

## Electronic Supplementary Information (ESI)

### A Hexameric $[\text{Mn}^{\text{III}}_{18}\text{Na}_6]$ Wheel Based on $[\text{Mn}^{\text{III}}_3\text{O}]^{7+}$ Sub-Units

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## Experimental

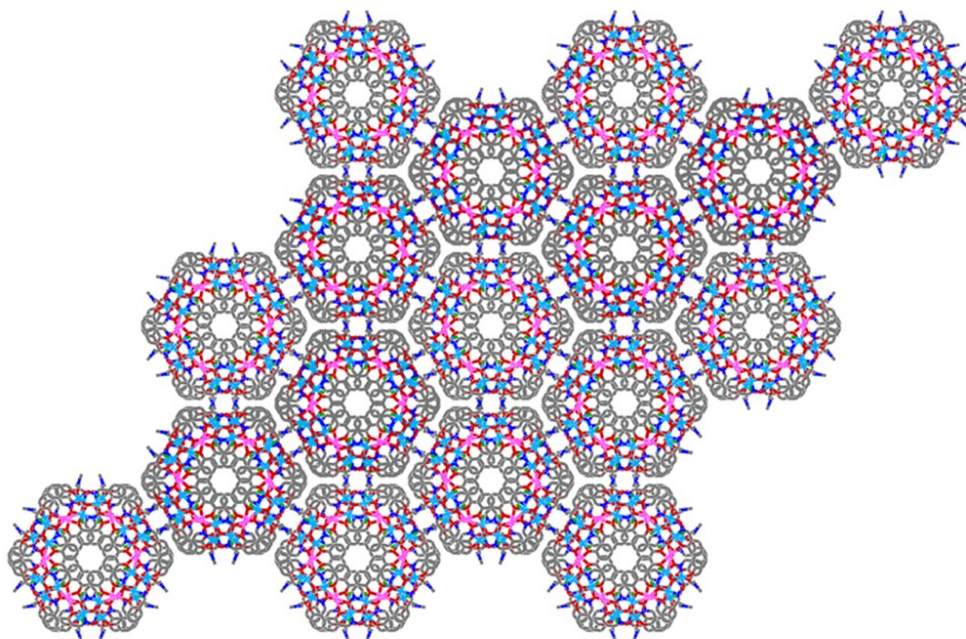
**Materials.** Reagent grade chemicals were obtained from Aldrich and used without further purification. Water was distilled in-house.

**Synthesis of  $[\text{Mn}^{\text{III}}_{18}\text{Na}_6(\mu_3\text{-O})_6(\text{sao})_{18}\text{Br}_{12}(\text{H}_2\text{O})_{18}(\text{DMF})_6]$  (**1**).** To a solution of  $\text{MnBr}_2 \cdot 4\text{H}_2\text{O}$  (0,231 g, 0.806 mmol) in MeCN/DMF 4:1 (8ml/2ml) was added 2-(hydroxymethyl)phenol (hpH<sub>2</sub>) (0,100 g, 0.806 mmol) and sodium cyanate (NaOCN) (0,0524 g, 0.806 mmol) and the reaction mixture was left under magnetic stirring for one hour. Then, salicylaldoxime (saoH<sub>2</sub>) (0,1104g / 0.806 mmol) was added to the resulting pale pink suspension and the mixture was left under magnetic stirring for twenty hours. The resulting dark green solution was filtered and layered with diethylether to afford single crystals of **1** in ~45% yield after 2 weeks. C, H, N elemental analysis details are included in the main part of the paper. Selected IR data (cm<sup>-1</sup>, KBr pellet):  $\nu = 3400$  (m, br), 2783 (w), 1723 (m), 1640 (m), 1597 (s), 1545 (s), 1474 (m), 1439 (s), 1400 (s), 1282 (s), 1204 (m), 1045 (s), 1030 (s), 920 (s), 830 (m), 745 (m), 687 (s), 650 (m), 536 (w), 478 (w).

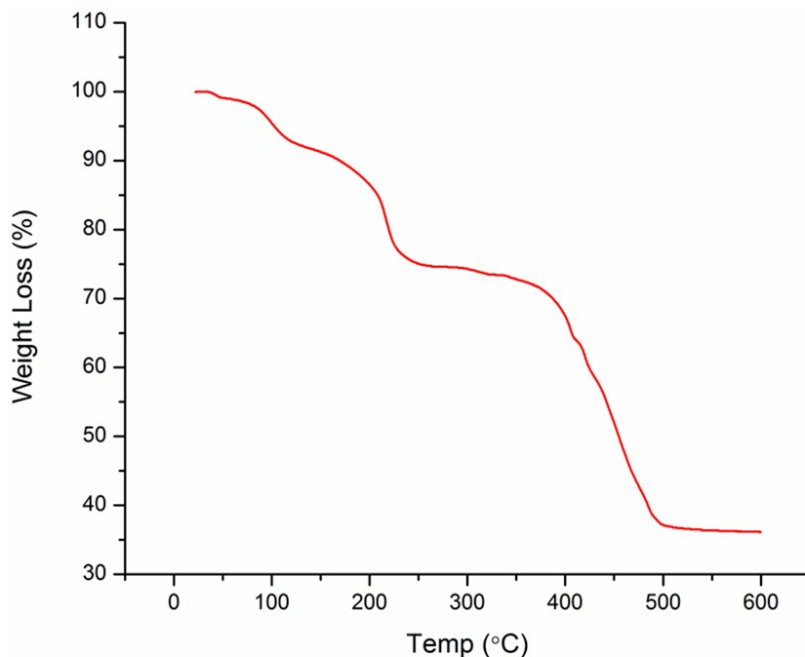
**X-ray Crystallography.** Data were collected on an Oxford Diffraction diffractometer, equipped with a CCD area detector and a graphite monochromator utilizing Cu K $\alpha$  radiation ( $\lambda = 1.54184$  Å). A suitable crystal was attached to a glass fiber using paratone-N oil and transferred to a goniostat that was cooled for data collection. Empirical absorption corrections (multi-scan based on symmetry-related measurements) were applied using CrysAlis RED software.<sup>1</sup> The structure was solved by direct methods using SIR92<sup>2</sup> and refined on  $F^2$  using full-matrix least squares with SHELXL97.<sup>3</sup> Software packages used: CrysAlis CCD for data collection,<sup>1</sup> CrysAlis RED for cell refinement and data reduction,<sup>1</sup> WINGX for geometric calculations,<sup>4</sup> and DIAMOND<sup>5</sup> 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. Unit cell data and structure refinement details are summarized in the main part of the paper. Full details can be found in the CIF file.

**Physical Measurements.** Elemental analysis (C, H, N) were performed by Medac Ltd, UK. IR spectra were recorded on KBr pellets in the 4000–400 cm<sup>-1</sup> range using a Shimadzu Prestige

-21 spectrometer. Thermal stability studies were performed with a Shimadzu TGA 50 thermogravimetric analyzer. Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 1.8 K were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants. Magnetic studies below 1.8 K were carried out on single crystals using a micro-SQUID apparatus operating down to 40 mK.<sup>6</sup>

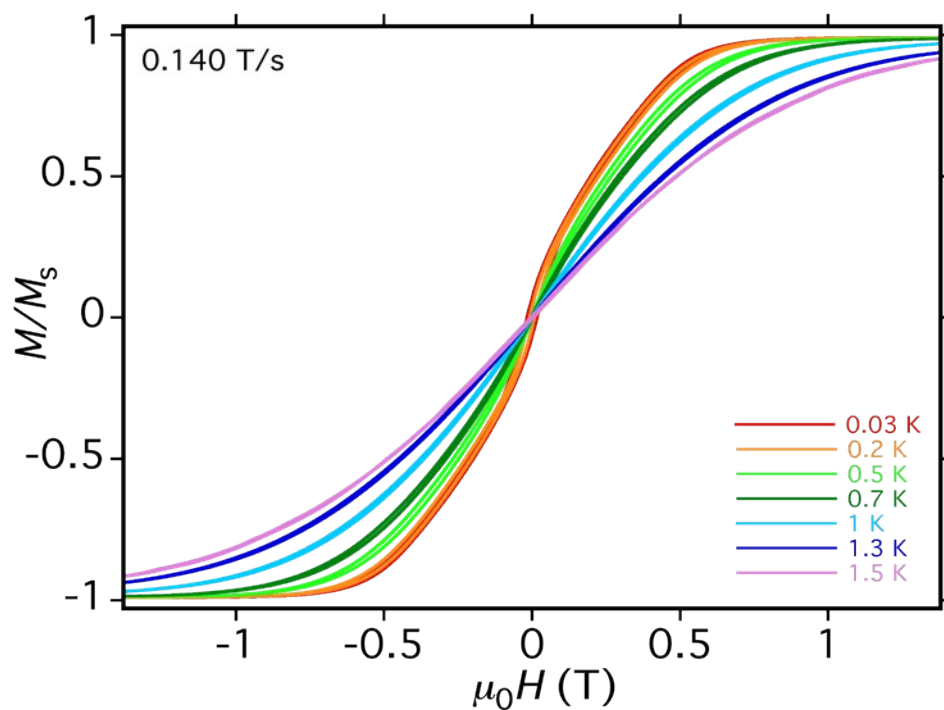
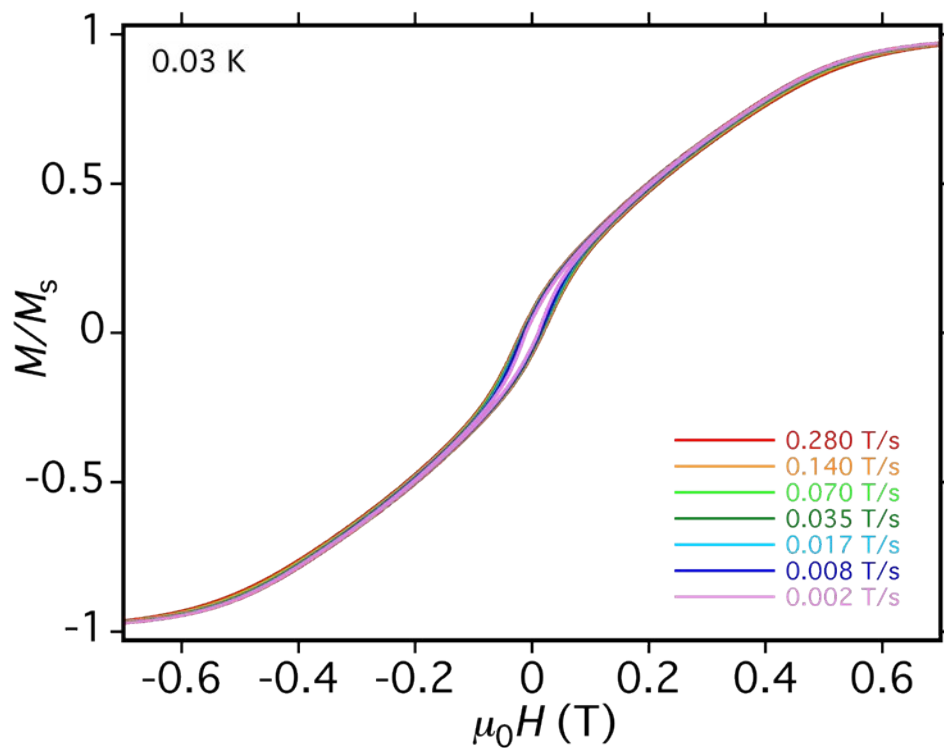


**Figure S1.** Representation of the packing of **1** along the *c*-axis. Colour code: Mn blue; Na, pink; Br, green; O, red; N, dark blue; C, grey. H atoms are omitted for clarity.



**Figure S2.** TGA curve of complex **1**.

**Discussion:** The thermal stability of **1** was investigated by means of thermogravimetric analysis (TGA). The TGA curve of **1** indicates the existence of three decomposition steps. The first one which is completed at  $\sim 130$  °C is attributed to the loss of lattice water molecules, the second one which ends at  $\sim 250$  °C corresponds to the loss of dmf (both coordinated and lattice) and ligated water molecules, and the last one that appears at higher temperatures is due to the elimination of the other ligands that are present in **1**. Notably the mass losses for the first two steps associated with the loss of bound and lattice solvent molecules ( $\text{H}_2\text{O}$  and DMF) indicates the presence of 3DMF and  $30\text{H}_2\text{O}$  in the crystal lattice of **1** in agreement with the fit of C,H,N elemental analysis data. In particular, the first mass loss corresponds to the loss of  $\sim 30$  lattice water molecules (experimental mass loss:  $\sim 8.5\%$ , calculated mass loss assuming the presence of  $30 \text{H}_2\text{O}$ ,  $\sim 8.8\%$ ), whereas the second mass loss corresponds to the loss of 9 DMF (6 bound and 3 lattice) and 18 bound  $\text{H}_2\text{O}$  molecules (experimental mass loss:  $\sim 16.3\%$  calculated mass loss: 16%).



**Figure S3.** Magnetization ( $M$ ) versus applied magnetic field ( $\mu_0 H$ ) hysteresis loops for a single crystal of **1** at the indicated field sweep rates at 0.03 K (top) and at the indicated temperatures and a fixed field sweep rate of 0.140 Ts<sup>-1</sup> (bottom).  $M$  is normalized to its saturation value ( $M_s$ ).

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## References:

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