Supplementary Information

Switching the orientation of Jahn-Teller axes in oxime-based Mn^{III} dimers and its effect upon magnetic exchange: a combined experimental and theoretical study

Priyanka Comar,[a] Thayalan Rajeshkumar,[b] Gary S. Nichol,[a] Mateusz B. Pitak,[c] Simon J. Coles,[c] Gopalan Rajaraman*[b] and Euan K. Brechin*[a]

[a]EaStCHEM School of Chemistry, The University of Edinburgh, David Brewster Road, Edinburgh, EH9 3FJ, Scotland, UK. Tel: +44 (0)131-650-7545; Email: E.Brechin@ed.ac.uk
[b]Department of Chemistry, Indian Institute of Technology Bombay, Mumbai, 400076, India. E-mail: rajaraman@chem.iitb.ac.in;
[c] UK National Crystallographic Service, Chemistry, University of Southampton, Highfield Campus, Southampton, SO17 1BJ, UK

Experimental Procedures

Synthesis of complex 1: $Mn(ClO_4)_2 \cdot 6H_2O$ (0.145 g, 0.4 mmol) and Et-saoH_2 (0.066 g, 0.4 mmol) were dissolved in MeOH (10 mL). NH_4OH (61.6 µL, 1.6 mmol) was then added to the solution and the reaction was left to stir for 40 minutes at room temperature. dpa (74.1 µL, 0.4 mmol) in EtOH (10 mL) was added to the reaction mixture, which was then filtered after a further 5 minutes of stirring. The black mother liquor was left to crystallise by slow evaporation for 4 days, producing black block crystals in approximately 30% yield. Elemental analysis (calculated) found C: (48.39) 48.26 %, H: (4.32) 4.45%, N: (10.75) 10.82%.

Synthesis of complex 2: $Mn(ClO_4)_2 \cdot 6H_2O$ (0.145g, 0.4 mmol) and Me-saoH_2 (0.06 g, 0.4 mmol) were dissolved in MeOH (10 mL). NH_4OH (61.6 µL, 1.6 mmol) was then added to the solution and the reaction was left to stir for 40 minutes at room temperature. dpa (142.32 µL, 0.8 mmol) in EtOH (10 mL) was added to the reaction mixture, which was then filtered after 5 minutes. The black mother liquor was left to crystallise by slow evaporation for 4 days, producing black block crystals in approximately 30% yield. Elemental analysis (calculated) found C: (44.96) 44.84 %, H: (3.56) 4.34 %, N: (10.49) 10.92 %.

Synthesis of complex 3: $Mn(ClO_4)_2 \cdot 6H_2O$ (0.145 g, 0.4 mmol) and Me_2-saoH_2 (0.066g, 0.4 mmol) were dissolved in MeOH (10 mL). NH_4OH (61.6 µL, 1.6 mmol) was then added to the solution and the reaction was left to stir for 40 minutes at room temperature. dpa (74.1 µL, 0.4 mmol) in EtOH (10 mL) was added to the reaction mixture, which was then filtered after 5 minutes. The black mother liquor was

left to crystallise by slow evaporation for 2-4 days, producing black block crystals in approximately 30% yield. Elemental analysis (calculated) found: C: (47.56) 47.32 %, H: (5.17) 5.93 %, N: (9.64) 9.87 %.

Synthesis of complex 4: $Mn(ClO_4)_2 \cdot 6H_2O$ (0.145 g, 0.4 mmol) and $saoH_2$ (0.055 g, 0.4 mmol) were dissolved in MeOH (10 mL). Benzyl trimethyl ammonium hydroxide (280 µL, 1.6 mmol) was then added to the solution and the reaction was left to stir for 40 minutes at room temperature. dpa (74.1 µL, 0.4 mmol) in EtOH (10 mL) was added to the reaction mixture, which was then filtered after 5 minutes. The black mother liquor was left to crystallise by slow evaporation for 4 days, producing black block crystals. Only a very small amount of **4** could be made, precluding calculation of a yield and CHN analysis.

Synthesis of complex 5: $Mn(ClO_4)_2 \cdot 6H_2O$ (0.145 g, 0.4 mmol) and Ph-$saoH_2$ (0.085 g, 0.4 mmol) were dissolved in a THF/MeOH mixture (6 mL / 4 mL). NH_4OH (61.6 µL, 1.6 mmol) was then added to the solution and the reaction was left to stir for 40 minutes at room temperature. dpa (74.1 µL, 0.4 mmol) in EtOH (10 mL) was added to the reaction mixture, which was then filtered after 5 minutes. The black mother liquor was left to crystallise by slow evaporation for 4 days, producing black block crystals. Elemental analysis (calculated) found C: (54.37) 54.62 %, H (4.57) 4.13 %, N: (8.99) 9.66 %.

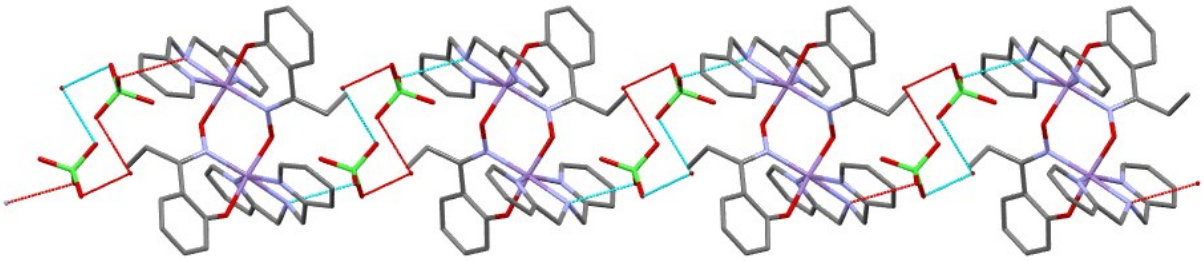

Figure S1. Packing diagram for complex **1** viewed along the *b* axis. Hydrogen bonding between the cages is mediated *via* the N-atom of the dpa ligand and the ClO_4^- anions, highlighted by the dashed lines, leading to the formation of 1D chains.

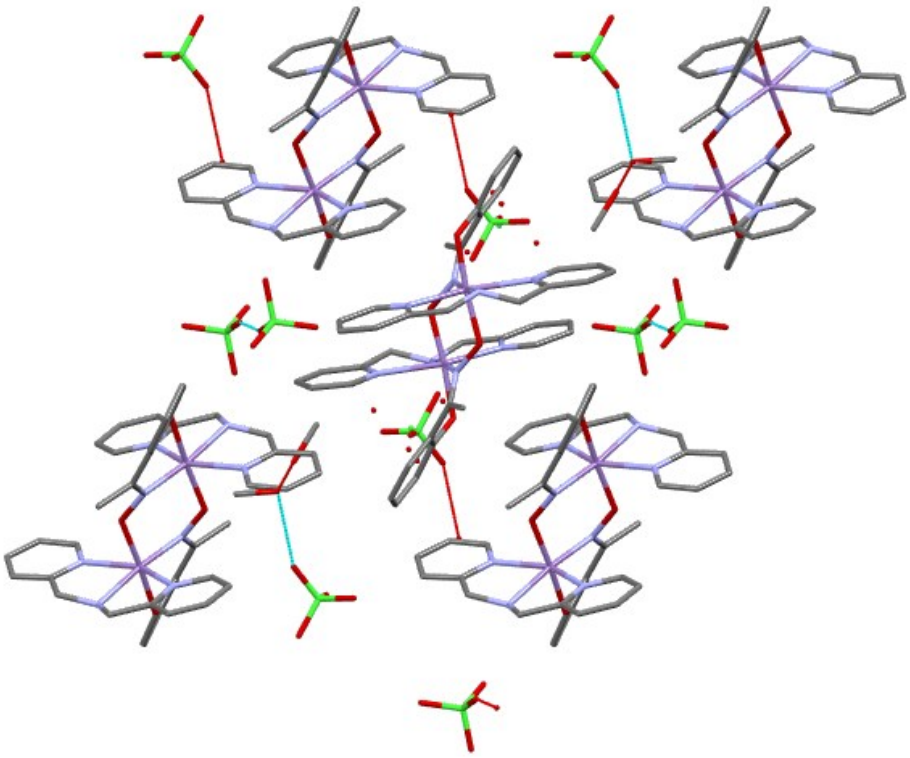

Figure S2. Packing diagram for complex **2** viewed along the *b* axis. Hydrogen bonding between the perchlorate anions and the MeOH molecules is highlighted by the dashed lines.

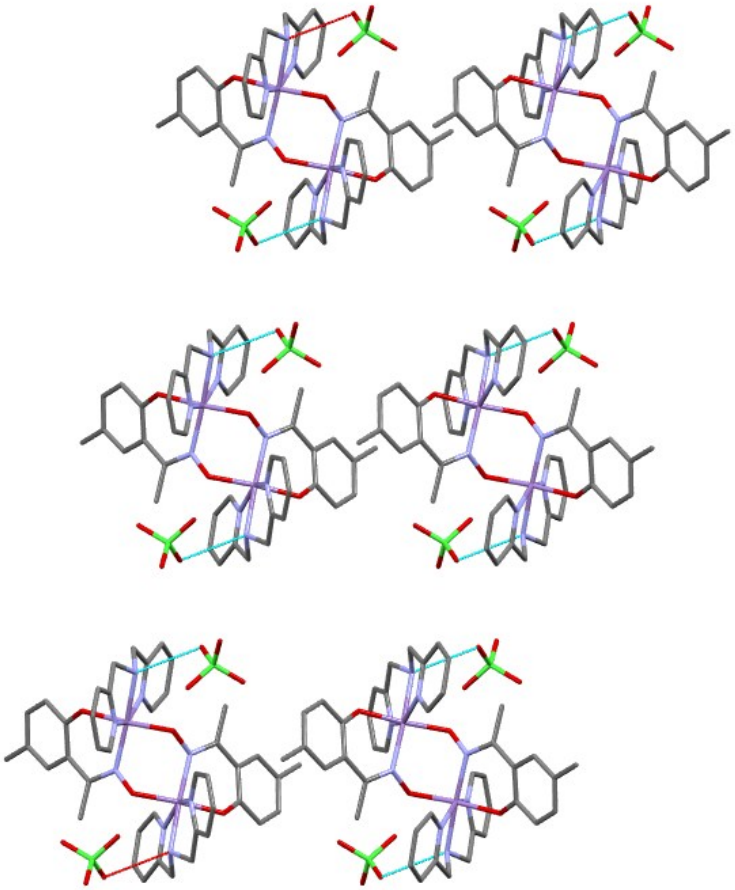

Figure S3. Packing diagram for complex **3** viewed along the *b* axis. Hydrogen bonding exists between the dpa N-atoms and the ClO_4^- anions, with π- π stacking between the phenyl rings of adjacent cationic cages.

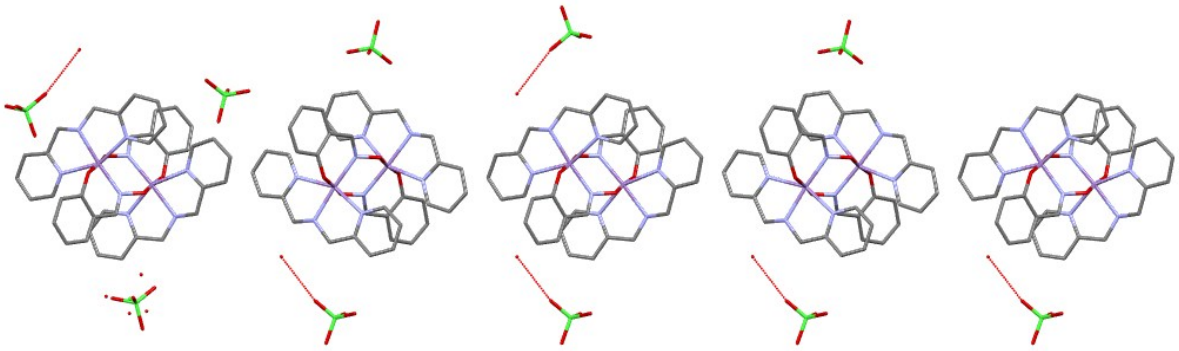

Figure S4. Packing diagram for complex **4** viewed along the *b* axis. Hydrogen bonding interactions between the perchlorate anions and THF solvent (3.16 Å), and between the perchlorate anions and ligand C-atoms are highlighted.

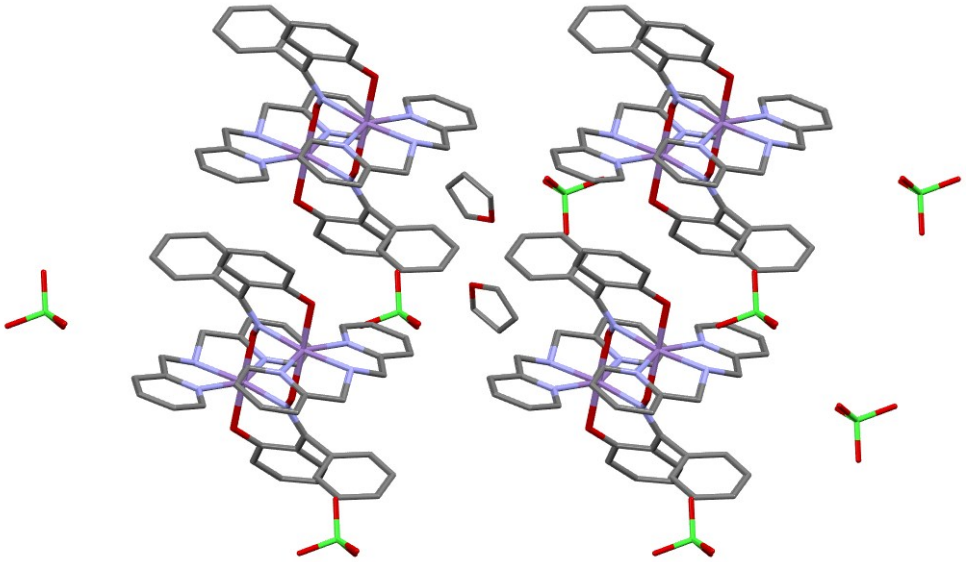

Figure S5. Packing diagram for complex **5** viewed along the *b* axis. Close contacts between neighbouring cages result in the formation of 1D chains.

Table S1. Crystallographic information for complexes **1**-**5**.

Identification code	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{42}H_{52}Cl_2Mn_2N_8O_{12.44}$	$C_{42}H_{46}Cl_2Mn_2N_8O_{14}$	$C_{46}H_{60}Cl_2Mn_2N_8O_{16}$	$C_{56.44}H_{56.87}Cl_2Mn_2N_8O_{13.61}$	$C_{40}H_{44}Cl_2Mn_2N_8O_{14}$
Formula weight	1041.5	1067.65	1161.8	1245.74	1041.61
Temperature	120.0 K	100.0 K	120.0 K	120.0 K	120.0 K
Wavelength	1.5418 Å	0.71073 Å	0.71073 Å	1.54184 Å	1.54184 Å
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	*C*2/*c*	*P*-1	*C*2/*c*	*P*-1	$P2_1/c$
Unit cell dimensions	a = 21.1082(7) Å b = 10.3582(3) Å c = 22.8139(7) Å α= 90°. β= 115.866(4)°. γ = 90°.	*a* = 13.1019(7) Å *b* = 14.5141(7) Å *c* = 14.8351(10) Å α = 105.116(7)° β = 110.267(8)° γ = 108.665(8)°	a = 25.9020(12) Å b = 10.4638(4) Å c = 21.9889(11) Å α= 90°. β= 103.471(5)°. γ = 90°.	a = 8.4822(4) Å b = 13.2500(4) Å c = 13.6070(5) Å α= 110.595(3)°. β= 103.803(4)°. γ = 92.048(3)°.	a = 14.2526(7) Å b = 22.2504(12) Å c = 15.7127(11) Å α= 90°. β= 116.936(8)°. γ = 90°.
Volume	4488.4(3) Å^3	2277.5(3) Å^3	5795.8(5) Å^3	1378.12(10) Å^3	4442.3(5) Å^3
Z	4	2	4	1	4
Theta range for data collection	4.307 to 76.096°.	3.037 to 25.242°	2.965 to 26.372°.	3.595 to 76.336°.	3.478 to 52.004°.
Reflections collected	34109	24513	28756	21371	19662
Independent reflections	4658 [R(int) = 0.0397]	6066 [R_{int} = 10.040]	5895 [R(int) = 0.0473]	5662 [R(int) = 0.0353]	4819 [R(int) = 0.0692]
Data / restraints / parameters	4658 / 0 / 318	6066 / 166 / 642	5895 / 0 / 304	5662 / 151 / 383	4819 / 47 / 605
Goodness-of-fit on F^2	1.057	1.009	1.084	1.051	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0913	R1 = 0.949, wR2 = 0.2502	R1 = 0.0492, wR2 = 0.1306	R1 = 0.0572, wR2 = 0.1539	R1 = 0.0692, wR2 = 0.1739
R indices (all data)	R1 = 0.0399, wR2 = 0.0928	R1 = 0.1417, wR2 = 0.2895	R1 = 0.0592, wR2 = 0.1359	R1 = 0.0632, wR2 = 0.1590	R1 = 0.1036, wR2 = 0.2073
Largest diff. peak and hole	0.331 and -0.719 e.Å^{-3}	1.443 and -0.937 e Å^{-3}	0.806 and -0.467 e.Å^{-3}	0.953 and -0.696 e.Å^{-3}	0.461 and -0.503 e.Å^{-3}

Table S2. Selected bond lengths (Å) for complexes **1**-**5**.

Bond	1	2	3	4	5
Mn1…Mn1	4.924	3.819	3.787	3.806	-
Mn1…Mn2	-	-	-	-	3.826
Mn1-N1	2.2727(18)	2.264(4)	2.238(2)	2.203(3)	2.207(6)
Mn1-N2	2.0971(18)	2.160(5)	2.110(2)	2.141(3)	2.116(6)
Mn1-N3	2.2979(18)	2.197(5)	2.258(2)	2.267(3)	2.245(6)
Mn1-N4	2.0081(17)	2.024(5)	2.009(2)	2.039(2)	2.002(6)
Mn1-O1	1.8590(14)	1.869(4)	1.8596(18)	1.867(2)	1.856(5)
Mn1-O2	1.9035(14)	1.895(4)	1.9080(18)	1.902(2)	1.886(5)
Mn2-N1’	-	-	-	-	2.213(6)
Mn2-N2’	-	-	-	-	2.148(6)
Mn2-N3’	-	-	-	-	2.162(6)
Mn2-N4’	-	-	-	-	2.026(6)
Mn2-O1’	-	-	-	-	1.847(5)
Mn2-O2’	-	-	-	-	1.884(5)

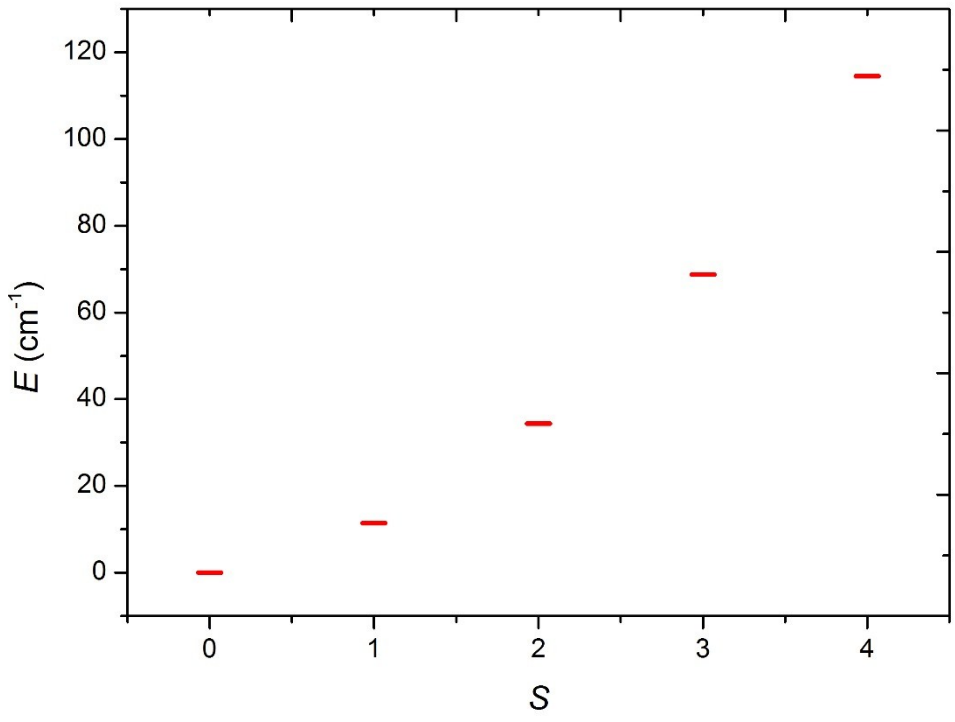

Figure S6. Energy spectrum of **1** at zero magnetic field for the isotropic spin-Hamiltonian (1) with the determined best fit parameters as described in the main text.

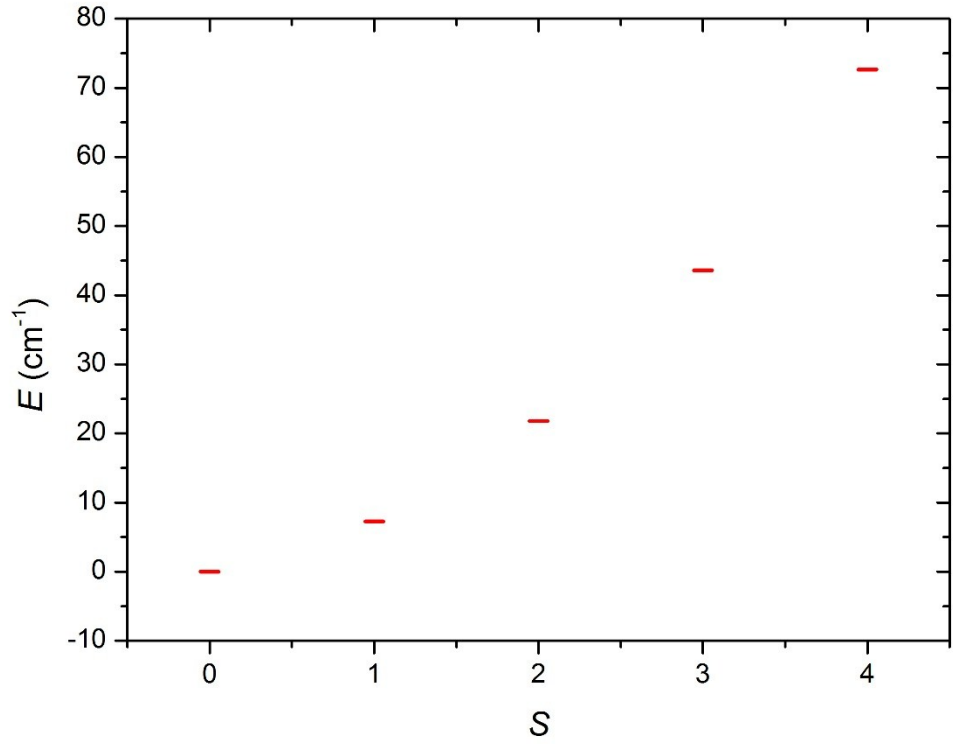

Figure S7. Energy spectrum of **2** at zero magnetic field for the isotropic spin-Hamiltonian (1) with the determined best fit parameters as described in the main text.

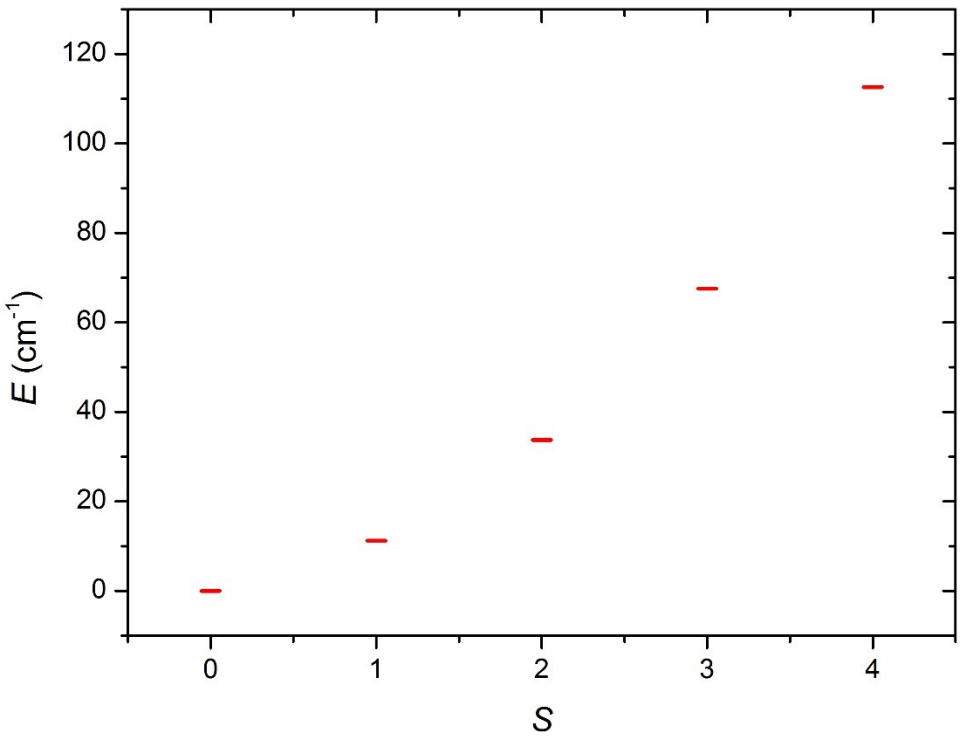

Figure S8. Energy spectrum of **3** at zero magnetic field for the isotropic spin-Hamiltonian (1) with the determined best fit parameters as described in the main text.

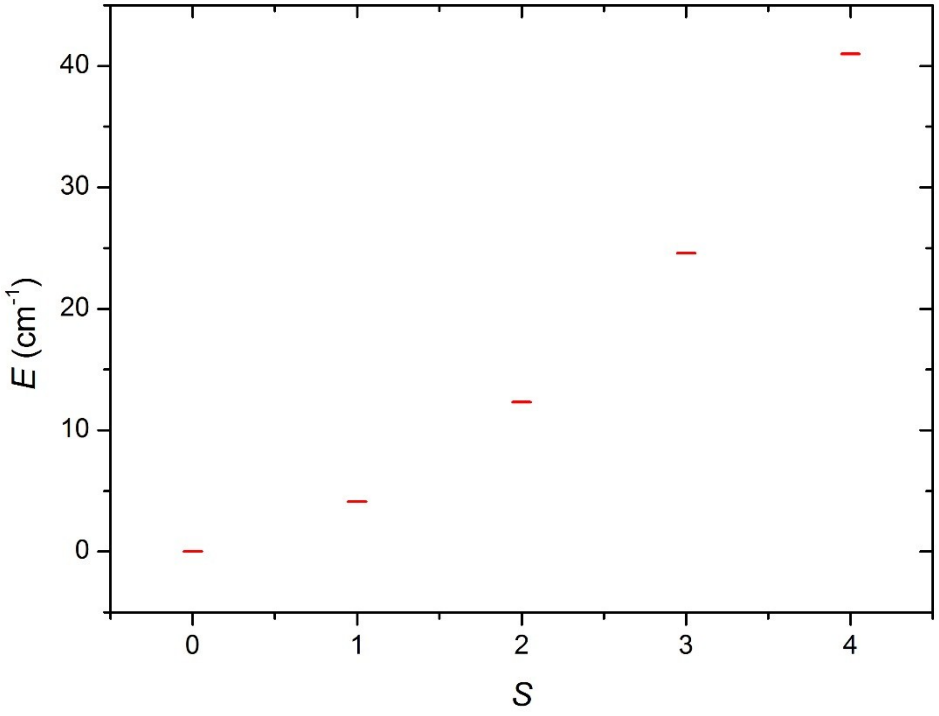

Figure S9. Energy spectrum of **5** at zero magnetic field for the isotropic spin-Hamiltonian (1) with the determined best fit parameters as described in the main text.

Table S3. Overlap integral values for complex **1**

α/β	d_{yz}	d_{xz}	d_{xy}	d_z^2	$d_{x^2-y^2}$
d_{yz}	-0.082	-0.021	-0.033	-0.029	0.031
d_{xz}	-0.018	0.268	0.054	-0.037	0.065
d_{xy}	-0.032	0.055	0.302	-0.043	0.006
d_z^2	0.029	0.040	0.044	0.107	0.038
$d_{x^2-y^2}$	-0.031	-0.068	-0.006	0.039	-0.082

Table S4. Overlap integral values for complex **2**

α/β	d_{xy}	d_{yz}	d_{xz}	d_z^2	$d_{x^2-y^2}$
d_{xy}	0.206	-0.112	-0.048	0.087	0.089
d_{yz}	0.115	-0.171	0.139	-0.023	0.028
d_{xz}	0.049	0.136	-0.224	-0.020	0.099
d_z^2	0.086	0.023	0.019	0.076	-0.051
$d_{x^2-y^2}$	0.087	-0.027	-0.098	-0.051	-0.013

Table S5. Overlap integral values for complex **3**

α/β	d_{xy}	d_{yz}	d_{xz}	d_z^2	$d_{x^2-y^2}$
d_{xy}	0.169	-0.083	-0.005	-0.062	0.091
d_{yz}	-0.084	-0.163	-0.191	0.033	-0.115
d_{xz}	-0.005	-0.192	-0.248	0.010	0.170
d_z^2	-0.062	0.033	0.011	-0.057	0.020
$d_{x^2-y^2}$	0.091	-0.115	0.170	0.020	0.256

Table S6. Overlap integral values for complex **4**

α/β	d_{xz}	d_{xy}	d_{yz}	d_z^2	$d_{x^2-y^2}$
d_{yz}	0.205	0.001	0.082	0.053	0.049
d_{xy}	-0.314	0.189	0.209	-0.091	-0.079
d_{xz}	0.362	0.195	-0.043	0.097	0.119
d_z^2	0.045	0.090	-0.010	0.081	0.069
$d_{x^2-y^2}$	-0.100	-0.121	0.066	-0.069	0.178

Table S7. Overlap integral values for Complex **5**

α/β	d_{xy}	d_{yz}	d_{xz}	dz^2	$d_{x^2-y^2}$
d_{xy}	0.445	-0.035	-0.016	0.043	-0.064
d_{yz}	-0.033	0.138	0.121	0.042	-0.084
d_{xz}	-0.015	0.124	-0.391	0.039	-0.070
d_z^2	0.043	0.040	0.035	-0.067	0.086
$d_{x^2-y^2}$	-0.064	-0.084	-0.070	0.086	0.015

Table S8. Overlap integral values for complex **6**

α/β	d_{xz}	d_{yz}	d_{xy}	d_z^2	$d_{x^2-y^2}$
d_{xz}	-0.109	-0.160	0.007	-0.002	-0.087
d_{yz}	-0.159	-0.096	0.059	-0.001	0.002
d_{xy}	-0.006	-0.059	-0.209	0.021	-0.020
d_z^2	-0.002	-0.001	-0.021	0.489	0.009
$d_{x^2-y^2}$	-0.087	0.003	0.020	0.009	-0.075

Table S9. Computed spin densities of selected atoms in complexes **1** and **6**.

	1	**6**
Mn(III)	3.889	3.831
O	-0.004	0.013
N	-0.042	0.073

Table S10. Overlap integral values for a model complex with a Mn-N-O-N torsion angle of 18.5°

α/β	d_{xy}	d_{xz}	d_{yz}	d_z^2	$d_{x^2-y^2}$
d_{xy}	0.245	-0.048	-0.185	-0.067	0.073
d_{xz}	0.049	-0.360	0.066	-0.026	-0.158
d_{yz}	0.189	0.060	0.220	0.074	0.050
d_z^2	-0.066	0.030	-0.075	0.019	-0.007
$d_{x^2-y^2}$	0.078	0.152	-0.045	-0.007	-0.032

Table S11. Overlap integral values for a model complex with Mn-N-O-N torsion angle of 41.8°

α/β	d_{xy}	d_{xz}	d_{yz}	d_z^2	$d_{x^2-y^2}$
d_{xy}	0.310	0.189	-0.028	0.039	0.092
d_{xz}	-0.195	0.013	0.332	0.005	0.085
d_{yz}	0.033	0.335	-0.068	-0.017	-0.100
d_z^2	0.037	-0.007	0.022	0.394	-0.017
$d_{x^2-y^2}$	0.089	-0.078	0.101	-0.019	-0.056

Table S12. Overlap integral values for a model complex Mn-N-O-N torsion angle of 92.8°

α/β	d_{xy}	d_{xz}	d_{yz}	d_z^2	$d_{x^2-y^2}$
d_{xy}	-0.333	0.031	0.238	0.074	0.076
d_{xz}	0.097	-0.302	0.015	-0.018	-0.088
d_{yz}	-0.425	0.043	0.012	-0.025	0.038
d_z^2	0.034	0.008	0.031	0.049	-0.070
$d_{x^2-y^2}$	0.047	0.081	-0.030	-0.077	-0.074