

Supplementary Data

Complex 2

Complex 2 (Figure S1) showed a μ_{eff} value of $10.9 \mu_{\text{B}}$ at 300 K which is close to the expected value associated with the sum of the {two spin 5/2 + two spin 4/2} sites ($10.86 \mu_{\text{B}}$). The sample showed a gradual increase in μ_{eff} between 20 and 100 K, then the moments became almost temperature independent above 100 K. The χ_M versus temperature plot was Curie-Weiss like in shape with no distinct max. at low temperature indicative of antiferromagnetic coupling. High field magnetisation isotherms (2 to 20 K, $H=0$ to 5 T) were measured to try to identify the ground state and are shown in Figure S2. Saturation in M was not achieved at 2 K and 5 T, the M value under these conditions being $8.8 N\mu_{\text{B}}$; it appears that saturation might occur above fields of 5 T. From the data obtained a ground state of $S_{\text{T}} \sim 4$ is suggested.

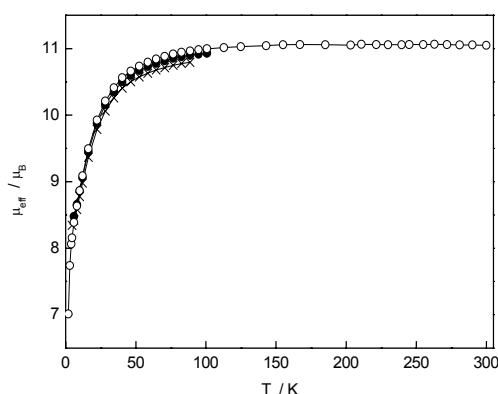


Fig. S1 Plots of magnetic moment versus temperature (300 – 2 K) for complex 2 in applied fields of 1 (O), 0.1 (●) and 0.01 T (X). The latter two fields were measured only in the range 100 – 4.2 K. The solid line just joins the points.

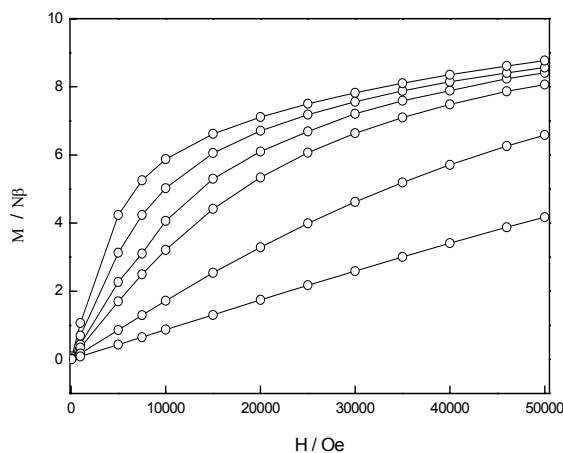


Fig. S2 Magnetisation versus field plots for complex 2 at temperatures of 2, 3, 4, 5.5, 10 and 20 K (top to bottom). The solid lines just join the points

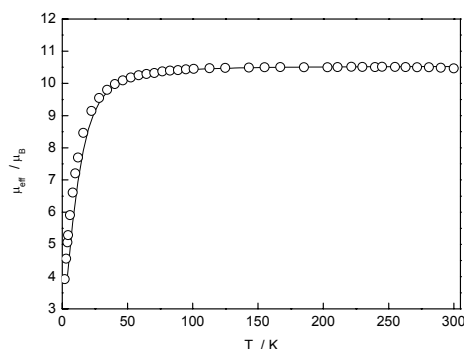


Fig. S3 Plots of magnetic moment *versus* temperature (300 – 2 K) for complex **3** in a field of 1 T. The solid line represents the best fit parameters: $g = 1.94$, $J_{wb} = -0.8 \text{ cm}^{-1}$ and $J_{bb} = +2.1 \text{ cm}^{-1}$.

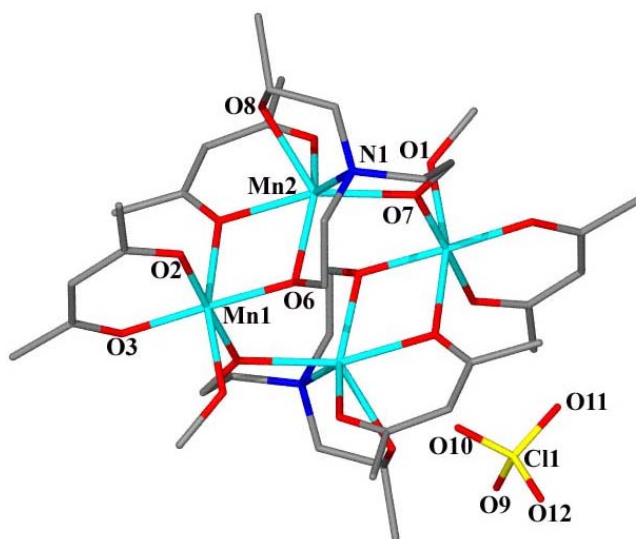
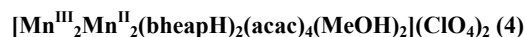


Fig. S4 Structure of **4**



The asymmetric unit of complex **4** contains half the cluster and a perchlorate counterion. The [Mn₄(bheapH)₂(acac)₄(MeOH)₂] cluster of **4** is shown in Figure S4. The peripheral Mn^{III} ions, Mn(1), are six coordinate with distorted octahedral geometry, showing the expected Jahn-Teller elongation in the form of an elongation of the O(1) – Mn(1) – O(4) axis (2.311(2) and 2.314(2) Å respectively). The central body Mn atoms, Mn(2), are also six coordinate, exhibiting distorted trigonal prismatic geometry, although a significant interaction between Mn(2) and the face capping O(1[′]) atom at a distance of ~ 2.62 Å forms a seven coordinate environment (commonly observed for Mn^{II} ions). Bond length analysis and BVS calculations were used to confirm the oxidation states of Mn(1) and Mn(2). All three arms of the doubly deprotonated bheapH²⁻ anions in **4** partake in bonding. Two arms link the wing-tip Mn^{III} ions (Mn(1)) to the central body Mn^{II} ions (Mn(2)) through μ_2 -bridges (*via* O(6) and O(7)) (Fig. S4) while the third arm, O(8), remains protonated, preferring to bond terminally to Mn(2), as does its amine nitrogen atom, N(1). Four acac⁻ anions are present in the structure and show two different bonding modes. While the first exhibits its traditional chelating mode (to Mn(1)), the second acac⁻ anion

bridges the peripheral Mn^{III} ions (Mn(1)) to the central body Mn^{II} ions (Mn(2)) *via* a μ_2 -bridge from one of its oxygen atoms, O(5), while the second oxygen, O(4), bonds terminally to Mn(2) (Fig. S4) . The coordination geometries at the wing-tip Mn positions (Mn(1)) are completed by terminal MeOH molecules. The ClO₄⁻ counter ions are hydrogen bonded to the protonated arm of the bheapH²⁻ ligand (O(8)...O(10) 2.759 Å). There are no hydrogen bonds between neighbouring clusters.