

## Electronic supplementary information (ESI)

# New High-Nuclearity Manganese Clusters Containing Mixed Chelating Ligands: Syntheses, Crystal Structures and Magnetochemical Characterization†

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## Experimental details

All chemicals and solvents used in the syntheses were commercially available as A.R. grade and used as received, without further purification.  $[\text{Mn}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{py})_3](\text{ClO}_4)$  and  $[\text{Mn}_4\text{O}_2(\text{O}_2\text{CPh})_9(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$  were synthesized as previously described.<sup>1,2</sup>

**Caution!** Perchlorates and azide salts is potentially explosive and should be used in small quantities and with utmost care at all times.

**1(ClO<sub>4</sub>)·6H<sub>2</sub>O:** Solid  $[\text{Mn}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{py})_3](\text{ClO}_4)$  (0.175 g, 0.20 mmol),  $\text{NaN}_3$  (0.013 g, 0.2 mmol), and di-2-pyridylketone (0.018 g, 0.10 mmol) were added to a stirred solution of 2-hydroxymethylpyridine (0.022 g, 0.2 mmol) in 15 ml  $\text{CH}_3\text{CN}$ . To this reaction mixture,  $\text{NMe}_4\text{OH}\cdot 5\text{H}_2\text{O}$  (0.036 g, 0.2 mmol) was added under vigorous stirring. The solution was stirred for a further 5 h, filtered, and the filtrate left undisturbed at ambient temperature. After ten days later, dark red crystal of  $1(\text{ClO}_4)\cdot 6\text{H}_2\text{O}$  were formed in about 30% yield, and they were collected by filtration, washed with cold  $\text{MeCN}$  ( $3 \times 10$  ml) and  $\text{Et}_2\text{O}$  ( $3 \times 10$  ml), and dried in air. Elemental analysis (%) calcd for  $1(\text{ClO}_4)\cdot 6\text{H}_2\text{O}$  ( $\text{C}_{70}\text{H}_{92}\text{ClMn}_{13}\text{N}_8\text{O}_{52}$ , no solvent  $\text{H}_2\text{O}$  were free): C 32.00, H 3.53, N 4.27; found: C 31.89, H 3.45, N 4.15. Selected IR (KBr): 3396 (s), 2068 (s), 1585 (s), 1479 (w), 1417 (s), 1340 (m), 1293 (m), 1242 (w), 1154 (m), 1044 (s), 913 (m), 818 (w), 773 (w), 659 (s), 614 (s), 575 (s), 466 (m)  $\text{cm}^{-1}$ .

**2·6H<sub>2</sub>O**: This compound was prepared in the same manner as compound **1** but using (NBu<sup>n</sup><sub>4</sub>)[Mn<sub>4</sub>O<sub>2</sub>(O<sub>2</sub>CPh)<sub>9</sub>(H<sub>2</sub>O)] (0.32 g, 0.2 mmol) and 2-pyridylketone oxime (0.027 g, 0.2 mmol) in place of [Mn<sub>3</sub>O(O<sub>2</sub>CCH<sub>3</sub>)<sub>6</sub>(py)<sub>3</sub>](ClO<sub>4</sub>) and 2-hydroxymethylpyridine. Dark-red crystals of **2·6H<sub>2</sub>O** were collected by filtration, washed with cold MeCN (3 × 10 ml) and Et<sub>2</sub>O (3 × 10 ml), and dried in air. The yield was very low (< 10%). Elemental analysis (%) calcd for **2·6H<sub>2</sub>O** (C<sub>170</sub>H<sub>142</sub>Mn<sub>16</sub>N<sub>16</sub>O<sub>54</sub>): C 49.18, H 3.45, N 5.40; found: C 49.20, H 3.42, N 5.51. Selected IR (KBr): 3391 (m), 3061 (m), 1600 (s), 1558 (s), 1474 (m), 1400 (s), 1216 (m), 1154 (w), 1122 (m), 1088 (m), 1041 (m), 818(w), 717 (w), 690 (s), 673 (m), 636 (m), 554 (m), 445 (m) cm<sup>-1</sup>.

Diffraction data for **1**(ClO<sub>4</sub>)·6H<sub>2</sub>O and **2·6H<sub>2</sub>O** were collected on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 291 K. The data reduction was made with the Bruker SAINT package. Absorption correction was performed using the SADABS program. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares using SHELXL-2000 with anisotropic displacement parameters for all non-hydrogen atoms. H atoms were introduced in calculations using the riding model. All computations were carried out using the SHELXTL-2000 program package.

#### References:

- (1) Synthetic method refer: Vincent, J. B.; Chang, H. -R.; Folting, K.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1987**, *109*, 5703.
- (2) Synthetic method refer: Wemple, M. W.; Tsai, H. -L.; Wang, S.; Claude, J. P.; Streib, W. E.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem.* **1996**, *35*, 6437.

#### Physical measurements

The IR spectra were obtained as KBr disks on a VECTOR 22 spectrometer. Elemental analyses were performed on a Perkin Elmer 240C elemental analyzer. Variable-temperature direct current (DC) magnetic susceptibility data down to 1.8 K on microcrystalline samples were carried out on a Quantum Design MPMP-XL7 superconducting quantum interference device (SQUID) magnetometer equipped with

a 7 T DC magnet. The alternating current (AC) susceptibility down to 1.8 K were also performed on a Quantum Design MPMP-XL7 magnetometer in a zero DC field and a 1.0 Oe field oscillating at frequencies in the 1-1488 Hz range. The alternating current (AC) magnetic susceptibility data down to 2.0 K were collected on PPMS-9T magnetometer in a zero DC field and a 1.0 Oe field oscillating at frequencies in the 511-9111 Hz range (for **2**: 1111-9111Hz). Diamagnetic corrections were made for both the sample holder as the background and the compound estimated from Pascal's constants.

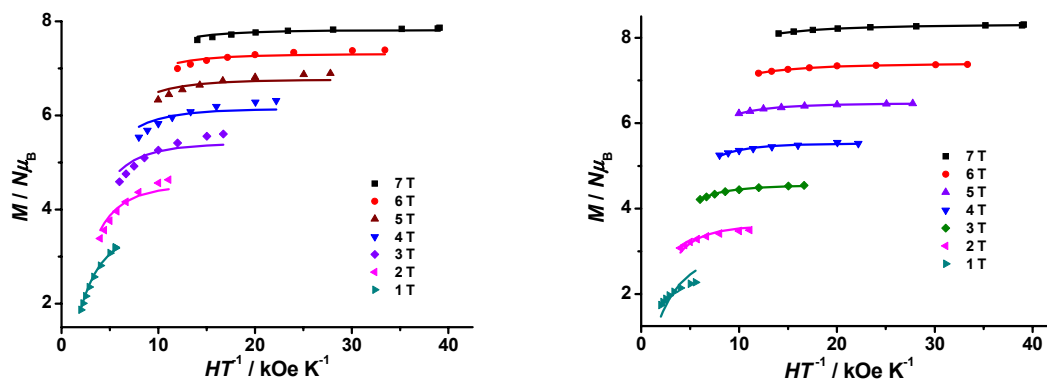
Table S1. Bond Valence Sum<sup>a</sup> for the Mn atoms in **1** and **2**

Complex <b>1</b>	Mn(II)	Mn(III)	Mn(IV)
Mn(1)	<u>2.05</u>	1.91	1.95
Mn(2)	3.29	<u>3.02</u>	3.17
Mn(3)	3.09	<u>2.83</u>	2.97
Mn(4)	<u>2.07</u>	1.91	1.97
Mn(5)	3.16	<u>2.89</u>	3.03
Mn(6)	3.25	<u>3.01</u>	3.11
Mn(7)	3.18	<u>2.91</u>	3.05

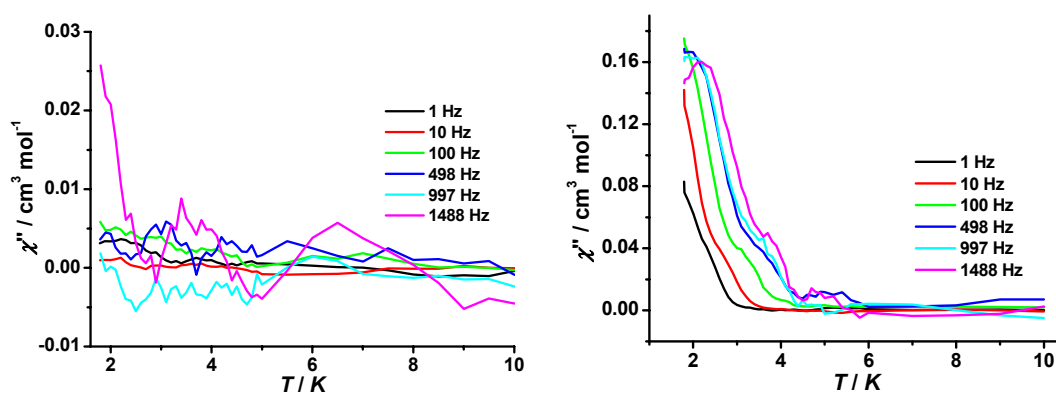
  

Complex <b>2</b>	Mn(II)	Mn(III)	Mn(IV)
Mn1	3.19	<u>2.95</u>	3.05
Mn2	3.24	<u>2.97</u>	3.09
Mn3	3.18	<u>2.96</u>	3.02
Mn4	3.11	<u>2.85</u>	2.99
Mn5	<u>1.97</u>	1.80	1.89
Mn6	3.15	<u>2.94</u>	2.98
Mn7	<u>1.99</u>	1.84	1.90
Mn8	<u>1.99</u>	1.84	1.91

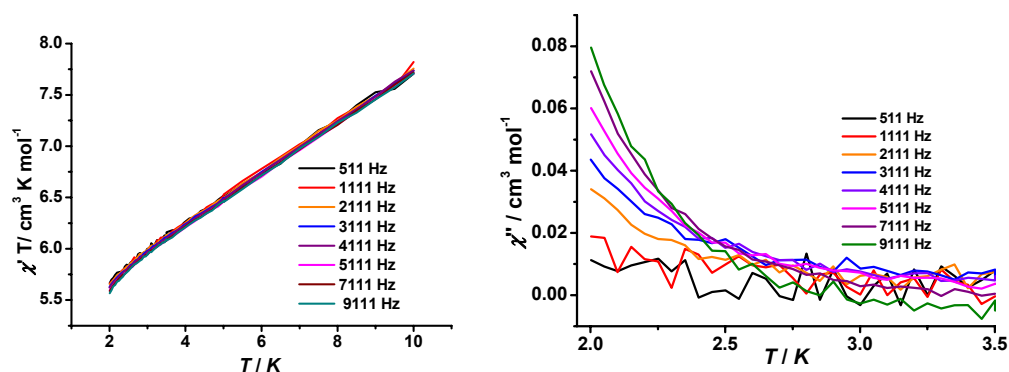
The underline value is the one closest to the charge for which it was calculated. The oxidation state of a particular atom can be taken as the nearest whole number to the underline value.



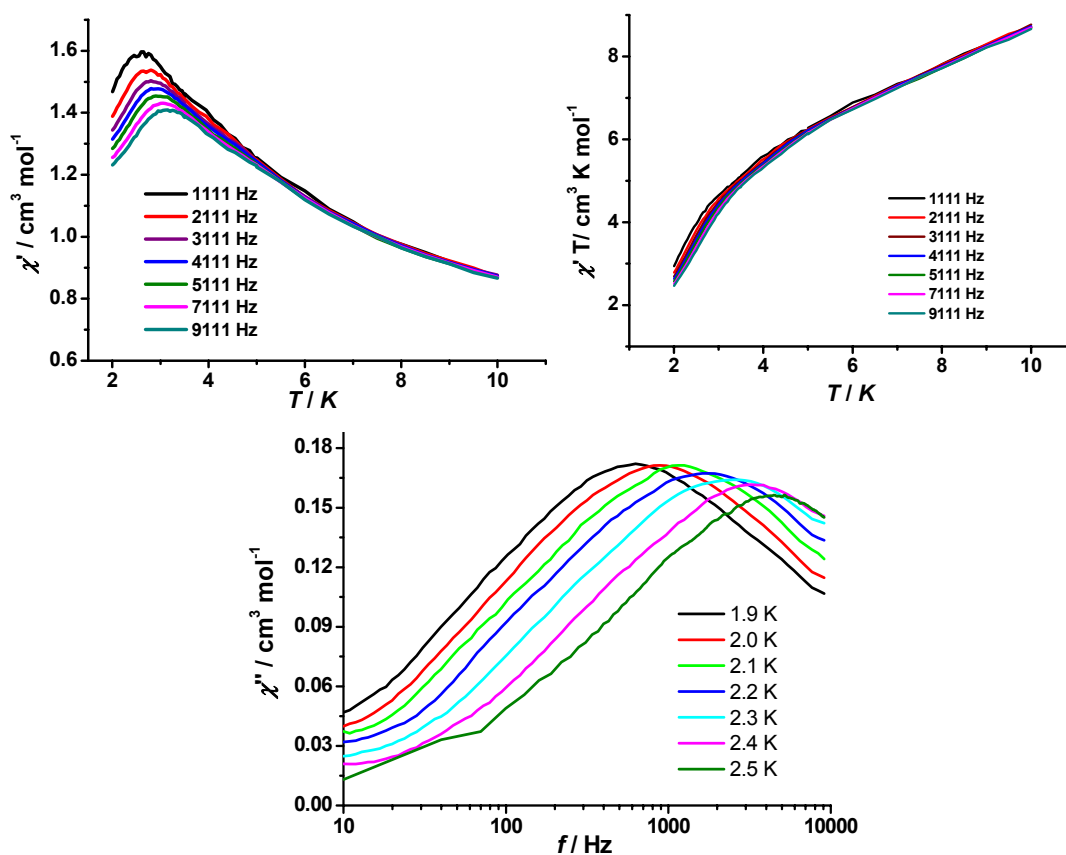
**Figure S1.** Plot of the reduced magnetization ( $M/N\mu_B$ ) vs  $H/T$  of  $1(\text{ClO}_4)\cdot 6\text{H}_2\text{O}$  (left) and  $2\cdot 6\text{H}_2\text{O}$  (right) at the indicated applied fields. The solid lines are the fit of the data.



**Figure S2.** Plots of the out-of-phase ( $\chi_M''$ ) signals versus temperature of  $1(\text{ClO}_4)\cdot 6\text{H}_2\text{O}$  (left) and  $2\cdot 6\text{H}_2\text{O}$  (right) in AC susceptibility studies in zero applied static field with an oscillating field of 1.0 Oe at the indicated frequencies.



**Figure S3.** Plots of the in-phase ( $\chi_M'T$ ) signals (left) and out-of-phase ( $\chi_M''$ ) signals (right) versus temperature of  $1(\text{ClO}_4)\cdot 6\text{H}_2\text{O}$  in AC susceptibility studies in zero applied static field with an oscillating field of 1.0 Oe at the indicated frequencies.



**Figure S4.** The upper two plots and the bottom plot shown the in-phase ( $\chi_M'$  and  $\chi_M'T$ ) signals versus temperature and the  $\chi_M''$  versus frequency for  $2 \cdot 6\text{H}_2\text{O}$ , respectively. The AC magnetic susceptibility data are measured in zero applied static fields with an oscillating field of 1.0 Oe.