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Rationalizing the Sign and Magnitude of the Magnetic Interaction and Anisotropy in Dinuclear Manganese(III) complexes

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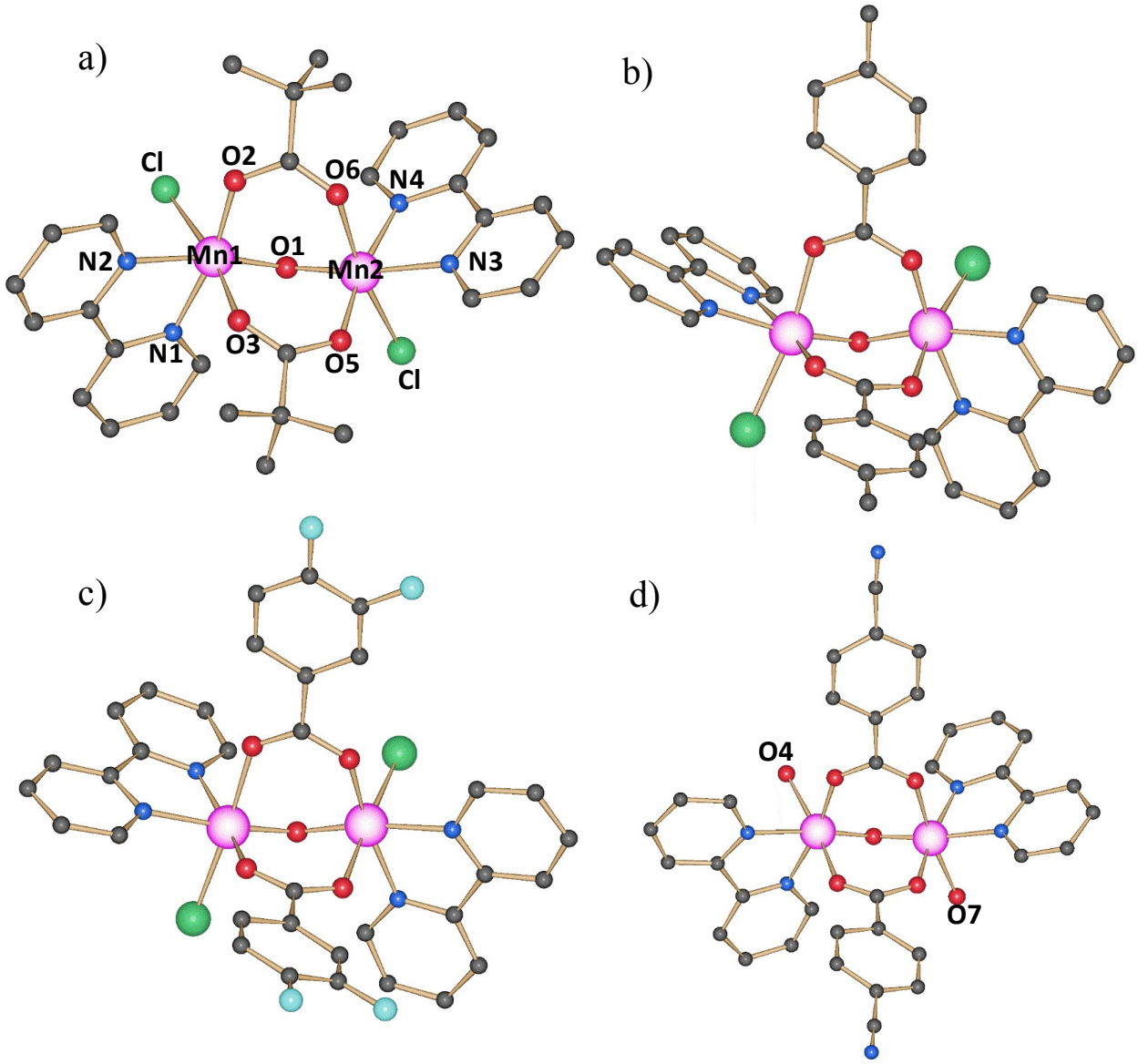

Figure S1. The molecular structure of complex (a) **2**, (b)**3**, (c) **4** and (d)**5**. The solvent and H atoms are omitted for clarity. Color scheme; Mn^{III}, pink; O, red; N, blue; C, light grey; Cl, green; F,cyan. Atom labelling is same for all complexes.

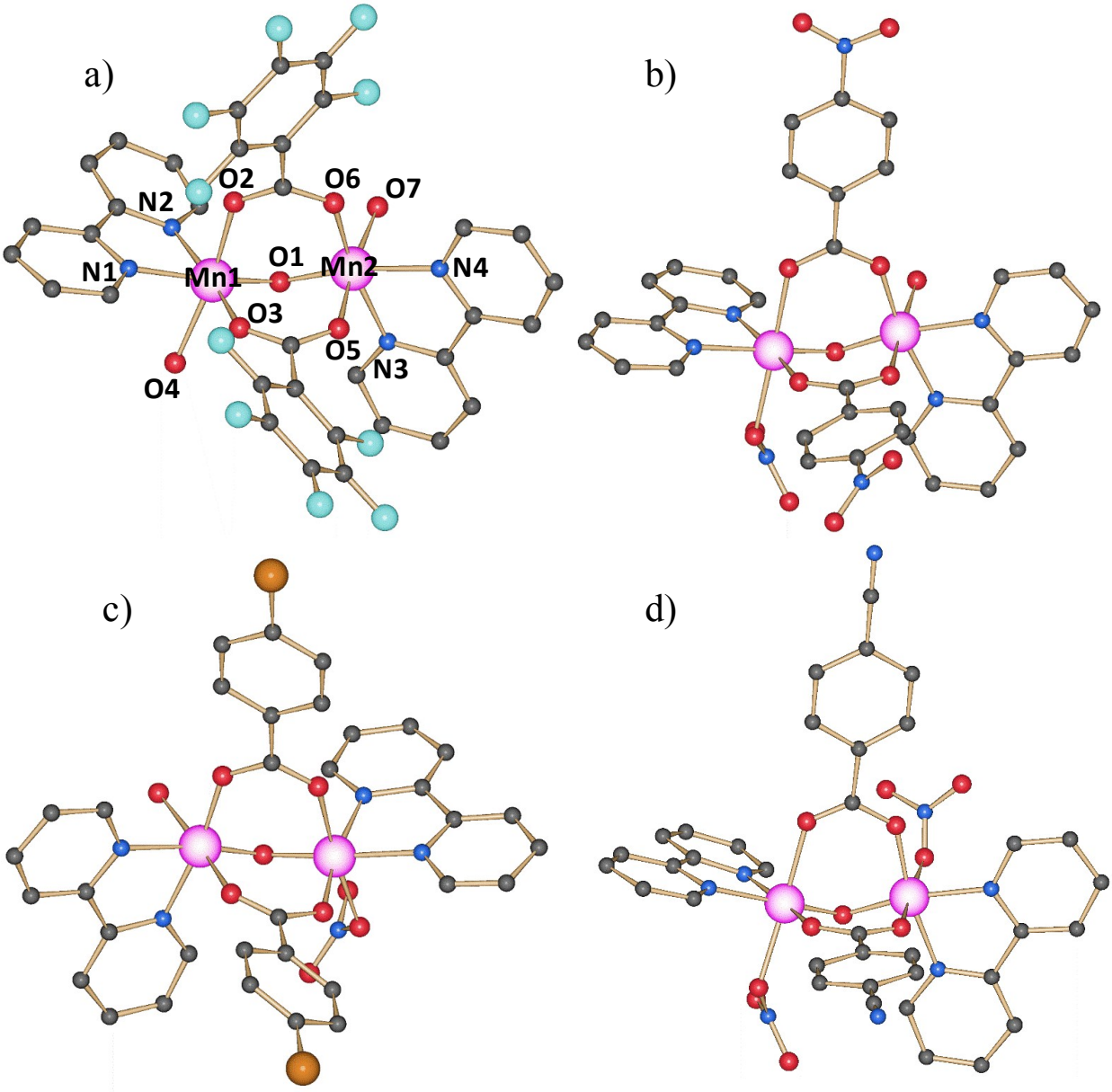

Figure S2. The molecular structure of complex (a) **6**, (b)**7**, (c) **8**and (d)**9**. The solvent and H atoms are omitted for clarity. Color scheme; Mn^{III}, pink; O, red; N, blue; C, light grey; Cl, green; F,cyan; Br, orange. Atom labelling is same for all complexes.

Table S1. Selected bond lengths (Å) and angles (°) for complexes **1**– **4** and **12** (See Figures 1 and S1 for atom labels).

	1	**2**	**3**	**4**		**12**
Mn1-N1	2.100	2.062	2.097	2.089	Mn1-N1	2.124
Mn1-O1	1.784	1.784	1.789	1.779	Mn1-O1	1.793
Mn1-N2	2.056	2.059	2.085	2.078	Mn1-N2	2.079
Mn1-O2	1.967	1.935	2.002	1.991	Mn1-O2	2.036
Mn1-O3	2.227	2.177	2.134	2.183	Mn1-O3	2.125
Mn1-Cl	2.448	2.559	2.464	2.483	Mn1-N5	2.136
Mn1-O1-Mn2	126.6	122.4	123.1	125.0	Mn1-O1-Mn2	122.6
Mn1···Mn2	3.188	3.128	3.156	3.160	Mn1···Mn2	3.145
Mn2-N3	2.077	2.065	2.084	2.082	Mn2-N4	2.124
Mn2-O1	1.784	1.785	1.800	1.784	Mn2-O1	1.793
Mn2-N4	2.096	2.055	2.062	2.075	Mn2-N3	2.079
Mn2-O5	1.979	1.940	2.004	1.996	Mn2-O4	2.036
Mn2-O6	2.218	2.159	2.179	2.196	Mn2-O5	2.125
Mn2-Cl	2.481	2.560	2.496	2.507	Mn2-N6	2.136
JT dihedral*	74.8 83.2	78.3 89.2	108.3 104.5	105.6 103.0		107.2 101.6

Table S2. Selected bond lengths (Å) and angles (°) for complexes **5**–**11**(See Figures 1, S1 and S2 for atom labels).

	5	**6**	**7**	**8**	**9**	**10**	**11**
Mn1-N1	2.062	2.081	2.078	2.080	2.072	2.069	2.056
Mn1-O1	1.793	1.796	1.784	1.784	1.789	1.790	1.786
Mn1-N2	2.065	2.062	2.063	2.050	2.063	2.047	2.052
Mn1-O2	1.961	2.010	1.942	1.955	1.950	1.947	1.945
Mn1-O3	2.141	2.136	2.197	2.149	2.180	2.166	2.187
Mn1-O4	2.214	2.128	2.195	2.217	2.284	2.245	2.283
Mn1-O1-Mn2	124.1	124.0	125.4	124.3	125.5	123.9	123.6
Mn1···Mn2	3.158	3.158	3.171	3.159	3.170	3.154	3.152
Mn2-N3	2.079	2.075	2.079	2.084	2.091	2.069	2.071
Mn2-O1	1.781	1.781	1.785	1.790	1.777	1.784	1.791
Mn2-N4	2.081	2.060	2.064	2.070	2.072	2.045	2.069
Mn2-O5	1.989	1.989	1.962	1.964	1.972	1.953	1.960
Mn2-O6	2.140	2.103	2.204	2.199	2.159	2.164	2.171
Mn2-O7	2.178	2.154	2.225	2.203	2.203	2.244	2.268
JT dihedral*	99.3 92.3	108.1 96.5	107.8 94.9	86.7 79.9	109.2 95.4	108.5 93.2	75.6 81.2
* The two JT dihedral angles are X-Mn-Mn-X (X is terminal ligand sites coordinated atoms such as Cl-, O-atom of in H_2O, $[NO_3]^-$, $[ClO_4]^-$ ligands or N-atom in $[N_3]^-$) and O-Mn-Mn-O where O is oxygen atom of carboxylate group.							

Table S3. Calculated cluster and single-ion anisotropy (*D* and E/D values) of complexes **1**-**12**.

Complexes	$D_{S=4}$	E/D	*D*-Mn1	E/D-Mn1	*D*-Mn2	E/D-Mn2
1			-3.0544	0.257723	-2.92454	0.292738
2			-2.86518	0.327167	-2.83927	0.328053
3	1.164116	0.199199	-3.05099	0.22785	-3.25344	0.194136
4	1.164829	0.161778	-2.96261	0.308694	-3.02729	0.268699
5			-3.29153	0.16288	-3.14625	0.171356
6	1.09289	0.20985	-3.16667	0.266091	-3.4007	0.187159
7			-3.23175	0.137002	-3.28018	0.10777
8			-2.93251	0.305684	-2.91839	0.29349
9	0.977711	0.158526	-3.29142	0.151743	-3.1856	0.104967
10			-3.33999	0.058856	-3.34026	0.05598
11			-3.23221	0.066383	-3.23221	0.066383
12	0.906495	0.133348	3.71777	0.023614	3.68559	0.058175

Table S4: Overlap integral values for complex **1**.

Alpha/Beta	d_{xy}	d_{xz}	d_{yz}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	0.0268	-0.0034	0.1629	-0.2212	-0.0761
d_{xz}	-0.0198	0.5328	-0.0646	-0.0238	-0.0315
d_{yz}	-0.0044	-0.0503	0.5043	0.0517	0.1869
d_{z^2}	-0.2888	0.0151	0.0027	-0.0022	0.0387
$d_{x^2-y^2}$	-0.0902	0.0201	-0.0843	-0.0212	-0.2998

Table S5: Overlap integral values for complex **2**.

Alpha/Beta	d_{xy}	d_{xz}	d_{yz}	d_z^2	$d_{x^2-y^2}$
d_{xy}	-0.0255	0.0806	-0.1034	-0.1794	-0.0872
d_{xz}	0.0663	-0.3697	0.1630	-0.0477	0.0114
d_{yz}	-0.1411	0.1264	0.2359	0.0984	0.1762
d_z^2	0.1590	0.0708	-0.0465	0.0231	0.0300
$d_{x^2-y^2}$	-0.1357	0.0189	0.2303	-0.0282	0.1475

Table S6: Overlap integral values for complex **3**.

Alpha/Beta	d_{xy}	d_{xz}	d_{yz}	d_z^2	$d_{x^2-y^2}$
d_{xy}	0.0767	-0.0520	-0.1622	0.1830	-0.1747
d_{xz}	-0.0066	0.1131	0.0631	0.0243	-0.0585
d_{yz}	-0.2212	0.0696	0.1162	0.2058	0.0892
d_z^2	-0.1829	0.0027	-0.2362	-0.0052	-0.0245
$d_{x^2-y^2}$	0.1252	0.0418	-0.0728	-0.0087	-0.1189

Table S7: Overlap integral values for complex **4**.

Alpha/Beta	d_{xy}	d_{xz}	d_{yz}	d_z^2	$d_{x^2-y^2}$
d_{xy}	-0.0379	0.0687	-0.1401	0.2213	0.1943
d_{xz}	-0.1224	0.0451	-0.0156	-0.1121	-0.0160
d_{yz}	0.1104	-0.0537	0.0694	0.1381	-0.1018
d_z^2	-0.0552	-0.1123	0.1467	-0.0354	-0.0013
$d_{x^2-y^2}$	0.1931	0.0117	0.0955	0.0116	-0.0604

Table S8: Overlap integral values for complex **5**.

Alpha/Beta	d_{xy}	d_{xz}	d_{yz}	d_z^2	$d_{x^2-y^2}$
d_{xy}	0.0455	-0.0671	0.0274	0.1408	-0.0520
d_{xz}	-0.2232	0.2768	-0.1540	0.0708	-0.0307
d_{yz}	-0.0334	-0.1874	-0.2495	0.0899	-0.1769
d_z^2	0.2461	0.0278	0.0588	-0.0413	0.0031
$d_{x^2-y^2}$	0.0272	0.0529	-0.1501	-0.0253	-0.1321

Table S9: Overlap integral values for complex **6**.

Alpha/Beta	d_{xy}	d_{xz}	d_{yz}	d_z^2	$d_{x^2-y^2}$
d_{xy}	0.0453	0.0928	0.0251	0.0491	0.2825
d_{xz}	-0.0414	0.0701	0.0607	-0.0144	0.0145
d_{yz}	-0.0281	-0.0619	0.1075	0.0852	0.0209
d_z^2	-0.0904	-0.0953	0.0665	-0.2362	-0.0034
$d_{x^2-y^2}$	-0.2971	0.0869	-0.0116	-0.0069	-0.0856

Table S10: Overlap integral values for complex **9**.

Alpha/Beta	d_{xy}	d_{xz}	d_{yz}	d_z^2	$d_{x^2-y^2}$
d_{xy}	0.0767	-0.0520	-0.1622	0.1830	-0.1747
d_{xz}	-0.0066	0.1531	0.0631	0.0243	-0.0585
d_{yz}	-0.2212	0.0696	0.1662	0.2058	0.0892
d_z^2	-0.1829	0.0027	-0.2362	-0.0052	-0.0245
$d_{x^2-y^2}$	0.1252	0.0418	-0.0728	-0.0087	-0.1189

Table S11: Overlap integral values for complex **12**.

Alpha/Beta	d_{xy}	d_{xz}	d_{yz}	$d_{x^2-y^2}$	d_{z^2}
d_{xy}	0.0106	-0.0931	0.0810	-0.0930	0.0813
d_{xz}	-0.0800	0.0552	-0.0119	-0.0321	0.2100
d_{yz}	0.0075	-0.0752	-0.0469	0.0706	-0.0527
$d_{x^2-y^2}$	-0.0618	0.0471	0.0765	-0.0227	0.0129
d_{z^2}	-0.1256	-0.1472	0.0009	-0.0091	-0.0465

Table S12. Cubical function employed for fitting and the relevant fitting parameters corresponding to the correlation developed for Mn-O-Mn bond angle.

	3	**11**
Exponential function	$y = A + B*x + C*x^2 + D*x^3$	
A	-7843.54674	-6559.73274
B	175.17326	147.19359
C	-1.27477	-1.08056
D	0.00301	0.00258

Table S13. Overlap integral values of bond angle of 108.8 (°) for complex **3**.

Alpha/Beta	d_{xy}	d_{xz}	d_{yz}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	-0.0610	0.1027	0.0280	-0.1337	0.0947
d_{xz}	0.1320	0.1301	-0.0096	-0.0045	0.0849
d_{yz}	0.0973	-0.0348	0.0165	0.2284	0.0319
d_{z^2}	-0.1379	0.0605	-0.1327	0.0013	0.0250
$d_{x^2-y^2}$	0.0634	0.0211	-0.0338	0.0387	-0.0832

Table S14. Overlap integral values of bond angle

of 138.8 (°) for complex **3**.

Alpha/Beta	d_{xy}	d_{xz}	d_{yz}	d_{z^2}	$d_{x^2-y^2}$
d_{xy}	-0.0041	-0.1129	0.1671	-0.0386	0.0258
d_{xz}	-0.1125	0.4324	0.2782	0.0120	0.1578
d_{yz}	0.1722	0.0771	-0.2804	0.0397	-0.1955
d_{z^2}	0.0391	-0.0128	-0.0396	-0.0761	0.0284
$d_{x^2-y^2}$	-0.0257	-0.1577	0.1935	0.0286	-0.1189

Table S15. Exponential function employed for fitting and the relevant fitting parameters corresponding to the correlation developed for Mn-O bond lengths.

	3	**11**
Exponential function	$y = y_0 + A*\exp(R_0*x)$	
y_0	23.77965	27.97444
A	-1125730.23	-158676.81
R_0	-6.29916	-4.65496