COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Controlling 'One-Pot' Transformations in the Assembly of Polyoxometalate Clusters: $\{Mo_{11}V_7\}$, $\{Mo_{17}V_8\}$ and $\{Mo_{72}V_{30}\}$

Haralampos N. Miras,[a] *Maria N. Corella Ochoa,*[a] *De-Liang Long*[a] *and Leroy Cronin*[a*]

WestCHEM, Department of Chemistry, The University of Glasgow, Glasgow, G12 8QQ, U.K.

L.Cronin@chem.gla.ac.uk

Redox Titrations

Compound **1** $(NH_4)_{10}[Mo^{VI}_{11}V^{V}_{5}V^{IV}_{2}O_{52}(\mu_9\text{-}SO_3)(Mo^{VI}_{6}V^{V}O_{22})]\cdot 14H_2O$, mass used =120 mg
Oxidant = 0.01 M Ce^{IV} in 0.5 M of sulphuric acid solution
Theoretical amount of oxidant for 2 electron reduced species in mL: 3.18
Experimental amount used in mL: 3.35

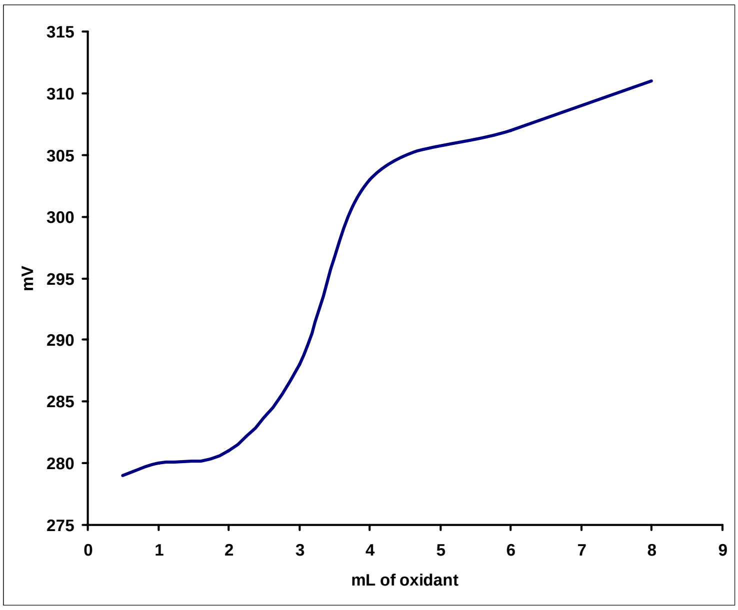

Fig. S1. Redox titration curve of Compound **1**

ESI-MS

The distribution envelope observed for **1**, is the result of the contribution of two species with different extend of protonation. More specifically, the first envelope can be assigned to the isolated species with three reduced vanadium centres, $\{(Pr_4N)_7[Mo^{VI}{}_{11}V^{V}{}_4V^{IV}{}_3O_{52}(\mu_9\text{-}SO_3)(Mo^{VI}{}_6V^{V}O_{22})](NH_4)_2(CH_3CN)\}^{2-}$ which gives an envelope centred at m/z *ca*. 2342.1, while the second envelope can be assigned to the singly protonated analogue with four reduced vanadium centres, $\{(Pr_4N)_7[HMo^{VI}{}_{11}V^{V}{}_3V^{IV}{}_4O_{52}(\mu_9\text{-}SO_3)(Mo^{VI}{}_6V^{V}O_{22})](NH_4)_2(CH_3CN)\}^{2-}$ which gives an envelope centred at m/z *ca*. 2342.6. During the course of the ESI-MS studies and due to the low intensity of the observed envelope for compound **1**, was not possible the graphic representation of two well resolved species. For the above reason, only the profile of the fitted envelopes is shown, highlighted red for $\{(Pr_4N)_7[Mo^{VI}{}_{11}V^{V}{}_4V^{IV}{}_3O_{52}(\mu_9\text{-}SO_3)(Mo^{VI}{}_6V^{V}O_{22})](NH_4)_2(CH_3CN)\}^{2-}$ and blue for $\{(Pr_4N)_7[HMo^{VI}{}_{11}V^{V}{}_3V^{IV}{}_4O_{52}(\mu_9\text{-}SO_3)(Mo^{VI}{}_6V^{V}O_{22})](NH_4)_2(CH_3CN)\}^{2-}$ respectively.

Infrared spectroscopy

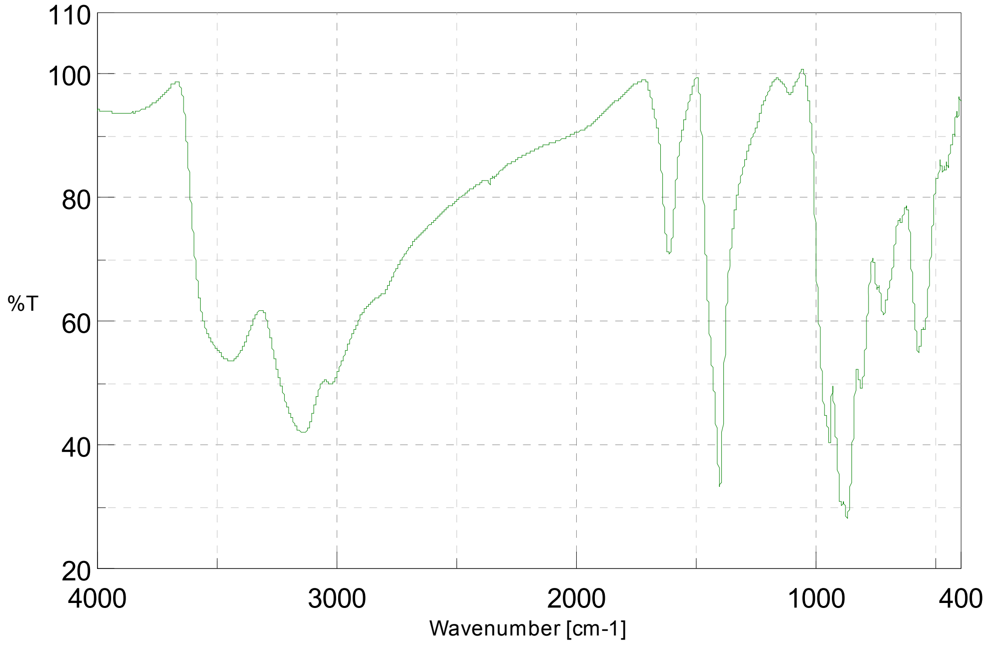

Fig. S1: Infrared spectrum of compound **1**.

Vis spectroscopy

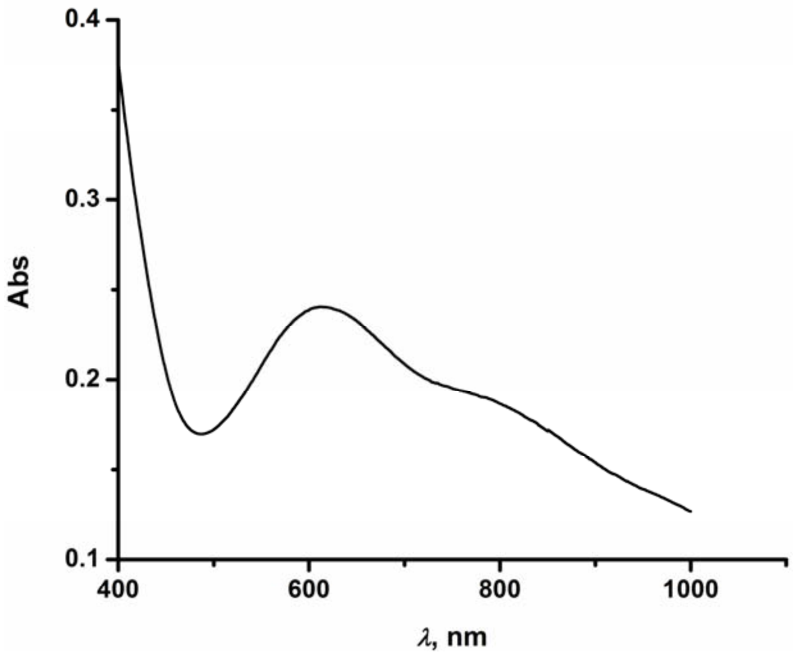

Fig. S2: Visible spectrum of compound **1**. The bands can be assigned to ML and IV charge transfer.

Thermogravimetric analysis

Weight loss between 25 – 200 °C can be assigned to approx. 14 water molecules in the crystal lattice, while between 200 – 600 °C, can be assigned to removal of 10 NH_4^+ cations as NH_3 molecules which is overlapping with the removal of SO_3^{2-} as gas SO_2), the remaining percentage (600 – 800 °C) can be assigned to the MoO_3 based phase transition.

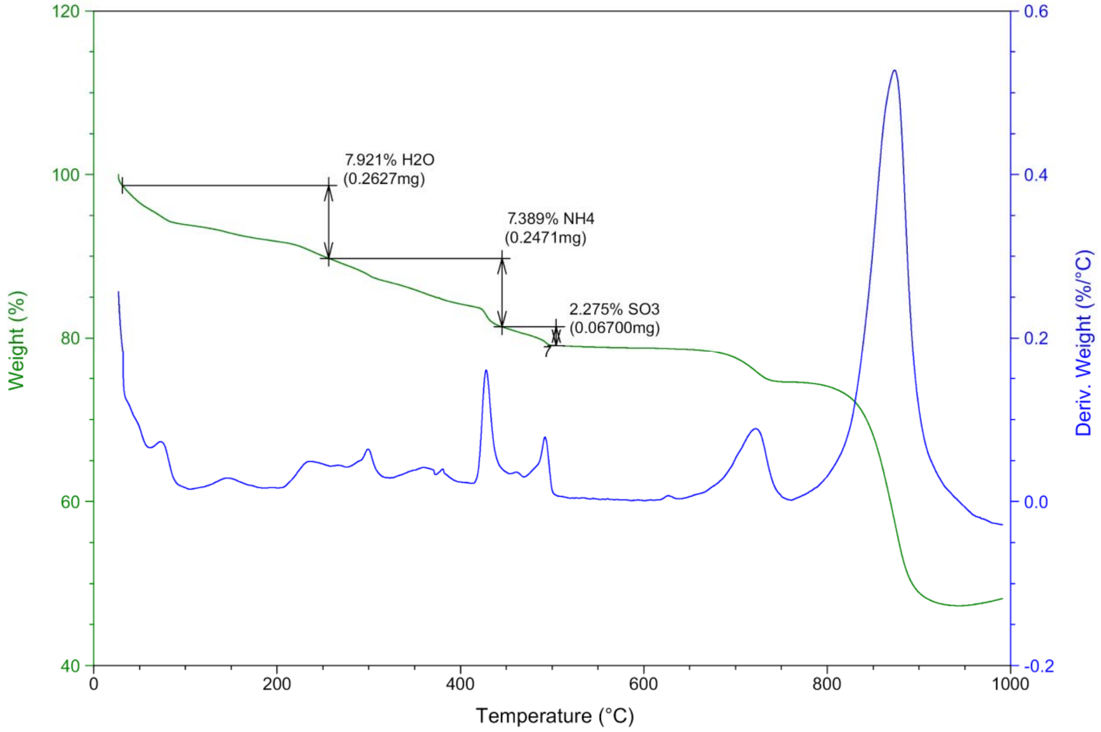

Fig. S3: Thermal gravimetric analysis of **1**, showing the loss of solvent content (RT - 180 °C) as well as of the NH_4^+ and SO_3^{2-} as SO_2 (200 - 600 °C) followed by the decomposition of the compound at temperature beyond 700°C. A phase transition is taking place at higher temperatures (m.p MoO_3 = 795 °C).

Synthesis of {$Mo_{72}V_{30}(SO_4)_{12}$}

Sodium molybdate dihydrate (0.60 g, 2.4 mmol) was dissolved in an HCl solution (37% HCl in water, 1:4 v/v, 25 mL, pH ~ 0), and then the solid sodium metavanadate (0.40 g, 3.2 mmol) was added in one portion to the solution under stirring. Upon dissolution of the $NaVO_3$ the solution turns to light yellow colour and the pH changed to 0.7. Then, solid triethanolamine (1.3 g, 8.7 mmol) added followed by Na_2SO_3 (9.33 g, 74.0 mmol) under magnetic stirring. A series of colour changes ensued, beginning from a green colour at pH 0.7, then light blue colour at pH 1.5, followed by a dark green colour at pH 2 and ending with a deep violet solution at pH 3.5. The Keplerate compound could be synthesized within the pH range of 2.5 – 4.5. The solution was filtered off and then treated with KCl (0.65 g, 8.72 mmol). The filtrate left in an open vessel (a 100 mL beaker) at room temperature (~25 °C) for 5 days, during which time dark purple crystals suitable for X-ray structure analysis were obtained. Yield: 0.20 g (30.4 % based on mo). The unit cell determination revealed dimensions identical to the previously reported compound with formula, $Na_8K_{24}Mo_{72}V_{32}S_{12}O_{538}H_{412}$ ({$Mo_{72}V_{30}$}). IR (KBr): 1625 (H_2O), 1201 (w), 1129 (w), 1049 (w), 966 v(Mo–O_t)/v(V–O_t)), 795 (vs), 631 (m).