## **Supplementary Information**

A combined high-field EPR and quantum chemical study on a weakly ferromagnetically coupled dinuclear Mn(III) complex. A complete analysis of the EPR spectrum beyond the strong coupling limit.

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	$c^i$	$c_+{}^{ii}$	$c_{-}^{iii}$	$C_A$	$C_B$	$d_A$	$d_B$	$d_{AB}$
<i>S</i> = 4	0	3/7	0	1/2	1/2	3/14	3/14	2/7
<i>S</i> = 3	0	1/5	0	1/2	1/2	1/10	1/10	2/5
<i>S</i> = 2	0	-3/7	0	1/2	1/2	-3/14	-3/14	5/7
<i>S</i> = 1	0	-21/5	0	1/2	1/2	-21/10	-21/10	13/5
S = 0	0	0	0	1/2	1/2	0	0	0

**Table S1.** The  $\mathbf{g}_A$  and  $\mathbf{g}_B$ -tensor coefficients,  $c_A$  and  $c_B$ , local  $\mathbf{D}_A$  and  $\mathbf{D}_B$ -tensor coefficients,  $d_A$  and  $d_B$  and the pair-interaction **D**-tensor coefficient,  $d_{AB}$  for a dinuclear system with  $S_A = S_B = 2$ .

 $^{i}c = \frac{S_{A}(S_{A}+1) - S_{B}(S_{B}+1)}{S(S+1)}$ 

$${}^{ii}c_{+} = \frac{3\left[S_{A}\left(S_{A}+1\right)-S_{B}\left(S_{B}+1\right)\right]^{2}+S\left(S+1\right)\left[3S\left(S+1\right)-2S_{A}\left(S_{A}+1\right)-2S_{B}\left(S_{B}+1\right)-3\right]}{(2S+3)(2S-1)S\left(S+1\right)}$$
$${}^{iii}c_{-} = \frac{4S\left(S+1\right)\left[S_{A}\left(S_{A}+1\right)-S_{B}\left(S_{B}+1\right)\right]}{(2S+3)(2S-1)S\left(S+1\right)}$$

**Table S2.** The Mn- $\mu$ O-Mn angle (°), Mn- $\mu$ O distance (Å) and  $\delta$  parameter derived from nine optimized geometries calculated from  $1^{opt}$  together with the magnetic exchange interaction *J* (cm<sup>-1</sup>) calculated for each structure with the "single geometry" approach.

∠(Mn-O-Mn)	d(Mn-µO)	$\delta$	J
117.40	1.8571	63.22	14.67
118.46	1.8467	64.15	13.09
119.53	1.8366	65.08	11.05
120.07	1.8316	65.56	9.88
120.62	1.8266	66.03	8.54
121.16	1.8217	66.51	7.08
121.71	1.8168	66.99	5.48
122.82	1.8071	67.97	1.87
123.94	1.7976	68.95	-2.35

## Table S3. xyz coordinates of 1<sup>opt</sup>.

## E -4339.507925292608

0	0.000001	0.000001	-0.681311
N	3 525443	-0 192961	1 127854
0	0.938992	-1 514968	1.682742
N	2 370503	-1 706937	-0.973/52
$\hat{0}$	-1 299286	-1.568211	1 389/80
N	2 816670	1 121034	1.302400
0	1 200286	1.121934	1 220/21
N	2.816670	1.306211	1.309401
N	-2.8100/9	-1.121955	-1.280304
N	-0.938992	1.314909	1.062/40
IN	-3.525441	0.192959	1.12/854
N	-2.370504	1.706937	-0.9/3453
C	-0.210117	-1.984335	1.932521
С	0.210117	1.984336	1.932520
С	-0.345605	-3.092876	2.948017
С	0.345603	3.092878	2.948014
С	3.452640	-0.281633	2.648692
С	3.854894	-1.709137	3.006949
С	4.881328	-2.058368	1.919772
С	4.268049	-1.440269	0.653807
С	3.297975	-2.397841	-0.033548
С	1.278445	-2.654793	-1.413633
С	1.081937	-2.380949	-2.900376
С	2.512316	-2.078250	-3.369167
C	3.053582	-1.197471	-2.230908
Ĉ	2 717858	0.280209	-2 492951
Ĉ	2 343662	2 519835	-1 525590
č	3 570642	3 272779	-2 044764
c	4 702638	2 713163	-1 161861
c	4.702058	1 282404	0.776522
c	4.230708	1.262404	0.722218
C	4.233447	2.510924	1 525501
C	-2.545001	-2.319634	-1.525591
C	-3.5/0641	-3.2/2//9	-2.044765
C	-4.702637	-2./13103	-1.101802
C	-4.230768	-1.282405	-0.776523
C	-4.233446	-1.062639	0./3231/
C	-3.452638	0.281631	2.648692
С	-3.854893	1.709135	3.006949
С	-4.881327	2.058366	1.919773
С	-4.268049	1.440267	0.653808
С	-3.297975	2.397840	-0.033548
С	-1.278447	2.654794	-1.413635
С	-1.081939	2.380950	-2.900378
С	-2.512318	2.078250	-3.369168
С	-3.053583	1.197471	-2.230910
С	-2.717859	-0.280208	-2.492953
Mn	1.585831	-0.054733	0.223454
Mn	-1.585830	0.054733	0.223453
Н	-1.106571	-3.816944	2.631782
Н	-0.685614	-2.654867	3.899066
н	0 614442	-3 591271	3 119298
н	1 106568	3 816948	2 631778
н	0.685613	2 654872	3 899064
н	-0.614445	3 591271	3 119295
и ц	2 445030	0.006823	2 076055
п u	4 167022	-0.000823	2.970933
п	4.107033	0.444221	3.003023
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н	2.979105	-2.369341	2.951358
Н	5.851472	-1.58//26	2.136506
Н	5.055998	-3.13/2//	1.810399
Н	5.044773	-1.124920	-0.054251
Н	3.863784	-3.187054	-0.560162
Н	2.664355	-2.875745	0.724391
Н	1.620985	-3.690002	-1.255545
Н	0.387095	-2.472592	-0.804617
Н	0.629099	-3.230899	-3.426198
Η	0.433794	-1.501522	-3.035458
Η	2.561025	-1.574804	-4.344156
Н	3.095192	-3.007659	-3.445020
Н	4.138001	-1.318458	-2.106496
Н	1.672961	0.352644	-2.826437

3.367904	0.645086	-3.307876
1.491957	2.503220	-2.212318
2.007082	2.927543	-0.560904
3.465449	4.361679	-1.958587
3.744787	3.041457	-3.105956
4.819234	3.326655	-0.255740
5.673164	2.700595	-1.671878
4.856663	0.528308	-1.270375
3.691848	1.885097	1.220182
5.267982	1.053387	1.117314
-1.491956	-2.503219	-2.212319
-2.007080	-2.927541	-0.560904
-3.465447	-4.361679	-1.958588
-3.744785	-3.041457	-3.105957
-4.819232	-3.326655	-0.255741
-5.673163	-2.700596	-1.671879
-4.856663	-0.528308	-1.270376
-3.691846	-1.885098	1.220181
-5.267980	-1.053389	1.117314
-2.445928	0.006821	2.976955
-4.167031	-0.444222	3.065023
-4.269897	1.774105	4.020346
-2.979163	2.369339	2.951357
-5.851471	1.587722	2.136508
-5.055998	3.137274	1.810400
-5.044773	1.124918	-0.054250
-3.863786	3.187053	-0.560161
-2.664355	2.875744	0.724391
-1.620988	3.690003	-1.255546
-0.387097	2.472594	-0.804619
-0.629102	3.230900	-3.426200
-0.433795	1.501524	-3.035460
-2.561027	1.574804	-4.344157
-3.095194	3.007659	-3.445022
-4.138002	1.318458	-2.106496
-1.672962	-0.352643	-2.826439
-3.367905	-0.645085	-3.307877
	3.367904 1.491957 2.007082 3.465449 3.744787 4.819234 5.673164 4.85663 3.691848 5.267982 -1.491956 -2.007080 -3.465447 -3.744785 -4.819232 -5.673163 -4.85663 -3.691846 -5.267980 -2.445928 -4.167031 -4.269897 -2.979163 -5.851471 -5.055998 -5.044773 -3.863786 -2.664355 -1.620988 -0.387097 -0.629102 -0.433795 -2.561027 -3.095194 -4.138002 -1.672962 -3.367905	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$



**Fig. S1**. Experimental (top, red) and simulated (middle, green and bottom, blue) HF-EPR spectra at 285 GHz and 5K. The green simulated spectrum has been calculated with the initial parameters (Table 3) while the blue simulated one with the fitted parameters (Table 3)



**Fig. S2**. Simulated HF-EPR spectra at 285 GHz and 15 K calculated using the initial parameters (Table 3) with (top, blue) or without (bottom, green) taking into account the  $D_{AB}$  contribution



**Fig. S3**. Energy levels with the magnetic field oriented along the x axis and experimental spectra at 285 GHz and 15 K. The forbiden transitions are grey colored.



**Fig. S4**. Energy levels with the magnetic field oriented along the y axis and experimental spectra at 285 GHz and 15 K. The forbiden transitions are grey colored.