Electronic Supporting Information File

The effect of the orientation of the Jahn-Teller distortion on the magnetic interactions of trinuclear mixed-valence Mn(II)/Mn(III) complexes

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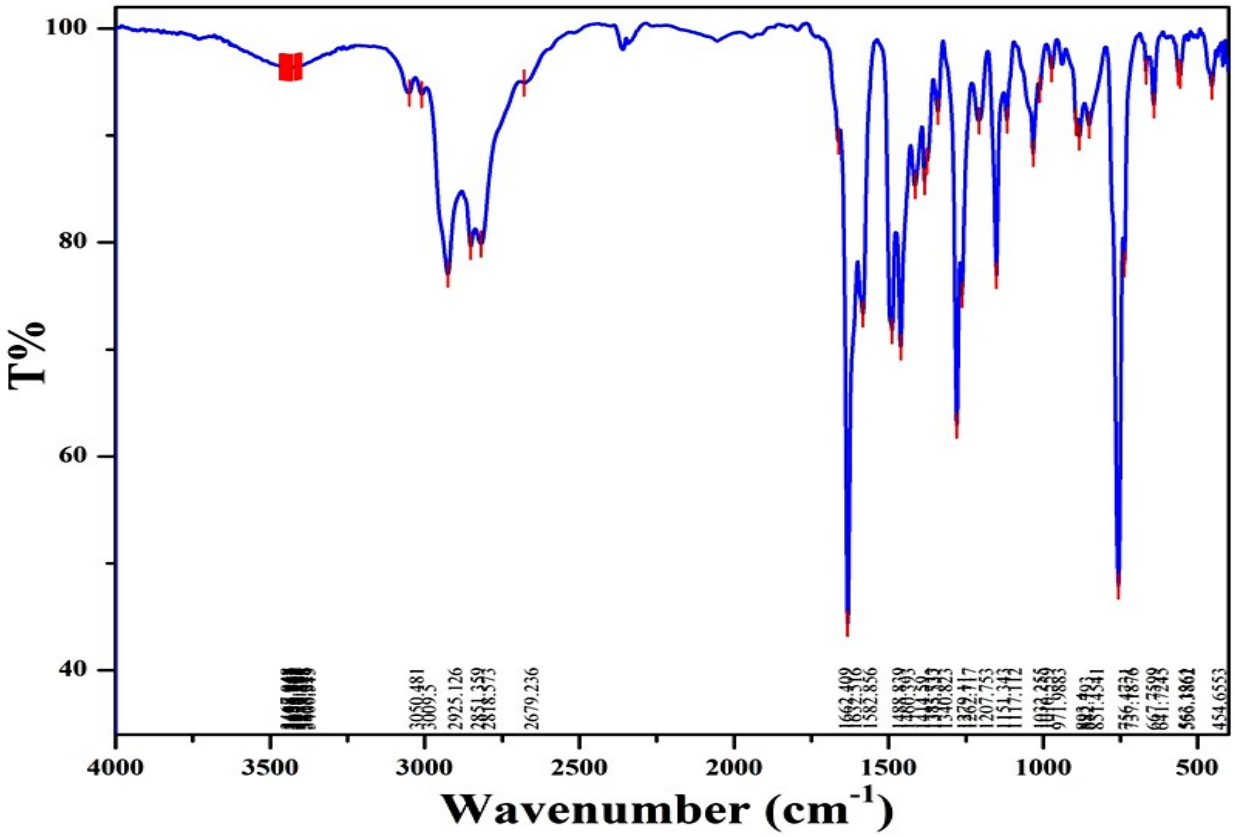


Fig. S1. FT-IR spectrum of the ligand H_4L^1 recorded as KBr disk.

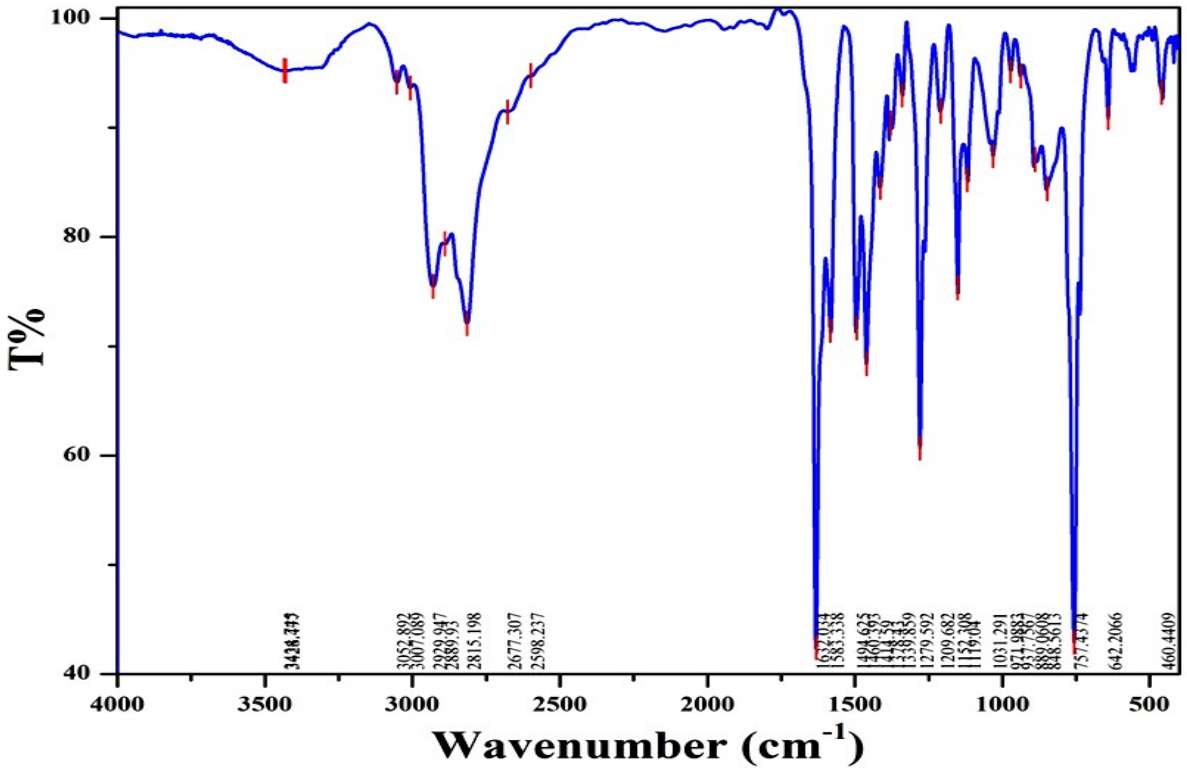


Fig. S2. FT-IR spectrum of the ligand H_4L^2 recorded as KBr disk.

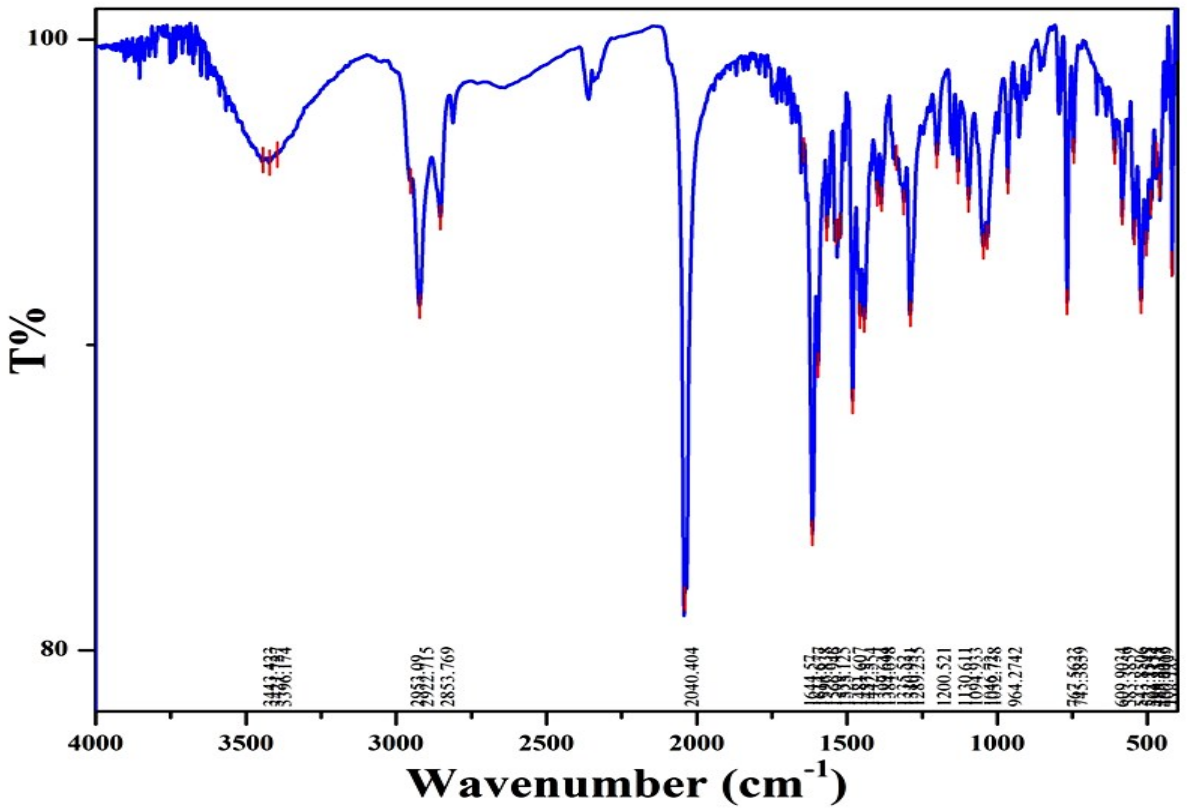


Fig. S3. FT-IR spectrum of complex **1** recorded as KBr disk.

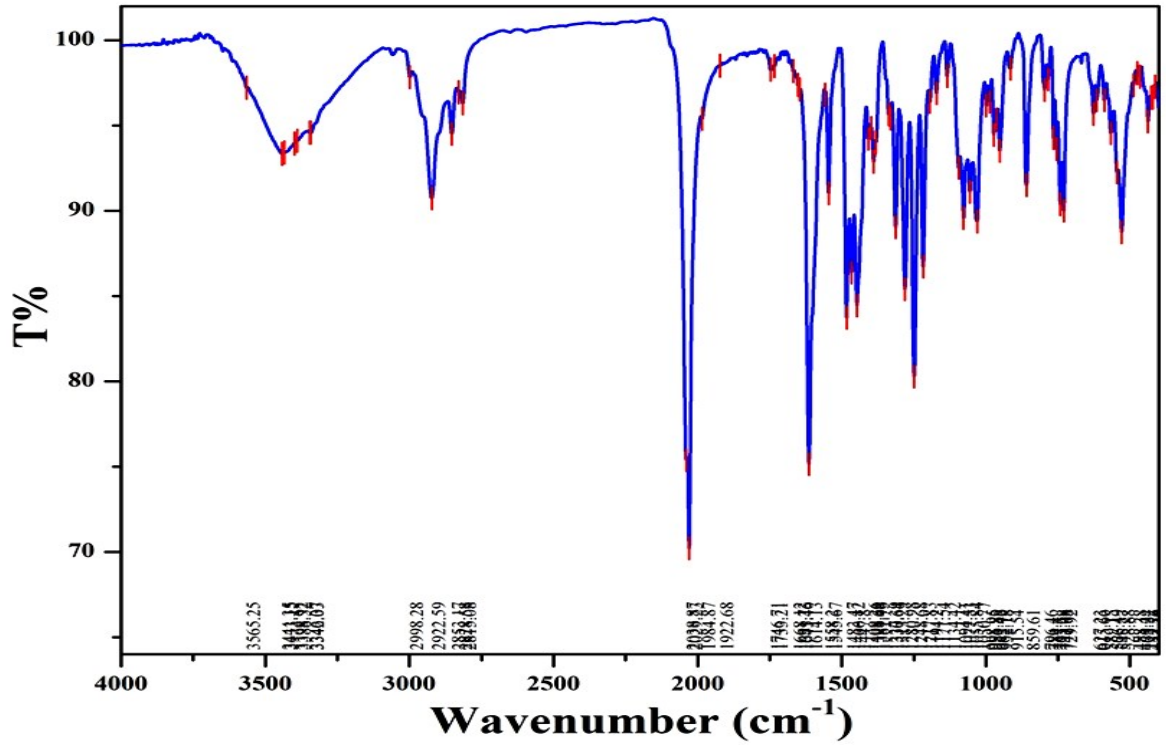


Fig. S4. FT-IR spectrum of complex **2** recorded as KBr disk.

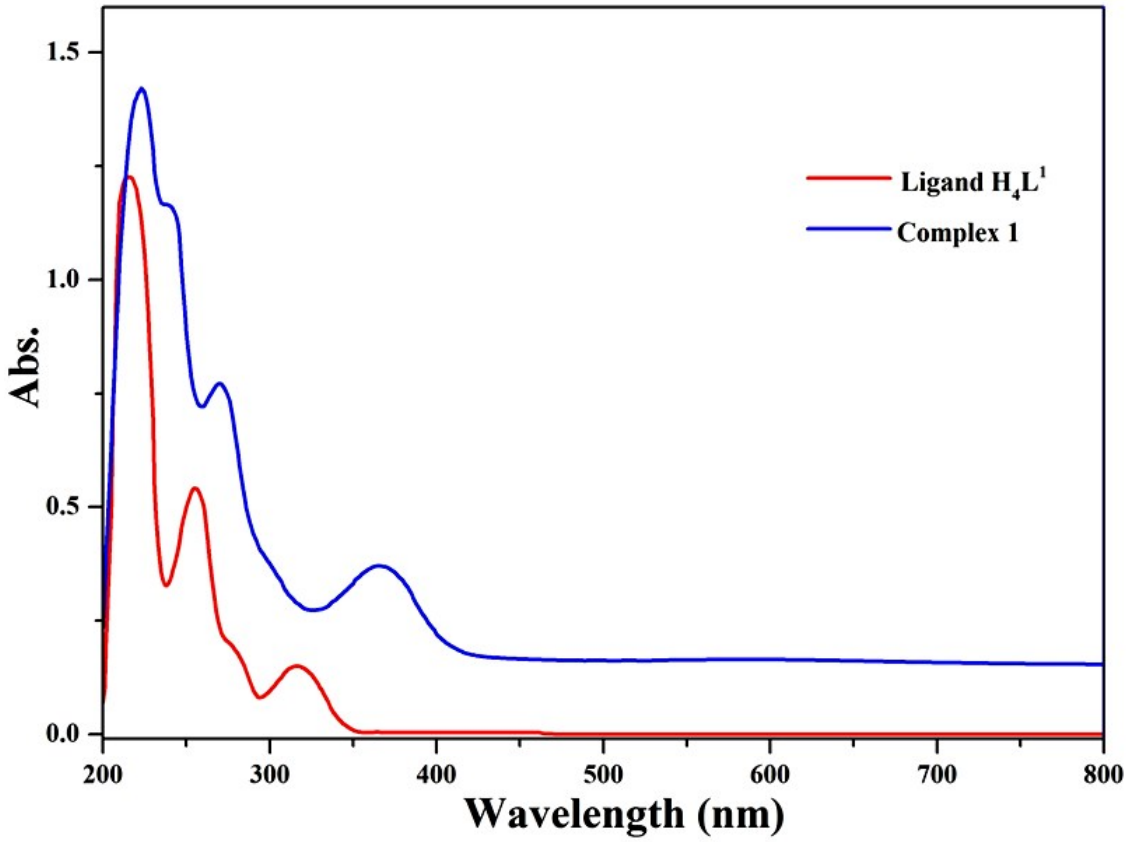


Fig. S5. Comparison of the electronic spectra of H_4L^1 and complex **1** in methanol.

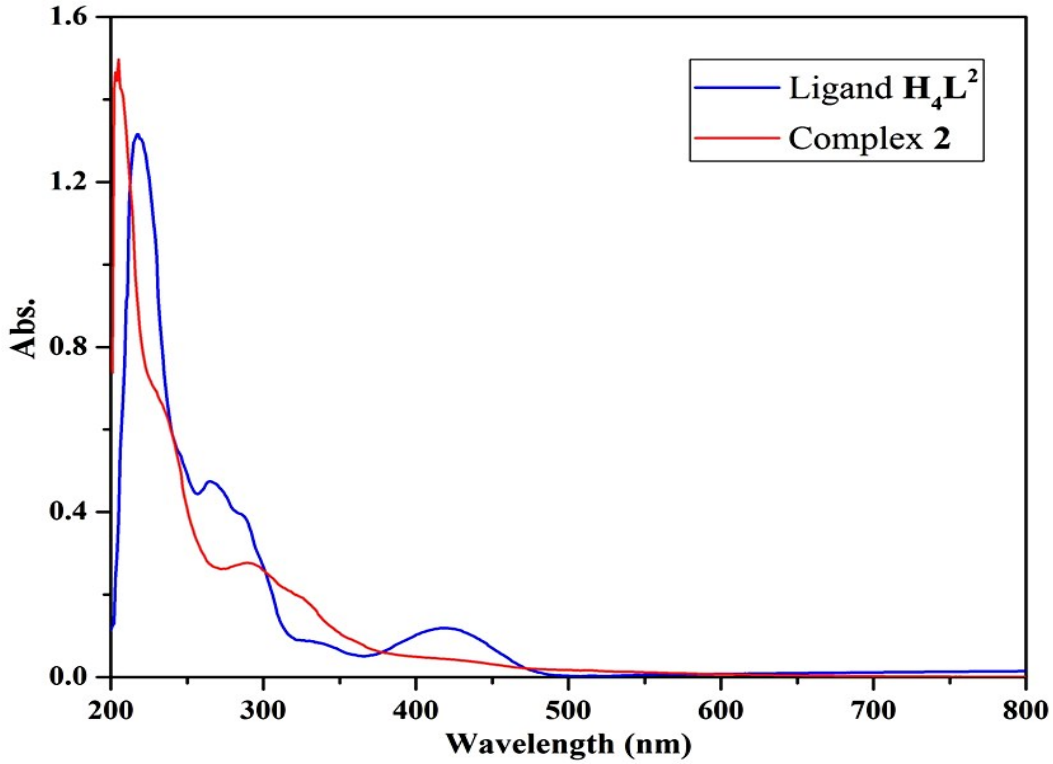


Fig. S6. Comparison of the electronic spectra of H_4L^2 and complex **2** in methanol.

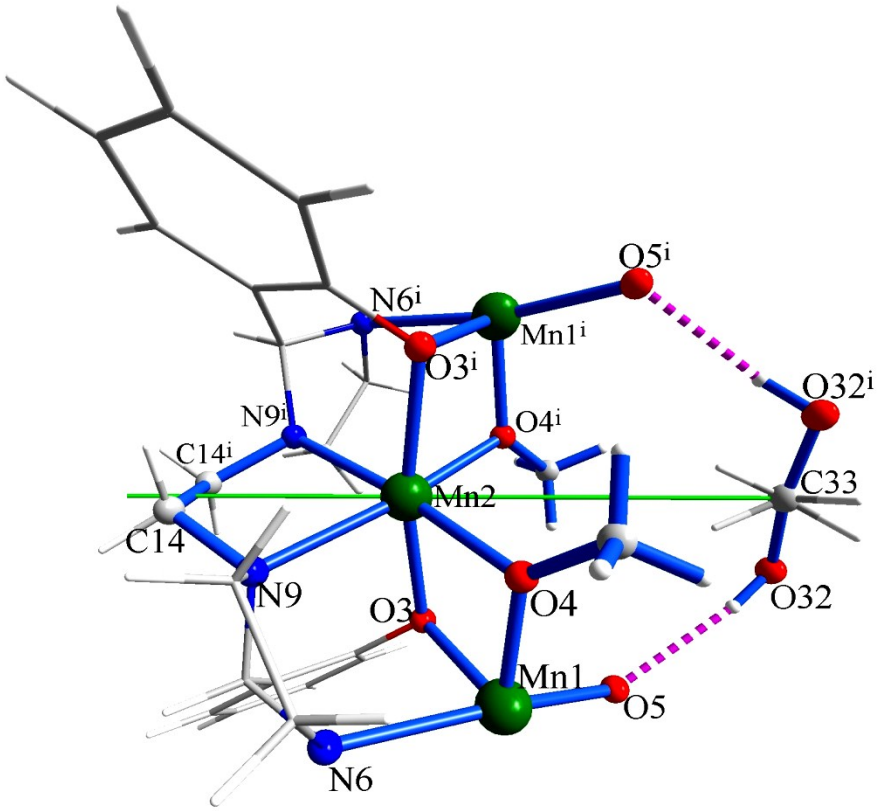
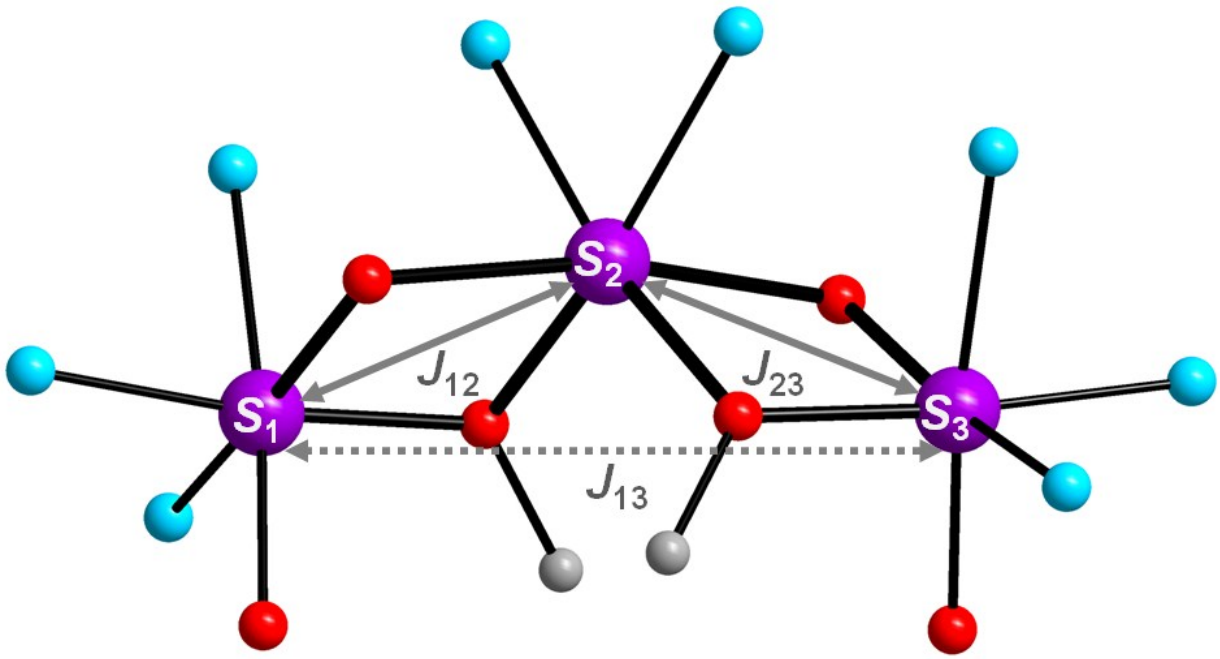


Fig. S7. Two-fold rotation axis in the crystal structure of complex **1**.



Scheme 2. Model for the magnetic exchange within a trinuclear complex adapted to complexes **1** and **2** ($J = J_{12} = J_{23}$, $J_{13} = 0$).

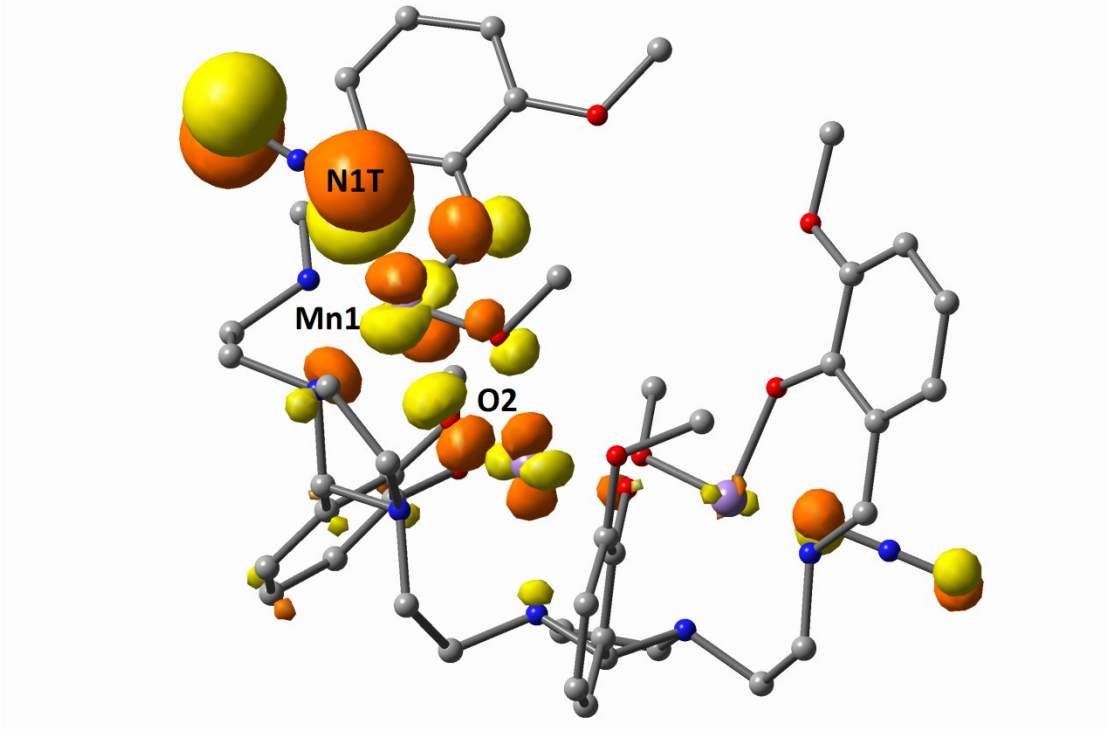


Fig S8. Surface plot of the d_z2 centered molecular orbital of Mn1 for complex **2**. The z axis is defined by the line N1T-Mn1-O2.

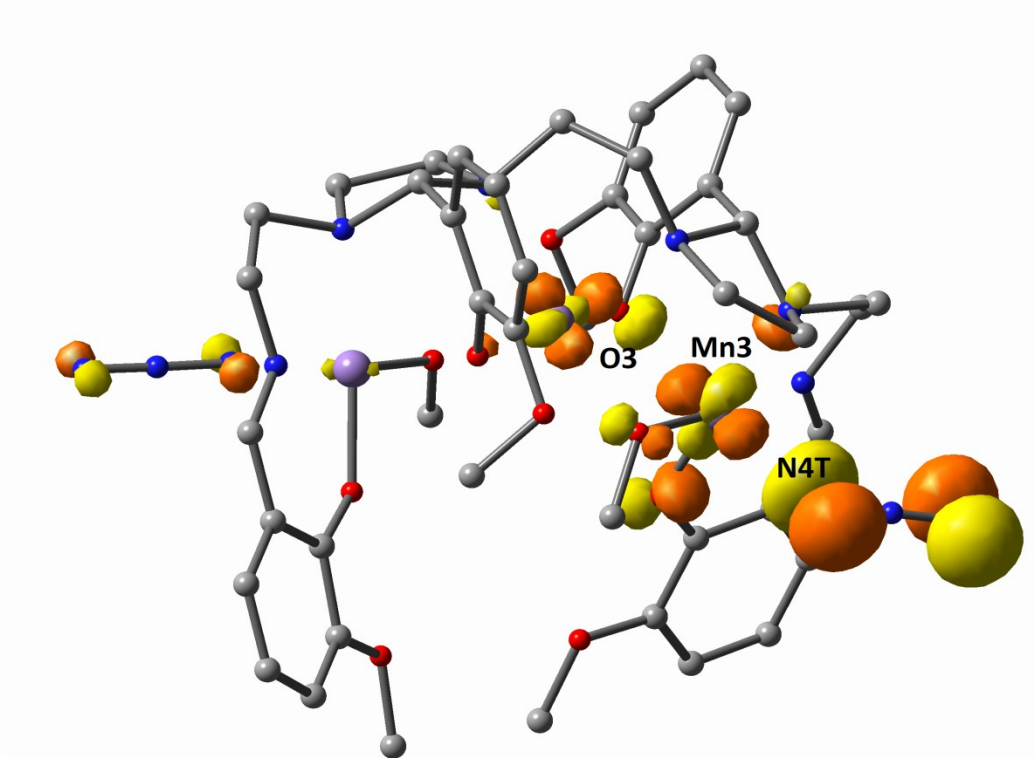


Fig. S9. Surface plot of the d_z2 centered molecular orbital of Mn3 for complex **2**

Table S1. Selected bond angles (˚) for complexes **1** and **2**

Complex 1		**Complex 2**		
	100 K		100 K	293 K
O1B—Mn1—O1	98.52(7)	O1B—Mn1—O1	93.81(6)	93.71(9)
O1B—Mn1—N1	171.04(7)	O1B—Mn1—N1	172.73(6)	172.59(9)
O1B—Mn1—N2	91.36(7)	O1B—Mn1—N2	91.97(6)	92.27(9)
O1B—Mn1—O2	83.94(6)	O1B—Mn1—O2	82.59(5)	81.86(7)
O1B—Mn1—N1T	93.32(8)	O1B—Mn1—N1T	93.77(7)	93.99(10)
O1—Mn1—N1	89.40(7)	O1—Mn1—N1	91.77(7)	91.57(10)
O1—Mn1—N2	168.26(7)	O1—Mn1—N2	174.18(6)	174.02(9)
O1—Mn1—O2	90.05(6)	O1—Mn1—O2	95.73(6)	95.50(9)
O1—Mn1—N1T	97.13(8)	O1—Mn1—N1T	91.74(7)	92.11(11)
N1—Mn1—N2	80.32(7)	N1—Mn1—N2	82.51(7)	82.48(10)
N1—Mn1—O2	91.91(7)	N1—Mn1—O2	92.23(6)	92.46(8)
N1—Mn1—N1T	89.82(8)	N1—Mn1—N1T	90.71(7)	91.01(11)
N2—Mn1—O2	84.68(6)	N2—Mn1—O2	85.61(5)	85.37(8)
N2—Mn1—N1T	88.56(8)	N2—Mn1—N1T	87.27(7)	87.44(11)
O2—Mn1—N1T	172.64(7)	O2—Mn1—N1T	171.88(6)	171.54(10)
O1B—Mn2—O1B^{i}	96.68(9)	O1B—Mn2—O2B	105.55(5)	106.42(8)
O1B—Mn2—O2	76.04(6)	O1B—Mn2—O2	79.00(5)	78.71(7)
O1B—Mn2—O2^{i}	96.39(6)	O1B—Mn2—O3	91.81(5)	92.74(7)
O1B—Mn2—N3	92.29(6)	O1B—Mn2—N3	86.62(5)	86.39(8)
O1B—Mn2—N3^{i}	170.87(7)	O1B—Mn2—N4	163.54(6)	163.05(8)
O1B^{i}—Mn2—O2	96.39(6)	O2B—Mn2—O2	97.44(5)	97.86(7)
O1B^{i}—Mn2—O2^{i}	76.04(6)	O2B—Mn2—O3	77.27(5)	76.80(7)
O1B^{i}—Mn2—N3^{i}	92.29(6)	O2B—Mn2—N4	89.23(5)	89.17(8)
O1B^{i}—Mn2—N3	170.87(7)	O2B—Mn2—N3	167.83(5)	167.17(8)
O2—Mn2—O2^{i}	168.79(8)	O2—Mn2—O3	167.88(5)	168.34(7)
O2—Mn2—N3^{i}	104.70(6)	O2—Mn2—N4	106.69(5)	106.22(7)
O2—Mn2—N3	84.10(6)	O2—Mn2—N3	84.32(5)	83.73(8)
O2^{i}—Mn2—N3^{i}	84.10(6)	O3—Mn2—N4	84.31(5)	84.24(7)
O2^{i}—Mn2—N3	104.70(6)	O3—Mn2—N3	103.18(5)	103.81(8)
N3—Mn2—N3^{i}	78.80(9)	N3—Mn2—N4	78.75(5)	78.20(8)
		O2B—Mn3—O4	94.45(6)	94.59(8)
		O2B—Mn3—N6	174.76(6)	174.92(9)
		O2B—Mn3—O3	82.59(5)	82.44(8)
		O2B—Mn3—N5	92.79(6)	93.05(8)
		O2B—Mn3—N4T	93.83(6)	94.34(9)
		O4—Mn3—N6	90.78(6)	90.48(9)
		O4—Mn3 —O3	94.80(6)	95.12(9)
		O4—Mn3—N5	172.62(6)	172.20(9)
		O4—Mn3—N4T	93.92(6)	93.91(10)
		N6—Mn3—O3	96.75(6)	96.78(9)
		N6—Mn3—N5	81.97(6)	81.87(9)
		N6—Mn3—N4T	86.05(6)	85.64(10)
		O3—Mn3—N5	84.76(5)	84.34(8)
		O3—Mn3—N4T	170.81(6)	170.62(9)
		N5—Mn3—N4T	86.98(6)	87.05(10)
Mn1—O1B—Mn2	101.66(7)	Mn1—O1B—Mn2	104.35(6)	105.02(8)
Mn1—O2—Mn2	95.88(6)	Mn1—O2—Mn2	92.06(5)	92.47(7)
		Mn2—O2B—Mn3	103.69(6)	103.95(9)
		Mn2—O3—Mn3	93.83(5)	94.18(7)

Symmetry code: *i*) −*x*+2, *y*, −*z*+1/2.

Table S2. Bond Valence Sum calculations for the Mn ions in crystal structure of complex **1**

Bond	Experimental Bond Distances	Bond Valence
Mn2-O1B	2.1259	0.3770395
Mn2-O1B^{i}	2.1259	0.3770395
Mn2-O2	2.1361	0.3667874
Mn-O2^{i}	2.1361	0.3667874
Mn2-N3	2.3419	0.263906
Mn2-N3^{i}	2.3419	0.263906
		2.0154657 Bond Valence Sum
Bond	Experimental Bond Distances	Bond Valence
Mn1-O1B	1.8748	0.6798073
Mn1-O1	2.0322	0.4442573
Mn1-O2	2.046	0.4279929
Mn1-N1	2.0067	0.6321373
Mn1-N1T	2.043	0.5730646
Mn1-N2	2.3156	0.2743053
		3.0315648 Bond Valence Sum

Table S3. Bond Valence Sum calculations for the Mn ions in crystal structure of complex **2**

Bond	Experimental Bond Distances	Bond Valence
Mn1—O1B	1.8695	0.6896151
Mn1—O1	1.8952	0.6433405
Mn1—N1	1.9829	0.6741354
Mn1—N2	2.1642	0.4129931
Mn1—O2	2.2118	0.2734171
Mn1—N1T	2.2286	0.3470181
		3.0405194 Bond Valence Sum
Bond	Experimental Bond Distances	Bond Valence
Mn2—O1B	2.1021	0.4020893
Mn2—O2B	2.1174	0.3858014
Mn2—O2	2.1512	0.3521198
Mn2—O3	2.1527	0.3506952
Mn2—N4	2.3247	0.2764637
Mn2—N3	2.3429	0.2631937
		2.0303632 Bond Valence Sum
Bond	Experimental Bond Distances	Bond Valence
Mn3—O2B	1.8762	0.6772399
Mn3—O4	1.8998	0.6353918
Mn3—N6	1.9968	0.6492796
Mn3—O3	2.1519	0.3214656
Mn3—N5	2.1966	0.3783665
Mn3—N4T	2.2363	0.339871
		3.0016143 Bond Valence Sum

Table S4. Parameters of Equations 1 and 2 for Mn^{III}–Mn^{II}–Mn^{III} trinuclear complexes.

i	S^*	S_T	a_i	b_i	E_i
1	4	13/2	682.5	14	-20J
2	4	11/2	429	12	-7J
3	4	9/2	247.5	10	4J
4	4	7/2	126	8	13J
5	4	5/2	52.5	6	20J
6	4	3/2	15	4	25J
7	3	11/2	429	12	-15J
8	3	9/2	247.5	10	-4J
9	3	7/2	126	8	5J
10	3	5/2	52.5	6	12J
11	3	3/2	15	4	17J
12	3	1/2	1.5	2	20J
13	2	9/2	247.5	10	-10J
14	2	7/2	126	8	-1J
15	2	5/2	52.5	6	6J
16	2	3/2	15.0	4	11J
17	2	1/2	1.5	2	14J
18	1	7/2	126	8	-5J
19	1	5/2	52.5	6	2J
20	1	3/2	15	4	7J
21	0	5/2	52.5	6	0