Supplementary Material (ESI) for Dalton Transactions

†Electronic Supplementary Information (ESI)

Decanuclear and Octadecanuclear Manganese(II/III)-Triethanolamine Single Molecule Magnets†

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Table S1. Bond valence sums for complex **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	**1.98**	1.84	1.80
Mn2	3.28	**3.01**	2.96
Mn3	3.41	**3.12**	3.07
Mn4	**1.97**	1.84	1.81
Mn5	3.31	**3.06**	3.03
Mn6	**1.80**	1.65	1.62
Mn7	3.36	**3.09**	3.05
Mn8	3.39	**3.11**	3.06
Mn9	3.39	**3.12**	3.06
Mn10	**1.98**	1.86	1.79

Table S2. Selected bond lengths (Å) for complex **1**.

Mn1-O2	2.167(4)	Mn3-O14	2.080(5)	Mn6-O22	2.055(4)	Mn9-O22	1.862(4)
Mn1-O3	2.183(5)	Mn3-O13	2.098(5)	Mn6-O8	2.066(4)	Mn9-O32	1.902(4)
Mn1-O6	2.256(4)	Mn3-O12	2.104(6)	Mn6-O23	2.077(4)	Mn9-O31	2.018(6)
Mn1-O5	2.310(5)	Mn4-O16	2.170(5)	Mn6-N5	2.229(6)	Mn9-O28	2.028(5)
Mn1-O4	2.328(6)	Mn4-O15	2.183(5)	Mn7-O23	1.842(4)	Mn9-O30	2.087(5)
Mn1-N1	2.339(6)	Mn4-O17	2.283(6)	Mn7-O2	1.915(4)	Mn9-O29	2.190(5)
Mn1-N2	2.388(6)	Mn4-O18	2.284(5)	Mn7-O7	2.060(5)	Mn10-O32	2.156(5)
Mn2-O8	1.860(4)	Mn4-O14	2.285(6)	Mn7-O24	2.072(5)	Mn10-O33	2.210(5)
Mn2-O3	1.919(4)	Mn4-N3	2.336(6)	Mn7-O25	2.085(6)	Mn10-O35	2.277(5)
Mn2-O9	2.051(6)	Mn4-N4	2.371(6)	Mn7-O6	2.143(4)	Mn10-O34	2.282(6)
Mn2-O10	2.099(5)	Mn5-O22	1.843(4)	Mn8-O23	1.852(4)	Mn10-O29	2.290(4)
Mn2-O7	2.115(5)	Mn5-O16	1.908(4)	Mn8-O33	1.915(4)	Mn10-N6	2.350(7)
Mn2-O6	2.155(5)	Mn5-O20	2.056(6)	Mn8-O27	2.033(5)	Mn10-N7	2.362(6)
Mn3-O8	1.846(4)	Mn5-O13	2.076(5)	Mn8-O29	2.060(5)		
Mn3-O15	1.914(5)	Mn5-O21	2.081(5)	Mn8-O26	2.109(5)		
Mn3-O11	2.039(5)	Mn5-O14	2.183(6)	Mn8-O28	2.111(5)		

Table S3. Bond valence sums for complex **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	**2.16**	2.04	1.98
Mn2	3.40	**3.16**	3.08
Mn3	3.32	**3.07**	3.02
Mn4	3.44	**3.18**	3.12
Mn5	3.25	**3.01**	2.96
Mn6	3.42	**3.16**	3.11
Mn7	3.39	**3.14**	3.08
Mn8	**1.90**	1.77	1.74
Mn9	3.35	**3.13**	3.07
Mn10	**2.10**	1.99	1.94
Mn11	3.35	**3.07**	3.01
Mn12	3.27	**3.03**	2.97
Mn13	3.42	**3.23**	3.18
Mn14	3.32	**3.08**	3.03
Mn15	3.09	**2.91**	2.87
Mn16	3.34	**3.12**	3.07
Mn17	3.50	**3.22**	3.16
Mn18	3.31	**3.10**	2.95

Table S4. Selected bond lengths (Å) for complex **1**

Mn1-O3	2.105(5)	Mn4-N8	2.481(3)	Mn9-O28	2.203(2)	Mn14-N34	1.956(3)
Mn1-O2	2.141(3)	Mn5-O16	1.892(2)	Mn9-N5	2.343(3)	Mn14-O28	1.981(2)
Mn1-N2	2.248(3)	Mn5-O13	1.925(3)	Mn10-O27	2.117(2)	Mn14-O19	2.256(3)
Mn1-O1	2.296(3)	Mn5-O11	1.935(3)	Mn10-O7	2.195(3)	Mn14-N27	2.469(2)
Mn1-O5	2.301(2)	Mn5-O12	2.108(2)	Mn10-O6	2.214(2)	Mn15-O27	1.850(2)
Mn1-O4	2.303(4)	Mn5-O14	2.210(3)	Mn10-O21	2.219(3)	Mn15-O32	1.959(3)
Mn1-N1	2.306(3)	Mn5-N11	2.354(3)	Mn10-N19	2.309(3)	Mn15-O31	1.969(3)
Mn1a-O1	1.782(4)	Mn5-O15	2.519(2)	Mn10-N16	2.349(3)	Mn15-O28	1.994(2)
Mn1a-O3a	2.193(5)	Mn6-O15	1.872(2)	Mn10-O20	2.369(3)	Mn15-N33	2.394(3)
Mn1a-N2	2.253(4)	Mn6-O9	1.918(2)	Mn11-O16	1.919(2)	Mn15-N16	2.413(3)
Mn1a-O5	2.300(4)	Mn6-O22	1.930(2)	Mn11O29	1.926(3)	Mn16-O27	1.836(3)
Mn1a-N1	2.337(4)	Mn6-O10	1.951(2)	Mn11-O17	1.957(2)	Mn16-O29	1.941(3)
Mn1a-O2	2.602(4)	Mn6-O12	2.144(2)	Mn11N20	1.959(3)	Mn16-N30	1.965(3)
Mn2-O7	1.874(2)	Mn6-N12	2.390(3)	Mn11-O14	2.220(2)	Mn16-O17	2.014(2)
Mn2-O5	1.904(2)	Mn7-O12	1.868(2)	Mn11-O24	2.331(2)	Mn16-O30	2.217(2)
Mn2-O6	1.914(2)	Mn7-O20	1.923(2)	Mn12-O16	1.890(2)	Mn16-O20	2.318(2)
Mn2-N2	1.991(3)	Mn7-O17	1.967(2)	Mn12-O25	1.930(2)	Mn17-O22	1.900(2)
Mn2-N5	2.332(3)	Mn7-O6	2.121(2)	Mn12-O15	2.007(2)	Mn17-O28	1.913(2)
Mn2-N8	2.418(3)	Mn7-N8	2.128(3)	Mn12-O26	2.153(2)	Mn17-O30	1.916(2)
Mn3-O1	1.886(3)	Mn7-O14	2.143(3)	Mn12-O24	2.223(2)	Mn17-O24	1.980(2)
Mn3-O8	1.896(2)	Mn8-O23	2.080(2)	Mn12-N23	2.246(3)	Mn17-O17	2.094(2)
Mn3-O5	1.928(2)	Mn8-O8	2.155(3)	Mn12-O22	2.286(2)	Mn17-N27	2.299(3)
Mn3-O9	1.963(2)	Mn8-O18	2.260(3)	Mn13-O23	1.845(2)	Mn18-O26	1.889(3)
Mn3-O10	2.302(2)	Mn8-O9	2.263(2)	Mn13-O25	1.934(2)	Mn18-O15	1.921(2)
Mn3-N5	2.366(3)	Mn8-O19	2.324(2)	Mn13-O22	1.950(2)	Mn18-N37	1.942(4)
Mn4- O2	1.872(3)	Mn8-N15	2.334(3)	Mn13-N24	1.968(3)	Mn18-N40	1.985(3)
Mn4-O11	1.891(3)	Mn9-O6	1.899(2)	Mn13-N12	2.310(3)	Mn18-O13	2.120(3)
Mn4- O5	1.909(3)	Mn9-O9	1.937(2)	Mn13-N27	2.344(3)		
Mn4-O12	1.920(2)	Mn9-O19	1.952(2)	Mn14-O23	1.857(2)		
Mn4-O10	2.255(2)	Mn9-N16	1.974(3)	Mn14-O31	1.945(2)		

Figure S1. Observed (red squares) and calculated (black diamonds) magnetisation isotherm values (y-axis in $N\beta$) for the Mn_{10} cluster **1** in fields up to 50,000 Oe (5 T) (x-axis) at 2 K. See the script and the equations in Scheme S1 for the model using $g = 2.0$, and spin states S =10, 11, 12, 13, 14, 9 with energies: 0, 1, 3, 6, 9, 1 cm^{-1}. No zero field splitting is included.

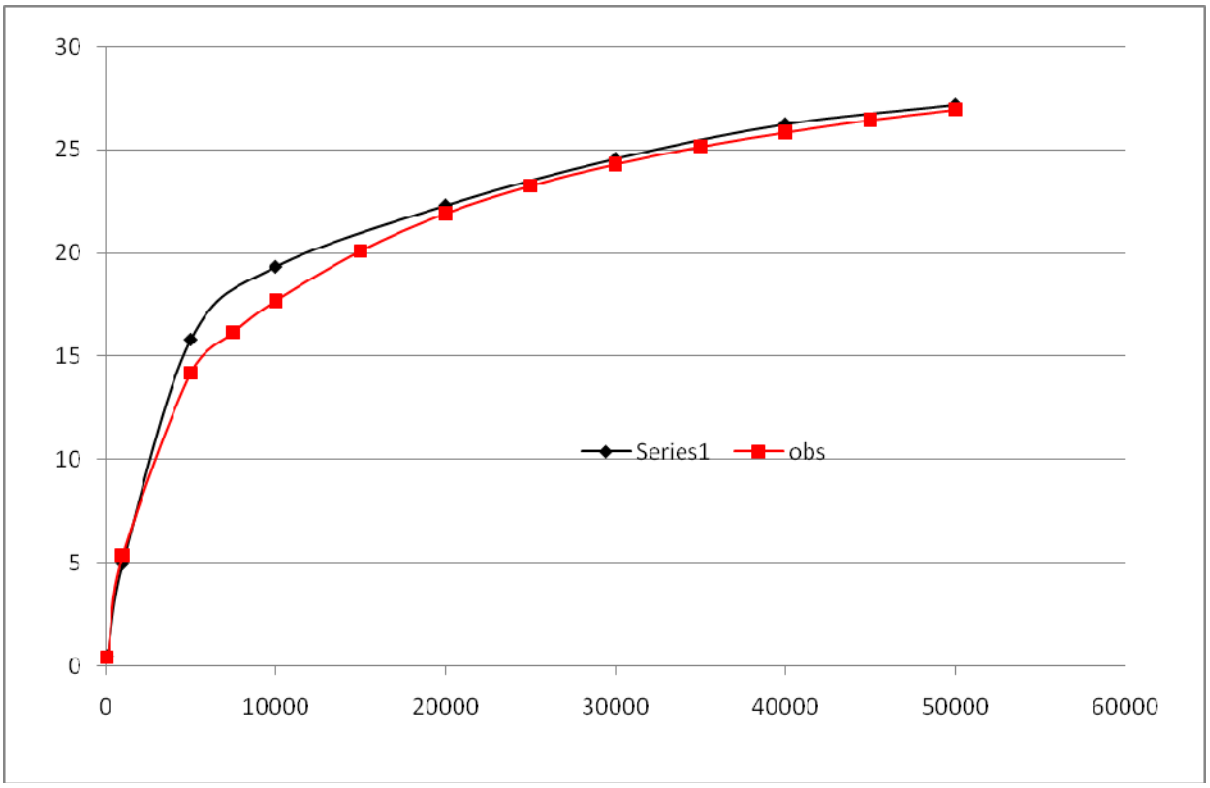


Figure S2 Observed (red squares) and calculated (black diamonds) magnetisation isotherm values (y-axis in $N\beta$) for the Mn_{10} cluster **1** in fields up to 50,000 Oe (5 T) (x-axis) at 3 K. See the script and the equations in Scheme S1 for the model using $g = 2.0$, and spin states S =10, 11, 12, 13, 14, 9 with energies: 0, 1, 3, 6, 9, 1 cm^{-1}. No zero field splitting is included.

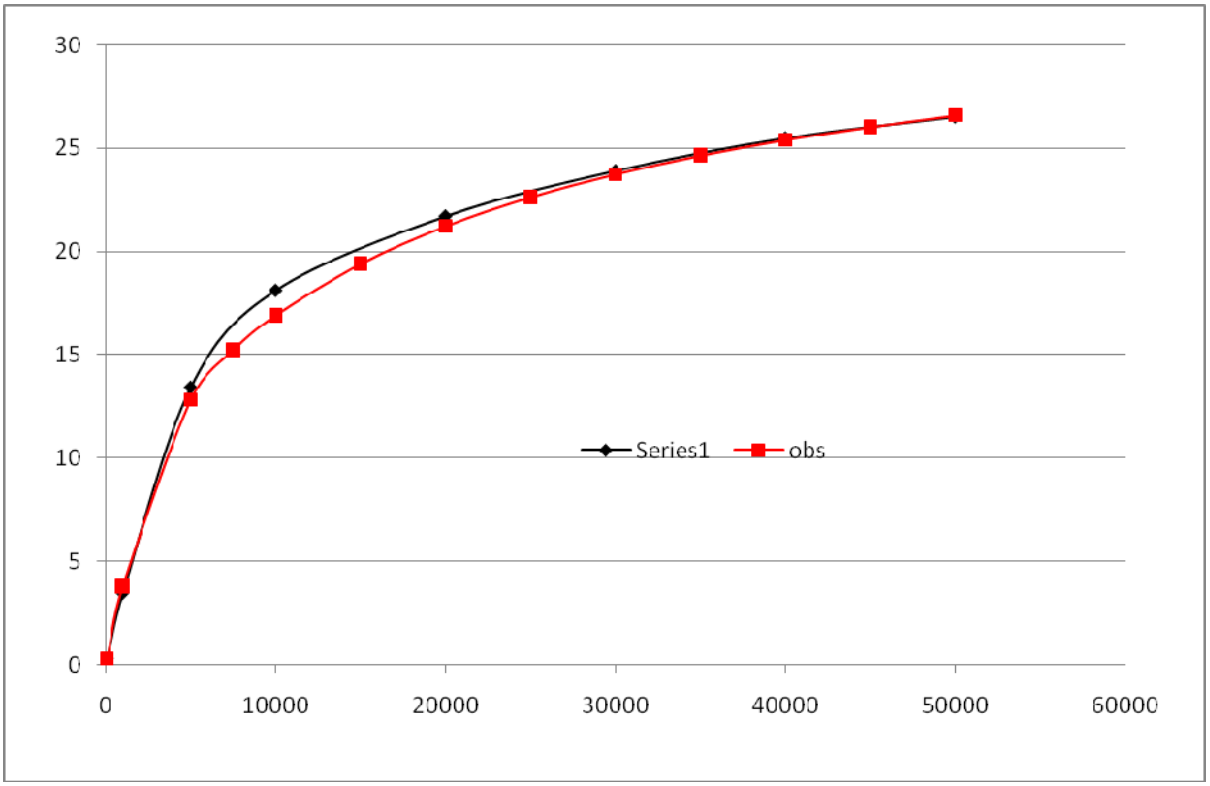


Figure S3 Observed (red squares) and calculated (black diamonds) magnetisation isotherm values (y-axis in $N\beta$) for the Mn_{10} cluster **1** in fields up to 50,000 Oe (5 T) (x-axis) at 4 K. See the script and the equations in Scheme S1 for the model using $g = 2.0$, and spin states S =10, 11, 12, 13, 14, 9 with energies: 0, 1, 3, 6, 9, 1 cm^{-1}. No zero field splitting is included.

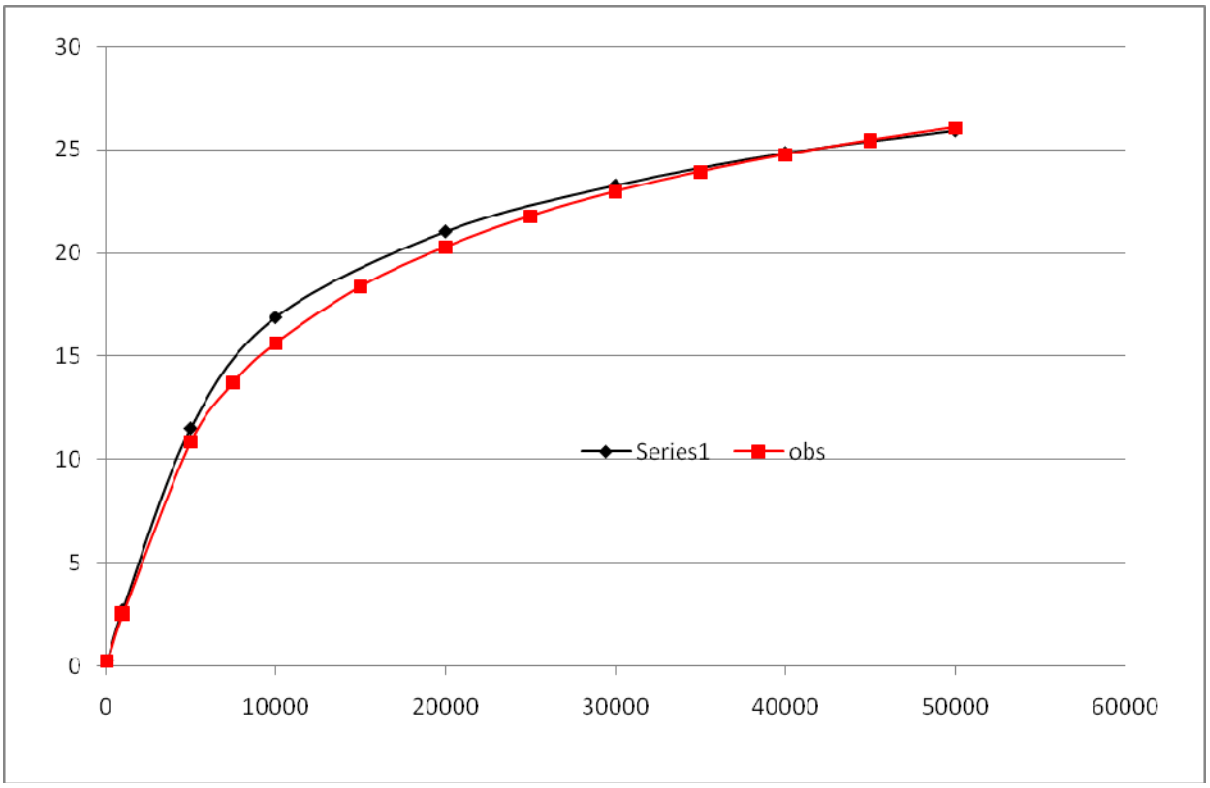


Figure S4 Observed (red squares) and calculated (black diamonds) magnetisation isotherm values (y-axis in $N\beta$) for the Mn_{10} cluster **1** in fields up to 50,000 Oe (5 T) (x-axis) at 5.5 K. See the script and the equations in Scheme S1 for the model using g = 2.0, and spin states S =10, 11, 12, 13, 14, 9 with energies: 0, 1, 3, 6, 9, 1 cm^{-1}. No zero field splitting is included.

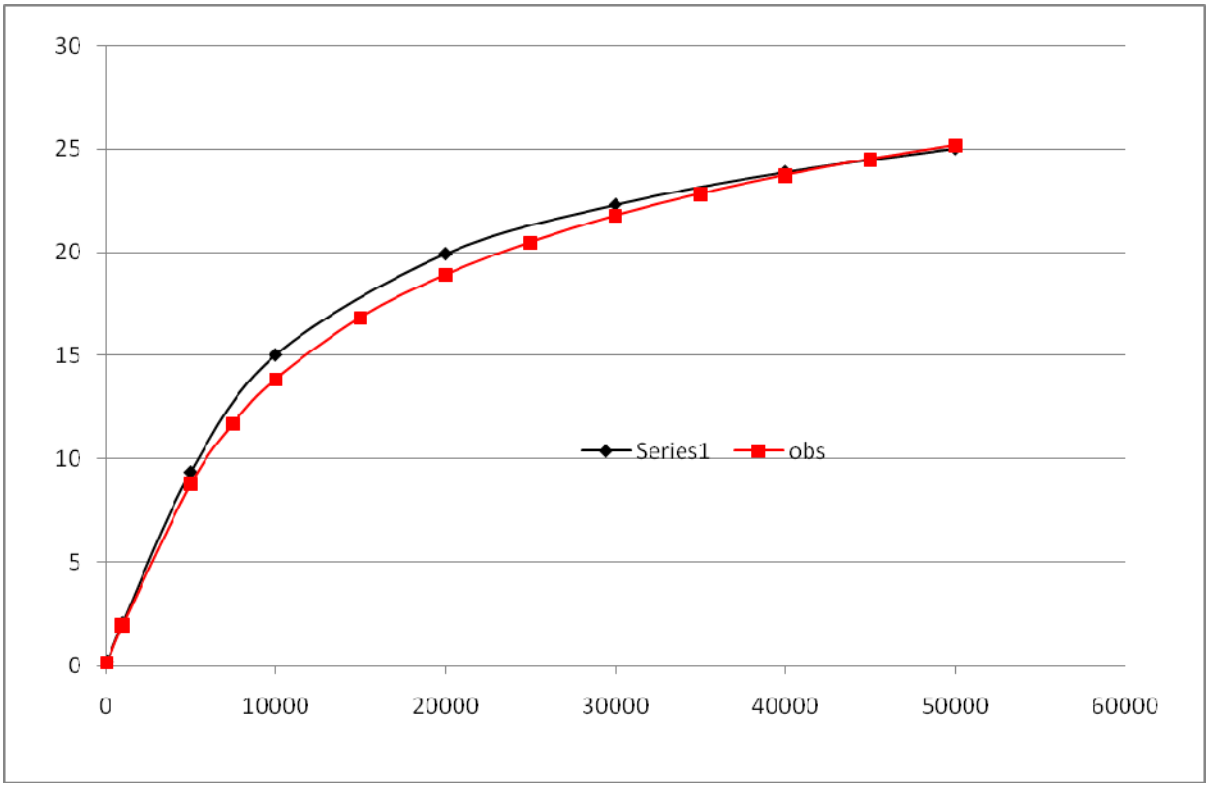


Figure S5 Observed (red squares) and calculated (black diamonds) magnetisation isotherm values (y-axis in $N\beta$) for the Mn_{10} cluster **1** in fields up to 50,000 Oe (5 T) (x-axis) at 10 K. See the script and the equations in Scheme S1 for the model using $g = 2.0$, and spin states S =10, 11, 12, 13, 14, 9 with energies: 0, 1, 3, 6, 9, 1 cm^{-1}. No zero field splitting is included. See the script for probable reasons for divergence between observed and calculated curves.

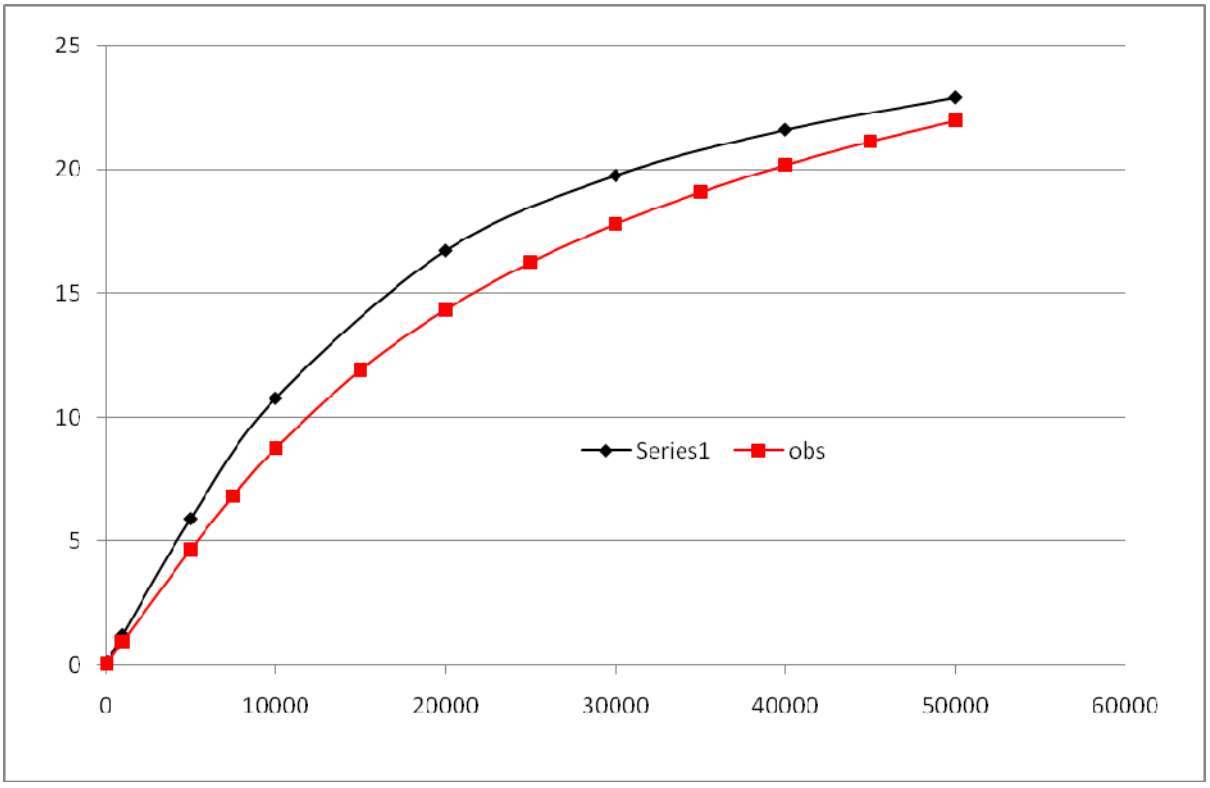


Figure S6 Observed (red squares) and calculated (black diamonds) magnetisation isotherm values (y-axis in $N\beta$) for the Mn_{10} cluster **1** in fields up to 50,000 Oe (5 T) (x-axis) at 20 K. See the script and the equations in Scheme S1 for the model using $g = 2.0$, and spin states S =10, 11, 12, 13, 14, 9 with energies: 0, 1, 3, 6, 9, 1 cm^{-1}. No zero field splitting is included. See the script for probable reasons for divergence between observed and calculated curves.

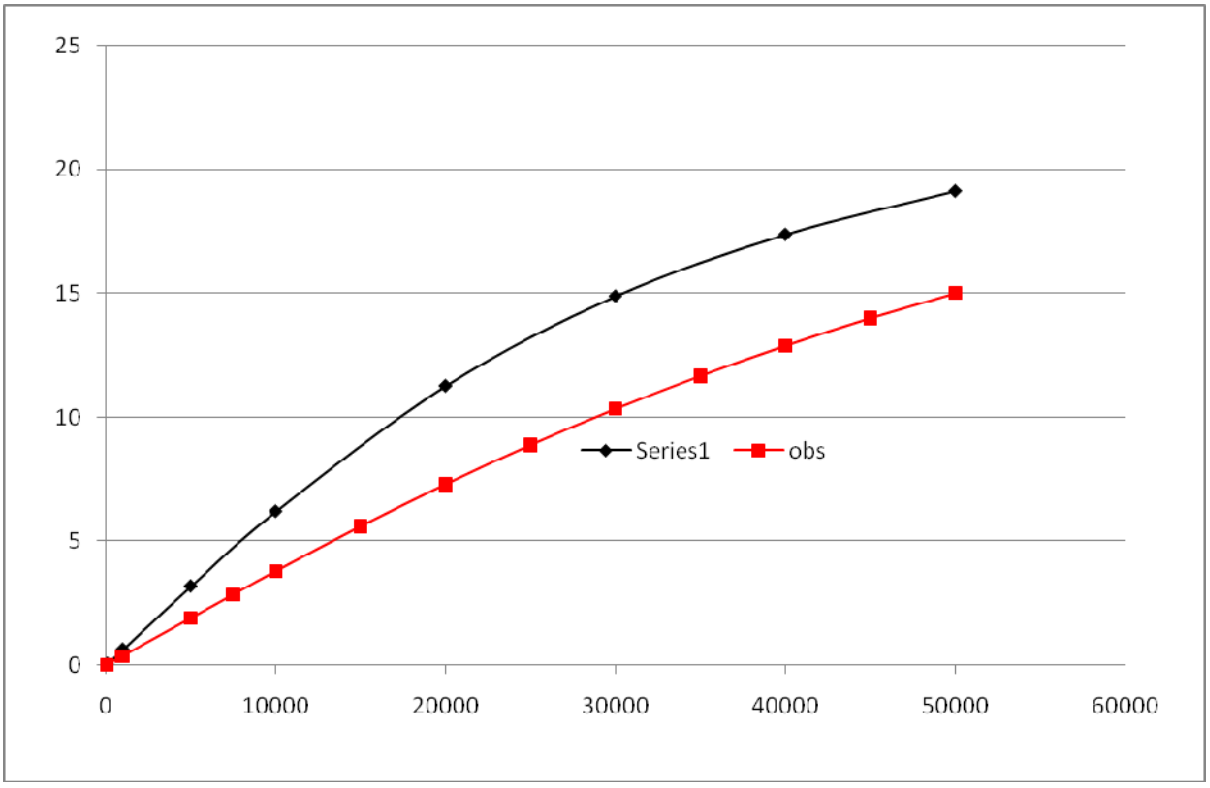


Figure S7 Observed magnetisation values, *M*, in *Nβ* (orange squares) for the Mn_{18} cluster, **2**, in a field of 0.1 T (1000 Oe), at temperatures between 2 to 20 K. The blue line is that calculated for *M* using the model given in the script and equations in Scheme S1. It assumes an isolated $S = 21/2$ state and $g = 1.97$. The calculations were carried out at 2, 3, 4, 5.5, 10 & 20K.

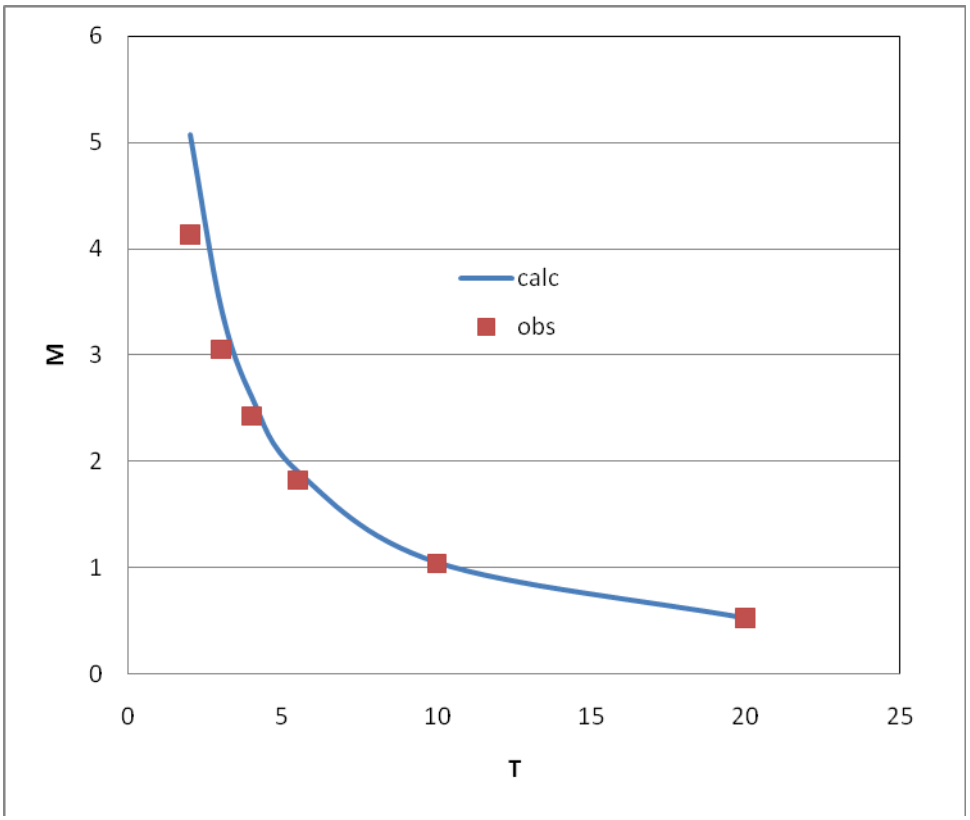
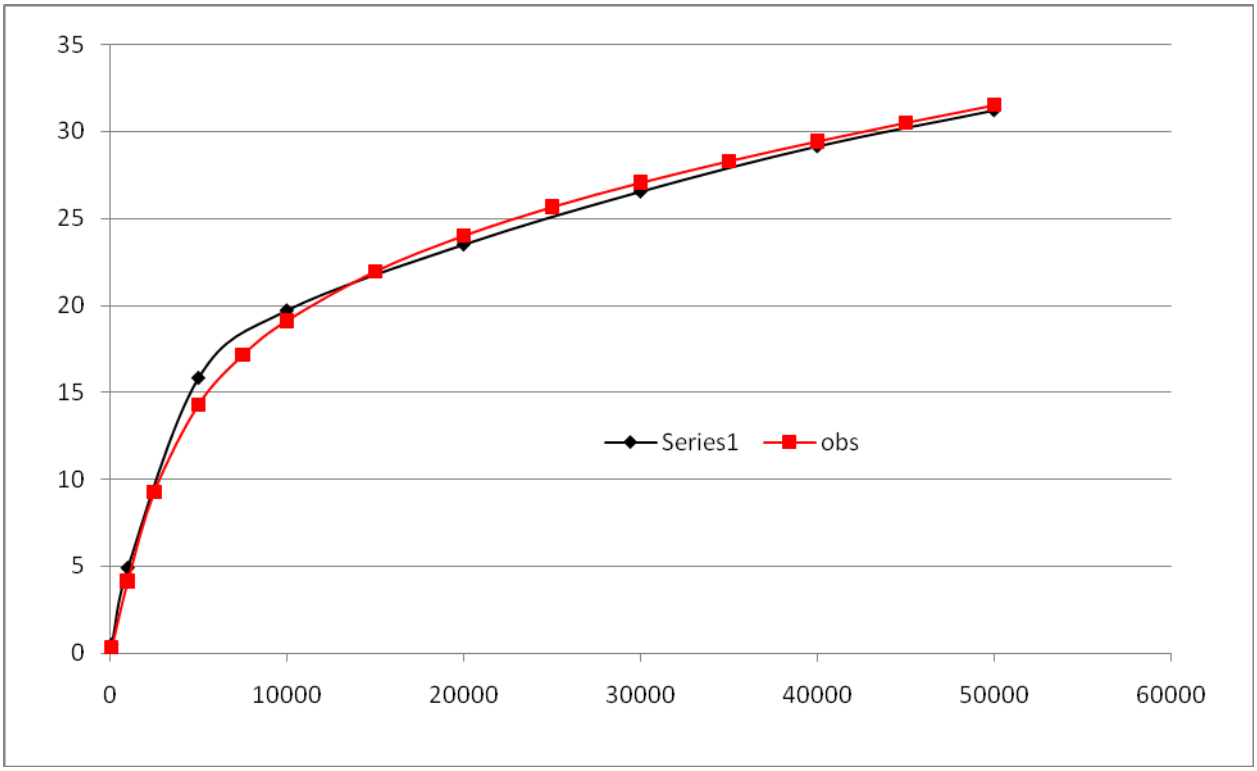


Figure S8. Observed (red squares) and calculated (black diamonds) magnetisation isotherm values (y-axis in $N\beta$) for the Mn_{18} cluster **2** in fields up to 50,000 Oe (5 T) (x-axis) at 2 K. See the script and the equations in Scheme S1 for the model using $g = 2.0$, and single S states from 17/2 through to 35/2 with energies: 1, 0, 0, 1, 3, 5, 8, 12, 16, 22 cm^{-1}. This is an exploratory calculation and degeneracies are not included. No zero field splitting is included. . For the above energies the respective lowest energy levels (S in parentheses) are:1 T and below (21/2), 2 T (23/2), 3 T(27/2), 4 T(29/2) and 5 T(33/2)



Scheme S1 The energies of the Zeeman M_S levels (for spin state S) and the magnetization, M, are calculated for clusters **1** and **2** using the equation given and the thermodynamic equation for M given.

$$E(M_S) = E + M_S g \beta H$$

$$M = -N\beta \frac{\sum_{-M}^{+M} M_s g \, e^{-E(M_s/kT)}}{\sum_{-M}^{+M} e^{-E(M_s/kT)}}$$