur. J. Inorg. Chem.*, 2004, 2036.

(4) a) M. Bosing, A. Noh, I. Loose and B. Krebs, *J. Am. Chem. Soc.*, 1998, **120**, 7252; b) B. Keita, I.M. Mbomekalle, Y.W. Lu, L. Nadjo, P. Berthet, T.M. Anderson and C.L. Hill, *Eur. J. Inorg. Chem.*, 2004, 3462.

(5) a) S. J. Dong, X. D. Xi and M. J. Tian, *Electroanal. Chem.*, 1995, **385**, 227; b) B. Keita and L. Nadjo, *J. Electroanal. Chem.*, 1987, **227**, 77; c) B. Keita, A. Belhouari, L. Nadjo and R. Contant, *J. Electroanal. Chem.*, 1988, **247**, 157.

(6) A. Belhouari, B. Keita, L. Nadjo, and R. Contant, *New J. Chem.*, 1998, **22**, 83.

(7) B. S. Bassil, U. Kortz, A. S. Tigan, J. M. Clemente-Juan, B. Keita, P. de Oliveira, and L. Nadjo, *Inorg. Chem.*, 2005, **44**, 9360.

(8) L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

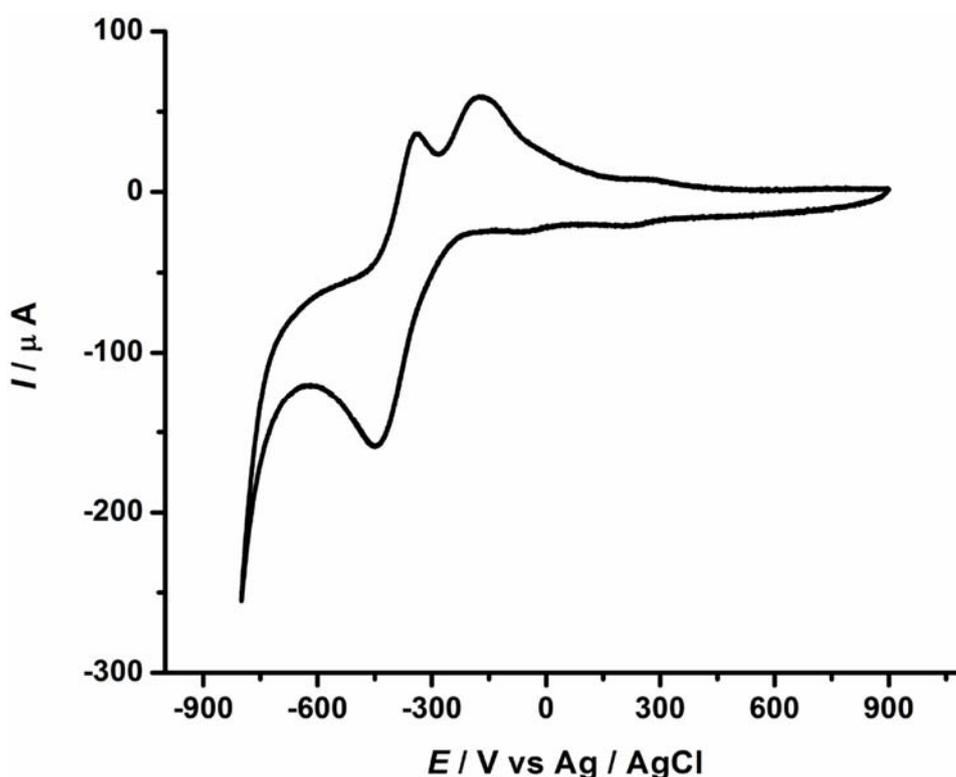


Fig S1. Cyclic voltammograms of **1** (2×10^{-3} M) in aqueous 0.2M Na₂SO₄ of 1M CH₃COOH/CH₃COONa buffer solution. The scan rate was 100 mV s⁻¹, the working electrode was glassy carbon (3 mm) and the reference electrode was Ag/AgCl.

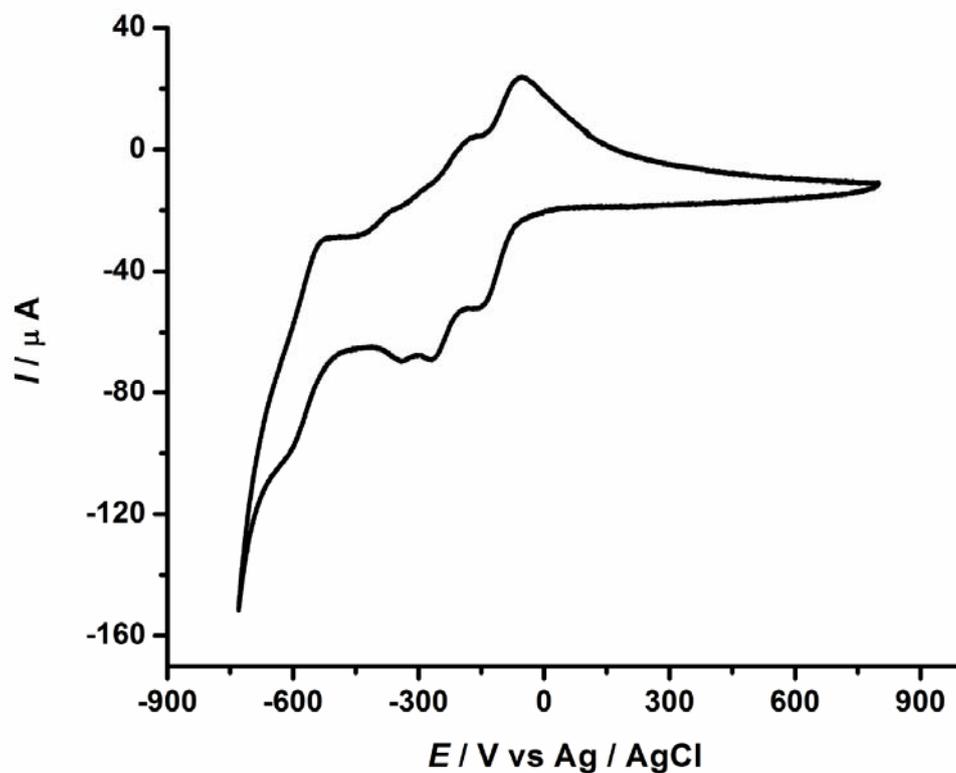


Fig S2. Cyclic voltammograms of compound **2** (2×10^{-3} M) in aqueous 0.2M Na₂SO₄ of 1 M CH₃COOH/CH₃COONa buffer solution. The scan rate was 100 mV s⁻¹, the working electrode was glassy carbon (3 mm) and the reference electrode was Ag/AgCl.

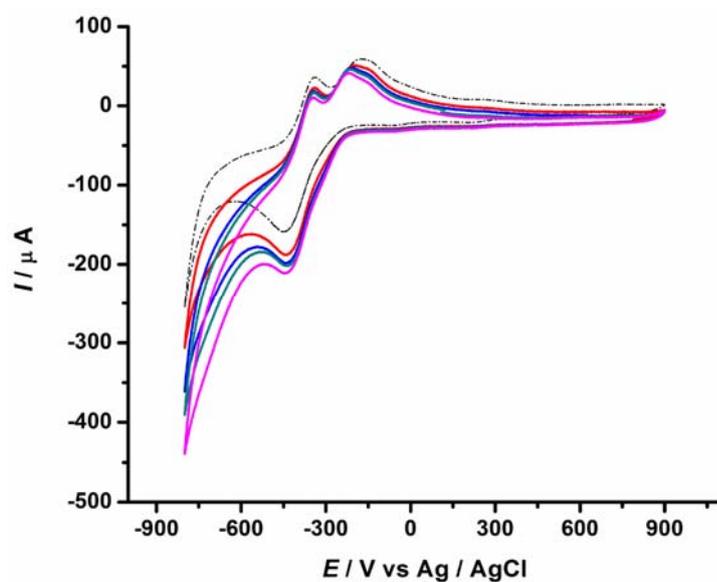


Fig S3 CVs of **1** addressing just the first redox processes of the W centers, in the absence of NO_2^- (dotted line) and after addition of specific amount of NO_2^- ; C = a) 1, b) 5, c) 7, and d) 10 mM.

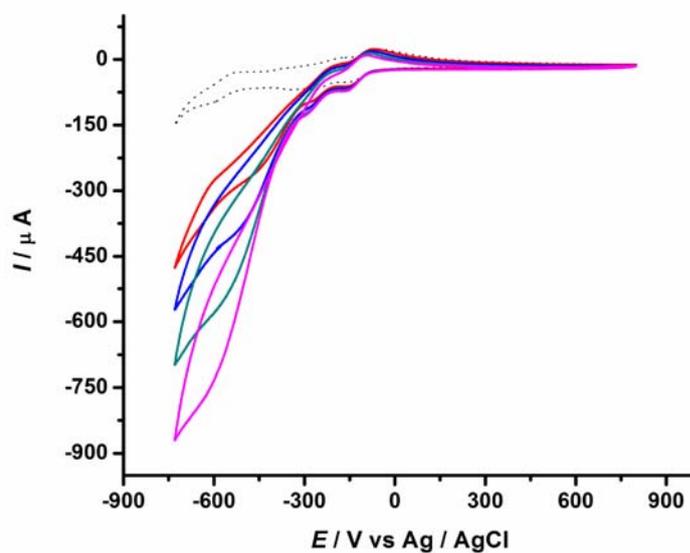


Fig. S4 CVs of **2** addressing just the first redox processes of the W centers, in the absence of NO_2^- (dotted line) and after addition of specific amount of NO_2^- ; C = a) 1, b) 5, c) 7, and d) 10 mM.

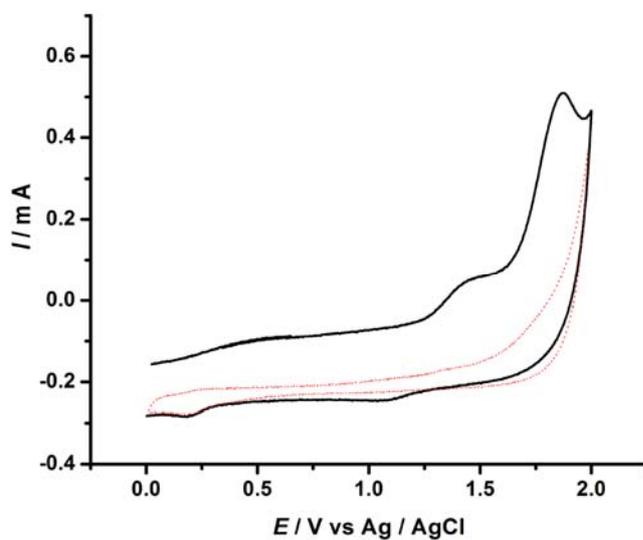


Fig. S5 Cyclic voltammograms of compound **1** (2×10^{-3} M) restricted to Mn-centred redox processes in aqueous 0.2 M Na_2SO_4 of 1 M $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ buffer solution. The potential is scanned initially in the negative direction and the positive going scan is extended up to electrolyte discharge limit; dotted line: background current; full line curve: CV of Mn^{III} centers. The scan rate was 100 mV s^{-1} , the working electrode was glassy carbon (3 mm) and the reference electrode was Ag/AgCl.