Supporting information

Synthesis of mixed-valence hexanuclear Mn(II/III) clusters from its Mn(II) precursor: Variations of catecholase-like activity and magnetic coupling

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Table ST1: Bond distances (Å) and angles (º) in the metal coordination spheres of complexes **2** and **3:**

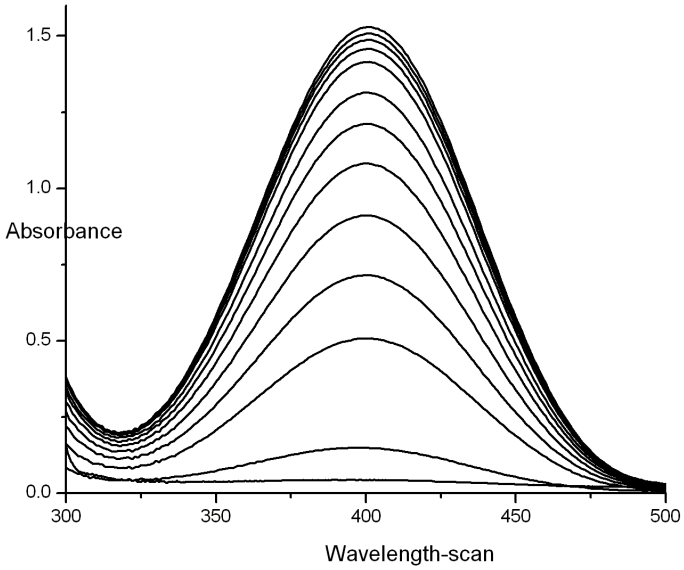
	2	**3**		**2**	**3**
Atom labels	**Distance**		**Atom labels**	**Distance**	
Mn(1)-O(1)	1.877(3)	1.888(2)	Mn(1)-O(2)	1.891(3)	1.892(2)
Mn(1)-O(21)	1.948(3)	1.964(2)	Mn(1)-O(83)	1.980(3)	1.963(2)
Mn(1)-O(61)	2.203(3)	2.227(3)	Mn(1)-O(11)	2.223(3)	2.229(3)
Mn(2)-O(2)	1.888(3)	1.899(2)	Mn(2)-O(1)	1.895(3)	1.883(2)
Mn(2)-O(91)	1.963(3)	1.946(2)	Mn(2)-O(43)	1.964(3)	1.972(2)
Mn(2)-O(53)	2.229(3)	2.246(2)	Mn(2)-O(101)	2.246(3)	2.235(2)
Mn(3)-O(71)	2.081(4)	2.094(3)	Mn(3)-O(51)	2.152(4)	2.105(3)
Mn(3)-O(23)	2.185(4)	2.140(3)	Mn(3)-O(2)	2.243(3)	2.196(2)
Mn(3)-O(61)	2.251(3)	2.372(2)	Mn(3)-N(1E)	a	2.233(4)
Mn(4)-O(31)	2.102(4)	2.114(3)	Mn(4)-O(63)	2.154(4)	2.150(3)
Mn(4)-O(41)	2.160(4)	2.175(3)	Mn(4)-O(1B)	2.187(5)	b
Mn(4)-O(1)	2.206(3)	2.215(2)	Mn(4)-O(53)	2.261(3)	2.271(2)
Mn(5)-O(73)	2.113(4)	2.117(3)	Mn(5)-O(13)	2.140(3)	2.182(3)
Mn(5)-O(93)	2.156(3)	2.198(3)	Mn(5)-X[c]	2.174(4)	2.221(4)
Mn(5)-O(2)	2.203(3)	2.201(2)	Mn(5)-O(101)	2.304(3)	2.281(2)
Mn(6)-O(33)	2.101(4)	2.138(3)	Mn(6)-O(103)	2.130(4)	2.134(3)
Mn(6)-O(81)	2.169(4)	2.152(3)	Mn(6)-Y(1A)	2.193(5)	2.353(2)
Mn(6)-O(1)	2.220(3)	2.205(2)	Mn(6)-O(11)	2.260(3)	2.327(3)
Mn(1)-Mn(2)	2.810(1)	2.804(1)	Mn(1)-Mn(6)	3.184(1)	3.198(1)
Mn(1)-Mn(3)	3.188(1)	3.183(1)	Mn(2)-Mn(4)	3.180(1)	3.178(1)
Mn(2)-Mn(5)	3.182(1)	3.190(1)			

	2	**3**		**2**	**3**
Atom labels	**Angles**		**Atom labels**	**Angles**	
O(1)-Mn(1)-O(2)	84.00(12)	84.28(9)	O(1)-Mn(1)-O(21)	170.33(14)	171.33(10)
O(2)-Mn(1)-O(21)	96.18(13)	96.65(10)	O(61)-Mn(1)-O(11)	173.86(13)	175.51(9)
O(83)-Mn(1)-O(11)	91.16(13)	91.82(10)	O(21)-Mn(1)-O(11)	85.85(13)	86.07(10)
O(2)-Mn(1)-O(11)	98.62(13)	97.91(9)	O(1)-Mn(1)-O(11)	84.56(13)	85.26(9)
O(83)- Mn(1)-O(61)	85.39(13)	84.66(9)	O(21)-Mn(1)-O(61)	88.95(14)	90.95(9)
O(2)-Mn(1)-O(61)	85.16(13)	85.77(9)	O(1)-Mn(1)-O(61)	100.70(13)	97.72(9)
O(21)-Mn(1)-O(83)	87.94(13)	87.06(10)	O(1)-Mn(1)-O(83)	93.53(13)	93.49(9)
O(2)-Mn(1)-O(83)	169.61(14)	169.79(10)	O(2)-Mn(2)-O(1)	83.62(12)	84.24(9)
O(2)-Mn(2)-O(91)	95.23(13)	97.23(10)	O(53)-Mn(2)-O(101)	176.66(13)	174.92(9)
O(43)-Mn(2)-(101)	85.82(14)	86.56(9)	O(91)-Mn(2)-O(101)	90.73(14)	89.06(9)
O(1)-Mn(2)-O(101)	98.75(13)	100.73(9)	O(2)-Mn(2)-O(101)	84.64(13)	84.10(8)
O(43)-Mn(2)-O(53)	92.70(14)	93.45(9)	O(91)-Mn(2)-O(53)	86.27(14)	85.87(9)
O(1)-Mn(2)-O(53)	84.30(13)	84.35(9)	O(2)-Mn(2)-O(53)	97.09(13)	96.27(9)
O(91)-Mn(2)-O(43)	89.88(14)	87.36(10)	O(1)-Mn(2)-O(43)	92.92(13)	92.85(9)
O(2)-Mn(2)-O(43)	169.23(14)	169.52(10)	O(1)-Mn(2)-O(91)	170.28(15)	170.21(9)
O(71)-Mn(3)-O(51)	98.96(14)	97.72(10)	O(71)-Mn(3)-O(23)	88.35(14)	90.78(11)
O(51)-Mn(3)-O(23)	170.24(14)	168.29(10)	O(51)-Mn(3)-O(2)	98.36(12)	96.85(9)
O(71)-Mn(3)-O(2)	94.02(13)	97.19(9)	O(51)-Mn(3)-O(61)	89.14(13)	87.46(9)
O(71)-Mn(3)-O(61)	168.34(15)	171.91(10)	O(23)-Mn(3)-O(2)	87.50(12)	90.04(9)
O(23)-Mn(3)-O(61)	84.64(13)	85.03(9)	O(2)-Mn(3)-O(61)	76.41(12)	75.94(8)
O(71)-Mn(3)-N(1S)	96.9(2)	93.12(13)	O(61)-Mn(3)-N(1S)	91.5(2)	93.28(12)
O(2)-Mn(3)-N(1S)	165.5(2)	167.97(12)	O(23)-Mn(3)-N(1S)	83.3(2)	83.62(12)
O(51)-Mn(3)-N(1S)	89.4(2)	87.86(12)	O(31)-Mn(4)-O(63)	100.77(15)	102.79(10)
O(31)-Mn(4)-O(41)	90.07(14)	85.29(10)	O(1)-Mn(4)-O(53)	76.94(12)	76.75(8)
O(1B)-Mn(4)-O(53)	98.06(15)	95.1(2)	O(41)-Mn(4)-O(53)	81.55(13)	81.85(9)
O(63)-Mn(4)-O(53)	89.50(13)	92.09(9)	O(31)-Mn(4)-O(53)	166.42(15)	162.78(9)
O(1B)-Mn(4)-O(1)	174.88(14)	171.9(2)	O(41)-Mn(4)-O(1)	90.72(13)	91.80(9)
O(63)-Mn(4)-O(1)	98.75(13)	98.57(9)	O(31)-Mn(4)-O(1)	92.59(13)	92.32(9)
O(41)-Mn(4)-O(1B)	87.45(16)	86.8(2)	O(63)-Mn(4)-O(1B)	82.13(15)	81.7(2)
O(31)-Mn(4)-O(1B)	92.19(16)	95.5(2)	O(63)-Mn(4)-O(41)	165.20(14)	166.50(10)
In **3** N(7S), rather than O(1B)					
O(73)-Mn(5)-O(13)	108.87(14)	105.77(10)	O(73)-Mn(5)-O(93)	83.36(14)	83.43(10)
O(13)-Mn(5)-O(93)	164.79(14)	168.74(10)	O(2)-Mn(5)-O(101)	76.64(12)	76.67(8)
O(3)-Mn(5)-O(101)	97.06(15)	95.99(11)	O(93)-Mn(5)-(101)	82.21(12)	81.09(9)
O(13)-Mn(5)O(101)	87.22(13)	90.55(9)	O(73)-Mn(5)-O(101)	162.00(14)	162.69(10)
O(3)-Mn(5)-O(2)	173.50(14)	172.19(11)	O(93)-Mn(5)-O(2)	92.25(13)	90.95(8)

O(13)-Mn(5)-O(2)	95.92(12)	94.46(9)	O(73)-Mn(5)-O(2)	93.26(13)	95.95(9)
O(93)-Mn(5)-O(3)	88.44(16)	90.55(12)	O(13)-Mn(5)-O(3)	82.02(15)	82.80(12)
O(73)-Mn(5)-O(3)	93.25(16)	91.83(12)			
N(5) in **3** rather than O(3)					
O(33)-Mn(6)-O(103)	106.34(15)	102.88(9)	O(33)-Mn(6)-O(81)	85.47(14)	88.07(9)
O(103)-Mn(6)-O(81)	164.95(15)	166.53(10)	O(33)-Mn(6)-O(1A)	100.18(17)	91.25(11)
O(103)-Mn(6)-O(1A)	83.47(16)	82.64(12)	O(81)-Mn(6)-O(1A)	85.29(16)	89.39(11)
O(33)-Mn(6)-O(1)	89.33(13)	92.29(9)	O(103)-Mn(6)-O(1)	99.14(12)	98.49(9)
O(81)-Mn(6)-O(1)	90.13(13)	88.75(8)	O(1A)-Mn(6)-O(1)	169.06(15)	175.94(11)
O(33)-Mn(6)-O(11)	161.21(14)	165.64(9)	O(103)-Mn(6)-(11)	88.18(13)	87.54(9)
O(81)-Mn(6)-O(11)	82.48(13)	83.15(9)	O(1A)-Mn(6)-O(11)	93.15(16)	99.96(11)
O(1)-Mn(6)-O(11)	76.39(12)	76.23(8)			
N(3S) in **3** rather than O(1A)					

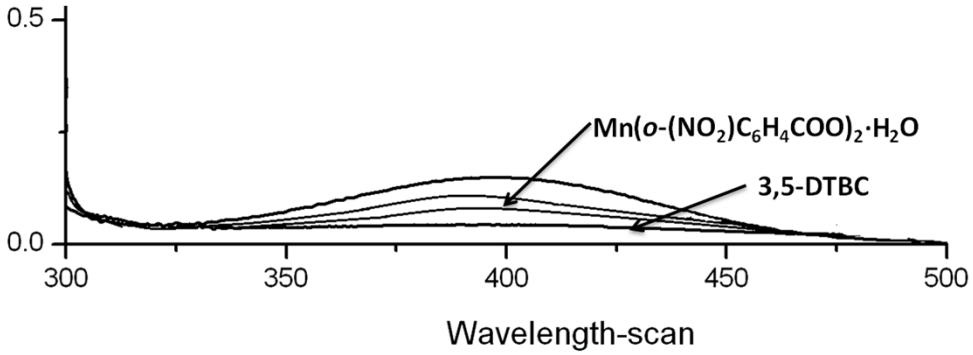
a disordered between N(1E) at 2.317(7) Å at 68% from ligand pyz, O(7E) at 2.101(16) Å from 0.32% methanol, b disordered between N(7S) at 2.216(6) Å at 72%, N(1A) at 2.353 (14) Å at 28%, c X = O(3) in **2** and N(5) in **3**, d Y = O in **2** and N in **3**

Fig. S1:



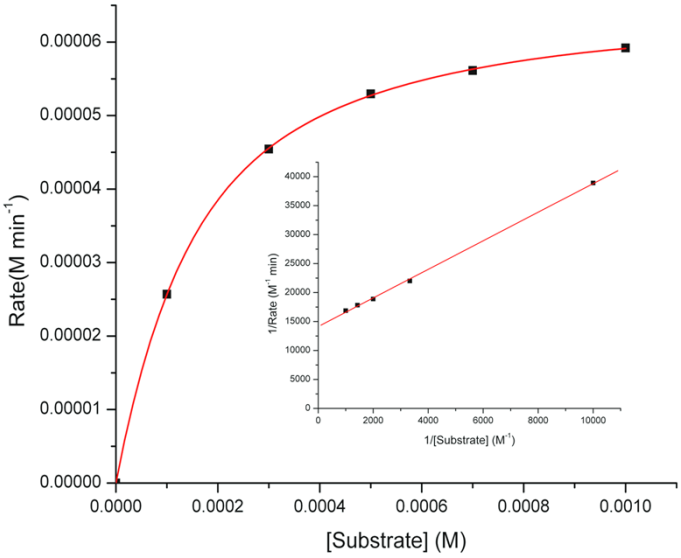
Increase of absorption spectra after addition of 100 equiv of 3,5-DTBC to a solution containing complex **3** (0.166×10^{-5} M) in acetonitrile. The spectra were recorded after every 5 min up to 1 h in CH_3CN.

Fig. S2:



Increase of absorption spectra after addition of 100 equiv of 3,5-DTBC to a solution containing $Mn(o\text{-}(NO_2)C_6H_4COO)_2 \cdot H_2O$ (0.166×10^{-5} M) in acetonitrile in 1h.

Fig. S3:



Plot of initial rates vs substrate concentration for the oxidation reaction catalyzed by complex **3**. Inset shows the Lineweaver−Burk plot.