

ELECTRONIC SUPPLEMENTARY INFORMATION

A Single-Chain Magnet Based on Linear $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}]$ Units

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[Mn₃(mpt)₂(EtCO₂)₂(MeOH)₂]_∞. A solution of 3-methylpentane-1,3,5-triol (H₃mpt; 0.220 g, 1.64 mmol) in MeOH (5 mL) was added under magnetic stirring to a solution of Mn(O₂CET)₂·2H₂O (0.200 g, 0.843 mmol) in MeOH (10 mL). The reaction mixture was heated in a 23 ml Teflon-lined autoclave at 100 °C for 24 h under autogenous pressure. The resulting dark red solution was cooled down to room temperature, filtered off and left to stand undisturbed in closed vials. Brown crystals of (1)_∞ suitable for X-ray structural determination appeared after 2 days. The crystals were isolated by filtration, washed with a copious amount of MeOH, and dried in vacuo; the yield was ca. 35%. Anal. Calcd. (Found) for (1)_∞: C, 37.69 (37.82); H, 6.33 (6.01) %. Selected IR data (cm⁻¹, KBr pellet): $\bar{\nu}$ = 2986 (w), 2938 (w), 2860 (w), 1561 (sm), 1430 (m), 1382 (sm), 1190 (mw), 1119 (s), 1071 (sm), 993 (w), 932 (s), 874 (s), 740 (mw), 671 (w), 580 (m), 530 (sm) 456 (w).

X-ray Crystallography. Data were collected on an Oxford Diffraction diffractometer, equipped with a CCD area detector and a graphite monochromator utilizing Cu K α radiation (λ = 1.54184 Å). A suitable crystal was attached to glass fiber using paratone-N oil and transferred to a goniostat that was cooled for data collection. Empirical absorption corrections (multi-scan based on symmetry-related measurements) were applied using CrysAlis RED software.¹ The structure was solved by direct methods using SIR92² and refined on F^2 using full-matrix least squares with SHELXL97.³ Software packages used: CrysAlis CCD for data collection,¹ CrysAlis RED for cell refinement and data reduction,¹ WINGX for geometric calculations,⁴ and DIAMOND and CrystalMaker⁵ for molecular graphics. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms, except the H atoms of the OH groups of the MeOH molecules that were located and refined anisotropically.

Magnetic Susceptibility measurements. Magnetic susceptibility measurements were performed using Quantum Design MPMS-XL SQUID magnetometer. The measurements were carried out on freshly filtered polycrystalline samples (12.57 mg) introduced in a sealed polyethylene bag (3 × 0.5 × 0.02 cm). dc measurements were conducted from 270 to 1.85 K and between ±70 kOe applied dc fields. The thermal dependence of the magnetic susceptibility was measured at 1000 Oe. An M vs. H measurement was performed at 100 K to confirm the absence of ferromagnetic impurities. The field dependence of the magnetisation was collected between 1.85 – 8 K while

sweeping the magnetic field between 0 and 7 T at about 100 to 400 Oe/min. ac susceptibility experiments were realized at ac frequencies ranging from 1 to 1500 Hz with an ac field amplitude of 3 Oe. Experimental data were corrected for the sample holder and for the diamagnetic contribution of the samples.

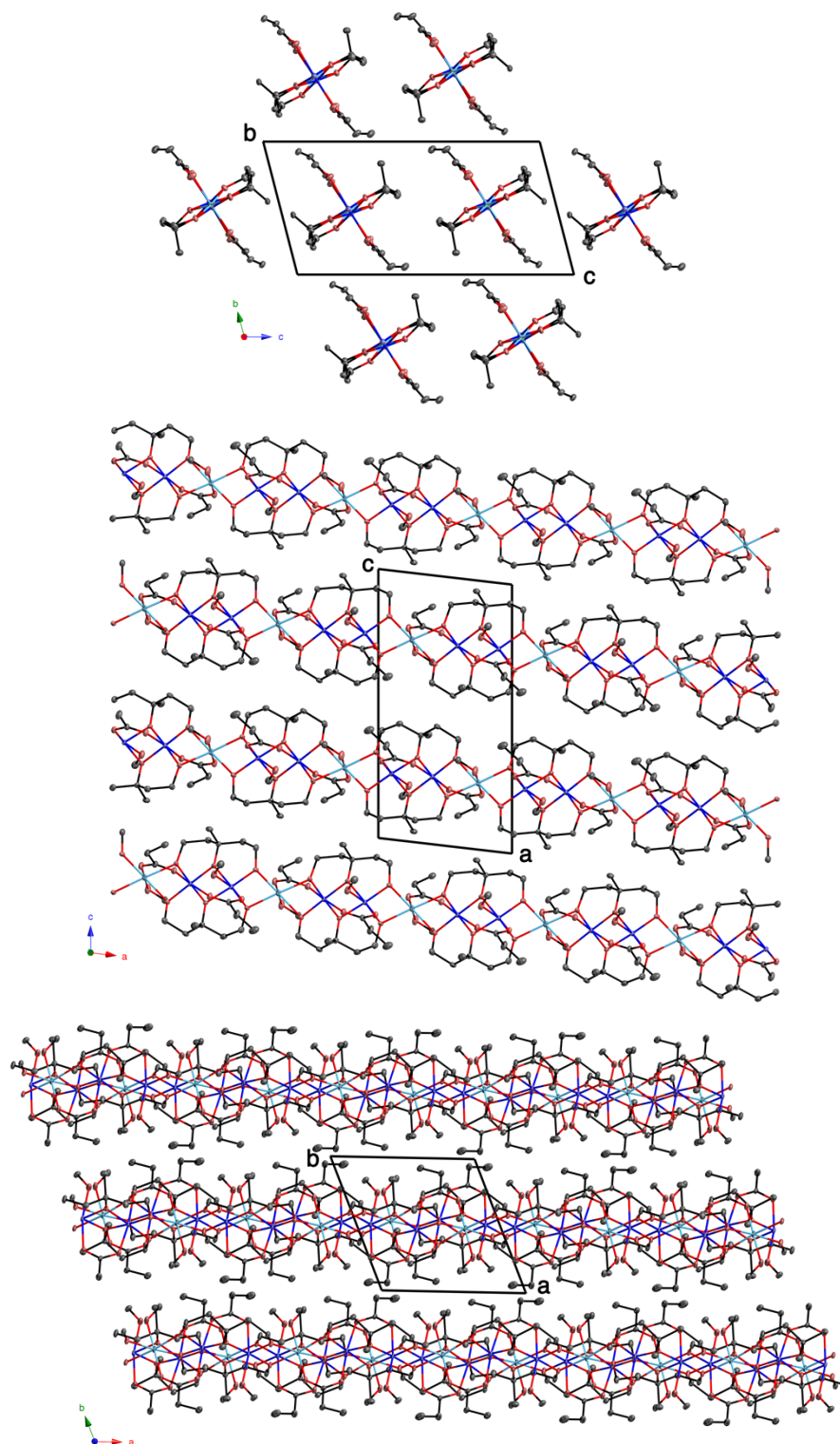


Figure S1. ORTEP-like view of the crystal packing of $(1)_{\infty}$ in the plane perpendicular to (top) the a axis (middle) the b axis and (bottom) the c axis with thermal ellipsoids fixed at 50 %. Color code: Mn^{II} , cyan; Mn^{III} , blue; O, red; C, grey. The hydrogen atoms are omitted for clarity.

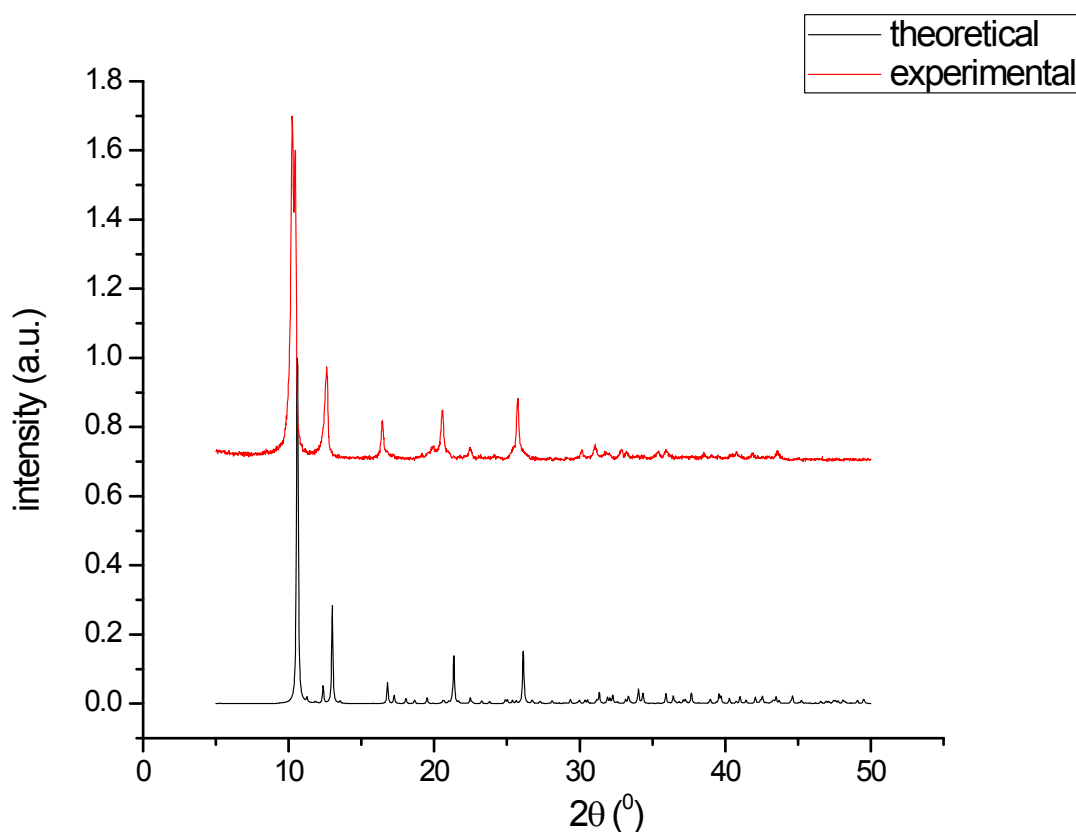


Figure S2. Comparison of the theoretical and experimental powder X-ray diffraction patterns of $(\mathbf{1})_{\infty}$.

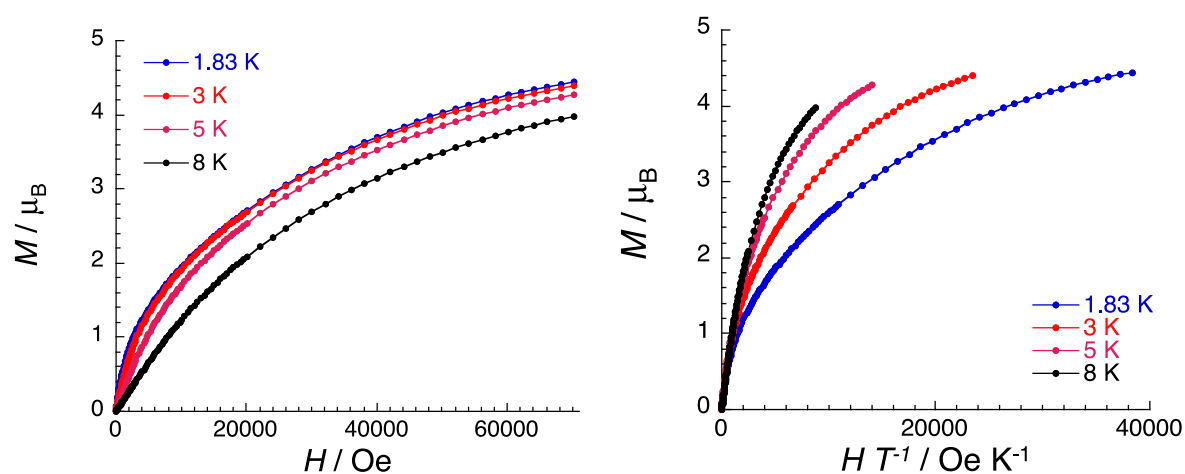
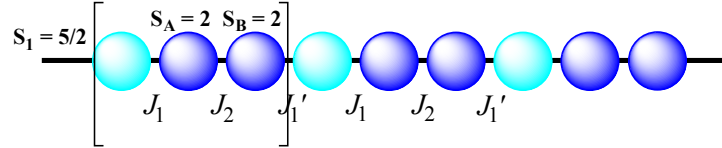


Figure S3. Field dependence of the magnetisation shown as M vs H (left) and M vs H/T (right) plots of $(\mathbf{1})_{\infty}$ in the temperature range from 1.83 to 8 K. The magnetisation increases continuously with applied field without saturation even at 1.8 K and under a 7-T dc field ($4.4 \mu_B$). This behavior reveals the existence of low lying excited states and/or significant magnetic anisotropy in $(\mathbf{1})_{\infty}$ as expected in presence of Mn^{III} magnetic centers.

Analytical expression of the magnetic susceptibility for a Heisenberg chain with a $[\text{Mn}^{\text{II}}_1 - \text{Mn}^{\text{III}}_{\text{A}} - \text{Mn}^{\text{III}}_{\text{B}}]$ repeating unit and considering magnetic centers as isotropic classical spins:

Based on Scheme S1 shown below, the used Hamiltonian in this one-dimensional model is:

$$\mathbf{H} = -2 \sum_{i=1}^N J_1 (\vec{S}_{1,i} \cdot \vec{S}_{A,i}) + J_2 (\vec{S}_{A,i} \cdot \vec{S}_{B,i}) + J'_1 (\vec{S}_{B,i} \cdot \vec{S}_{1,i+1})$$



Scheme S1. Magnetic interaction and spin topologies of the one-dimensional system observed in compounds $(\mathbf{1})_{\infty}$.

Extending the work of Fisher⁶ for the spin chain topology given in Scheme S1, a Heisenberg classical spin chain model was developed to obtain an analytical expression of the magnetic susceptibility:

$$\chi T = \frac{Ng^2 \mu_B^2}{k_B} \left[\frac{\frac{83}{12} [1 + u_1 u_2 u'_1] + 4 [u_1 u'_1 + u_2] + \frac{\sqrt{210}}{3} [u_1 + u'_1] [1 + u_2]}{1 - u_1 u_2 u'_1} \right]$$

with $u_i = \frac{1}{\tanh\left(\frac{\alpha_i J_i}{k_B T}\right)} - \frac{k_B T}{\alpha_i J_i}$, $u'_1 = \frac{1}{\tanh\left(\frac{\alpha_1 J'_1}{k_B T}\right)} - \frac{k_B T}{\alpha_1 J'_1}$ considering J_i and J'_1 defined by

Scheme S1, $\alpha_1 = 2\sqrt{S_{A/B}(S_{A/B} + 1)S_1(S_1 + 1)} = \sqrt{210}$ and $\alpha_2 = 2\sqrt{S_A(S_A + 1)S_B(S_B + 1)} = 12$.

References:

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