

Electronic supplementary information (ESI)

Unusual oxidation state distributions observed for two mixed-valence heptanuclear manganese disc-like clusters.

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Table 1. Bond valence sum calculations for **1**. The oxidation state for each metal is the whole number closest to the value in bold.

Atoms	Mn(II)	Mn(III)	Mn(IV)
Mn1	2.19	2.03	1.98
Mn2	4.44	4.09	4.02
Mn3	1.99	1.84	1.80

Table 2. Selected bond lengths for compound **1**. Symmetry transformation: (^I) $-x + y, 1 - x, z$ and (^{II}) $1 - y, 1 + x - y, z$.

Mn1-O1 ^I	2.216(3)	Mn2-O7	1.910(3)
Mn1-O1	2.216(3)	Mn2-O2	1.953(3)
Mn1-O1 ^{II}	2.216(3)	Mn2-O1	1.969(3)
Mn1-O2	2.218(3)	Mn3-O7	2.186(3)
Mn1-O2 ^I	2.218(3)	Mn3-O9	2.205(3)
Mn1-O2 ^{II}	2.218(3)	Mn3-O8	2.219(3)
Mn1-N1	2.297(6)	Mn3-O1 ^I	2.250(3)
Mn2-O5	1.852(3)	Mn3-O3 ^I	2.271(3)
Mn2-O4	1.860(3)	Mn3-O2	2.314(3)
Mn2-O3	1.878(3)	Mn3-O2	2.430(4)

Table 3. Bond valence sum calculations for **2**. The oxidation state for each metal is the whole number closest to the value in bold.

Atoms	Mn(II)	Mn(III)	Mn(IV)
Mn1	1.94	1.79	1.72
Mn2	1.92	1.77	1.72
Mn3	3.39	3.12	3.05
Mn4	2.10	1.93	1.88
Mn5	1.92	1.77	1.72
Mn6	3.28	3.01	2.92
Mn7	3.24	2.98	2.89

Table 4. Selected bond lengths for compound **2**.

Mn1-F5	2.159(3)	Mn3-O12	1.903(4)	Mn5-O3	2.223(4)
Mn1-O3	2.225(4)	Mn3-O11	1.932(4)	Mn5-N7	2.535(6)
Mn1-F6	2.250(3)	Mn3-O2	1.966(4)	Mn5-O17	2.539(8)
Mn1-O4	2.262(4)	Mn3-O13	2.178(4)	Mn6-O20	1.863(4)
Mn1-O2	2.268(4)	Mn3-F5	2.200(3)	Mn6-F23	1.919(4)
Mn1-N1	2.272(4)	Mn4-O16	2.114(4)	Mn6-O21	1.998(4)
Mn1-O1	2.308(4)	Mn4-O14	2.128(4)	Mn6-O4	2.045(4)
Mn2-O1	2.158(4)	Mn4-O17	2.135(5)	Mn6-O3	2.102(4)
Mn2-O7	2.177(4)	Mn4-O15	2.159(4)	Mn6-O24	2.121(5)
Mn2-F5	2.189(3)	Mn4-F6	2.205(3)	Mn7-O7	1.889(4)
Mn2-O8	2.278(4)	Mn4-O2	2.276(4)	Mn7-F23	1.928(4)
Mn2-O1	2.311(4)	Mn5-O19	2.112(6)	Mn7-O1	1.968(3)
Mn2-O9	2.320(4)	Mn5-F6	2.186(3)	Mn7-O25	1.990(4)
Mn2-N3	2.479(5)	Mn5-O20	2.213(4)	Mn7-O26	2.071(4)
Mn3-O15	1.897(4)	Mn5-O18	2.217(5)	Mn7-O4	2.275(4)

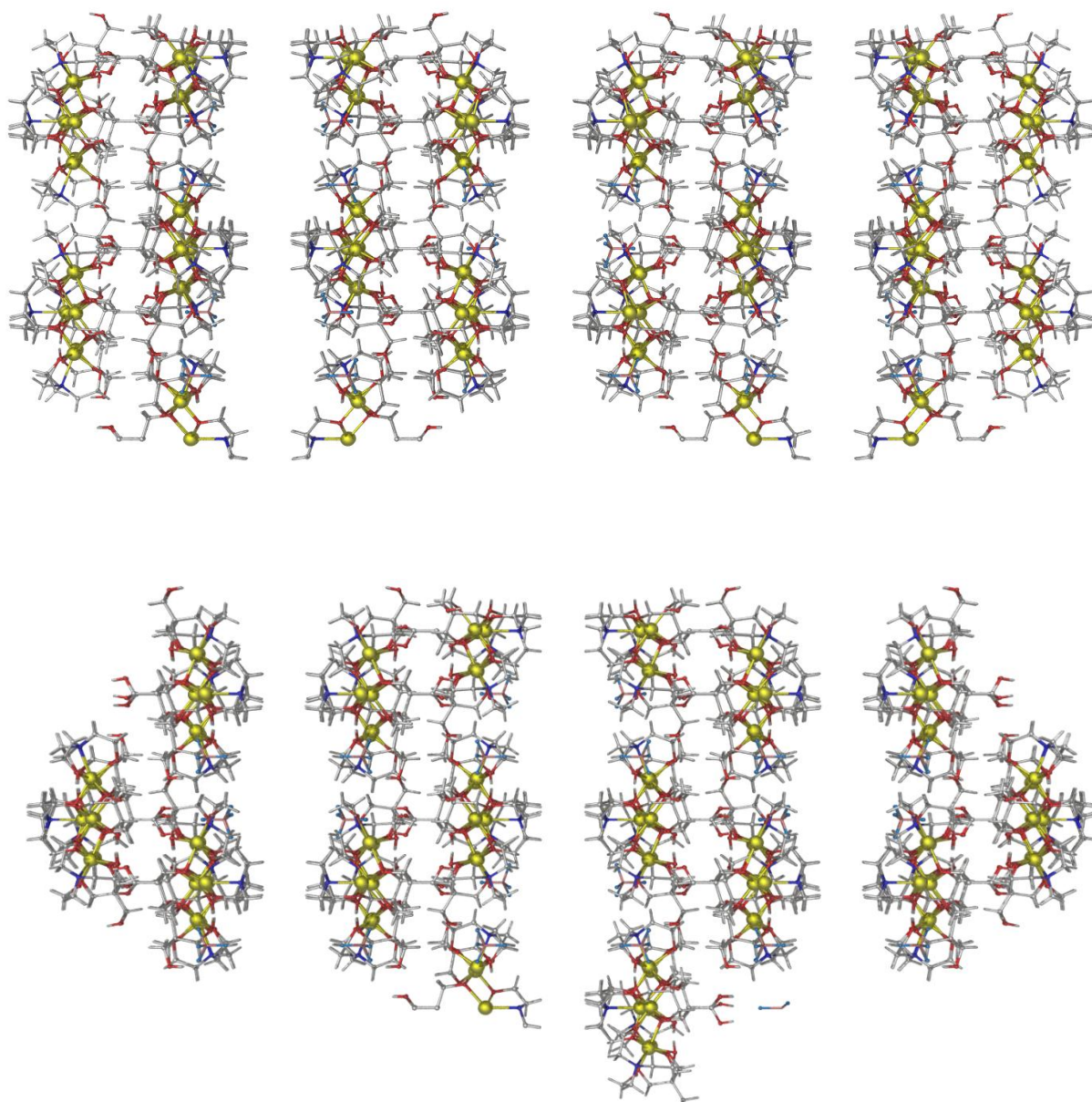


Fig. S1. Crystal packing of **1**, highlighting the void channels present.

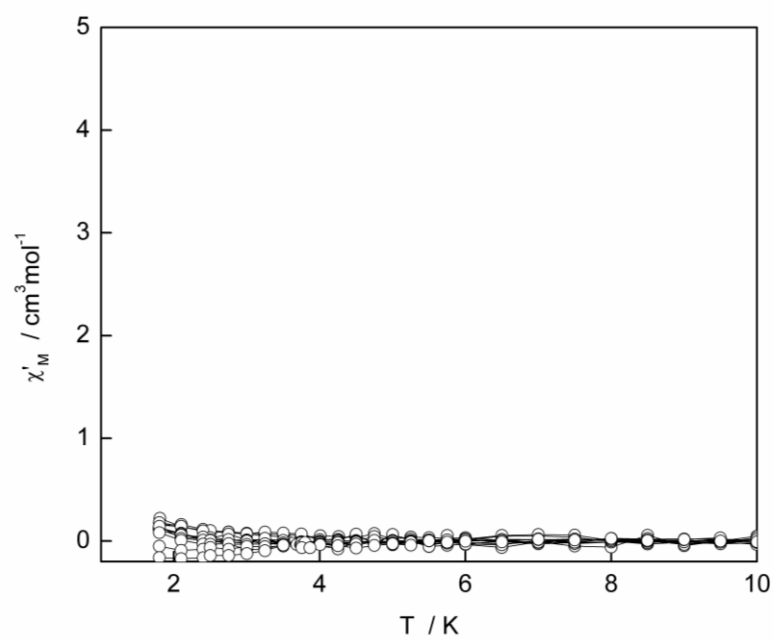


Fig. S2. Plot of χ'_M vs. T for cluster **1**, with AC frequencies of 1500, 1250, 1000, 750, 500 and 250 Hz.

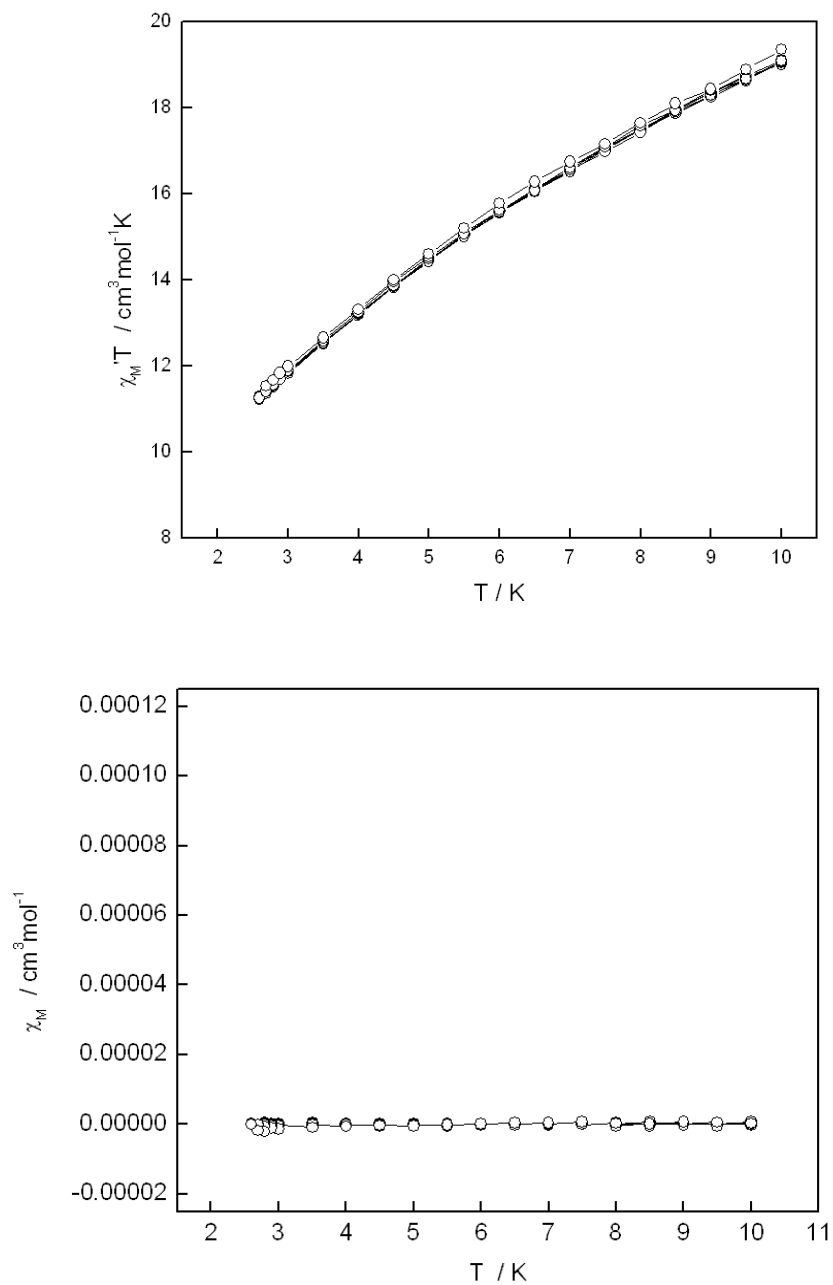


Fig S3. Plots of $\chi_M' T$ vs. T (top) and χ_M'' vs. T (bottom) for cluster **2**. with AC frequencies 1500, 1250, 1000, 750, 500 and 250 Hz. The solid lines are guides to the eye.