Supporting Information

Tuning of exchange coupling by Mn-O distance and phenoxido bridging angle: experimental and theoretical study for family of Mn(III) dimmers with salen type ligand

Piya Seth, Sanjib Giri and Ashutosh Ghosh

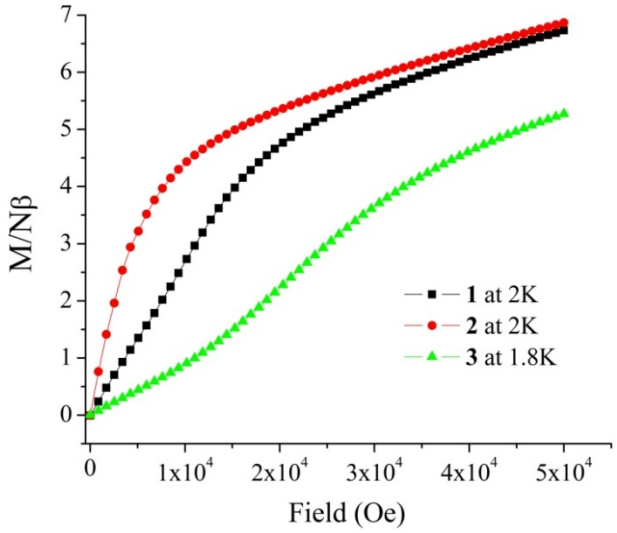


Figure S1: Variation of molar magnetization with field at 2K for complex **1** & **2**; at 1.8K for **3**.

Table ST1. Dimensions in the metal coordination spheres in **1-3** (distances, Å; angles, °).

	1	**2**
Mn(1)-O(1)	1.894(2)	1.909(3)
Mn(1)-O(2)	1.840(2)	1.851(3)
Mn(1)-O(3)	2.300(3)	––
Mn(1)-N(1)	1.981(2)	1.983(4)
Mn(1)-N(2)	1.985(2)	1.994(4)
Mn(1)-O(1)'	2.337(2)	2.418(3)
Mn(1)-N(3)	––	2.182(4)
O(1)-Mn(1)-O(2)	93.86(8)	94.96(11)

O(1)-Mn(1)-O(3)	98.00(8)	––
O(1)-Mn(1)-N(1)	88.49(9)	87.54(13)
O(1)-Mn(1)-N(2)	170.12(9)	166.95(13)
O(1)-Mn(1)-N(3)	––	96.02(13)
O(1)-Mn(1)-O(1)′	80.80(7)	80.03(10)
O(2)-Mn(1)-O(3)	87.15(8)	––
O(2)-Mn(1)-N(1)	177.22(9)	172.62(13)
O(2)-Mn(1)-N(2)	92.24(9)	91.62(13)
O(2)-Mn(1)-N(3)	––	96.26(13)
O(1)′-Mn(1)-O(2)	91.39(7)	88.65(10)
O(3)-Mn(1)-N(1)	94.02(9)	––
O(3)-Mn(1)-N(2)	90.06(9)	––
O(1)′-Mn(1)-O(3)	178.05(8)	––
N(1)-Mn(1)-N(2)	85.24(1)	84.61(15)
N(1)-Mn(1)-N(3)	––	90.37(15)
N(2)-Mn(1)-N(3)	––	94.44(14)
O(1)′-Mn(1)-N(1)	87.49(8)	84.95(12)
O(1)′-Mn(1)-N(2)	91.29(8)	88.90(12)
O(1)′-Mn(1)-N(3)	––	173.98(12)
Mn(1)-O(1)-Mn(1)′	99.20(7)	99.98(11)

Where ' = 1-x,-y,1-z in **1,** -x,-y,1-z in **2**.

Complex **3**

Mn(1) –O(1)	1.851(2)	O(1)-Mn(1)-O(2)	94.30(9)
Mn(1) –O(2)	1.908(2)	O(1)-Mn(1)-N(1)	92.03(10)
Mn(1) –N(1)	2.001(2)	O(1)-Mn(1)-N(2)	174.68(10)
Mn(1) –N(2)	1.990(3)	O(1)-Mn(1)-N(5)	91.75(13)
Mn(1) –N(5)	2.251(3)	O(1)-Mn(1)-O(2)′	87.81(9)

Mn(1) –O(2)′	2.373(2)	O(2)-Mn(1)-N(1)	171.93(10)
Mn(2)-O(3)	1.848(2)	O(2)-Mn(1)-N(2)	88.60(10)
Mn(2)-O(4)	1.897(2)	O(2)-Mn(1)-N(5)	93.97(11)
Mn(2)-N(3)	1.996(3)	O(2)-Mn(1)-O(2)′	78.50(8)
Mn(2)-N(4)	1.989(2)	N(1)-Mn(1)-N(2)	84.72(10)
Mn(2)-N(6)	2.210(4)	N(1)-Mn(1)-N(5)	90.84(11)
Mn(2)-O(4)′′	2.553(2)	O(2)′-Mn(1)-N(1)	96.76(8)
Mn(1)-O(2)-Mn(1)′	101.50(9)	N(2)-Mn(1)-N(5)	92.51(13)
Mn(2)-O(4)-Mn(2)′′	99.96(8)	O(2)′-Mn(1)-N(2)	88.40(9)
O(3)-Mn(2)-O(4)	93.27(10)	O(2)′-Mn(1)-N(5)	172.40(10)
O(3)-Mn(2)-N(3)	91.10(10)	O(3)-Mn(2)-N(4)	172.77(10)
O(3)-Mn(2)-O(4)′′	88.66(9)	O(3)-Mn(2)-N(6)	93.09(11)
O(4)-Mn(2)-N(3)	166.53(10)	O(4)-Mn(2)-O(4)′′	80.04(8)
O(4)-Mn(2)-N(4)	88.84(10)	N(3)-Mn(2)-N(4)	85.35(10)
O(4)-Mn(2)-N(6)	98.27(12)	N(3)-Mn(2)-N(6)	94.21(12)
N(4)-Mn(2)-N(6)	93.45(11)	O(4)′′-Mn(2)-N(3)	87.34(9)
O(4)′′-Mn(2)-N(4)	84.89(9)	O(4)′′-Mn(2)-N(6)	177.64(11)

Where ′= 2-x,1-y,-z and ′′= 1-x,1-y,1-z.

Table ST2. DFT calculations performed by changing Mn-O bond length for Complex **2**.

Mn-O distance (Å)	Coupling constant (*J*) Ruiz (cm^{-1})
2.3	0.294
2.35	0.168
2.418	0.093
2.45	0.128
2.51	0.306
2.55	0.392
2.7	0.78
2.9	1.0815
3.3	0.9007
3.5	0.6573
3.7	0.4344

Table ST3. DFT calculations performed by changing Mn-O bond length for Complex **3** with Mn-O distance 2.373 Å.

Mn-O distance (Å)	Coupling constant (*J*) Ruiz (cm^{-1})
2.25	-1.352
2.3	-1.575
2.35	-1.66
2.3737	-1.65
2.4	-1.626
2.45	-1.525
2.5	-1.33
2.6	-0.9403
2.7	-0.449
2.85	0.074
3	0.362
3.2	0.526
3.6	0.3769
3.8	0.2663

Table ST4. DFT calculation performed by changing Mn-O-Mn angle for Complex **2**

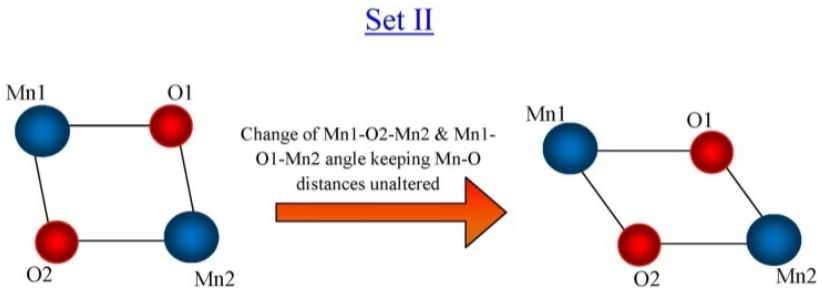
Mn-O-Mn angle (º)	Coupling constant (*J*) Ruiz (cm^{-1})
99.0	1.2356
99.2	1.0317
99.4	0.8087
99.6	0.5833
99.8	0.3715
100.01	0.093
100.2	-0.0918
100.4	-0.3223
100.6	-0.5724
100.8	-0.8296
101	-1.0784

Representation of variation of Mn-O distance and Mn-O-Mn angle independently keeping the rest of the structure unaltered.

Set 1. We have varied the Mn-O bond distance from 2.25Å to 3.7 Å keeping the Mn-O-Mn angle fixed at 99.98˚. This variation of bond length was made by changing the distance of two monomeric MnO_2N_2 units along the Mn-O bond. It is worth to note that the operation also causes a change in Mn...Mn distance as shown in following Scheme.

All the angle (Mn1-O2-Mn2 , Mn1-O1-Mn2, O1-Mn1-O2 & O1-Mn2-O2) angles are remain constant throughout the operation.

Set 2. Similarly, we have varied the Mn-O-Mn bond angle from 99 to 101˚with an interval of 0.2˚ keeping the Mn-O fixed distances of 2.418Å. This variation of bond angle was made by moving one of Mn-O_2N_2 units along the Mn-O bond. The operation is quite similar with the transformation of square to rhombus keeping the lengths of the sides constant. In this case also, an effective change of Mn...Mn distance occurred. Thus in both cases Mn...Mn distance altered to accommodate the desired changes.



All the distances (Mn1-O2, Mn1-O1, Mn1-O2 & Mn2-O2) are remain constant throughout the operation.