Electronic Supplementary Information (ESI)

"Squaring the clusters": A $Mn^{III}_4Ni^{II}_4$ molecular square from nickel(II)-induced structural transformation of a $Mn^{II/III/IV}_{12}$ cage

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Experimental Section

Syntheses. All manipulations were performed under aerobic conditions using materials and solvents as received. ***Caution!*** *Although no such behavior was observed during the present work, perchlorate salts are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with utmost care at all times.*

$[Mn_{12}O_8(OH)_2(ppko)_{12}(H_2O)_2](OH)(ClO_4)_3$ (1). To a stirred solution of ppkoH (0.20 g, 1.0 mmol) and NEt_3 (0.14 mL, 1.0 mmol) in MeCN (20 mL) was added solid $Mn(ClO_4)_2\cdot 6H_2O$ (0.36 g, 1.0 mmol). The mixture was stirred for a further 30 min, which caused a rapid color change from orange to dark brown. The solution was filtered, and the filtrate was allowed to slowly evaporate at room temperature. After 6 days, X-ray quality brown crystals of **1**·2MeCN were collected by filtration, washed with cold MeCN (2 x 3 mL) and Et_2O (2 x 5 mL), and dried under vacuum; the yield was 80%. Anal. Calcd (Found) for **1**: C, 48.87 (48.70); H, 3.28 (3.09); N 9.50 (9.77). Selected IR data (cm^{-1}): 3414 (mb), 1618 (m), 1596 (m), 1538 (w), 1488 (w), 1466 (m), 1442 (m), 1384 (w), 1340 (w), 1258 (w), 1196 (m), 1108 (s), 1080 (vs), 1028 (m), 976 (m), 788 (m), 746 (m), 710 (s), 626 (s), 598 (w), 578 (m), 490 (w), 465 (w), 410 (w).

$[Mn_4Ni_4(OH)_8(ppko)_8(H_2O)_4](ClO_4)_4$ (2). To a dark brown solution of **1** (0.35 g, 0.1 mmol) in CH_2Cl_2 (30 mL) was added solid $Ni(ClO_4)_2\cdot 6H_2O$ (0.22 g, 0.6 mmol). The mixture was stirred overnight, during which time a red microcrystalline solid formed. This was collected by filtration. Dissolution of the solid in MeCN (25 mL) and careful layering with Et_2O (50 mL, 1:1 v/v) gave red crystals of **2** after 12 days. The crystals were collected by filtration, washed with cold MeCN (2 x 3 mL) and Et_2O (2 x 5 mL), and dried under vacuum; the yield was 45%. Anal. Calcd (Found) for **2**: C, 43.71 (44.02); H, 3.36 (3.49); N 8.49 (8.27). Selected IR data (cm^{-1}): 3284 (s), 1596 (m), 1546 (w), 1462 (m), 1440 (m), 1336 (w), 1265 (w), 1194 (m), 1076 (vs), 1024 (m), 970 (m), 790 (m), 743 (m), 706 (s), 624 (m), 562 (mb), 466 (m), 424 (w).

Table 1 Bond Valence Sum (BVS)[a,b] calculations for Mn and selected oxygen atoms in complex **1**

Atom	Mn^{II}	Mn^{III}	Mn^{IV}
Mn1	<u>2.071</u>	1.965	1.948
Mn2	3.216	<u>2.985</u>	3.064
Mn3	<u>1.850</u>	1.730	1.754
Mn4	3.167	<u>2.897</u>	3.041
Mn5	4.202	3.908	<u>3.998</u>
Mn6	3.253	<u>3.021</u>	3.098

	BVS	assignment
O7	0.99	OH^-
O8	1.84	O^{2-}
O9	1.76	O^{2-}
O10	1.75	O^{2-}
O11	1.65	O^{2-}

[a] The underlined value is the one closest to the charge for which it was calculated. The oxidation state of a particular atom is the nearest whole number to the underlined value. [b] A BVS in the ~1.8-2.0, ~1.0-1.2, and ~0.2-0.4 ranges for an O atom is indicative of non-, single- and double-protonation, respectively, but these values can be altered somewhat by H-bonding.

Table 2 Bond Valence Sum (BVS) calculations for Mn and selected oxygen atoms in complex **2**

Atom	Mn^{II}	Mn^{III}	Mn^{IV}
Mn1	2.928	2.778	2.811

	BVS	assignment
O1	0.98	OH^-
O3	0.26	H_2O

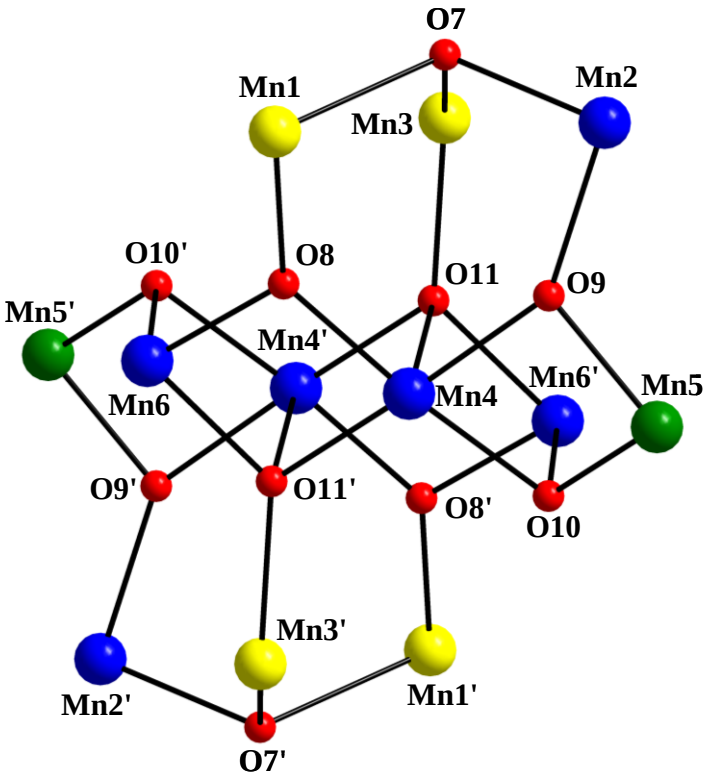

Fig. S1 Labeled PovRay representation of the $[Mn_{12}O_8(OH)_2]^{16+}$ core of **1** created by monoatomic bridges. Symmetry code: (′) = -*x*, 1-*y*, 2-*z*. O7 and O7′ are the hydroxido oxygen atoms. Colour scheme: Mn^{II} yellow; Mn^{III} blue; Mn^{IV} olive; O red.

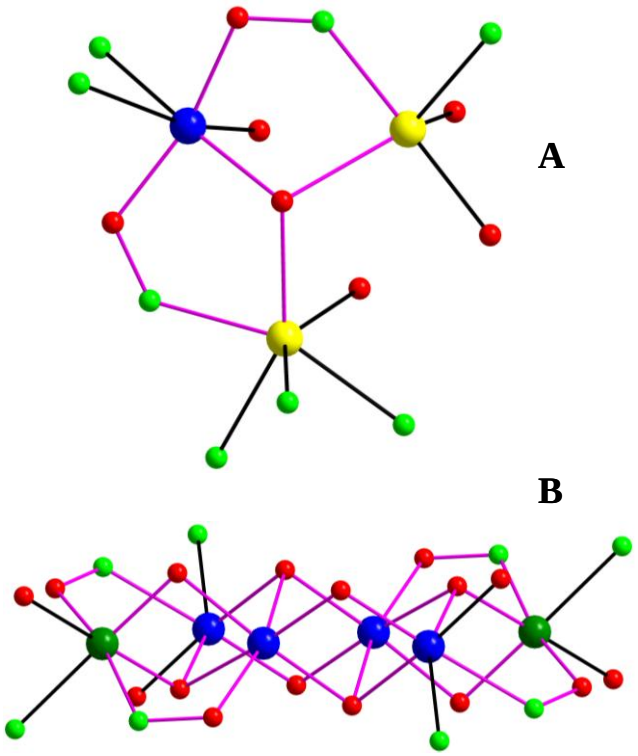

Fig. S2 The two layers of the core of **1**. Colour scheme: Mn^{II} yellow; Mn^{III} blue; Mn^{IV} olive; O red; N green.

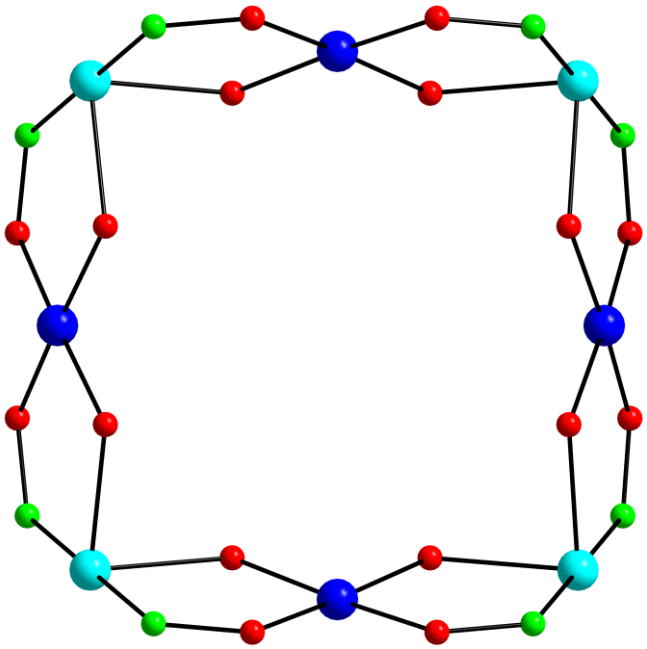

Fig. S3 PovRay representation of the complete $[Mn_4Ni_4(\mu\text{-}OH)_8(\mu\text{-}ON)_8]^{4+}$ core of **2**. Colour scheme: Mn^{III} blue; Ni^{II} cyan; O red; N green.

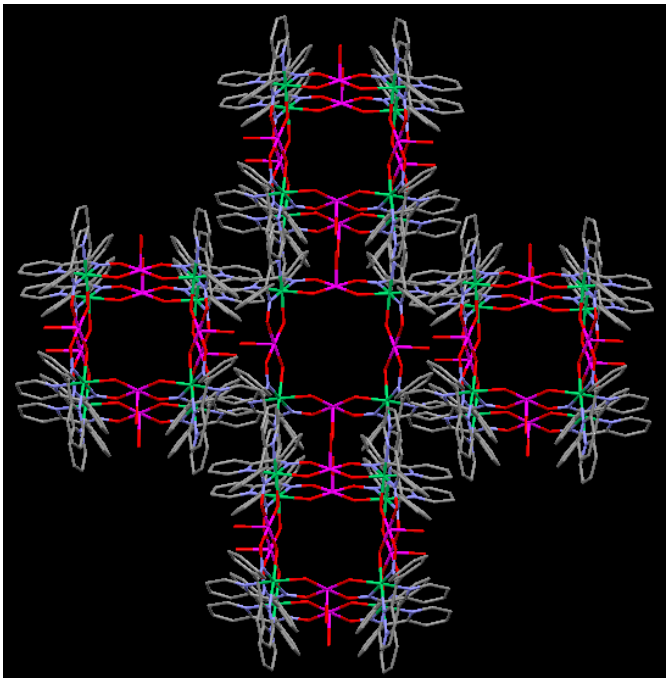

Fig. S4 Packing diagram of **2** along the c-axis.

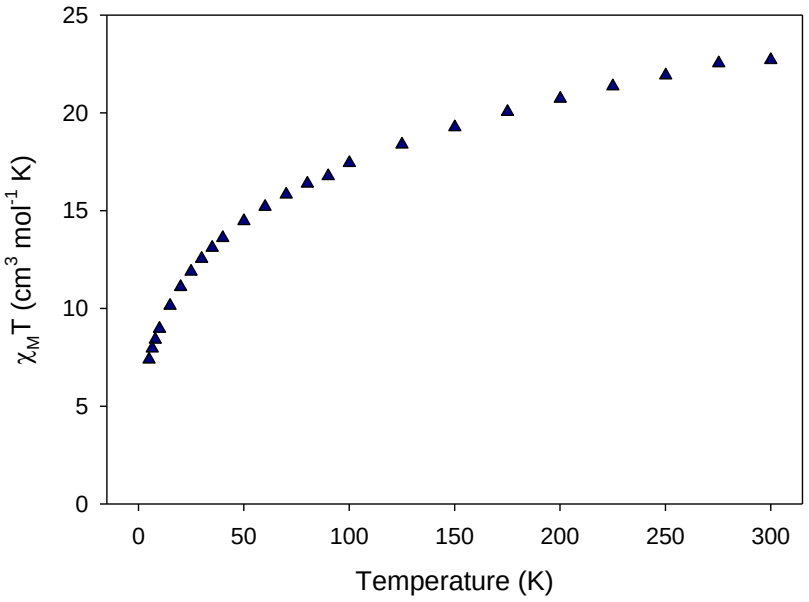

Fig. S5 $\chi_M T$ vs T data for **1** in a 0.1 T dc field.

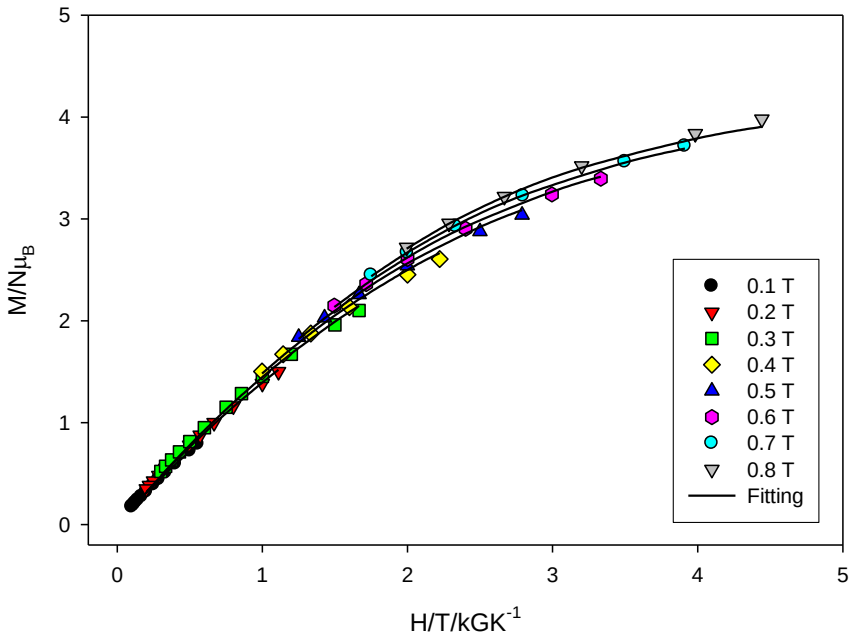

Fig. S6 Plot of $M/N\mu_B$ vs H/T for complex **2** at the indicated applied fields. The solid lines are the fit of the data; see the text for the fit parameters.

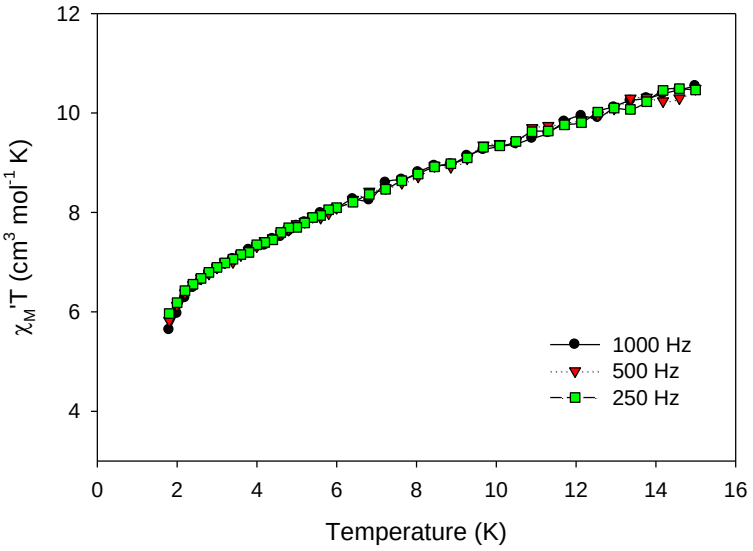

Fig. S7 Plot of the in-phase (χ'_M) (as $\chi'_M T$) ac susceptibility signals for **1**, measured in a 3.5 G field oscillating at the indicated frequencies. Extrapolation of the data above ~3 K (to avoid the effects of magnetization relaxation phenomena at lower temperatures) down to 0 K gives ~6 cm^3 K mol^{-1}, indicating an S = 3 ground state with g ~ 2.

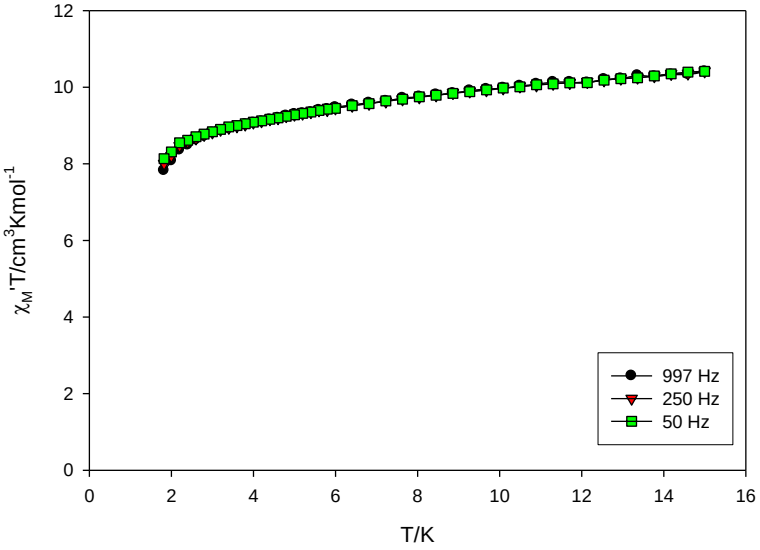

Fig. S8 Plot of the in-phase (χ'_M) (as $\chi'_M T$) ac susceptibility signals for **2**, measured in a 3.5 G field oscillating at the indicated frequencies. Extrapolation of the data above ~3 K (to avoid the effects of magnetization relaxation phenomena at lower temperatures) down to 0 K gives ~9 cm^3 K mol^{-1}, indicating an S = 4 ground state with g ~ 1.9, in excellent agreement with the dc magnetization fits.

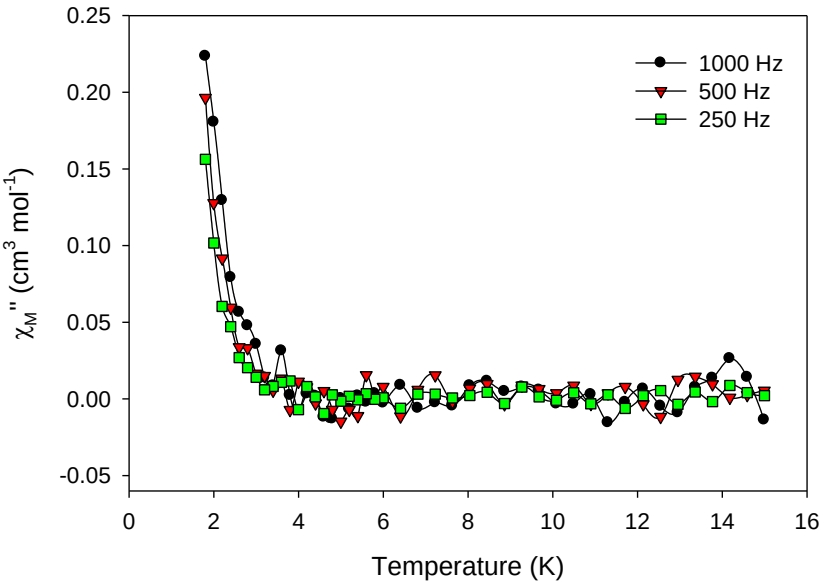

Fig. S9 Out-of-phase χ_M'' vs T ac susceptibility signals for **1** in a 3.5 G field oscillating at the indicated frequencies.