

Supporting Information

Constructing Octa- and Hexadecanuclear Manganese Clusters from Tetrahedral $\text{Mn}^{\text{III}}_3\text{Mn}^{\text{II}}$ Cores Bridged by Quinquedentate Schiff Base and Versatile Azide Groups

Dan Liu, Qi Zhou, Yan Chen, Fen Yang, Yang Yu, Zhan Shi* and Shouhua Feng

State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China. Fax: +86 431 85168624; E-mail: zshi@mail.jlu.edu.cn

Table S1. Bond valence sum calculation for Mn atoms in **1**.

Mn site	Mn ^{II}	Mn ^{III}	Mn ^{IV}
Mn1	<u>2.046</u>	1.926	1.873
Mn2	<u>2.076</u>	1.955	1.901
Mn3	3.410	<u>3.211</u>	3.122
Mn4	3.397	<u>3.199</u>	3.110
Mn5	3.395	<u>3.197</u>	3.108
Mn6	3.272	<u>3.081</u>	2.995
Mn7	3.422	<u>3.222</u>	3.132
Mn8	3.429	<u>3.229</u>	3.139

Table S2. Bond valence sum calculation for Mn atoms in **2**.

Mn site	Mn ^{II}	Mn ^{III}	Mn ^{IV}
Mn1	3.251	<u>3.022</u>	3.094
Mn2	2.996	<u>2.787</u>	2.851
Mn3	3.243	<u>3.019</u>	3.084
Mn4	<u>1.891</u>	1.747	1.806
Mn5	3.269	<u>3.053</u>	3.103
Mn6	3.220	<u>2.995</u>	3.064
Mn7	3.270	<u>3.044</u>	3.109
Mn8	<u>1.972</u>	1.851	1.867

Note. The underlined 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 underlined value.

Table S3. Bond valence sum calculation for oxygen atoms in **1**.

Atom	OH-	atom	OH-
O6	0.6889	O7	0.8390
O11	0.9246	O12	1.0845
O16	0.9423	O17	0.9073
O21	0.9073	O22	0.9097
O26	1.0933	O27	1.5704
O31	1.3572	O32	0.8807

Table S4. Bond valence sum calculation for oxygen atoms in **2**.

Atom	OH ⁻	atom	OH ⁻	Atom	OH ⁻	atom	H ₂ O
O6	0.8879	O16	0.7250	O30	1.0081	O19	0.308
O7	0.9271	O17	0.9474	O31	0.8619	O21	0.258
O11	0.8879	O25	1.0410	O35	1.1293		
O12	1.0584	O26	1.0962	O36	0.9423		

Note. The bond valence sum values for O atoms of O²⁻, OH⁻, and H₂O groups are typically 1.8–2.0, 1.0–1.2, and 0.2–0.4, respectively, but can be affected somewhat by hydrogen bonding.

Figure S1. Plot of reduced magnetization ($M/N\mu_B$) versus H/T for **1** (a) and **2** (b) in the temperature range 2.0-10 K.

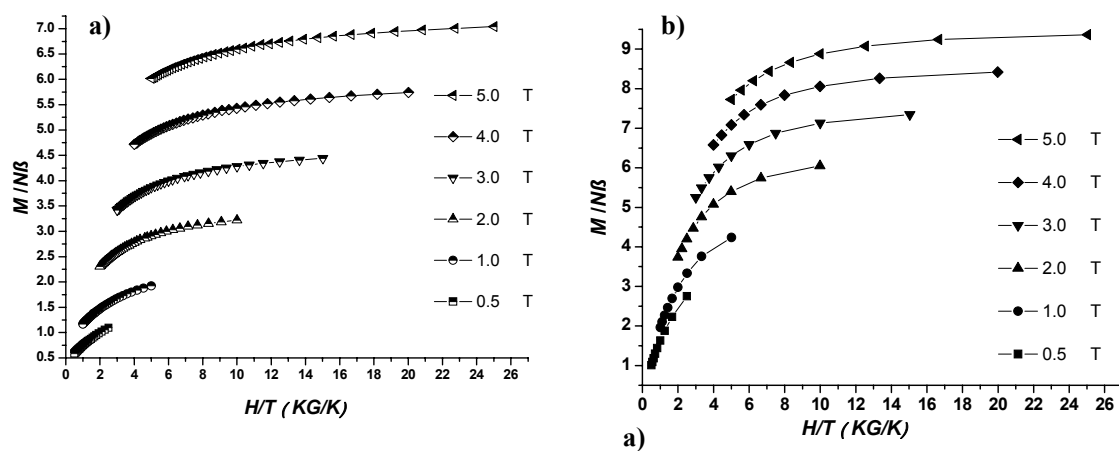


Figure S2. Temperature dependence of the in-phase (χ_M') versus T for **1** (a) and **2** (b) in a 3.0-G oscillating field at the indicated frequencies.

