ELECTRONIC SUPPORTING INFORMATION

Supramolecular chains of high nuclearity $\{Mn^{III}_{25}\}$ barrel-like single molecule magnets

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Experimental Section

Syntheses. All manipulations were performed under aerobic conditions using materials as received. The organic ligand mpraoH was synthesized by following the same procedure with that reported previously for the similar ligand praoH$_2$.[1] ***Caution!*** *Although no such behavior was observed during the present work, perchlorate and azide salts are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times.*

[Mn$_{25}$NaO$_{20}$(OMe)$_{12}$(N$_3$)$_{12}$(mprao)$_{12}$(H$_2$O)$_2$]$_n$ (1): To a stirred, colorless solution of mpraoH (0.12 g, 1.0 mmol) and NEt$_3$ (0.14 mL, 1.0 mmol) in MeCN/MeOH (20 mL, 2:1 v/v) were added solid Mn(ClO$_4$)$_2$·6H$_2$O (0.36 g, 1.0 mmol) and NaN$_3$ (0.07 g, 1.0 mmol). The resulting orange solution was stirred for 6 h, during which time all the solids dissolved and the color of the solution changed to dark brown. The solution was filtered, and the filtrate was layered with Et$_2$O (40 mL, 1:1 v/v). After four days, X-ray quality dark-brown plate-like crystals of **1**·8MeOH had appeared and were collected by filtration, washed with cold MeCN (1 x 3 mL) and Et$_2$O (2 x 5 mL), and dried in air. The yield was 30 %. Selected IR data (KBr): ν= 3338 (sb), 2078 (m), 2057 (vs), 1600 (m), 1481 (m), 1405 (m), 1307 (m), 1060 (m), 989 (m), 670 (mb), 570 (m).

[1] M. M. Hania, *Asian J. Chem.*, 2002, **14**, 1074.

Table S1 Bond Valence Sum (BVS)[a,b] Calculations for Mn Atoms in Complex **1**

Atom	Mn^{II}	Mn^{III}	Mn^{IV}
Mn1	3.16	<u>2.93</u>	3.01
Mn2	3.10	<u>2.83</u>	2.97
Mn3	3.36	<u>3.13</u>	3.19
Mn4	3.26	<u>3.04</u>	3.10
Mn5	3.13	<u>2.91</u>	2.99
Mn6	2.67	<u>2.46</u>	2.42
Mn7	3.17	<u>2.94</u>	3.02
Mn8	3.15	<u>2.88</u>	3.02
Mn9	3.21	<u>2.98</u>	3.06
Mn10	3.17	<u>2.90</u>	3.05
Mn11	3.05	<u>2.84</u>	2.90
Mn12	3.18	<u>2.96</u>	3.02
Mn13	3.25	<u>3.02</u>	3.10

[a] The underlined value is the one closest to the charge for which it was calculated. The oxidation state is the nearest whole number to the underlined value.

[b] An O BVS in the ~1.7-2.0, ~1.0-1.2, and ~0.2-0.4 ranges is indicative of non-, single- and double-protonation, respectively.

BVS calculations for selected oxygen atoms in **1** gave values of: 1.70-1.85 for O^{2-}, 1.91-1.97 for MeO^{-}, and 0.23 for H_2O.

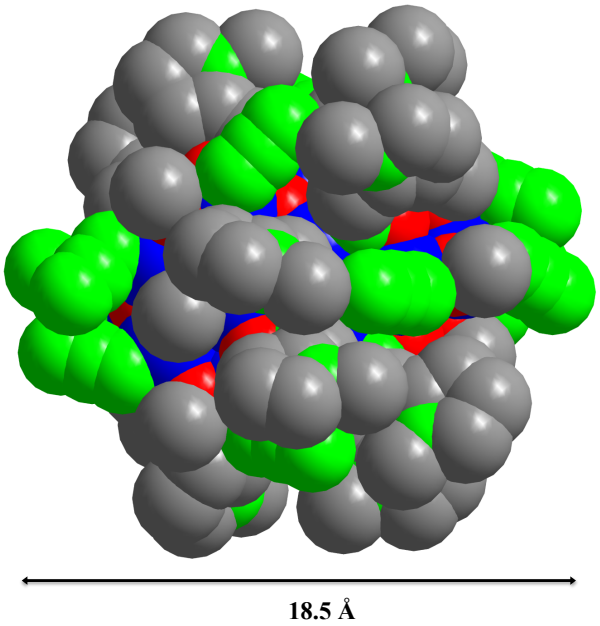

Fig. S1 Space-filling representation of the Mn_{25} cluster unit of the 1D coordination polymer **1**, indicating the length of the molecule. Colour scheme: Mn^{III} blue; O red; N green; C gray.

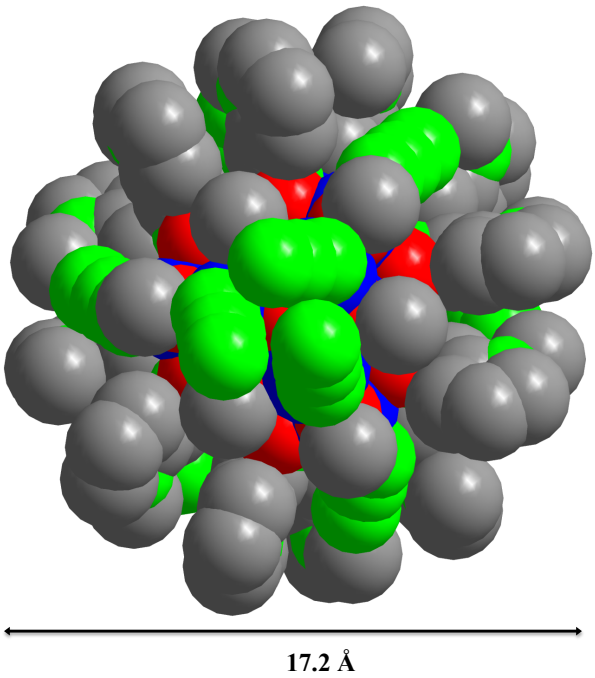

Fig. S2 Space-filling representation and width of the Mn_{25} cluster unit of the 1D coordination polymer **1**, viewed approximately along the virtual C_3 axis.

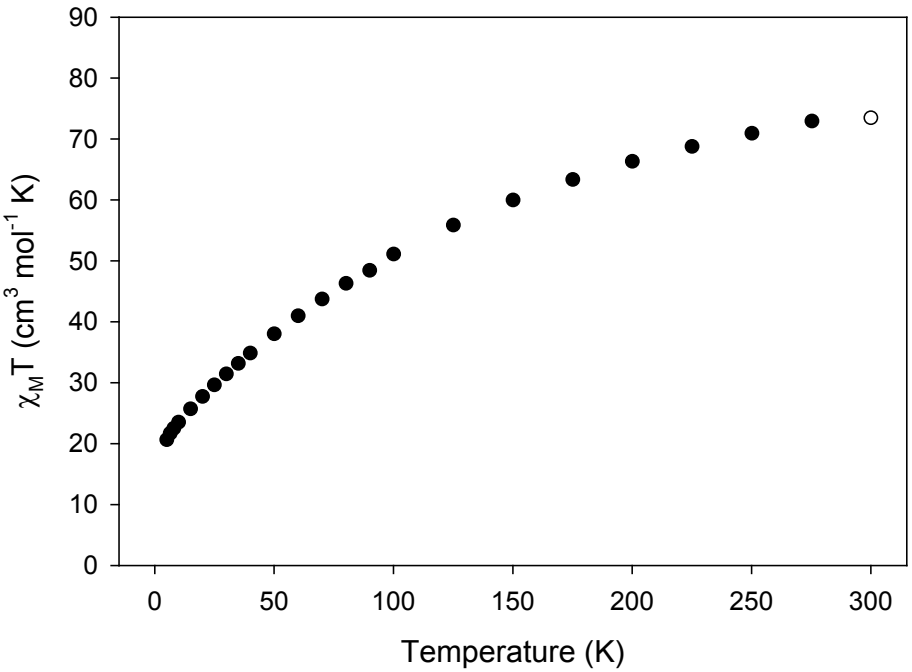

Fig. S3 $\chi_M T$ vs T plot for complex **1**.

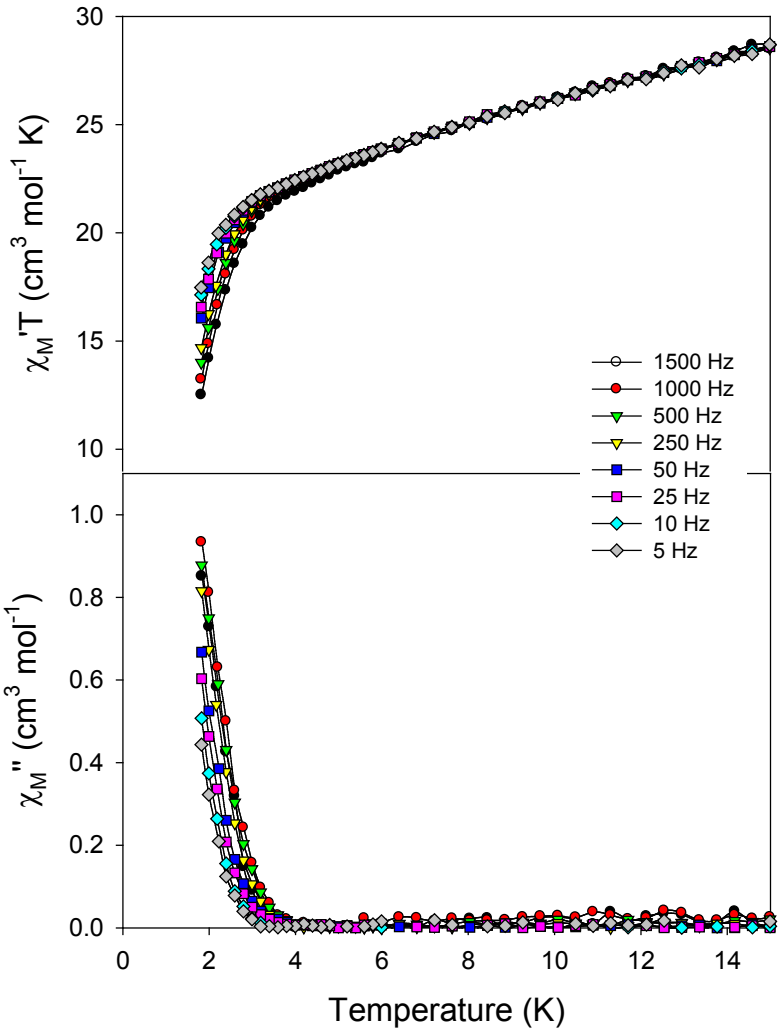

Fig. S4 The in-phase (χ_M') (as $\chi_M'T$, top) and out-of-phase (χ_M'', bottom) vs T ac susceptibility signals for **1**.