Supporting Information

3 Tables.

Cambridge Crystal Data Bank reference codes:

ACESMN, BAZBOT, BZATMN10, DCTAMN, DOPTAD, DURDUP, FOGHAK, GAYMAU, HEHVEV, HENLER, HEWJEY, HEWJIC, HEWJOI, JATMIA, JEFWIA, JIHLIV, JOCZIK10, KASZIN, KAWCIU, KAWLID10, KEGNUF, KEPZEK, KETBOB, LEJCEI, PAHLAL, PAHLIT, POLDID, SAJLiY, SOCKIE, SOZBAK, VAGCAH, VEPLUX, VEPMAE, VEPMEI, VIZYIM, WATVES, WATVIW, WATVOC, YAGBIR, YANWEP, YIYVEH, YIZRII, YOWGUM, ZIFJIH, ZIGKEF, ZIPNOB.

Table S1: Bond lengths and angles of Mn(III)complexes from Cambridge Data base

	Mn-N	N-Mn-N	Mn-O	O-Mn-O	Mn-Cl
VEPMAE	2.011/1.986	83.8	1.871/1.853	90.3	2.391
YOWGUM	1.973/1.985	83.1	1.883/1.874	91.3	2.573
YIZRII	2.016/1.959	82.0	1.871/1.853	90.1	2.390

Table S2: Comparison of X-ray data to calculated values for model systems.

VEPMAE	Mn-N	N-Mn-N	Mn-O	O-Mn-O	Mn-Cl
X-ray	2.011/1.986	83.8	1.871/1.853	90.3	2.391
B3LYP/3-21G	1.945/1.929	82.7	1.873/1.867	90.6	2.352
B3LYP/6-31G* [Mn(dz)]	1.958/1.952	82.6	1.900/1.900	92.1	2.239
B3LYP/6-31G* [Mn(tz)]	1.967/1.961	82.1	1.905/1.904	92.1	2.231

YOWGUM	Mn-N	N-Mn-N	Mn-O	O-Mn-O	Mn-Cl
X-ray	1.973/1.985	83.1	1.883/1.874	91.3	2.573
B3LYP/3-21G	1.954/1.969	83.8	1.939/1.919	94.9	2.476
B3LYP/6-31G* [Mn(dz)]	1.973/1.997	82.5	1.972/1.935	94.2	2.373
B3LYP/6-31G* [Mn(tz)]	1.981/2.100	82.1	1.978/1.938	93.9	2.351

Table S3: Becke3LYP total energies (a.u.) and relative energies (kcal/mol) for **2 - 5**

	Basis Set 3-21G	ΔE	s^2	Basis Set 6-31G(d)/ Mn(dz)	ΔE	s^2	Basis Set 6-31G(d)/ Mn(tz)	ΔE	s^2
2_s Mn(III)	-1713.05091	48.4	-	-1721.43851	43.6	-	-1721.62744	45.7	-
2_t	-1713.08395	27.6	2.7	-1721.47202	22.6	2.6	-1721.65716	27.1	2.6
2_q	-1713.12797	0.0	6.0	-1721.50806	0.0	6.1	-1721.70033	0.0	6.1
3_s Mn(V)O	-1787.89066	0.8	-	-1796.68123	0.0	-	-1796.84499	0	-
3_t	-1787.89187	0.0	2.1	-1796.67439	4.3	2.1	-1796.83937	3.5	2.1
3_q	-1787.86586	16.3	6.0	-1796.66526	10.0	6.1	-1796.82708	11.2	6.1
4_s Mn(III)Cl	-2171.31027	53.1	-	-2181.90068	35.4	-	-2182.08759	40.2	-
4_t	-2171.34626	30.5	2.1	-2181.93027	26.8	2.0	-2182.12051	19.5	2.1
4_q	-2171.39487	0.0	6.0	-2181.95708	0	6.1	-2182.15162	0.0	6.1
5_s Mn(V)O,Cl	-2246.11547	11.7	-	-2257.09738	8.2	-	-2257.26097	10.2	-
5_t	-2246.13414	0.0	2.9	-2257.11044	0	2.9	-2257.27725	0	2.9
5_q	-2246.12770	4.0	6.1	-2257.10858	1.2	6.1	-2257.27412	2.0	6.1