

Supplementary information

High-Spin Tetranuclear Mn^{II}₂Mn^{IV}₂ Clusters with Unique Mn(II)-Mn(IV) Magnetic Exchange. Synthesis, Structures and Magnetism of Mn₄ and Fe₄ Clusters with Tetrakis(2-hydroxyethyl)ethylenediamine †

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1. Bond valence sum calculations

Bond valence sum calculations for complexes **1** and **2** are based on the program BVS*. *d* is the bond distances around metal center in angstrom unit.

Complex 1:

Mn1	2.089	$d_{\text{average}} = 2.269$
Mn1-O1	0.402	$d = 2.127(2)$
Mn1-O3	0.375	$d = 2.153(2)$
Mn1-O2	0.313	$d = 2.220(2)$
Mn1-O5	0.293	$d = 2.245(2)$
Mn1-O4	0.217	$d = 2.355(3)$
Mn1-N2	0.257	$d = 2.373(3)$
Mn1-N1	0.232	$d = 2.411(3)$
Mn2	4.436	$d_{\text{average}} = 1.907$
Mn2-O10	0.902	$d = 1.828(2)$
Mn2-O9	0.846	$d = 1.852(2)$
Mn2-O11	0.803	$d = 1.871(2)$

Mn2-O6	0.661	$d = 1.943(2)$
Mn2-O3	0.661	$d = 1.943(2)$
Mn2-O2	0.562	$d = 2.003(2)$
Mn3	2.082	$d_{\text{average}} = 2.270$
Mn3-O6	0.393	$d = 2.136(2)$
Mn3-O8	0.366	$d = 2.162(2)$
Mn3-O5	0.312	$d = 2.221(2)$
Mn3-O2	0.301	$d = 2.234(2)$
Mn3-N4	0.267	$d = 2.358(3)$
Mn3-O7	0.214	$d = 2.360(3)$
Mn3-N3	0.229	$d = 2.416(3)$
Mn4	4.449	$d_{\text{average}} = 1.906$
Mn4-O13	0.905	$d = 1.827(2)$
Mn4-O12	0.853	$d = 1.849(2)$
Mn4-O14	0.793	$d = 1.876(2)$
Mn4-O1	0.672	$d = 1.937(2)$
Mn4-O8	0.665	$d = 1.941(2)$
Mn4-O5	0.562	$d = 2.003(2)$
Mn5	2.067	$d_{\text{average}} = 2.271$
Mn5-O17	0.394	$d = 2.135(2)$
Mn5-O15	0.370	$d = 2.159(2)$
Mn5-O18	0.291	$d = 2.247(2)$
Mn5-O20	0.279	$d = 2.262(2)$
Mn5-O16	0.226	$d = 2.341(3)$
Mn5-N5	0.267	$d = 2.358(3)$
Mn5-N6	0.241	$d = 2.397(3)$
Mn6	4.450	$d_{\text{average}} = 1.905$
Mn6-O24	0.888	$d = 1.834(2)$
Mn6-O23	0.855	$d = 1.848(2)$
Mn6-O25	0.778	$d = 1.883(2)$
Mn6-O15	0.683	$d = 1.931(2)$
Mn6-O19	0.667	$d = 1.940(2)$
Mn6-O18	0.579	$d = 1.992(2)$
Mn7	2.069	$d_{\text{average}} = 2.271$
Mn7-O19	0.387	$d = 2.141(2)$
Mn7-O21	0.372	$d = 2.156(2)$
Mn7-O20	0.298	$d = 2.238(2)$
Mn7-O18	0.281	$d = 2.260(2)$
Mn7-O22	0.229	$d = 2.335(3)$

Mn7-N8	0.270	$d = 2.354(3)$
Mn7-N7	0.232	$d = 2.411(3)$
Mn8	4.432	$d_{\text{average}} = 1.907$
Mn8-O27	0.885	$d = 1.835(2)$
Mn8-O26	0.862	$d = 1.845(2)$
Mn8-O28	0.778	$d = 1.883(2)$
Mn8-O21	0.669	$d = 1.939(2)$
Mn8-O17	0.665	$d = 1.941(2)$
Mn8-O20	0.573	$d = 1.996(2)$

Complex 2:

Mn1	2.075	$d_{\text{average}} = 2.271$
Mn1-O2	0.406	$d = 2.1231(18)$
Mn1-O3	0.367	$d = 2.1613(18)$
Mn1-O1	0.314	$d = 2.2191(18)$
Mn1-O1	0.262	$d = 2.2854(19)$
Mn1-O4	0.233	$d = 2.329(2)$
Mn1-N2	0.263	$d = 2.364(2)$
Mn1-N1	0.230	$d = 2.413(2)$
Mn2	4.480	$d_{\text{average}} = 1.902$
Mn2-O7	0.871	$d = 1.841(2)$
Mn2-O6	0.856	$d = 1.8476(19)$
Mn2-O5	0.799	$d = 1.873(2)$
Mn2-O2	0.694	$d = 1.925(2)$
Mn2-O3	0.667	$d = 1.940(2)$
Mn2-O1	0.593	$d = 1.9836(18)$

* Bond-Valence Parameters for Solids, N. E. Brese and M. O'keeffe, *Acta Cryst.*, 1991, **B47**, 192-197.