



Supporting Information

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Design of A Polyoxometalate Single Molecule Magnet Using Lacunary

Building Blocks: $\{[\text{XW}_9\text{O}_{34}]_2[\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2\text{O}_4(\text{H}_2\text{O})_4]\}^{11-}$

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Experimental data:

All chemicals were of analytical grade and used as supplied. Synthesis of $\text{Na}_4\text{K}_1(\text{C}_4\text{H}_{10}\text{NO})_7[\text{Ge}_2\text{W}_{18}\text{O}_{72}\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2] \cdot 15\text{H}_2\text{O}$ **1**: Morpholine (56.25 ml, 0.637 M) was added to 2.5 L of 1M NaCl, and the solution acidified to pH 7.9 using 4.5M H_2SO_4 . To this solution was added $\text{K}_8\text{GeW}_{10}\text{O}_{36} \cdot 6\text{H}_2\text{O}$ (3.635 g, 1.4 mmol) followed by the addition of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (0.845 g, 0.5 mmol) resulting in a clear bright yellow solution. The pH of the solution was then finely adjusted to exactly 7.7 using dilute sulphuric acid. The reaction mixture was then left to crystallize by slow evaporation. Over a 1 month period the yellow solution gradually deepened to a dark brown colour, indicating the partial oxidation of the Mn^{II} to Mn^{III} . After the initial 1 month, dark brown needles crystallize rapidly over the course of 3 days. Yield = (900 mg, 15 μmol , 19.19% based on W). Elemental analysis for $\text{Na}_4\text{K}_1(\text{C}_4\text{H}_{10}\text{NO})_7[\text{Ge}_2\text{W}_{18}\text{O}_{72}\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2] \cdot 15\text{H}_2\text{O}$, $\text{C}_{28}\text{H}_{100}\text{Ge}_2\text{K}_1\text{Mn}_6\text{N}_7\text{Na}_4\text{O}_{94}\text{W}_{18}$, MW = 5954 g mol⁻¹, calcd. (found) %: C 5.65 (5.35), H 1.69 (1.32), N 1.65 (1.53), Na 1.54 (1.67), K 0.66 (0.58). FTIR (KBr pellet), cm⁻¹: 3426 (br), 2739 (sh), 1634 (m), 1569 (m), 1445 (m), 1384 (wk), 1305 (wk), 1226 (wk), 1192 (wk), 1090 (m), 1041 (wk), 946 (m), 875 (s), 788 (m), 698 (m), 611 (m), 566 (wk), 512 (wk), 453 (wk).

2: $(\text{C}_4\text{H}_{10}\text{NO})_{12}[\text{Si}_2\text{W}_{18}\text{O}_{72}\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2] \cdot 15\text{H}_2\text{O}$. Morpholine (0.45 ml, 5.16 mmol) was added to 20ml of 1M NaCl and the pH adjusted to 7.6 using 4.5M H_2SO_4 . The solution was then split into two equal portions. $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (0.0338 g, 0.2 mmol) was added to one portion yielding solution (A), and $\text{K}_8\text{SiW}_{10}\text{O}_{36} \cdot 12\text{H}_2\text{O}$ (0.1486 g, 0.5 mmol) added to the other and its pH lowered to 7.3 yielding solution (B). Solution (A) was then added to solution (B), with a final pH of 7.2. The resulting yellow reaction mixture was then heated to 50°C for 10 minutes then cooled to room temperature. Over a 1 month period the yellow solution gradually deepened to a dark brown colour, indicating the partial oxidation of the Mn^{II} to Mn^{III} , with brown plate crystals forming over a 3 month period. Yield = (85 mg, 13.7 μmol , 49.55 %) Elemental analysis for $(\text{C}_4\text{H}_{10}\text{NO})_{12}[\text{Si}_2\text{W}_{18}\text{O}_{72}\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2] \cdot 15\text{H}_2\text{O}$, $\text{C}_{48}\text{H}_{150}\text{Mn}_6\text{N}_{12}\text{O}_{99}\text{W}_{18}$, MW = 6174 g / mol⁻¹ calcd (found) %: C 9.34 (9.97), H 2.45 (2.14), N 2.72 (2.91), FTIR (KBr pellet), cm⁻¹: 3422 (br), 3062 (wk), 2935 (wk), 2721 (wk), 1611 (m), 1450 (wk), 1311 (wk), 1101 (wk), 1045 (wk), 947 (wk), 894 (m), 771 (wk), 703 (m), 620 (wk), 515 (wk).

Crystallographic data and structure refinements for $\{[\text{GeW}_9\text{O}_{34}]_2[\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2\text{O}_4(\text{H}_2\text{O})_4][\text{Na}_4\text{K}_1(\text{C}_4\text{H}_{10}\text{NO})_7]\} \cdot 15\text{H}_2\text{O}$ **1**: $\text{C}_{28}\text{H}_{100}\text{Ge}_2\text{K}_1\text{Mn}_6\text{N}_7\text{Na}_4\text{O}_{94}\text{W}_{18}$, MW = 5954 g / mol⁻¹; brown rod crystal: $0.2 \times 0.1 \times 0.04 \text{ mm}^3$. Triclinic, space group *P*-1, $a = 11.9515(5)$, $b = 16.3463(8)$, $c = 16.8912(8) \text{ \AA}$, $\alpha = 108.749(3)$, $\beta = 99.702(2)$, $\gamma = 105.202(2)$ $V = 2897.8(2) \text{ \AA}^3$, $Z = 1$, $\rho = 3.412 \text{ g cm}^{-3}$, $\lambda (\text{MoK}\alpha) = 19.076 \text{ mm}^{-1}$, $F(000) = 2678$, 48405 reflections measured, 11382 unique ($R_{\text{int}} = 0.0412$), 733 refined parameters, $R1 = 0.0376$, $wR2 = 0.1008$. $\{[\text{SiW}_9\text{O}_{34}]_2[\text{Mn}^{\text{III}}_4\text{Mn}^{\text{II}}_2\text{O}_4(\text{H}_2\text{O})_4][(\text{C}_4\text{H}_{10}\text{NO})_{12}]\} \cdot 15\text{H}_2\text{O}$ **2**: $\text{C}_{48}\text{H}_{150}\text{Si}_2\text{Mn}_6\text{N}_{12}\text{O}_{99}\text{W}_{18}$, MW = 6175 g / mol⁻¹; brown rod crystal: $0.2 \times 0.1 \times 0.05 \text{ mm}^3$. Triclinic, space group *P*-1, $a = 12.045(3)$, $b = 14.251(3)$, $c = 19.377(4) \text{ \AA}$, $\alpha = 86.397(6)$, $\beta = 79.488(6)$, $\gamma = 67.882(5)$ $V = 3029.7(11) \text{ \AA}^3$, $Z = 1$, $\rho = 3.384 \text{ g cm}^{-3}$, $\lambda (\text{MoK}\alpha) = 17.746 \text{ mm}^{-1}$, $F(000) = 2824$, 27887 reflections measured, 9373 unique ($R_{\text{int}} = 0.0572$), 744 refined parameters, $R1 = 0.0428$, $wR2 = 0.0863$.

Crystal data were measured on a Bruker Apex II CCD diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 100(2) K. CCDC XXXXX – XXXXX contain the supplementary crystallographic data for **1** and **2** respectively. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ; fax:(+44) 1223-336-033; or deposit@ccdc.cam.ac.uk. Magnetic susceptibility data were recorded using a Quantum Design MPMS5-XL SQUID magnetometer. Susceptibility data were corrected for diamagnetic and TIP contributions ($\chi_{\text{dia/TIP}}(\mathbf{1}) = -445 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, $\chi_{\text{dia/TIP}}(\mathbf{2}) = -441 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) Heisenberg exchange Hamiltonian of the type $H = -2\mathcal{J}_i\mathcal{S}_i$.

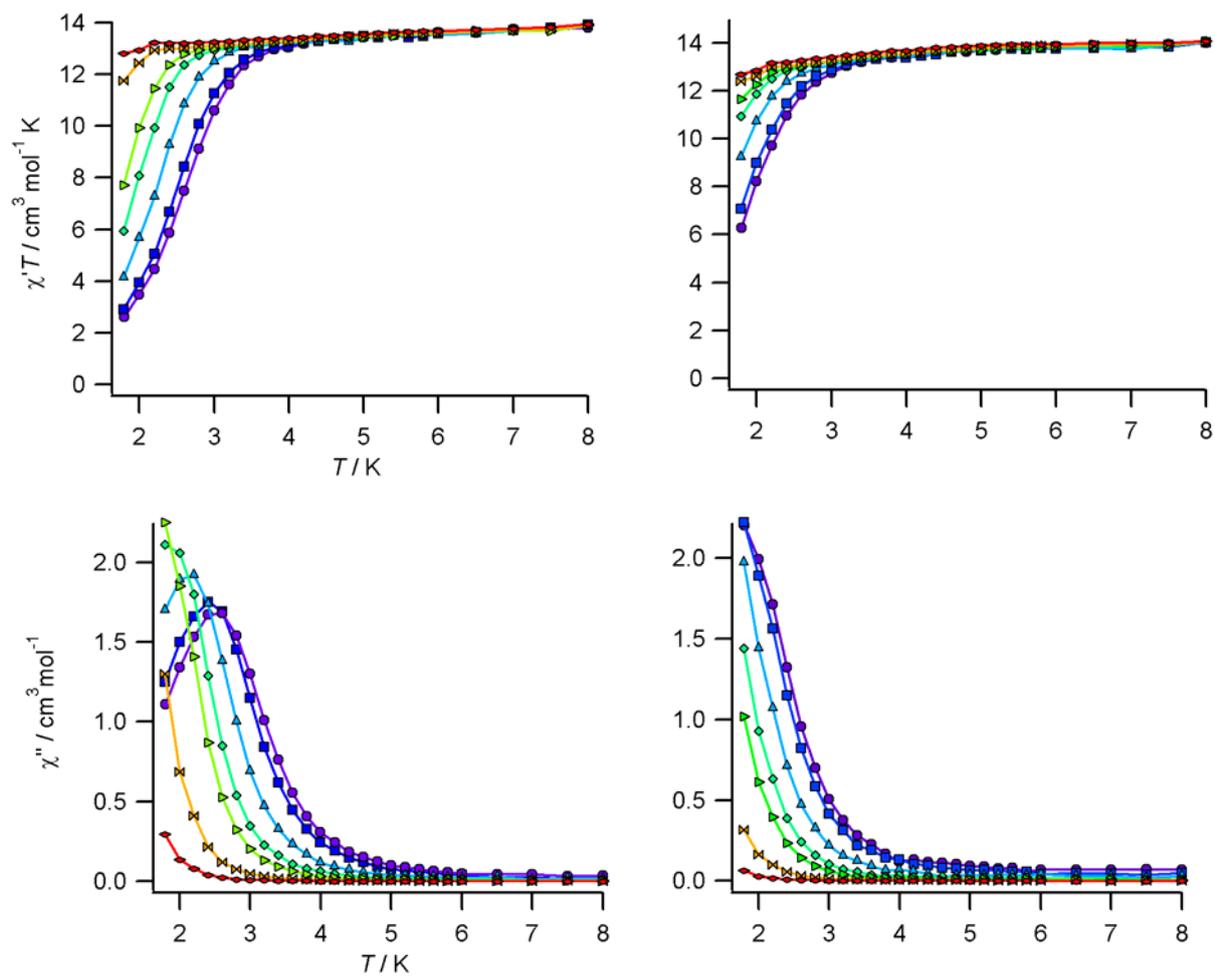


Fig. S1. Ac susceptibility for **1** (left) and **2** (right) measured in zero dc field, with a 3 G ac drive field $\{\omega = 5 \text{ Hz}$ (red), 28, 130, 225, 476, 977 and 1267 Hz (purple)} and plotted as $\chi' T$ versus T (upper) and χ'' versus T (lower).

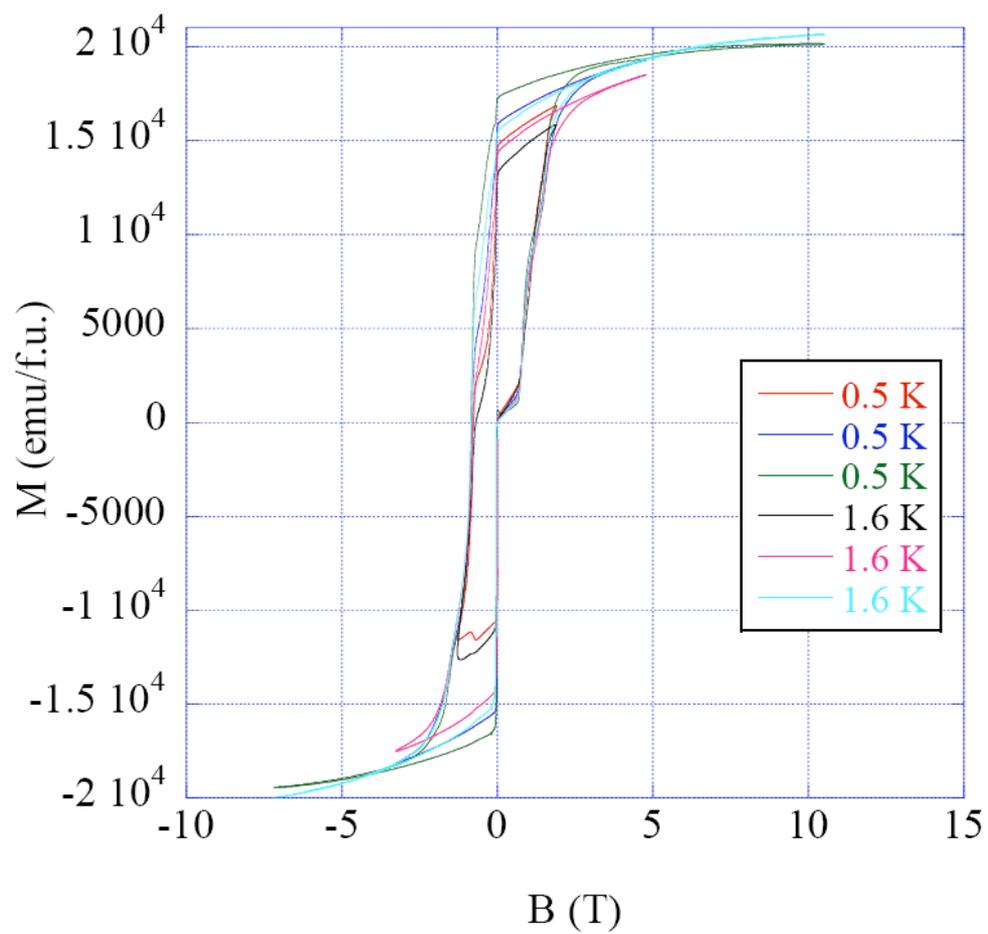


Fig. S2. Temperature dependent hysteresis loops for compound 1 between 1.6 and 0.5 K.

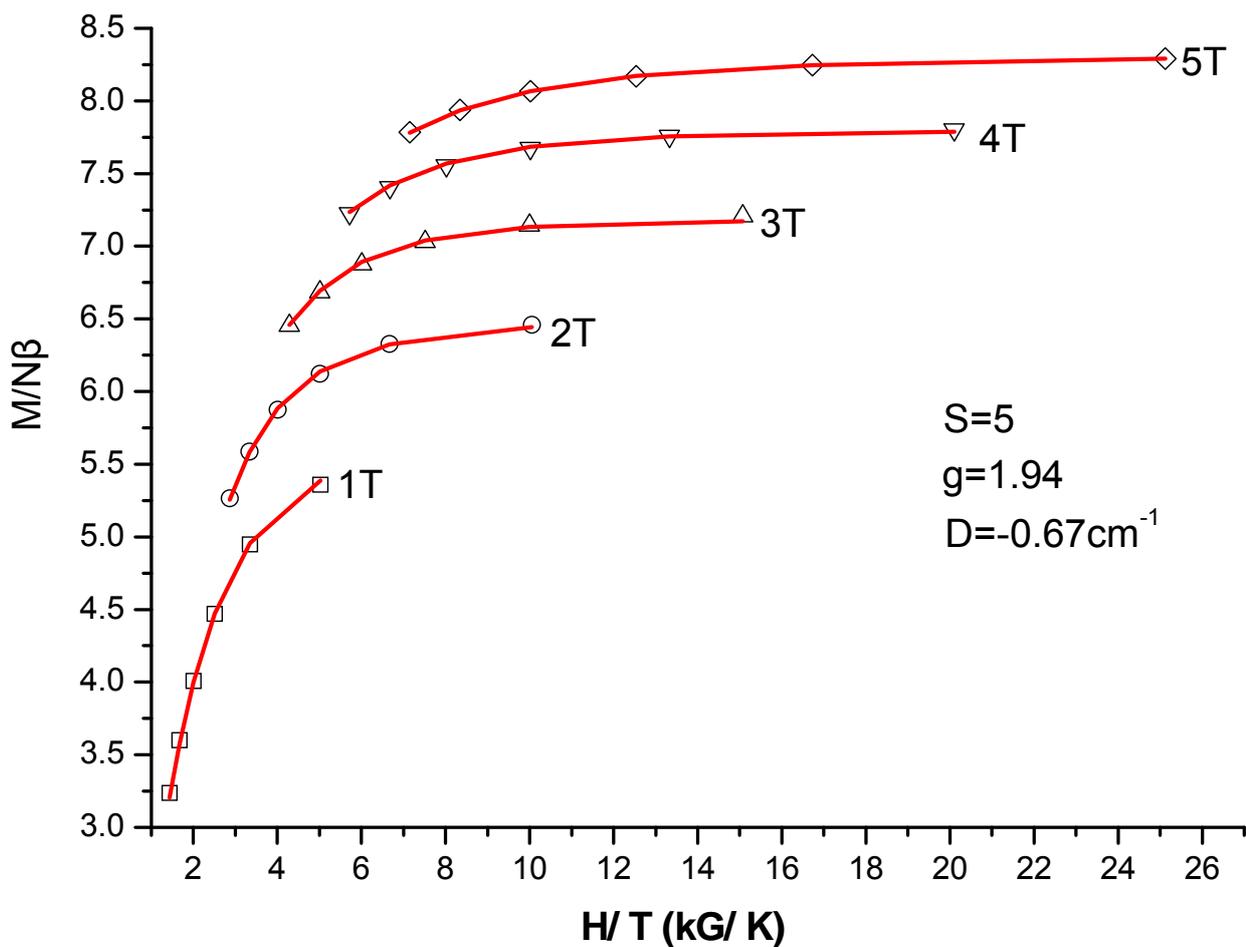


Fig. S3. To further verify the magnitude of the spin ground state for complexes 1 and 2, magnetization data were collected in the ranges 1 – 5 Tesla and 1.8 – 7.0 K and these are plotted as reduced magnetization ($M/N\beta$) vs H/T in. For a complex entirely populating the ground state and experiencing no zero-field splitting, the observed isofield lines should superimpose and saturate at a value ($M/N\beta$) equal to gS . The fitting of the experimental data with the axial ZFS plus Zeeman Hamiltonian^[20] given in Equation (1) over the whole field and temperature range afforded the parameters: 1: $S = 5$, $g = 1.94$, $D = -0.67\text{ cm}^{-1}$ and for 2: $S = 5$, $g = 1.99$, $D = -0.62\text{ cm}^{-1}$.