

Solution Discovery and Solid State Characterisation of a Heterometallic Polyoxometalate $\{\text{Mo}_{11}\text{V}_7\}$: $[\text{Mo}^{\text{VI}}_{11}\text{V}^{\text{V}}_5\text{V}^{\text{IV}}_2\text{O}_{52}(\mu_9\text{-SO}_3)]^{7-}$

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Experimental and Analytical Data

$(\text{NH}_4)_6\text{Mo}_7^{\text{VI}}\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.60 g, 0.4 mmol) was dissolved in an HCl solution (37 % HCl in water, 1:4 v/v, 25 ml, pH ~ 0) and then solid NH_4VO_3 (0.60 g, 5.1 mmol) was added in one portion to the solution under stirring. Upon dissolution of NH_4VO_3 the light red colour of the solution changed to light green and the pH changed to 0.7. Then, solid $(\text{NH}_4)_2\text{SO}_3$ (6.20 g, 46.2 mmol) was gradually added to it, under magnetic stirring. A series of colour changes ensued beginning from green colour at pH = 0.7, then light blue at pH = 1.5, followed by the formation of a deep violet (pH = 3) solution. The compound **1** can be synthesized within the pH range 2.5 – 5, although the highest yield has been obtained at a pH value of 3. The solution was filtered off and the filtrate left in an open vessel (a 250 ml beaker) at room temperature (~25 °C) for 3 days, during which deep green crystals suitable for X-ray structure analysis, were obtained. Yield: 0.95 g (21 % based on Mo). Elemental analysis calcd for: $\text{H}_{52}\text{Mo}_{11}\text{N}_7\text{O}_{67}\text{SV}_7$: H: 1.97, N: 3.68, S: 1.20, Mo: 39.58, V: 13.37; found: H: 1.88, N: 3.82, S: 1.22, Mo: 39.48, V: 13.40. IR bands (KBr): cm^{-1} 3400 (br) [$\nu(\text{O-H})$ from H_2O], 1401s [$\nu(\text{NH}_4)$], 1037 [$\nu(\text{SO}_3^{2-})$], 970 (sh) [$\nu(\text{V=O})$], 944 (s) [$\nu(\text{Mo=O})$], 886 (s) [$\nu(\text{SO}_3^{2-})$], 861 (s) [$\nu(\text{SO}_3^{2-})$], 817 (vs) [$\nu(\text{SO}_3^{2-})$]; UV-Vis (H_2O): 243(21106), 587(532) $\text{nm}(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$; UV-Vis (reflectance): 249(19987); TGA: percentage weight loss (temperature (°C)): 8.10 (25 - 200, assigned to H_2O), 4.92 (200 - 420 °C, assigned to removal of NH_4^+ cations as NH_3 molecules), 2.69 (420 - 510, assigned to removal of SO_3^{2-} as gas SO_2). -ve (negative) mode cryospray ionisation mass spectrometry (CSIMS) at 20°C in CH_3CN $\{(\text{Pr}_4\text{N})_4[\text{H}_{1-n}\text{V}_{5+n}^{\text{V}}\text{V}_{2-n}^{\text{IV}}\text{Mo}_{11}\text{O}_{52}(\text{SO}_3)]\}^{2-}$ where $n = 1$ gives an envelope centred at m/z ca. 1534.5 and where $n = 0$ an envelope centred at m/z ca. 1635.0 as confirmed by isotopic fitting of the envelopes to the bifurcated isotopic distribution shown between 1522 and 1547 mass units.

§ Crystal data for **1**: $(\text{NH}_4)_7[\text{Mo}^{\text{VI}}_{11}\text{V}^{\text{V}}_5\text{V}^{\text{IV}}_2\text{O}_{52}(\text{SO}_3)]\cdot 12\text{H}_2\text{O}$: $\text{H}_{52}\text{Mo}_{11}\text{N}_7\text{O}_{67}\text{SV}_7$, $M_r = 2666.47$, monoclinic, space $P2_1/m$, $a = 12.140(2)$, $b = 19.148(2)$, $c = 13.492(2)$ Å, $V = 3020.1(1)$ Å³, $Z = 2$, $\rho_{\text{calc}} = 2.898 \text{ Mg cm}^{-3}$, $T = 150(2)$ K. $R1(\text{final}) = 0.0301$, $wR2 = 0.0846$. Further details on the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (+49) 7247-808-132, email: crysdata@fiz-karlsruhe.de).

Redox Titrations

- (1) Compound **1** $(\text{NH}_4)_7\text{Mo}_{11}\text{V}_5\text{V}^{\text{IV}}_2(\text{SO}_3)\text{O}_{52}\cdot 12\text{H}_2\text{O}$, mass used =47 mg
Oxidant = 0.01 M Ce^{IV} in 0.5 M of sulphuric acid solution
Theoretical amount of oxidant for *two electron* reduced species in mL: 3.72
Experimental amount used in mL: 3.35

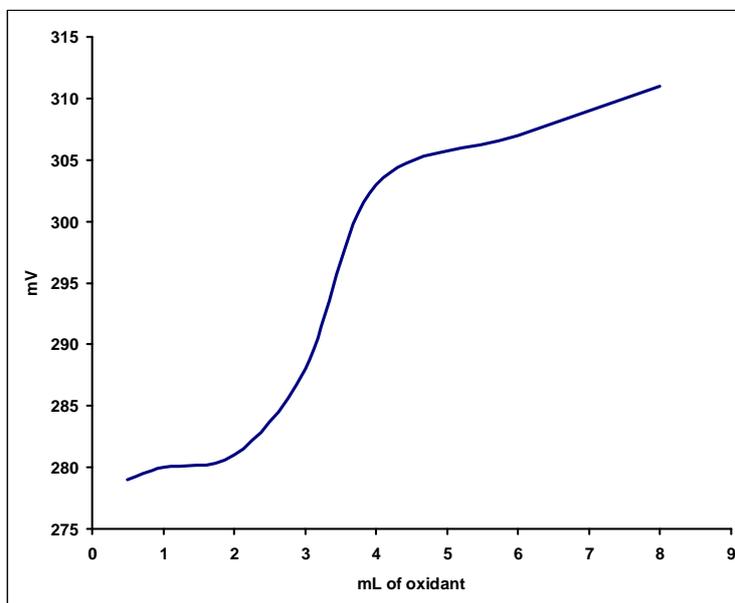


Figure S1. Redox titration curve of Compound **1**

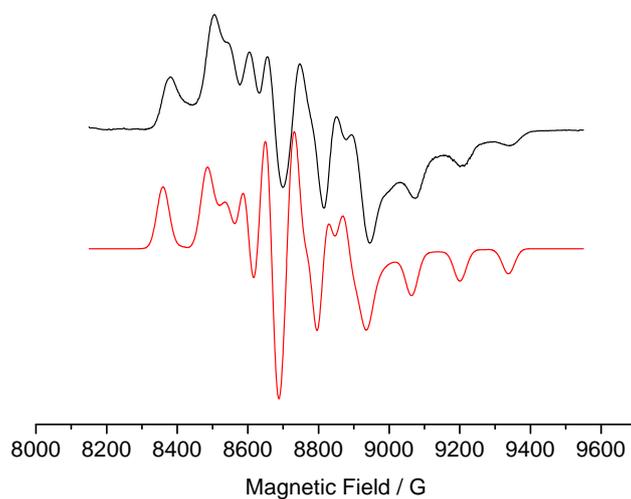


Figure S2. Solid state K-band EPR spectrum of **1** at 10 K (black) and simulation (red).

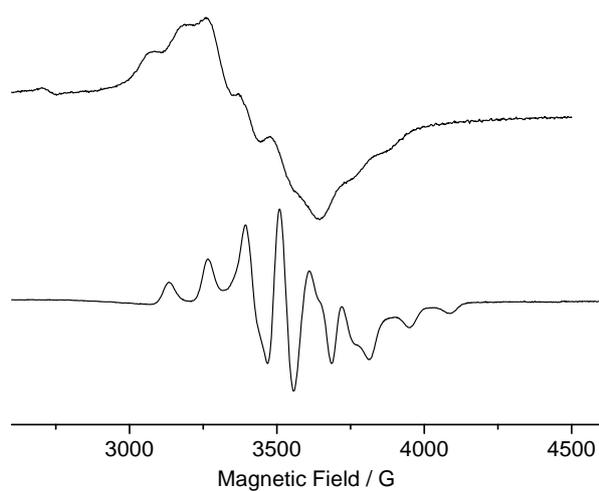


Figure S3. Solid state EPR spectra of **1** at 300 K (top) and 10 (bottom)

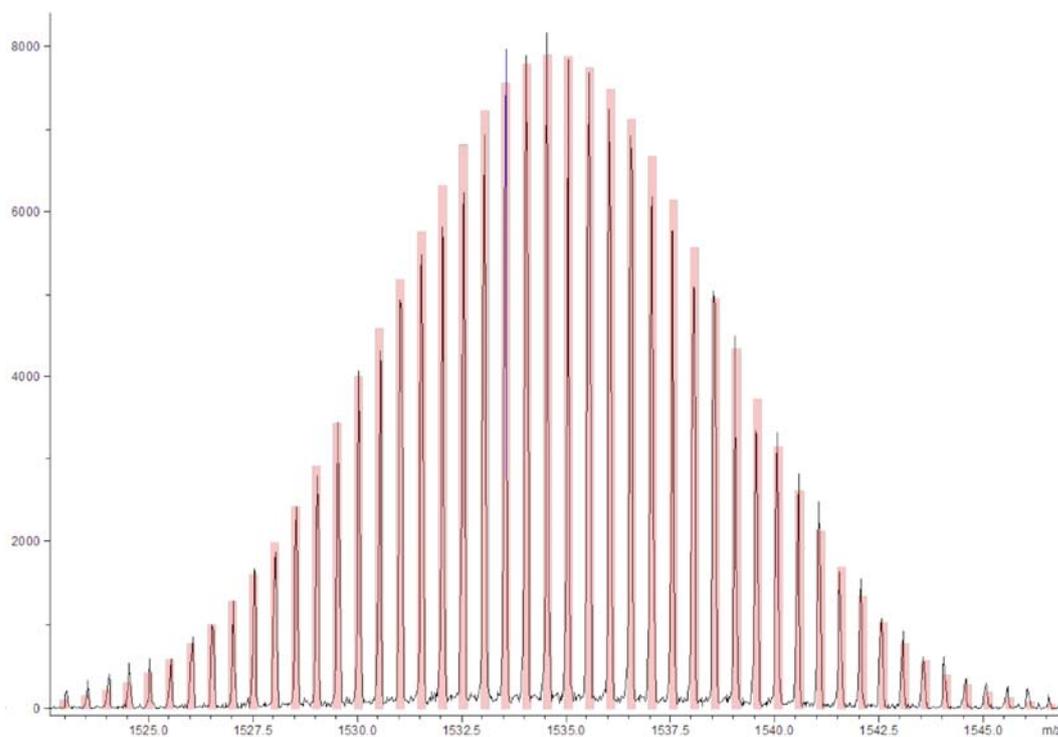


Figure S4. Negative ion mass spectrum in acetonitrile solution of $\{(\text{Pr}_4\text{N})_4[\text{H}_{1-n}\text{V}_{5+n}^{\text{V}}\text{V}_{2-n}^{\text{IV}}\text{Mo}_{11}\text{O}_{52}(\text{SO}_3)]\}^{2-}$. Two envelopes can be seen where $n = 1$ (with only one vanadium ion in oxidation state IV) giving an envelope centred at m/z ca. 1534.5, and where $n = 0$ (with 2 vanadium ions in oxidation state IV, requiring one proton) giving an envelope centred at m/z ca. 1535.0. Black line: experimental data, Red bars: simulation of isotope pattern.