

# **Chemistry—A European Journal**

## **Supporting Information**

### **Exchange Interactions and Magnetic Properties of a Molecular Mn<sub>18</sub>-Ring Complex**

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## Powder X-ray Diffraction Analysis

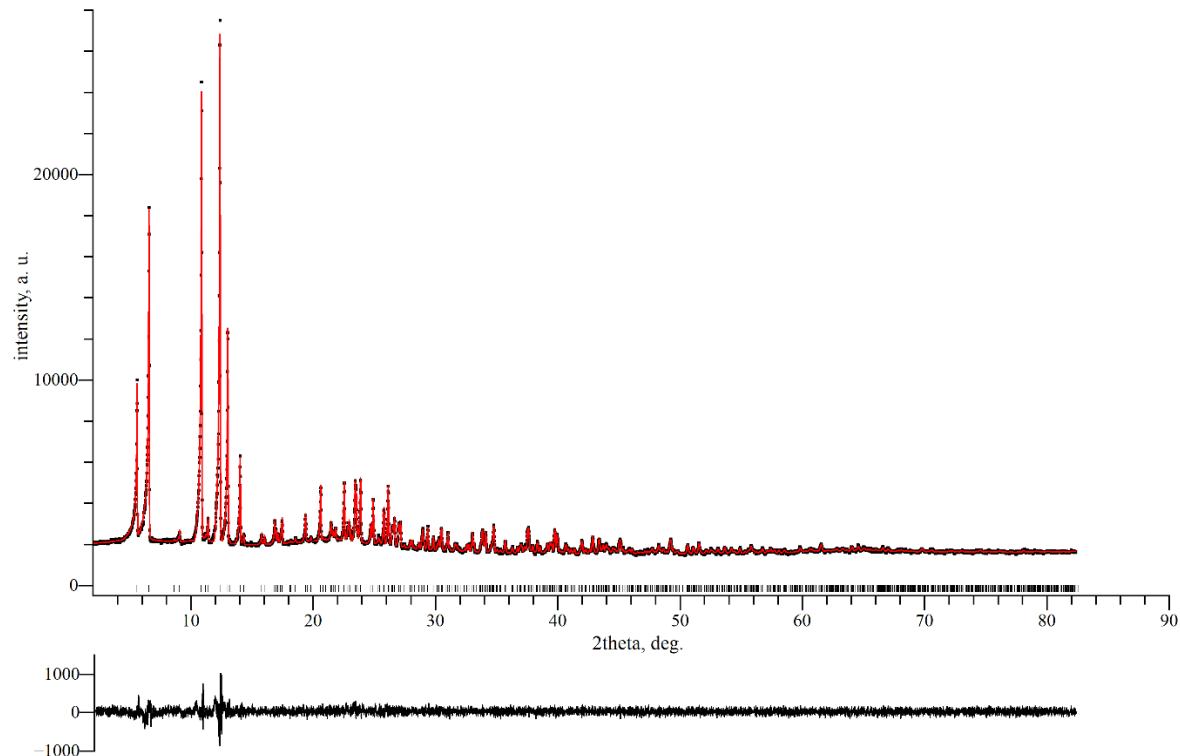


Figure S 1. Observed (black) and calculated (red) powder X-ray diffraction pattern of  $[\text{Mn}_3\text{O}(\text{OAc})_7(\text{HOAc})]_6 \cdot x\text{AcOH}$  ( $x = 6-9$ ) after Le Bail fit. The calculated reflection positions are indicated by the vertical bars below the pattern. The curve at the bottom represents the difference between the observed and the calculated intensities.  $R_p = 1.73$ ,  $R_{wp} = 2.33$  (not background corrected R values),  $S = 1.05$ .

## Single Crystal Structure Determination

Table S 1. Atomic coordinates ( $\cdot 10^4$ ) and equivalent isotropic displacement parameters  $U(\text{eq})$  ( $\text{\AA}^2 \cdot 10^3$ ) for  $[\text{Mn}_3\text{O}(\text{OAc})_7(\text{HOAc})]_6 \cdot 6\text{AcOH}$ .  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	$x$	$y$	$z$	$U(\text{eq})$
Mn(1)	5060(1)	5600(1)	3340(1)	22(1)
Mn(2)	6415(1)	6554(1)	3253(1)	18(1)
Mn(3)	5426(1)	6986(1)	3155(1)	20(1)
O(1)	5647(1)	6347(1)	3270(1)	19(1)
O(2)	4364(1)	4829(1)	3398(1)	31(1)
O(3)	3715(1)	3921(1)	3404(1)	29(1)
O(4)	5345(1)	5468(1)	4136(1)	33(1)
O(5)	6304(1)	5938(1)	3967(1)	29(1)
O(6)	5473(1)	5246(1)	2760(1)	32(1)
O(7)	6347(1)	6021(1)	2581(1)	28(1)
O(8)	4511(1)	5844(1)	3900(1)	34(1)
O(9)	4995(1)	6816(1)	3933(1)	30(1)
O(10)	4684(1)	5670(1)	2563(1)	22(1)
O(11)	4704(1)	6514(1)	2697(1)	23(1)
O(12)	6097(1)	7574(1)	3610(1)	25(1)
O(13)	6595(1)	7142(1)	3921(1)	24(1)
O(14)	5790(1)	7198(1)	2347(1)	22(1)
O(15)	6616(1)	7196(1)	2529(1)	25(1)
O(16A)	5213(5)	7730(4)	2987(4)	25(1)
O(17A)	5139(1)	8503(1)	2896(1)	34(1)
C(15A)	5227(1)	8144(1)	3251(2)	22(1)
C(16A)	5336(2)	8277(2)	3933(2)	31(1)
O(16B)	5224(16)	7643(13)	3122(12)	24(4)
O(17B)	5068(4)	7755(4)	4141(3)	43(3)
C(15B)	5186(5)	7942(6)	3550(4)	34(3)
C(16B)	5271(6)	8529(6)	3468(7)	46(3)
C(1)	4236(1)	4301(1)	3449(1)	28(1)
C(2)	4691(1)	4145(1)	3556(2)	54(1)
C(3)	5958(1)	5493(1)	2504(1)	29(1)
C(4)	6126(2)	5150(2)	2069(2)	49(1)
C(5)	5868(1)	5647(1)	4303(1)	32(1)
C(6)	5956(2)	5497(2)	4965(2)	64(1)
C(7)	4599(1)	6312(1)	4115(1)	33(1)
C(8)	4219(2)	6316(2)	4647(2)	68(1)
C(9)	4530(1)	6031(1)	2423(1)	21(1)
C(10)	4113(1)	5888(1)	1886(1)	31(1)
C(11)	6476(1)	7543(1)	3943(1)	24(1)
C(12)	6817(1)	8033(1)	4391(1)	35(1)
C(13)	6279(1)	7251(1)	2173(1)	19(1)
C(14)	6423(1)	7383(1)	1486(1)	29(1)

Table S 2. Anisotropic displacement parameters  $U_{ij}$  in  $\text{\AA}^2$  for  $[\text{Mn}_3\text{O}(\text{OAc})_7(\text{HOAc})_6 \cdot 6\text{AcOH}]$ .

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
Mn(1)	20(1)	17(1)	19(1)	1(1)	-2(1)	2(1)
Mn(2)	15(1)	23(1)	14(1)	-1(1)	-1(1)	7(1)
Mn(3)	17(1)	18(1)	18(1)	-4(1)	1(1)	5(1)
O(1)	15(1)	18(1)	20(1)	0(1)	0(1)	4(1)
O(2)	33(1)	17(1)	29(1)	2(1)	-1(1)	2(1)
O(3)	32(1)	19(1)	23(1)	3(1)	-1(1)	3(1)
O(4)	31(1)	32(1)	24(1)	8(1)	-2(1)	6(1)
O(5)	31(1)	34(1)	23(1)	3(1)	-3(1)	17(1)
O(6)	38(1)	25(1)	30(1)	-5(1)	-5(1)	15(1)
O(7)	27(1)	38(1)	21(1)	-6(1)	-2(1)	17(1)
O(8)	31(1)	29(1)	28(1)	-1(1)	6(1)	5(1)
O(9)	23(1)	30(1)	26(1)	-10(1)	4(1)	6(1)
O(10)	22(1)	19(1)	22(1)	-2(1)	-4(1)	7(1)
O(11)	20(1)	22(1)	26(1)	-7(1)	-4(1)	9(1)
O(12)	20(1)	20(1)	29(1)	-6(1)	-1(1)	6(1)
O(13)	22(1)	26(1)	19(1)	-5(1)	-3(1)	9(1)
O(14)	25(1)	22(1)	20(1)	1(1)	2(1)	13(1)
O(15)	19(1)	30(1)	21(1)	4(1)	1(1)	8(1)
O(16A)	30(2)	20(3)	30(4)	-3(2)	-3(2)	16(2)
O(17A)	52(2)	31(1)	31(1)	-8(1)	-10(1)	31(1)
C(15A)	17(1)	23(2)	27(2)	-4(1)	-2(1)	11(1)
C(16A)	41(2)	27(2)	26(2)	-7(1)	-5(1)	19(2)
O(16B)	32(6)	16(8)	24(10)	-4(6)	1(7)	13(5)
O(17B)	69(7)	40(5)	32(4)	-2(3)	7(4)	36(5)
C(15B)	32(6)	39(7)	38(7)	9(6)	7(5)	23(5)
C(16B)	56(8)	37(7)	59(9)	6(6)	14(7)	34(6)
C(1)	32(1)	22(1)	21(1)	2(1)	1(1)	6(1)
C(2)	35(2)	30(2)	91(3)	12(2)	2(2)	12(1)
C(3)	37(1)	36(1)	22(1)	-9(1)	-10(1)	24(1)
C(4)	60(2)	64(2)	44(2)	-27(2)	-16(2)	46(2)
C(5)	37(1)	31(1)	21(1)	4(1)	-5(1)	12(1)
C(6)	55(2)	82(3)	32(2)	24(2)	-7(2)	16(2)
C(7)	24(1)	38(1)	24(1)	-7(1)	4(1)	6(1)
C(8)	51(2)	64(2)	58(2)	-19(2)	32(2)	5(2)
C(9)	14(1)	21(1)	21(1)	-2(1)	2(1)	4(1)
C(10)	30(1)	26(1)	33(1)	-9(1)	-14(1)	13(1)
C(11)	21(1)	21(1)	19(1)	-2(1)	4(1)	2(1)
C(12)	32(1)	28(1)	32(1)	-12(1)	-4(1)	5(1)
C(13)	24(1)	15(1)	18(1)	-1(1)	2(1)	8(1)
C(14)	43(2)	36(1)	18(1)	5(1)	8(1)	27(1)

Table S 3. Selected crystallographic data and details of the structure determination of  $[\text{Mn}_3\text{O}(\text{OAc})_7(\text{HOAc})_6] \cdot 6\text{AcOH}$ . The squeezed molecules are not considered in this table.

Formula	$\text{C}_{16}\text{H}_{24}\text{Mn}_3\text{O}_{17}$
Molar mass / $\text{g}\cdot\text{mol}^{-1}$	653.18
Space group (No.)	$R\bar{3}$ (148)
$a$ / Å	26.6001(11)
$c$ / Å	21.1673(9)
$V$ / Å <sup>3</sup>	12970.7(12)
$Z$	18
Pearson symbol	$hR1080$
$\rho_{\text{calc.}}$ / $\text{g}\cdot\text{cm}^{-3}$	1.507
$\mu$ / mm <sup>-1</sup>	1.362
Color	black
Crystal morphology	block
Crystal size / mm <sup>3</sup>	0.142 · 0.089 · 0.075
$T$ / K	129
$\lambda$ / Å	0.71073 (Mo-K <sub>α</sub> )
No. of reflections	141121
$\theta$ range / °	2.529 - 30.598
Range of Miller indices	$-37 \leq h \leq 38$ $-38 \leq k \leq 37$ $-30 \leq l \leq 30$
Absorption correction	multi-scan
$T_{\text{max}}, T_{\text{min}}$	0.9431, 0.8888
$R_{\text{int}}, R_{\sigma}$	0.0691, 0.0313
Completeness of the data set	0.999
No. of unique reflections	8837
No. of parameters	373
No. of restraints	2
No. of constraints	0
$S$ (all data)	1.060
$R(F)$ ( $I \geq 2\sigma(I)$ , all data)	0.0460, 0.0661
$wR(F^2)$ ( $I \geq 2\sigma(I)$ , all data)	0.0939, 0.1016
Extinction coefficient	-
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ / $\text{e}\cdot\text{\AA}^{-3}$	0.838, -0.916

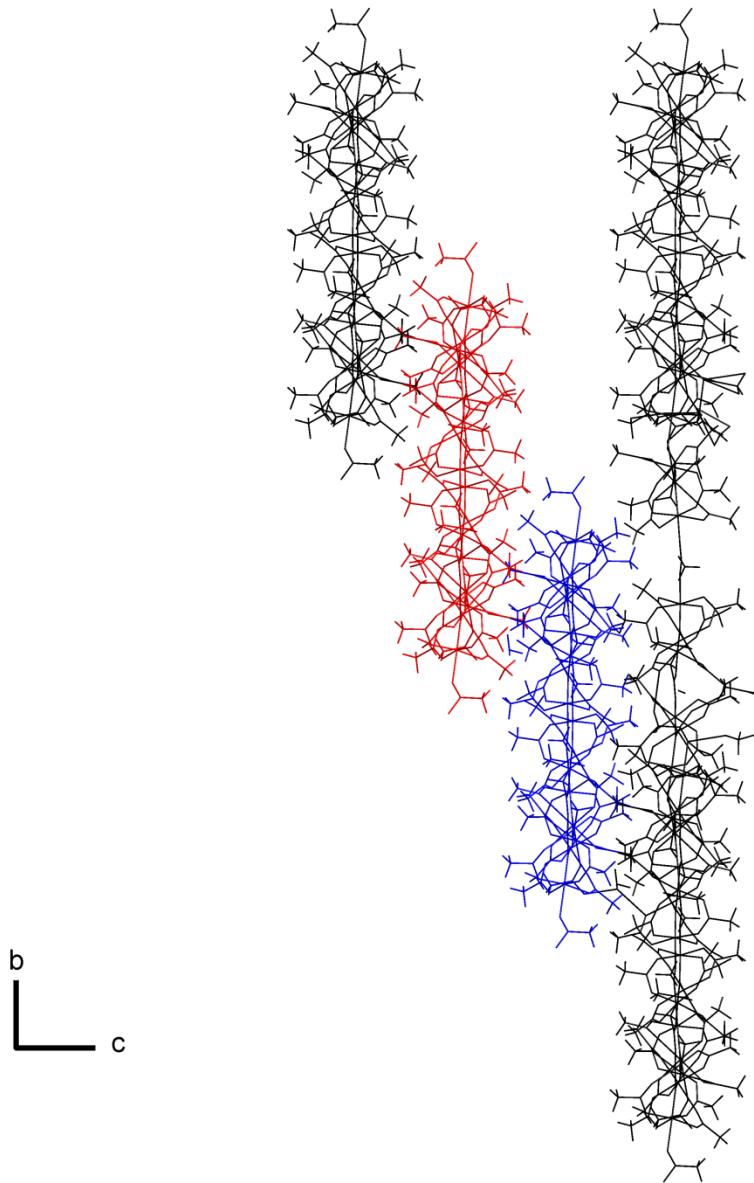


Figure S 2. Stacking of the  $\text{Mn}_{18}$  molecular rings along the  $c$  axis. View along the  $a$  axis. For simplicity the stick model was used, and all atoms, independent from their identity, are colored the same, when they belong to the same molecular ring.

## Thermogravimetric Analysis

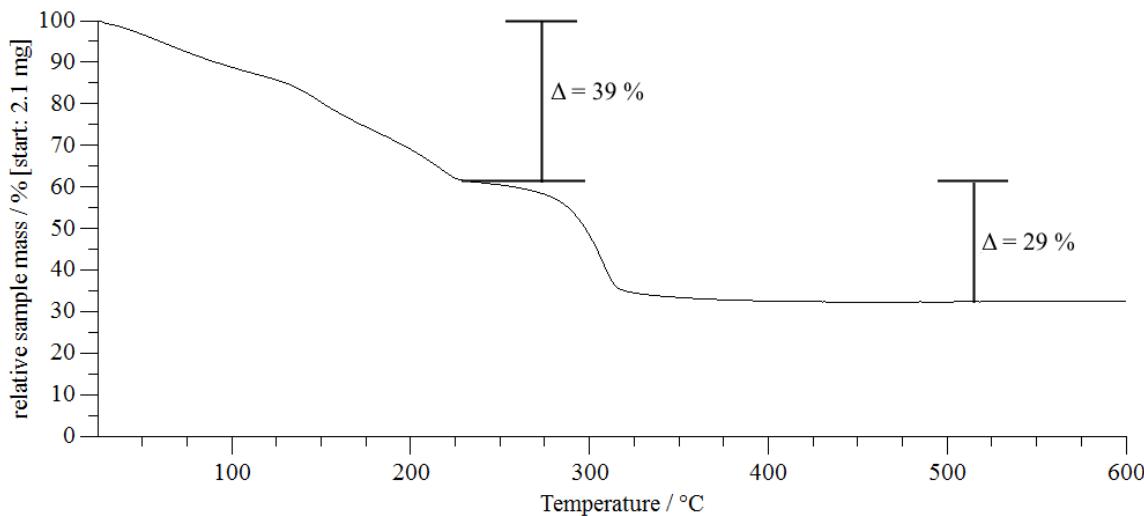


Figure S 3. Thermogram of the decomposition of  $[\text{Mn}_3\text{O}(\text{OAc})_7(\text{HOAc})]_6 \cdot x\text{AcOH}$  ( $x = 6-9$ ), measured with a heating rate of 10 K/min inside a corundum crucible under  $\text{N}_2$  (30 mL/min). After the decomposition experiment  $\text{MnO}$  could be detected as the residue by powder X-ray diffraction measurements.

Table S4. Mass loss of the thermal decomposition of  $[\text{Mn}_3\text{O}(\text{OAc})_7(\text{HOAc})]_6 \cdot x\text{AcOH}$  ( $x = 6-9$ ) and possible residuals for all steps.

	Mass loss (complete)	Mass loss (step)	Possible residual	Theo. mass loss (complete)	
				$x = 6$	$x = 9$
Step I	39 %		$\text{Mn}_2(\text{CO}_3)_3$	38 %	40 %
Step II	68 %	29 %	$\text{MnO}^*$	70%	71 %

\*identified using powder X-ray diffraction analysis.

## Vibrational Spectroscopy

During the Raman measurements the compound showed decomposition and no meaningful spectra were obtained. The decomposition could be observed visually (Figure S4).

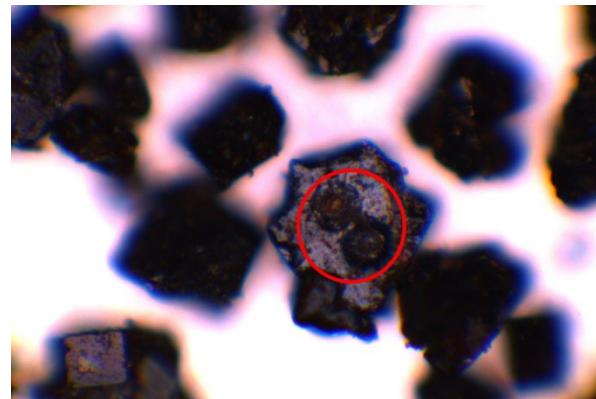


Figure S 4. A photography of crystals of  $[\text{Mn}_3\text{O}(\text{OAc})_7(\text{HOAc})]_6 \cdot \text{xAcOH}$  ( $\text{x} = 6-9$ ). The small circular parts inside the red circle are due to the irradiation damage of the laser.

The infrared spectrum is shown in Figure S 5 and the band positions including their assignments are shown in Table S5.

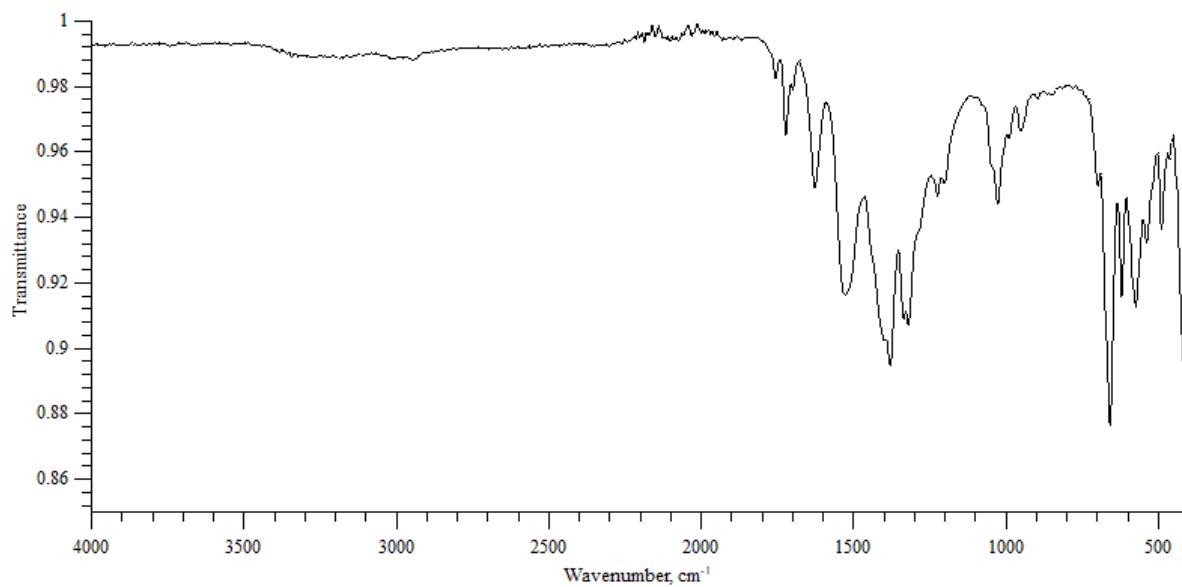


Figure S 5. ATR-IR spectrum of  $[\text{Mn}_3\text{O}(\text{OAc})_7(\text{HOAc})]_6 \cdot \text{xAcOH}$  ( $\text{x} = 6-9$ ).

The stretching vibrations of the OH and CH groups are of low intensity and appear above 2900 cm<sup>-1</sup>. Below 1000 cm<sup>-1</sup> the rocking vibrations of the methyl groups, stretching vibration of C—C bonds and deformation bands of the COO groups can be observed. The deformation bands of the OH groups are at approximately 1700 cm<sup>-1</sup>, the stretching vibrations of the carbonyl group are around 1500 cm<sup>-1</sup>, and the deformation modes of the methyl groups are between 1200 and 1400 cm<sup>-1</sup>. IR bands of the starting materials, like acetic acid, acetic anhydride, or acetate anions would be overlapping with the respective IR bands of the product and thus IR spectroscopy is not a fully suitable tool to estimate compound purity in this case. Also, decomposition products like manganese oxides would also not be detectable due to band overlap.

Table S5. IR and Raman bands recorded for  $[\text{Mn}_3\text{O}(\text{OAc})_7(\text{HOAc})]_6 \cdot x\text{AcOH}$  ( $x = 6-9$ ).

$[\text{Mn}_3\text{O}(\text{OAc})_7(\text{HOAc})]_6 \cdot x\text{AcOH}$ ( $x = 6-9$ )	Assignment <sup>[24]</sup>
Observed (ATR-IR)	
3410–3020 (broad, weak)	$\nu(\text{OH})$
3014	
2943	$\nu(\text{CH})$
1754	
1719	$\delta(\text{OH})$
1697	
1623	
1525	$\nu(\text{COO})$
1399	
1379	
1334	$\delta(\text{CH}_3)$
1319	
1224	
1199	
1044	$\rho(\text{CH}_3)$
1026	
987	$\nu(\text{CC})$
948	
665	
655	
616	
571	
534	$\delta(\text{COO})$
486	
461	
412	

## Quantum-Chemical Calculations

### Computational Details

For the present computations, scalar relativistic effects were calculated using a Douglas Kroll Hess Hamiltonian<sup>[1]</sup>. The Ahlrichs polarized def2-TZVP basis sets<sup>[2]</sup> optimized for DKH<sup>[3]</sup> were used for nearly all calculations. In the case of DFT calculations, the def2-SVP basis sets optimized for DKH were used for the ligand only. Resolution of identity approximation along with the appropriate auxiliary basis sets<sup>[4]</sup> were used for computational speedup. For the broken-symmetry DFT calculation BP86 and WB97X-D4 functionals were used since the functional of TPSSh and B3LYP failed to yield reasonable spin-configurations for the studied complex.

The spin-orbit coupling was calculated using the Breit-Pauli operator<sup>[5]</sup>. This consists of the one- and two-electron parts.

$$\hat{H}_{SO} = \frac{\alpha^2}{2} \sum_A \sum_i \frac{Z_A}{|\vec{R}_A - \vec{r}_i|^3} \hat{\vec{l}}_i^A \hat{\vec{s}}_i - \frac{\alpha^2}{2} \sum_i \hat{\vec{s}}_i \sum_{i \neq j} \frac{1}{|\vec{r}_i - \vec{r}_j|^3} (\hat{\vec{l}}_i^j + \hat{\vec{l}}_j^i)$$

where  $\alpha$  is the fine structure constant,  $\hat{\vec{l}}_i^A = (\vec{r}_i - \vec{R}_A) \times \vec{p}_i$  is the angular momentum for the electron  $i$  at position  $r_i$  with respect to nucleus  $A$  of charge  $Z_A$  at position  $R_A$  and  $\hat{\vec{l}}_j^i = (\vec{r}_i - \vec{r}_j) \times \vec{p}_i$  is the angular momentum of the electron  $i$  with respect to electron  $j$ . The one- and two-electron integrals in the present study were computed using a mean-field approximation (SOMF)<sup>[6]</sup>.

The Zeeman and spin-orbit matrix elements are given by<sup>[7]</sup>:

$$\langle \Psi_I^{SM_S} | \hat{H}_{BO} + \hat{H}_{SOC} + \hat{H}_Z | \Psi_J^{S'M'S} \rangle = \delta_{IJ} \delta_{SS} \delta_{M_S M'_S} E_I^S \\ + \langle \Psi_I^{SM_S} | \hat{H}_{SOC} + \beta \vec{B} (\hat{\vec{L}} + g_e \hat{\vec{S}}) | \Psi_J^{S'M'S} \rangle$$

Where  $\hat{H}_{BO}$  is the Born-Oppenheimer Hamiltonian,  $\hat{H}_{SOC}$  is the Spin-Orbit coupling hamiltonian and  $\hat{H}_Z$  is the Zeeman operator,  $E_I^S$  is the energy of the wavefunction with spin S and index I,  $g_e$  is the gyromagnetic ratio of the electron and  $\beta$  is the bohr magneton. By taking the first and second numerical derivatives of the energy on the basis of CASSCF/NEVPT2 wavefunctions, the magnetization and magnetic susceptibility can be calculated along a fixed direction.

The zero-field splitting tensor  $\mathbf{D}_i$  is extracted for each site using an effective Hamiltonian theory implemented in Orca<sup>[8]</sup>. However, including the zero-field splitting in the spin Hamiltonian breaks the block diagonal nature of the Hamiltonian matrix and increases the computational cost. To offset this one must consider a smaller, three-site model and the equation becomes:

$$H = -2J_{12}\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 - 2J_{13}\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_3 - 2J_{23}\hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_3 + \hat{\mathbf{S}}_1 \mathbf{D}_1 \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2 \mathbf{D}_2 \hat{\mathbf{S}}_2 + \hat{\mathbf{S}}_3 \mathbf{D}_3 \hat{\mathbf{S}}_3$$

where  $\hat{\mathbf{S}}_i$  is the spin operator on the  $i^{\text{th}}$  site,  $J_{ij}$  is the exchange coupling between sites i and j and  $\mathbf{D}_i$  is the zero-field splitting tensor on the  $i^{\text{th}}$  site. The three-site model is further validated by the

low degree of exchange between site 3 and 6 (Table 1). However, the inclusion of the zero field splitting did not significantly alter the magnetic properties of the system (Figure 8).

In the course of the evaluation of this work an anonymous reviewer proposed to carry out CASSCF/NEVPT2 calculations for the three-nuclear Mn(III)<sub>3</sub> building block of the Mn<sub>18</sub> wheel complex to prove transferability of exchange coupling parameter from Mn<sub>2</sub>Ga to the Mn<sub>3</sub> cluster. Results have been included in the main text. Details about the computational protocol are included below.

## DFT Calculations

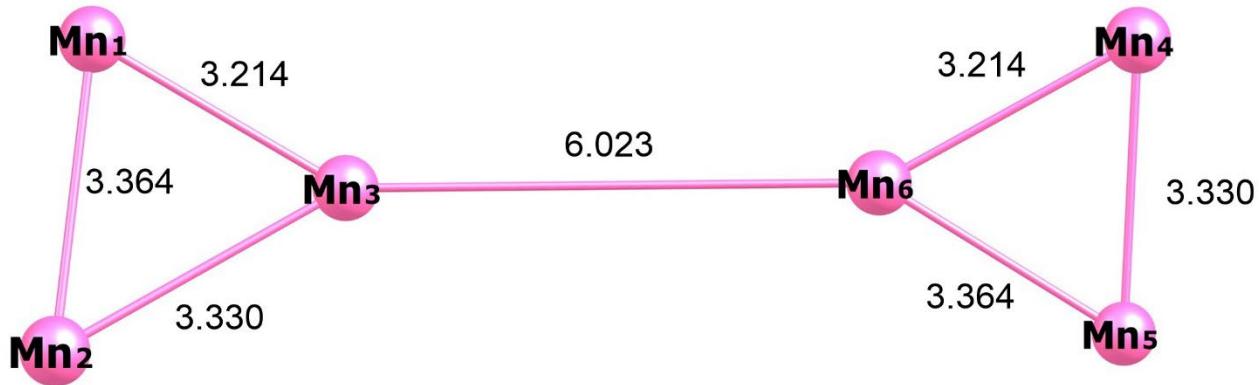


Figure S6. Exchange geometry and labelling of Mn centers in the Mn<sub>6</sub> model complex used for the extraction of magnetic exchange parameters from broken symmetry DFT.

Calculations of broken symmetry DFT spin-configurations start with the high-spin (parallel alignment of all Mn(III) M<sub>s</sub>=2 spins; the “gbw” file from the output is used then to compute energies of Slater determinants flipping first one spin, two spins and three spins.

Input for high-spin M<sub>s</sub>=6x2=12;

```
"mn6hsfkwB97XDhs.inp"
!UKS wB97X-D4 D3BJ DKH2 DKH-def2-SVP VeryTightSCF Autoaux

%basis
newgto Mn "dkh-def2-tzvp" end
end

%pal nprocs 16 end

%maxcore 8000
```

```

%rel method DKH
picturechange 2
end

#%MaxCore 4096

%scf maxiter 500 shift shift 0.5 erroff 0 end end

*xyz -1 25
25      1.046851347    4.846786110   -3.221476347
25      1.172594117    6.116990252   -0.109042101
25      0.532567575    2.905231909   -0.712864331
25      -0.318051807   -5.865140776    0.954653928
25      -0.800817655   -4.693088801    4.034079144
25      -0.250062270   -2.682427771    1.393930374
8       1.345686512    5.805139891   -7.197910162
6       1.320116137    4.964656479   -6.240154639
8       1.188711993    5.408047774   -5.087967155
1       2.375149629    3.245001452   -6.470835156
6       1.431705010    3.509808345   -6.495947460
1       1.058130547    3.303386544   -7.378105237
1       0.936250247    3.018066180   -5.808141272
1       -1.771359250   8.232904129   -3.409887477
6       -1.079273546   8.522199430   -2.779065979
1       -0.504161647   9.189370465   -3.208680894
1       -1.502524628   8.916465915   -1.988071015
1       5.090349077    6.929401924   -2.949015726
6       4.887476424    6.515103756   -2.084277996
1       5.227720188    7.083556784   -1.362063212
8       -0.250701495   6.343339645   -3.127218701
6       -0.254317501   7.342780511   -2.367964067
8       0.396844787    7.453836342   -1.285760029
8       2.956174019    6.387986724   -0.727843706
1       5.314785923    5.634559638   -2.035756579
6       3.401586068    6.359165197   -1.940430164
8       2.691636559    6.208690920   -2.938330143
1       -0.349130881   9.902137074   0.653535616
6       -0.292613722   9.375892882   1.477440786
8       1.540724001    7.894305670   1.280056889
1       -0.866379299   8.584887088   1.400770156
6       1.079323561    8.957821783   1.690978886
1       -0.588759750   9.921626352   2.235696712
8       1.884123509    9.808690358   2.376419255
1       1.424175427    10.639023451  2.570610987
8       2.372374787    3.455390598   -3.546404156
1       4.157473034    1.756619276   -4.052354836
1       2.869307483    1.079613482   -4.718176174
6       3.300201389    1.318150181   -3.870381184
1       -2.745706672   2.318359177   -4.290661759
6       -2.777608011   2.739473948   -3.405514254
1       -3.235544603   2.143536443   -2.777224644
1       3.452287139    0.508110064   -3.341739077

```

1	-3.262940932	3.588129604	-3.465313770
6	-1.372468643	2.996407827	-2.921912110
8	-0.559203515	3.524051874	-3.711201791
8	1.759284660	1.839465077	-2.126907509
6	2.402267444	2.265802868	-3.097638916
8	-1.121401747	2.662672090	-1.722106762
8	0.871915627	4.543749848	-1.423511177
8	2.123675981	3.022732101	0.457606932
8	-0.690057014	3.732694596	0.939104099
8	-0.551902175	5.962080595	0.736897591
8	1.966889997	5.078315112	1.332234023
6	3.497083380	3.564167705	2.304224649
1	4.385593824	3.718685434	1.920571389
1	3.379837918	4.130181899	3.095369876
1	3.411515882	2.622127752	2.560751077
6	-1.063826254	4.881053727	1.198895741
6	-2.233491483	5.083017526	2.137531466
1	-2.921280628	4.410042472	1.953723321
1	-1.927815898	4.992054750	3.065159290
6	2.448833494	3.902212184	1.288433313
1	-2.608801331	5.978724980	2.005071415
8	0.201429813	1.232010384	0.256783136
6	0.000000000	0.000000000	0.000000000
8	-0.031095767	-0.790322520	0.956986627
6	-0.178839739	-0.471802725	-1.392796642
1	0.321186701	0.110623538	-2.001995586
1	-1.130581066	-0.448145449	-1.626184918
1	0.153945436	-1.390133530	-1.472083837
1	2.812494600	-1.388899309	4.290677075
1	1.607226071	-0.859075197	5.200466594
6	2.048309718	-1.657626996	4.842418690
1	2.361157885	-2.217868621	5.583037219
6	1.077216345	-2.431759726	4.006784798
8	1.124617452	-2.271739910	2.762795378
8	0.263297478	-3.180048803	4.627357616
8	-1.808873243	-1.954656404	2.690359818
1	3.928790380	-3.885957387	0.250825806
8	1.308582733	-3.207735727	0.028813299
1	3.461774636	-3.706656938	-1.269305108
6	3.376254944	-4.261731596	-0.465301204
1	3.674171530	-5.173262381	-0.665189674
6	-1.802160432	-3.798063347	-0.810681068
8	-1.367110806	-4.953002078	-0.690851641
6	-2.627261848	-3.435919012	-2.031140386
1	-3.405060945	-2.908097384	-1.754165679
1	-2.079190770	-2.909079277	-2.650320716
1	-2.928485674	-4.254270220	-2.476477033
6	1.933755602	-4.288899130	-0.026260200
8	-1.605173902	-2.839866848	0.002005047
8	1.458780344	-5.428685899	0.272454331
8	-0.405019836	-4.396085731	2.022001947
8	-2.069984332	-6.511796074	1.608877306

8	0.668425517	-7.095819210	2.510546173
6	-2.461789406	-6.730664498	2.778521567
6	1.080543426	-6.825590086	3.643268314
8	-1.904781419	-6.282683660	3.830406299
1	2.547386809	-7.262588676	5.021364856
6	2.087066687	-7.743648466	4.302072487
1	1.623116770	-8.522651358	4.676385461
1	2.741951279	-8.042735948	3.637689470
1	-4.485760835	-7.001353534	2.899320838
1	-3.721342402	-8.262950145	2.278728889
6	-3.689373062	-7.568256823	2.969341631
1	-3.663975605	-7.988172736	3.854245954
8	0.738976928	-5.808967332	4.346076245
8	-1.259731344	-4.941592155	6.259300516
6	-2.663285176	-2.600930643	3.302556279
8	-2.428040557	-3.703292029	3.934256770
1	-4.583115661	-2.519862973	2.593929345
6	-4.087036154	-2.127405607	3.342386124
1	-4.499357571	-2.402770906	4.187764151
1	-4.108442657	-1.150099572	3.271767109
6	-0.793563180	-4.857885326	7.394419334
8	-1.634351005	-4.878073870	8.459397647
1	0.828036815	-5.160053132	8.528987553
1	-1.151040547	-4.723160309	9.284703511
6	0.622862701	-4.725208873	7.674999840
1	0.858095200	-3.776000881	7.726160340
1	1.138508263	-5.152232747	6.959085229
8	-0.285543457	-7.570506302	-0.014992117
6	-0.139425002	-7.990491795	-1.209406124
8	-0.331422665	-9.198368115	-1.422878155
6	0.234936225	-7.066206573	-2.304857247
1	-0.149607918	-7.385598298	-3.147755716
1	1.211357375	-7.031560645	-2.383867165
1	-0.108603391	-6.169775134	-2.107975564

\*

The following a sample input for flipping spin on Mn1 (notice: ORCA counts starting from 0, i.e. this is center “0” used in the spin-flip command “%scf; FlipSpin 0; FinalMs 8; end)

Input file: “mn6fflip0.inp”

```
!UKS wb97x-d4 D3BJ DKH2 DKH-def2-SVP VeryTightSCF Autoaux moread
%moinp "mn6hsfkwB97XD.gbw"
```

```
%basis
newgto Mn "dkh-def2-tzvp" end
end
```

```
%pal nprocs 16 end
```

```
%maxcore 8000
```

```

%rel method DKH
picturechange 2
end

#%MaxCore 4096

%scf maxiter 500 shift shift 0.5 erroff 0 end end

*xyz -1 25
25      1.046851347      4.846786110      -3.221476347
25      1.172594117      6.116990252      -0.109042101
25      0.532567575      2.905231909      -0.712864331
25      -0.318051807     -5.865140776      0.954653928
25      -0.800817655     -4.693088801      4.034079144
25      -0.250062270     -2.682427771      1.393930374
8       1.345686512      5.805139891      -7.197910162
6       1.320116137      4.964656479      -6.240154639
8       1.188711993      5.408047774      -5.087967155
1       2.375149629      3.245001452      -6.470835156
6       1.431705010      3.509808345      -6.495947460
1       1.058130547      3.303386544      -7.378105237
1       0.936250247      3.018066180      -5.808141272
1       -1.771359250     8.232904129      -3.409887477
6       -1.079273546     8.522199430      -2.779065979
1       -0.504161647     9.189370465      -3.208680894
1       -1.502524628     8.916465915      -1.988071015
1       5.090349077      6.929401924      -2.949015726
6       4.887476424      6.515103756      -2.084277996
1       5.227720188      7.083556784      -1.362063212
8       -0.250701495     6.343339645      -3.127218701
6       -0.254317501     7.342780511      -2.367964067
8       0.396844787      7.453836342      -1.285760029
8       2.956174019      6.387986724      -0.727843706
1       5.314785923      5.634559638      -2.035756579
6       3.401586068      6.359165197      -1.940430164
8       2.691636559      6.208690920      -2.938330143
1       -0.349130881     9.902137074      0.653535616
6       -0.292613722     9.375892882      1.477440786
8       1.540724001      7.894305670      1.280056889
1       -0.866379299     8.584887088      1.400770156
6       1.079323561      8.957821783      1.690978886
1       -0.588759750     9.921626352      2.235696712
8       1.884123509      9.808690358      2.376419255
1       1.424175427      10.639023451      2.570610987
8       2.372374787      3.455390598      -3.546404156
1       4.157473034      1.756619276      -4.052354836
1       2.869307483      1.079613482      -4.718176174
6       3.300201389      1.318150181      -3.870381184
1       -2.745706672     2.318359177      -4.290661759
6       -2.777608011     2.739473948      -3.405514254
1       -3.235544603     2.143536443      -2.777224644

```

1	3.452287139	0.508110064	-3.341739077
1	-3.262940932	3.588129604	-3.465313770
6	-1.372468643	2.996407827	-2.921912110
8	-0.559203515	3.524051874	-3.711201791
8	1.759284660	1.839465077	-2.126907509
6	2.402267444	2.265802868	-3.097638916
8	-1.121401747	2.662672090	-1.722106762
8	0.871915627	4.543749848	-1.423511177
8	2.123675981	3.022732101	0.457606932
8	-0.690057014	3.732694596	0.939104099
8	-0.551902175	5.962080595	0.736897591
8	1.966889997	5.078315112	1.332234023
6	3.497083380	3.564167705	2.304224649
1	4.385593824	3.718685434	1.920571389
1	3.379837918	4.130181899	3.095369876
1	3.411515882	2.622127752	2.560751077
6	-1.063826254	4.881053727	1.198895741
6	-2.233491483	5.083017526	2.137531466
1	-2.921280628	4.410042472	1.953723321
1	-1.927815898	4.992054750	3.065159290
6	2.448833494	3.902212184	1.288433313
1	-2.608801331	5.978724980	2.005071415
8	0.201429813	1.232010384	0.256783136
6	0.000000000	0.000000000	0.000000000
8	-0.031095767	-0.790322520	0.956986627
6	-0.178839739	-0.471802725	-1.392796642
1	0.321186701	0.110623538	-2.001995586
1	-1.130581066	-0.448145449	-1.626184918
1	0.153945436	-1.390133530	-1.472083837
1	2.812494600	-1.388899309	4.290677075
1	1.607226071	-0.859075197	5.200466594
6	2.048309718	-1.657626996	4.842418690
1	2.361157885	-2.217868621	5.583037219
6	1.077216345	-2.431759726	4.006784798
8	1.124617452	-2.271739910	2.762795378
8	0.263297478	-3.180048803	4.627357616
8	-1.808873243	-1.954656404	2.690359818
1	3.928790380	-3.885957387	0.250825806
8	1.308582733	-3.207735727	0.028813299
1	3.461774636	-3.706656938	-1.269305108
6	3.376254944	-4.261731596	-0.465301204
1	3.674171530	-5.173262381	-0.665189674
6	-1.802160432	-3.798063347	-0.810681068
8	-1.367110806	-4.953002078	-0.690851641
6	-2.627261848	-3.435919012	-2.031140386
1	-3.405060945	-2.908097384	-1.754165679
1	-2.079190770	-2.909079277	-2.650320716
1	-2.928485674	-4.254270220	-2.476477033
6	1.933755602	-4.288899130	-0.026260200
8	-1.605173902	-2.839866848	0.002005047
8	1.458780344	-5.428685899	0.272454331
8	-0.405019836	-4.396085731	2.022001947

8	-2.069984332	-6.511796074	1.608877306
8	0.668425517	-7.095819210	2.510546173
6	-2.461789406	-6.730664498	2.778521567
6	1.080543426	-6.825590086	3.643268314
8	-1.904781419	-6.282683660	3.830406299
1	2.547386809	-7.262588676	5.021364856
6	2.087066687	-7.743648466	4.302072487
1	1.623116770	-8.522651358	4.676385461
1	2.741951279	-8.042735948	3.637689470
1	-4.485760835	-7.001353534	2.899320838
1	-3.721342402	-8.262950145	2.278728889
6	-3.689373062	-7.568256823	2.969341631
1	-3.663975605	-7.988172736	3.854245954
8	0.738976928	-5.808967332	4.346076245
8	-1.259731344	-4.941592155	6.259300516
6	-2.663285176	-2.600930643	3.302556279
8	-2.428040557	-3.703292029	3.934256770
1	-4.583115661	-2.519862973	2.593929345
6	-4.087036154	-2.127405607	3.342386124
1	-4.499357571	-2.402770906	4.187764151
1	-4.108442657	-1.150099572	3.271767109
6	-0.793563180	-4.857885326	7.394419334
8	-1.634351005	-4.878073870	8.459397647
1	0.828036815	-5.160053132	8.528987553
1	-1.151040547	-4.723160309	9.284703511
6	0.622862701	-4.725208873	7.674999840
1	0.858095200	-3.776000881	7.726160340
1	1.138508263	-5.152232747	6.959085229
8	-0.285543457	-7.570506302	-0.014992117
6	-0.139425002	-7.990491795	-1.209406124
8	-0.331422665	-9.198368115	-1.422878155
6	0.234936225	-7.066206573	-2.304857247
1	-0.149607918	-7.385598298	-3.147755716
1	1.211357375	-7.031560645	-2.383867165
1	-0.108603391	-6.169775134	-2.107975564

\*

```
%scf FlipSpin 0 FinalMs 8
end
```

“\*.gbw” files were used to visualize spin-density for the high-spin and “flip 0” spins (contour plot value 0.05 electron/bohr<sup>3</sup>):

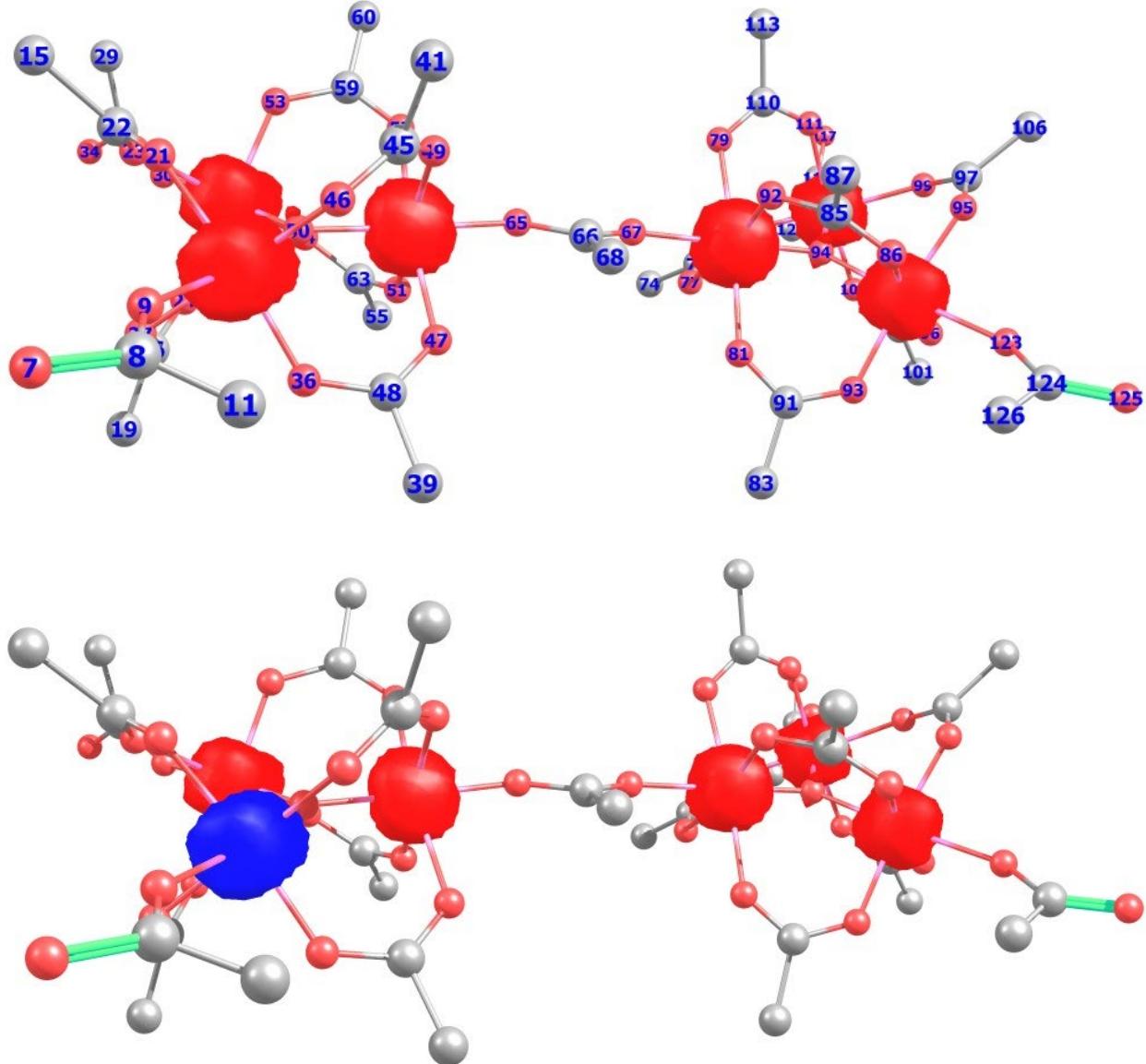


Figure S7: Spin-densities for the high-spin ( $M_s=12$ ) and flip spin on Mn1 ( $M_s=8$ ) from DFT-WB97XD4 calculations (contour plots with contour value of 0.05 electron/ $\text{bohr}^3$ , plotted with ChemCraft).

Calculations using broken spin DFT not always yield expected solutions with spin-configurations as desired. This can result in huge(!) artefacts. One should therefore check if desired  $M_s$  values on each magnetic center are really obtained. If not, such results should not be used when fitting  $J$  values from the set of the broken symmetry determinants. Table S6 below lists sets of  $M_s$  values of the 23 calculations.

Table S6 Set of  $M_s$  values for centers  $Mn_1$  to  $Mn_6$  resulting from broken-symmetry DFT-WB97XD4 calculations of various spin-flip configurations starting from the high-spin  $M_s=12$  local spin arrangement.

High-spin	Number of surviving spin-configurations used on the MatLab script to extract $J_{12}, J_{13}, J_{23}, J_{36}$	$M_s$ on $Mn_1$	$M_s$ on $Mn_2$	$M_s$ on $Mn_3$	$M_s$ on $Mn_4$	$M_s$ on $Mn_5$	$M_s$ on $Mn_6$
High-Spin	1	3.84	3.84	3.84	3.84	3.84	3.84
Flip $Mn_1$	2	-3.80	3.83	3.81	3.85	3.84	3.84
Flip $Mn_2$	6	3.82	-3.82	3.82	3.85	3.84	3.84
Flip $Mn_3$	14	3.82	3.83	-3.79	3.85	3.84	3.84
Flip $Mn_4$	13	3.84	3.84	3.84	-3.81	3.83	3.80
Flip $Mn_5$	15	3.84	3.84	3.84	3.83	-3.82	3.81
Flip $Mn_6$	-	3.83	2.00	3.84	3.83	3.83	-1.91
Flip $Mn_1, 2$	-	-1.93	-3.83	3.79	3.84	2.00	3.82
Flip $Mn_1, 3$	-	-1.94	3.82	-1.93	3.84	0.02	3.84
Flip $Mn_1, 4$	5	-3.80	3.83	3.81	-3.81	3.83	3.80
Flip $Mn_1, 5$	4	-3.80	3.83	3.81	3.82	-3.82	3.81
Flip $Mn_1, 6$	3	-3.80	3.83	3.81	3.82	3.83	-3.78
Flip $Mn_2, 3$	-	3.80	-3.83	-1.93	3.84	2.00	3.83
Flip $Mn_2, 4$	9	3.82	-3.82	3.82	-3.81	3.83	3.80
Flip $Mn_2, 5$	8	3.82	-3.82	3.82	3.83	-3.82	3.81
Flip $Mn_2, 6$	7	3.82	-3.82	3.82	3.82	3.83	-3.78
Flip $Mn_3, 4$	12	3.82	3.83	-3.79	-3.81	3.83	3.80
Flip $Mn_3, 5$	11	3.82	3.83	-3.79	3.83	-3.82	3.81
Flip $Mn_3, 6$	10	3.82	3.83	-3.79	3.82	3.83	-3.78
Flip $Mn_4, 5$	-	1.94	2.00	3.84	-1.94	-1.98	3.81
Flip $Mn_4, 6$	-	3.84	0.02	3.83	-1.94	3.82	-1.93
Flip $Mn_5, 6$	-	3.83	2.00	3.84	3.83	-1.98	-3.80
Flip $Mn_1, 2, 3$	-	-1.95	-2.00	-1.94	3.84	-1.95	3.82

Out of the 23 spin-alignments only 15 are surviving the desired magnitude of  $M_s$  close to 4 and the correct sign. Energies of only these spin-configuration can be used for the extraction of the values of  $J$ .

Energies of DFT broken symmetry Slater determinants are:

% 1 mn6hsfkwB97XD.mpi16.out  $M_s=12$

-10988.280478668305

% 2 mn6flip0.mpi16.out

-10988.282098805063  
% 3 mn6flip05.mpi16.out  
-10988.283758146143  
% 4 mn6flip04.mpi16.out  
-10988.284547214236  
% 5 mn6flip03.mpi16.out  
-10988.283665219673  
% 6 mn6flip1.mpi16.out  
-10988.282958011212  
% 7 mn6flip15.mpi16.out  
-10988.284616499288  
% 8 mn6flip14.mpi16.out  
-10988.285406479419  
% 9 mn6flip13.mpi16.out  
-10988.284524393734  
% 10 mn6flip25.mpi16.out  
-10988.283642036486  
% 11 mn6flip24.mpi16.out  
-10988.284610957064  
% 12 mn6flip23.mpi16.out  
-10988.283729266044  
% 13 mn6flip3.mpi16.out  
-10988.282045931721  
% 14 mn6flip2.mpi16.out  
-10988.282158891530

```
% 15 mn6flip4.mpi16.out
```

```
-10988.282928209237
```

The following MatLab script was used to extract the J12, J13, J23 and J36 parameters from a best fit to the data base of the listed 15 Slater Determinant energies.

MatLab script used to extract the J parameters from a best fit to energies of DFT-WB97XD4 broken symmetry Slater determinants:

```
clear all
clc
%
% wB97XD-4
energies_wb=[
%  1 mn6hsfkwB97XD.mpi16.out  Ms=12
-10988.280478668305
%  2 mn6flip0.mpi16.out
-10988.282098805063
%  3 mn6flip05.mpi16.out
-10988.283758146143
%  4 mn6flip04.mpi16.out
-10988.284547214236
%  5 mn6flip03.mpi16.out
-10988.283665219673
%  6 mn6flip1.mpi16.out
-10988.282958011212
%  7 mn6flip15.mpi16.out
-10988.284616499288
%  8 mn6flip14.mpi16.out
-10988.285406479419
%  9 mn6flip13.mpi16.out
-10988.284524393734
% 10 mn6flip25.mpi16.out
-10988.283642036486
% 11 mn6flip24.mpi16.out
-10988.284610957064
% 12 mn6flip23.mpi16.out
-10988.283729266044
%13 mn6flip3.mpi16.out
-10988.282045931721
% 14 mn6flip2.mpi16.out
-10988.282158891530
```

```

% 15 mn6flip4.mpi16.out
-10988.28292820923
];
energies=energies_wb;
ln_ener=max(size(energies))
energies=(energies-energies(1,:))*8065*27.211;
Y=energies(2:ln_ener,1);
disp(Y)

spinconf_wb=[+2 +2 +2 +2 +2 +2;
             -2 +2 +2 +2 +2 +2;
             -2 +2 +2 +2 +2 -2;
             -2 +2 +2 +2 -2 +2;
             -2 +2 +2 -2 +2 +2;
             +2 -2 +2 +2 +2 +2;
             +2 -2 +2 +2 +2 -2;
             +2 -2 +2 +2 -2 +2;
             +2 -2 +2 -2 +2 +2;
             +2 +2 -2 +2 +2 -2;
             +2 +2 -2 +2 -2 +2;
             +2 +2 -2 -2 +2 +2;
             +2 +2 -2 +2 +2 +2;
             +2 +2 +2 +2 -2 +2;
             +2 +2 +2 +2 +2 +2;

];
spinconf=spinconf_wb ;

% exchange pathways (J parameters)
% Ji 1,3;4,6
% Ji' 2,3;5,6
% Jl 1,2;4,5
% Jb 3,6
% Jnn 1,6;3,4
% Jnn' 2,6;3,5

% general equation for the spin-configuration energy
% using the -2J12 S1 S2 definition:
%           Ji           Ji'           Jl
Jb           Jnn           Jnn1
% (-
2) * ( (M1*M3+M4*M6) * Ji + (M2*M3+M5*M6) * Ji' + (M1*M2+M4*M5) * Jl + M3*M
6 * Jb + (M1*M6+M3*M4) * Jnn + (M2*M6+M3*M5) * Jnn1);

B(ln_ener,4)=zeros;

```

```

% B(9,4)=zeros;
% set up the energies of the nine spin-configurations, the
HS reference and the nine BS spin-config.

for i=1:ln_ener
M1=spinconf(i,1);
M2=spinconf(i,2);
M3=spinconf(i,3);
M4=spinconf(i,4);
M5=spinconf(i,5);
M6=spinconf(i,6);
B(i,1)=(-2)*(M1*M3+M4*M6); % Ji
B(i,2)=(-2)*(M2*M3+M4*M5); % Ji'
B(i,3)=(-2)*(M1*M2+M6*M5); % Jl
B(i,4)=(-2)*M3*M6; % Jb

end

A(ln_ener-1,4)=zeros;
for i=1:ln_ener-1
A(i,:)=B(i+1,:)-B(1,:);
end

X=pinv(A)*Y;
disp(X);
Ycalc=A*X;
result=[Y Ycalc];
disp(result)

diff=Y-Ycalc;

standdev=sqrt(diff'*diff/(ln_ener-1));
disp(standdev)
x=[-1100:100:-300];
y=x;
plot(Ycalc,Y,'s',x,y,'-')

```

Best fit values of J and root mean square deviation between computed using these values and the DFT data set are shown in Figure S7 along with a comparison between computed and DFT values.

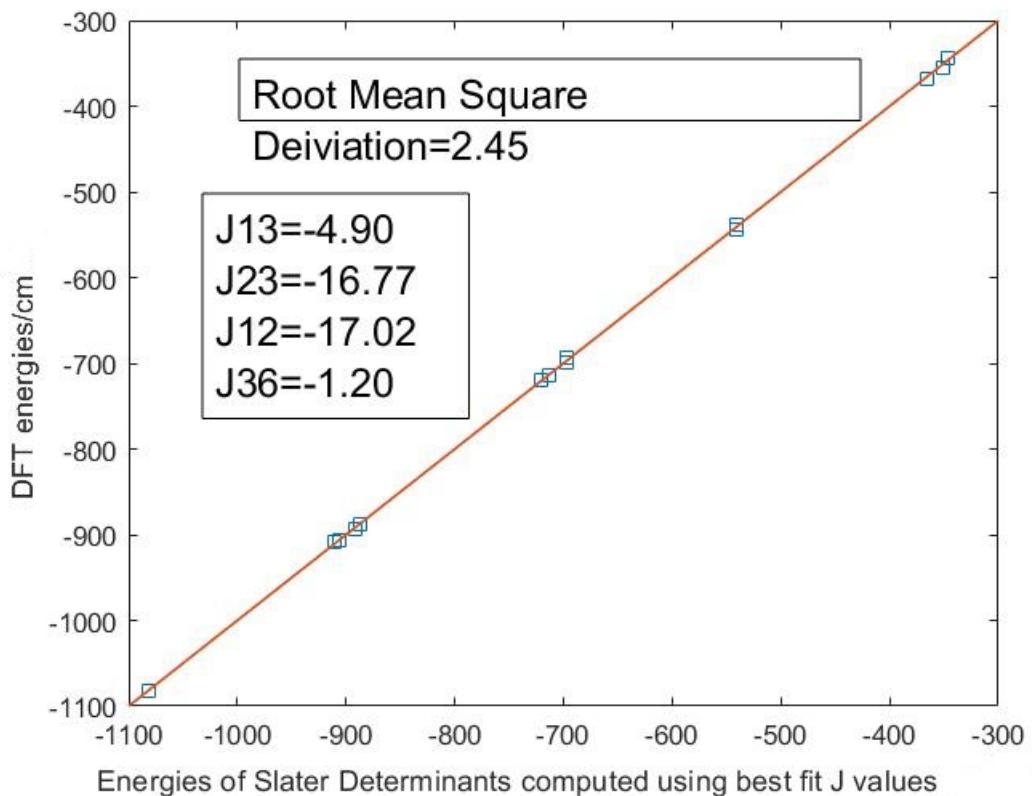


Figure S7 J parameters extracted from a best fit to energies of broken symmetry WB97XD4 Slater Determinants along with root mean square deviation between DFT and computed values (all energies are given in cm<sup>-1</sup>).

J values have been used to simulate the magnetic data with the program PHI [9].

## CASSCF/NEVPT2 Inputs for two magnetic sites

The following input file was used to prepare initial guess of orbitals for state specific CASSCF/NEVPT2 calculations of the ground states for each spin of the Mn<sub>1</sub>Mn<sub>2</sub>Ga<sub>3</sub> pair (similar input files for ORCA calculations were obtained for the Mn<sub>1</sub>Ga<sub>2</sub>Mn<sub>3</sub> and Ga<sub>1</sub>Mn<sub>2</sub>Mn<sub>3</sub> clusters, used to extract J<sub>13</sub> and J<sub>23</sub> exchange energy parameters, respectively).

mnmngahs.inp

```
!DKH DKH-def2-TZVP AutoAux NoFrozenCore PAL16
%rel method DKH
picturechange 2
```

```

end

%scf
MaxCore 16000
end

%casscf
nel 8
norb 10
mult 9
nroots 25
trafostep ri
actorbs locorbs
orbstep superci
                                switchstep diis
shiftup 1
shiftdn 1
end

*xyz -1 9
25      0.514283772   1.941554201   -2.508612016
25      0.640026542   3.211758343    0.603822230
31      0.000000000   0.000000000    0.000000000
8       0.813118937   2.899907982   -6.485045831
6       0.787548562   2.059424570   -5.527290308
8       0.656144418   2.502815865   -4.375102824
1       1.842582054   0.339769543   -5.757970825
6       0.899137435   0.604576436   -5.783083129
1       0.525562972   0.398154635   -6.665240906
1       0.403682672   0.112834271   -5.095276941
1       -2.303926825  5.327672220   -2.697023146
6       -1.611841121  5.616967521   -2.066201648
1       -1.036729222  6.284138556   -2.495816563
1       -2.035092203  6.011234006   -1.275206684
1       4.557781502   4.024170015   -2.236151395
6       4.354908849   3.609871847   -1.371413665
1       4.695152613   4.178324875   -0.649198881
8       -0.783269070  3.438107736   -2.414354370
6       -0.786885076  4.437548602   -1.655099736
8       -0.135722788  4.548604433   -0.572895698
8       2.423606444   3.482754815   -0.014979375
1       4.782218348   2.729327729   -1.322892248
6       2.869018493   3.453933288   -1.227565833
8       2.159068984   3.303459011   -2.225465812
1       -0.881698456  6.996905165   1.366399947
6       -0.825181297  6.470660973   2.190305117
8       1.008156426   4.989073761   1.992921220
1       -1.398946874  5.679655179   2.113634487
6       0.546755986   6.052589874   2.403843217
1       -1.121327325  7.016394443   2.948561043
8       1.351555934   6.903458449   3.089283586
1       0.891607852   7.733791542   3.283475318

```

8	1.839807212	0.550158689	-2.833539825
1	3.624905459	-1.148612633	-3.339490505
1	2.336739908	-1.825618427	-4.005311843
6	2.767633814	-1.587081728	-3.157516853
1	-3.278274247	-0.586872732	-3.577797428
6	-3.310175586	-0.165757961	-2.692649923
1	-3.768112178	-0.761695466	-2.064360313
1	2.919719564	-2.397121845	-2.628874746
1	-3.795508507	0.682897695	-2.752449439
6	-1.905036218	0.091175918	-2.209047779
8	-1.091771090	0.618819965	-2.998337460
8	1.226717085	-1.065766832	-1.414043178
6	1.869699869	-0.639429041	-2.384774585
8	-1.653969322	-0.242559819	-1.009242431
8	0.339348052	1.638517939	-0.710646846
8	1.591108406	0.117500192	1.170471263
8	-1.222624589	0.827462687	1.651968430
8	-1.084469750	3.056848686	1.449761922
8	1.434322422	2.173083203	2.045098354
6	2.964515805	0.658935796	3.017088980
1	3.853026249	0.813453525	2.633435720
1	2.847270343	1.224949990	3.808234207
1	2.878948307	-0.283104157	3.273615408
6	-1.596393829	1.975821818	1.911760072
6	-2.766059058	2.177785617	2.850395797
1	-3.453848203	1.504810563	2.666587652
1	-2.460383473	2.086822841	3.778023621
6	1.916265919	0.996980275	2.001297644
1	-3.141368906	3.073493071	2.717935746
8	-0.331137762	-1.673221525	0.969647467
6	-0.532567575	-2.905231909	0.712864331
8	-0.563663342	-3.695554429	1.669850958
6	-0.711407314	-3.377034634	-0.679932311
1	-0.211380874	-2.794608371	-1.289131255
1	-1.663148641	-3.353377358	-0.913320587
1	-0.378622139	-4.295365439	-0.759219506

\*

Using this initial guess of orbitals, we list a sample input file used to compute the energy of the S=0 ground state of the Mn<sub>1</sub>Mn<sub>2</sub>Ga<sub>3</sub> model cluster taking the X-ray geometry of the Mn<sub>3</sub> unit.

mnmngas0nev.inp

```

!DKH DKH-def2-TZVP AutoAux  NoFrozenCore PAL16 moread
!xyzfile normalprint
!nevpt2

%moinp "mnmngahs.gbw"

%scf rotate {184,188,90} {185,190,90} end end

```

```

%rel method DKH
picturechange 2
end

%scf
MaxCore 16000
end

%casscf
nel 8
norb 10
mult 1
nroots 1
trafostep ri
actorbs unchanged
actconstraints 1
printgstate 1
ptsettings
d4tpre 1e-14
end
ci
maxiter 300
nguessmat 4500
end
orbstep superci
      switchstep diis
      shiftup 1
      shiftdn 1
end

*xyz -1 9
25      0.514283772   1.941554201   -2.508612016
25      0.640026542   3.211758343    0.603822230
31      0.000000000   0.000000000    0.000000000
8       0.813118937   2.899907982   -6.485045831
6       0.787548562   2.059424570   -5.527290308
8       0.656144418   2.502815865   -4.375102824
1       1.842582054   0.339769543   -5.757970825
6       0.899137435   0.604576436   -5.783083129
1       0.525562972   0.398154635   -6.665240906
1       0.403682672   0.112834271   -5.095276941
1       -2.303926825  5.327672220  -2.697023146
6       -1.611841121  5.616967521  -2.066201648
1       -1.036729222  6.284138556  -2.495816563
1       -2.035092203  6.011234006  -1.275206684
1       4.557781502   4.024170015  -2.236151395
6       4.354908849   3.609871847  -1.371413665
1       4.695152613   4.178324875  -0.649198881
8       -0.783269070  3.438107736  -2.414354370
6       -0.786885076  4.437548602  -1.655099736
8       -0.135722788  4.548604433  -0.572895698
8       2.423606444   3.482754815  -0.014979375

```

1	4.782218348	2.729327729	-1.322892248
6	2.869018493	3.453933288	-1.227565833
8	2.159068984	3.303459011	-2.225465812
1	-0.881698456	6.996905165	1.366399947
6	-0.825181297	6.470660973	2.190305117
8	1.008156426	4.989073761	1.992921220
1	-1.398946874	5.679655179	2.113634487
6	0.546755986	6.052589874	2.403843217
1	-1.121327325	7.016394443	2.948561043
8	1.351555934	6.903458449	3.089283586
1	0.891607852	7.733791542	3.283475318
8	1.839807212	0.550158689	-2.833539825
1	3.624905459	-1.148612633	-3.339490505
1	2.336739908	-1.825618427	-4.005311843
6	2.767633814	-1.587081728	-3.157516853
1	-3.278274247	-0.586872732	-3.577797428
6	-3.310175586	-0.165757961	-2.692649923
1	-3.768112178	-0.761695466	-2.064360313
1	2.919719564	-2.397121845	-2.628874746
1	-3.795508507	0.682897695	-2.752449439
6	-1.905036218	0.091175918	-2.209047779
8	-1.091771090	0.618819965	-2.998337460
8	1.226717085	-1.065766832	-1.414043178
6	1.869699869	-0.639429041	-2.384774585
8	-1.653969322	-0.242559819	-1.009242431
8	0.339348052	1.638517939	-0.710646846
8	1.591108406	0.117500192	1.170471263
8	-1.222624589	0.827462687	1.651968430
8	-1.084469750	3.056848686	1.449761922
8	1.434322422	2.173083203	2.045098354
6	2.964515805	0.658935796	3.017088980
1	3.853026249	0.813453525	2.633435720
1	2.847270343	1.224949990	3.808234207
1	2.878948307	-0.283104157	3.273615408
6	-1.596393829	1.975821818	1.911760072
6	-2.766059058	2.177785617	2.850395797
1	-3.453848203	1.504810563	2.666587652
1	-2.460383473	2.086822841	3.778023621
6	1.916265919	0.996980275	2.001297644
1	-3.141368906	3.073493071	2.717935746
8	-0.331137762	-1.673221525	0.969647467
6	-0.532567575	-2.905231909	0.712864331
8	-0.563663342	-3.695554429	1.669850958
6	-0.711407314	-3.377034634	-0.679932311
1	-0.211380874	-2.794608371	-1.289131255
1	-1.663148641	-3.353377358	-0.913320587
1	-0.378622139	-4.295365439	-0.759219506

\*

Using the same input file and repacing "mult 1" by "mult 3", "mult 5", "mult 9" and "mult 9" energies of the lowest S=1,2,3 and 4 states for the Mn1Mn2 pair in the diamagnetically substituted "Mn1Mn2Ga3"

cluster have been calculated. These energies have been used to extract the parameter  $J_{12}$  from a best fit to these energies. To this end, the following MatLab script was used:

```

clear all
clc

% % NEVPT2
eref=[%
% S=0
-6389.108864
% S=1
-6389.108775
% S=2
-6389.108610
% S=3
-6389.108389
% S=4
-6389.108144
] ;

eref2=eref;
eref2=(eref2-eref2(1,1))*8065*27.211;
% eref22=eref2-eref2(5)

%
S=[0    1    2    3    4]

% fit to an isotropic non-Heisenberg exchange hamiltonian:
% -2Jab(Sa*Sb)-2J1ab*(Sa*Sb)^2
% with the Heisenberg exchange (the first term) and the biquadratic
% exchange (the second term)
A(5,2)=zeros;
for i=1:5
A(i,1)=-S(i)*(S(i)+1);
A(i,2)=-(S(i)*(S(i)+1))^2;
end

B(4,2)=zeros;
A(1:5,:)=A(1:5,:)-A(1,:);
B(1,:)=A(2,:);
B(2,:)=A(3,:);
B(3,:)=A(4,:);
B(4,:)=A(5,:);
Y(1,1)=eref2(2,1);
Y(2,1)=eref2(3,1);
Y(3,1)=eref2(4,1);
Y(4,1)=eref2(5,1);
eref2

```

```

X=pinv(B)*Y
Ycalc=B*X;
plot(Y,Ycalc,'o')
compar=[Y Ycalc]
diff=Y-Ycalc
stand_dev=sqrt(diff'*diff/3)
plot(Y,Ycalc,'o')

```

A value of  $J_{12}=-9.9 \text{ cm}^{-1}$  results along with a biquadratic exchange parameter  $J_{12}'=0.099 \text{ cm}^{-1}$ . In simulations of magnetic data  $J_{12}'$  was neglected.

## CASSCF/NEVPT2 Inputs for three magnetic sites $\text{Mn}_1\text{Mn}_2\text{Mn}_3$

In order to check the transferability of the J parameters computed Mn2+Ga dimers toward trimer clusters the following sets of input files were used:

1. Initial orbital guess:

```

"mn3hs_corr.inp"
!DKH DKH-def2-TZVP AutoAux NoFrozenCore PAL16

%rel method DKH
picturechange 2
end

%scf
MaxCore 16000
end

%casscf
nel 12
norb 15
mult 13
nroots 1
trafostep ri
actorbs locorbs
orbstep superci
                     switchstep diis
                     shiftup 1
                     shiftdn 1
end

*xyz -1 13
25      0.125742770    1.270204142    3.112434246
25      -0.514283772   -1.941554201    2.508612016
25      0.000000000    0.000000000    0.000000000
8       0.298835165    0.958353781   -3.976433815
6       0.273264790    0.117870369   -3.018678292
8       0.141860646    0.561261664   -1.866490808

```

1	1.328298282	-1.601784658	-3.249358809
6	0.384853663	-1.336977765	-3.274471113
1	0.011279200	-1.543399566	-4.156628890
1	-0.110601100	-1.828719930	-2.586664925
1	-2.818210597	3.386118019	-0.188411130
6	-2.126124893	3.675413320	0.442410368
1	-1.551012994	4.342584355	0.012795453
1	-2.549375975	4.069679805	1.233405332
1	4.043497730	2.082615814	0.272460621
6	3.840625077	1.668317646	1.137198351
1	4.180868841	2.236770674	1.859413135
8	-1.297552842	1.496553535	0.094257646
6	-1.301168848	2.495994401	0.853512280
8	-0.650006560	2.607050232	1.935716318
8	1.909322672	1.541200614	2.493632641
1	4.267934576	0.787773528	1.185719768
6	2.354734721	1.512379087	1.281046183
8	1.644785212	1.361904810	0.283146204
1	-1.395982228	5.055350964	3.875011963
6	-1.339465069	4.529106772	4.698917133
8	0.493872654	3.047519560	4.501533236
1	-1.913230646	3.738100978	4.622246503
6	0.032472214	4.111035673	4.912455233
1	-1.635611097	5.074840242	5.457173059
8	0.837272162	4.961904248	5.597895602
1	0.377324080	5.792237341	5.792087334
8	1.325523440	-1.391395512	-0.324927809
1	3.110621687	-3.090166834	-0.830878489
1	1.822456136	-3.767172628	-1.496699827
6	2.253350042	-3.528635929	-0.648904837
1	-3.792558019	-2.528426933	-1.069185412
6	-3.824459358	-2.107312162	-0.184037907
1	-4.282395950	-2.703249667	0.444251703
1	2.405435792	-4.338676046	-0.120262730
1	-4.309792279	-1.258656506	-0.243837423
6	-2.419319990	-1.850378283	0.299564237
8	-1.606054862	-1.322734236	-0.489725444
8	0.712433313	-3.007321033	1.094568838
6	1.355416097	-2.580983242	0.123837431
8	-2.168253094	-2.184114020	1.499369585
8	-0.174935720	-0.303036262	1.797965170
8	1.076824634	-1.824054009	3.679083279
8	-1.736908361	-1.114091514	4.160580446
8	-1.598753522	1.115294485	3.958373938
8	0.920038650	0.231529002	4.553710370
6	2.450232033	-1.282618405	5.525700996
1	3.338742477	-1.128100676	5.142047736
1	2.332986571	-0.716604211	6.316846223
1	2.364664535	-2.224658358	5.782227424
6	-2.110677601	0.034267617	4.420372088
6	-3.280342830	0.236231416	5.359007813
1	-3.968131975	-0.436743638	5.175199668

1	-2.974667245	0.145268640	6.286635637
6	1.401982147	-0.944573926	4.509909660
1	-3.655652678	1.131938870	5.226547762
8	-0.845421534	-3.614775726	3.478259483
6	-1.046851347	-4.846786110	3.221476347
8	-1.077947114	-5.637108630	4.178462974
6	-1.225691086	-5.318588835	1.828679705
1	-0.725664646	-4.736162572	1.219480761
1	-2.177432413	-5.294931559	1.595291429
1	-0.892905911	-6.236919640	1.749392510
*			

Input for state-specific CASSCF/NEVPT2 calculations of the lowest S=0 state of the Mn(III)<sub>3</sub> cluster:

```
„mn3s0nev.inp“
!DKH DKH-def2-TZVP AutoAux NoFrozenCore PAL16 moread

%moinp "mn3hs_corr.gbw"

%rel method DKH
picturechange 2
end

%scf
MaxCore 25000
end

%casscf
nel 12
norb 15
mult 1
nroots 1
trafostep ri
actorbs unchanged
actconstraints 1
orbstep superci
                                switchstep diis
                                shiftup 1
                                shiftdn 1
printgstate 1
ptsettings
d4tpre 1e-14
end
#maxiter 100
##gtol 1e-6
##etol 1e-11
nevpt2 true
ci
nguessmat 4500
maxiter 300
end
```

end

\*xyz -1 13

25	0.125742770	1.270204142	3.112434246
25	-0.514283772	-1.941554201	2.508612016
25	0.000000000	0.000000000	0.000000000
8	0.298835165	0.958353781	-3.976433815
6	0.273264790	0.117870369	-3.018678292
8	0.141860646	0.561261664	-1.866490808
1	1.328298282	-1.601784658	-3.249358809
6	0.384853663	-1.336977765	-3.274471113
1	0.011279200	-1.543399566	-4.156628890
1	-0.110601100	-1.828719930	-2.586664925
1	-2.818210597	3.386118019	-0.188411130
6	-2.126124893	3.675413320	0.442410368
1	-1.551012994	4.342584355	0.012795453
1	-2.549375975	4.069679805	1.233405332
1	4.043497730	2.082615814	0.272460621
6	3.840625077	1.668317646	1.137198351
1	4.180868841	2.236770674	1.859413135
8	-1.297552842	1.496553535	0.094257646
6	-1.301168848	2.495994401	0.853512280
8	-0.650006560	2.607050232	1.935716318
8	1.909322672	1.541200614	2.493632641
1	4.267934576	0.787773528	1.185719768
6	2.354734721	1.512379087	1.281046183
8	1.644785212	1.361904810	0.283146204
1	-1.395982228	5.055350964	3.875011963
6	-1.339465069	4.529106772	4.698917133
8	0.493872654	3.047519560	4.501533236
1	-1.913230646	3.738100978	4.622246503
6	0.032472214	4.111035673	4.912455233
1	-1.635611097	5.074840242	5.457173059
8	0.837272162	4.961904248	5.597895602
1	0.377324080	5.792237341	5.792087334
8	1.325523440	-1.391395512	-0.324927809
1	3.110621687	-3.090166834	-0.830878489
1	1.822456136	-3.767172628	-1.496699827
6	2.253350042	-3.528635929	-0.648904837
1	-3.792558019	-2.528426933	-1.069185412
6	-3.824459358	-2.107312162	-0.184037907
1	-4.282395950	-2.703249667	0.444251703
1	2.405435792	-4.338676046	-0.120262730
1	-4.309792279	-1.258656506	-0.243837423
6	-2.419319990	-1.850378283	0.299564237
8	-1.606054862	-1.322734236	-0.489725444
8	0.712433313	-3.007321033	1.094568838
6	1.355416097	-2.580983242	0.123837431
8	-2.168253094	-2.184114020	1.499369585
8	-0.174935720	-0.303036262	1.797965170
8	1.076824634	-1.824054009	3.679083279
8	-1.736908361	-1.114091514	4.160580446

8	-1.598753522	1.115294485	3.958373938
8	0.920038650	0.231529002	4.553710370
6	2.450232033	-1.282618405	5.525700996
1	3.338742477	-1.128100676	5.142047736
1	2.332986571	-0.716604211	6.316846223
1	2.364664535	-2.224658358	5.782227424
6	-2.110677601	0.034267617	4.420372088
6	-3.280342830	0.236231416	5.359007813
1	-3.968131975	-0.436743638	5.175199668
1	-2.974667245	0.145268640	6.286635637
6	1.401982147	-0.944573926	4.509909660
1	-3.655652678	1.131938870	5.226547762
8	-0.845421534	-3.614775726	3.478259483
6	-1.046851347	-4.846786110	3.221476347
8	-1.077947114	-5.637108630	4.178462974
6	-1.225691086	-5.318588835	1.828679705
1	-0.725664646	-4.736162572	1.219480761
1	-2.177432413	-5.294931559	1.595291429
1	-0.892905911	-6.236919640	1.749392510

\*

Lowest S=1,2,3,4,5 and 6 have been computed using the same input as for S=0 just replacing “mult 1” by “mult 3”, “mult 5”, “mult 7” and “mult 9”, “mult 11” and “mult 13”, respectively.

From the output files the following energies result:

S=0

---

Total Energy Correction : dE = -9.52720728012355

---

Reference Energy : E0 = -5594.82779542774915

---

Total Energy (E0+dE) : E = -5604.35500270787270

---

TOTAL RUN TIME: 0 days 19 hours 14 minutes 52 seconds 934 msec

S=1

---

Total Energy Correction : dE = -9.52729864008506

---

Reference Energy : E0 = -5594.82787952095441

---

Total Energy (E0+dE) : E = -5604.35517816103948

---

TOTAL RUN TIME: 1 days 15 hours 27 minutes 14 seconds 144 msec

S=2

---

Total Energy Correction : dE = -9.52744475312920

---

Reference Energy : E0 = -5594.82798802036086

---

Total Energy (E0+dE) : E = -5604.35543277349007

---

TOTAL RUN TIME: 0 days 23 hours 11 minutes 11 seconds 107 msec

S=3

---

Total Energy Correction : dE = -9.52734133590729

---

Reference Energy : E0 = -5594.82782983818288

---

Total Energy (E0+dE) : E = -5604.35517117409017

---

TOTAL RUN TIME: 0 days 10 hours 36 minutes 51 seconds 707 msec

S=4

---

Total Energy Correction : dE = -9.52722776780774

---

Reference Energy : E0 = -5594.82763113433975

---

Total Energy (E0+dE) : E = -5604.35485890214750

---

TOTAL RUN TIME: 0 days 5 hours 55 minutes 35 seconds 382 msec

S=5

---

Total Energy Correction : dE = -9.52710718015442

---

Reference Energy : E0 = -5594.82740242354339

---

Total Energy (E0+dE) : E = -5604.35450960369781

---

TOTAL RUN TIME: 0 days 2 hours 2 minutes 34 seconds 499 msec

S=6

---

Total Energy Correction : dE = -9.52697874159458

---

Reference Energy : E0 = -5594.82715722446392

---

Total Energy (E0+dE) : E = -5604.35413596605849

---

TOTAL RUN TIME: 0 days 1 hours 34 minutes 48 seconds 566 msec

NEVPT2

```

S=0 -5604.35500270787270
S=1 -5604.35517816103948
S=2 -5604.35543277349007
S=3 -5604.35517117409017
S=4 -5604.35485890214750
S=5 -5604.35450960369781
S=6 -5604.35413596605849

```

The following three MatLab script has been used to extract the  $J_{12}$ ,  $J_{13}$ ,  $J_{23}$  parameters from a best fit to the NEVPT2 spin energies.

Main Script:"mn3call.m"

```

clear all
clc
format short
close all
j1=[-9.88,-10.35,-2.36]
vals=mn3fun(j1(1),j1(2),j1(3))

aivals=100*[    0.943807876214733
               0.558764122041266
                           0.0
               0.574097449461743
               1.259399198720200
               2.025958099963277
               2.845930991200243
]
mn3fun(-9.88,-10.35,-2.36)-aivals
options =
optimset('Display','iter','PlotFcns',@optimplotfval,'MaxIter',
',300);
rms=@(j) sqrt(mean((mn3fun(j(1),j(2),j(3))-aivals).^2));
j2=fminsearch(rms,j1,options)
mn3fun(j2(1),j2(2),j2(3))
aivals
vals
j1
j2

```

Below we list two Matlab Functions which should be in the same directory as "mn3call.m":

"mn3fun.m"

```

function vals2 = mn3fun(j12,j23,j13)
% clear all
% clc

```

```

% format short
t0=cputime;
% matrices of the spin-operator within the S=2 manifold
spin=2;
smult=2*spin+1
ms=[2 1 0 -1 -2];
for i=1:smult
    ms1=ms(i);
    for j=1:smult
        ms2=ms(j);
        [msx,msy,msz]=smatrix(ms1,ms2,spin);
        sx(i,j)=msx;
        sy(i,j)=msy;
        sz(i,j)=msz;
    end
end
% spin wavefunctions: spin-uncoupled basis iw(:, centers 1
2 3 4)
%
% j k l
% fast l-slow
sume=0;
% for l=1:smult
    for k=1:smult
        for j=1:smult
            for i=1:smult
                sume=sume+1;
                % Fe1
                iw(sume,1)=i;
                % Fe2
                iw(sume,2)=j;
                % Fe3
                iw(sume,3)=k;
                % Fe4
                iw(sume,4)=l;
            end
        end
    end
% end
ndim=max(size(iw));
im=sqrt(-1);
sum1=0;
sum2=0;

```

```

sum3=0;
for i=1:smult
    for j=1:smult
        if sx(i,j)~=0.0
            sum1=sum1+1;
            sxoper(sum1,:)=[i j sx(i,j)];
        end
        if sy(i,j)~=0.0
            sum2=sum2+1;
            syoper(sum2,:)=[i j sy(i,j)];
        end
        if sz(i,j)~=0.0
            sum3=sum3+1;
            szoper(sum3,:)=[i j sz(i,j)];
        end
    end
end
nopersx=sum1;
opersy=sum2;
opersz=sum3;
% spin-matrices within the spin-uncoupled basis
% Fe1
s1x=zeros(ndim,ndim);
s1y=zeros(ndim,ndim);
s1z=zeros(ndim,ndim);
% Fe2
s2x=zeros(ndim,ndim);
s2y=zeros(ndim,ndim);
s2z=zeros(ndim,ndim);
% Fe3
s3x=zeros(ndim,ndim);
s3y=zeros(ndim,ndim);
s3z=zeros(ndim,ndim);
% % Fe4
% s4x=zeros(ndim,ndim);
% s4y=zeros(ndim,ndim);
% s4z=zeros(ndim,ndim);
% center 1
for i=1:nopersx
    % Fe(II) spin 1 left
    i1=sxoper(i,1);
    % Fe(II) spin 2 right
    i2=sxoper(i,2);

```

```

% matrix element spin 2 -> spin 1 i.e. sx=<spin
1|sx|spin 2>
    sxx=sxoper(i,3);
        for k=1:ndim
            if iw(k,1)==i2
                iw4=iw(k,:);
% replaces orbital i2 by orbital i1
                iw4(1,1)=i1;
                for m=1:k
                    if k>m&iw4(1,:)==iw(m,:)
                        s1x(m,k)=s1x(m,k)+sxx;
                        s1x(k,m)=conj(s1x(m,k));
                    end
                end
            end
% end k
        end
% end noperlf
end
for i=1:nopersy
    % Fe(II) spin 1 left
    i1=syoper(i,1);
    % Fe(II) spin 2 right
    i2=syoper(i,2);
    % matrix element spin 2 -> spin 1 i.e. sx=<spin
1|sx|spin 2>
    syy=syoper(i,3);
        for k=1:ndim
            if iw(k,1)==i2
                iw4=iw(k,:);
% replaces orbital i2 by orbital i1
                iw4(1,1)=i1;
                for m=1:k
                    if k>m&iw4(1,:)==iw(m,:)
                        s1y(m,k)=s1y(m,k)+sy;
                        s1y(k,m)=conj(s1y(m,k));
                    end
                end
            end
% end k
        end
% end noperlf
end

```

```

for i=1:nopersz
    % Fe(II) spin 1 left
    i1=szoper(i,1);
    % Fe(II) spin 2 right
    i2=szoper(i,2);
    % matrix element spin 2 -> spin 1 i.e. sx=<spin
1|sx|spin 2>
    szz=szoper(i,3);
    for k=1:ndim
        % % the orbital operator is diagonal:
        if iw(k,1)==i2
            s1z(k,k)=s1z(k,k)+szz;
        end
    end
    % end k
    end
end noperlf
% center 2
for i=1:nopersx
    % Fe(II) spin 1 left
    i1=sxoper(i,1);
    % Fe(II) spin 2 right
    i2=sxoper(i,2);
    % matrix element spin 2 -> spin 1 i.e. sx=<spin
1|sx|spin 2>
    sxz=sxoper(i,3);
    for k=1:ndim
        if iw(k,2)==i2
            iw4=iw(k,:);
    % replaces orbital i2 by orbital i1
            iw4(1,2)=i1;
            for m=1:k
                if k>m&iw4(1,:)==iw(m,:)
                    s2x(m,k)=s2x(m,k)+sxz;
                    s2x(k,m)=conj(s2x(m,k));
                end
            end
        end
    end
    % end k
    end
end noperlf
% end nopersy
for i=1:nopersy
    % Fe(II) spin 1 left

```

```

        i1=syoper(i,1);
% Fe(II) spin 2 right
        i2=syoper(i,2);
% matrix element spin 2 -> spin 1 i.e. sx=<spin
1|sx|spin 2>
        syy=syoper(i,3);
        for k=1:ndim
            if iw(k,2)==i2
                iw4=iw(k,:);
% replaces orbital i2 by orbital i1
                iw4(1,2)=i1;
                for m=1:k
                    if k>m&iw4(1,:)==iw(m,:)
                        s2y(m,k)=s2y(m,k)+syy;
                        s2y(k,m)=conj(s2y(m,k));
                    end
                end
            end
% end k
        end
% end noperlf
end

for i=1:nopersz
    % Fe(II) spin 1 left
    i1=szoper(i,1);
    % Fe(II) spin 2 right
    i2=szoper(i,2);
    % matrix element spin 2 -> spin 1 i.e. sx=<spin
1|sx|spin 2>
    szz=szoper(i,3);
    for k=1:ndim
% % the orbital operator is diagonal:
        if iw(k,2)==i2
            s2z(k,k)=s2z(k,k)+szz;
        end
    end
    % end k
    end
% end noperlf
end

% center 3
for i=1:nopersx
    % Fe(II) spin 1 left

```

```

        i1=sxoper(i,1);
% Fe(II) spin 2 right
        i2=sxoper(i,2);
% matrix element spin 2 -> spin 1 i.e. sx=<spin
1|sx|spin 2>
        sxx=sxoper(i,3);
        for k=1:ndim
            if iw(k,3)==i2
                iw4=iw(k,:);
% replaces orbital i2 by orbital i1
                iw4(1,3)=i1;
                for m=1:k
                    if k>m&iw4(1,:)==iw(m,:)
                        s3x(m,k)=s3x(m,k)+sxx;
                        s3x(k,m)=conj(s3x(m,k));
                    end
                end
            end
% end k
        end
% end noperlf
end
for i=1:nopersy
    % Fe(II) spin 1 left
    i1=syoper(i,1);
    % Fe(II) spin 2 right
    i2=syoper(i,2);
    % matrix element spin 2 -> spin 1 i.e. sx=<spin
1|sx|spin 2>
    syy=syoper(i,3);
    for k=1:ndim
        if iw(k,3)==i2
            iw4=iw(k,:);
% replaces orbital i2 by orbital i1
            iw4(1,3)=i1;
            for m=1:k
                if k>m&iw4(1,:)==iw(m,:)
                    s3y(m,k)=s3y(m,k)+syy;
                    s3y(k,m)=conj(s3y(m,k));
                end
            end
        end
    end
% end k
end

```

```

% end noperlf
end

for i=1:nopersz
    % Fe(II) spin 1 left
    i1=szoper(i,1);
    % Fe(II) spin 2 right
    i2=szoper(i,2);
    % matrix element spin 2 -> spin 1 i.e. sx=<spin
    1|sx|spin 2>
    szz=szoper(i,3);
    for k=1:ndim
        % % the orbital operator is diagonal:
        if iw(k,3)==i2
            s3z(k,k)=s3z(k,k)+szz;
        end
    end
end
% end noperlf
end

hexch12=-2*j12*(s1x*s2x+s1y*s2y+s1z*s2z);
hexch13=-2*j13*(s1x*s3x+s1y*s3y+s1z*s3z);
hexch23=-2*j23*(s2x*s3x+s2y*s3y+s2z*s3z);

hexch=hexch12+hexch13+hexch23;
[c,e]=eig(hexch); [e,ie]=sort(real(diag(e)));
e=e-e(1)*ones(size(e)); c=c(:,ie);
sxt=s1x+s2x+s3x;
syt=s1y+s2y+s3y;
szt=s1z+s2z+s3z;
szt2=szt*szt;
s2t=sxt*sxt+syt*syt+szt*szt;
s2eig=diag(c'*s2t*c);
szeig=diag(c'*szt*c);
% sort according to multiplicities
i0=1;i1=0;
for i=2:ndim
    if abs(e(i)-e(i-1))>0.001
        i1=i1+1;w(i1)=e(i-1);mul(i1)=i-i0;i0=i;
    end
end
i1=i1+1;w(i1)=e(i0);mul(i1)=ndim-i0+1;
% print result

```

```

fprintf(' _____ \n')
fprintf(' Multiplicity      E \n') 
fprintf(' _____ \n')
for i=1:i1
fprintf('     %3i      %12.3f\n',mul(i),w(i))
end
fprintf(' _____ \n')
sizew=max(size(w));
fitvals=zeros(1,7);
for i2=1:sizew
if (mul(sizew-i2+1)-1)/2==6
    fitvals(7)=w(sizew-i2+1);
end
if (mul(sizew-i2+1)-1)/2==5
    fitvals(6)=w(sizew-i2+1);
end
if (mul(sizew-i2+1)-1)/2==4
    fitvals(5)=w(sizew-i2+1);
end
if (mul(sizew-i2+1)-1)/2==3
    fitvals(4)=w(sizew-i2+1);
end
if (mul(sizew-i2+1)-1)/2==2
    fitvals(3)=w(sizew-i2+1);
end
if (mul(sizew-i2+1)-1)/2==1
    fitvals(2)=w(sizew-i2+1);
end
if (mul(sizew-i2+1)-1)/2==0
    fitvals(1)=w(sizew-i2+1);
end

end
fitvals
vals2=fitvals;
Elapsed_time=cputime-t0
end

“smatrix.m”

```

```
function [msx, msy, msz]=smatrix(ms1,ms2,s)
```

```

msx=0.0;
msy=0.0;
msz=0.0;
%
<ms1|sx|ms2>
if ms2<s&ms2==ms1-1;
    msx=0.5 *sqrt((s+ms1)*(s-
ms1+1));
end
if ms2>-s&ms2==ms1+1;
    msx=0.5 *sqrt((s-
ms1)*(s+ms1+1));
end
%
<ms1|sy|ms2>
if ms2<s&ms2==ms1-1;
    msy=-i*0.5 *sqrt((s+ms1)*(s-
ms1+1));
end
if ms2>-s&ms2==ms1+1;
    msy=i*0.5 *sqrt((s-
ms1)*(s+ms1+1));
end
%
<ms1|sz|ms2>
if ms2==ms1;
    msz=ms2;
end

```

The execution of the main script “mn3call.m” under MatLab yields the values of  $J_{12}, J_{23}, J_{13}$  of -8.18, -8.18 and  $2.27 \text{ cm}^{-1}$ , respectively.

Model of spin  $S = 2$ , approximating the spin of each  $(\text{Mn(III)}, S = 2)_3$  unit

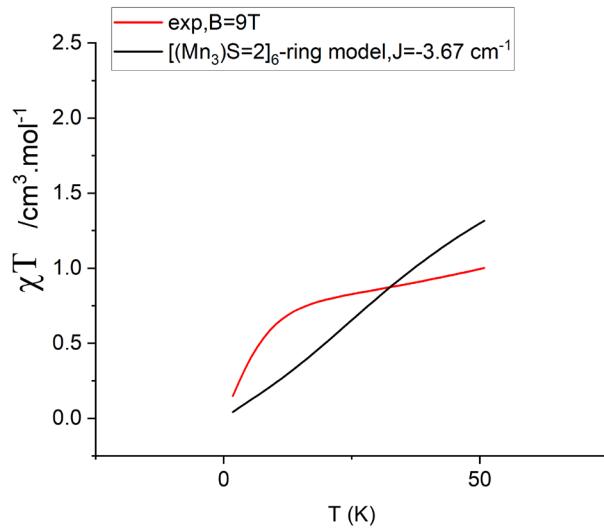


Figure S8: Simulation of the  $\chi_T$  vs  $T$  data using a simple model with a spin  $S = 2$ , approximating the spin of each  $(\text{Mn(III)}, S = 2)_3$  unit within the  $\text{Mn}_{18}$ -ring excluding data above 50K leads to improved  $J$  values.

## Literature for Supporting Information

- [1] (a) B. A. Hess, *Physical Review A* **1986**, *33*, 3742-3748; (b) M. Reiher, A. Wolf, *The Journal of Chemical Physics* **2004**, *121*, 10945-10956; (c) A. Wolf, M. Reiher, *The Journal of Chemical Physics* **2006**, *124*, 064102; (d) A. Wolf, M. Reiher, B. A. Hess, *The Journal of Chemical Physics* **2002**, *117*, 9215-9226.
- [2] (a) F. Weigend, R. Ahlrichs, *PCCP* **2005**, *7*, 3297-3305; (b) A. Schäfer, H. Horn, R. Ahlrichs, *The Journal of Chemical Physics* **1992**, *97*, 2571-2577; (c) A. Schäfer, C. Huber, R. Ahlrichs, *The Journal of Chemical Physics* **1994**, *100*, 5829-5835.
- [3] D. A. Pantazis, X.-Y. Chen, C. R. Landis, F. Neese, *Journal of Chemical Theory and Computation* **2008**, *4*, 908-919.
- [4] F. Neese, *The Journal of Chemical Physics* **2003**, *119*, 9428-9443.
- [5] (a) G. Breit, *Physical Review* **1932**, *39*, 616-624; (b) G. Breit, *Physical Review* **1929**, *34*, 553-573; (c) G. Breit, L. A. Wills, *Physical Review* **1933**, *44*, 470-490.
- [6] D. Ganyushin, F. Neese, *The Journal of Chemical Physics* **2013**, *138*, 104113.
- [7] M. Atanasov, D. Ganyushin, D. A. Pantazis, K. Sivalingam, F. Neese, *Inorg. Chem.* **2011**, *50*, 7460-7477.
- [8] (a) F. Neese, L. Lang, V. G. Chilkuri, *Topology, Entanglement, and Strong Correlations*, **2020**; (b) R. Maurice, R. Bastardis, C. d. Graaf, N. Suaud, T. Mallah, N. Guihéry, *Journal of Chemical Theory and Computation* **2009**, *5*, 2977-2984; (c) V. Vallet, L. Maron, C. Teichteil, J.-P. Flament, *The Journal of Chemical Physics* **2000**, *113*, 1391-1402.
- [9] N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini, K. S. Murray, *J. Comput. Chem.* **2013**, *34*, 1164–1175.