

Electronic Supplementary Information for Dalton Transactions

High nuclearity manganese(III) compounds containing phenol-pyrazole ligands: the influence of the ligand on the core geometry

Marta Viciano-Chumillas, Graham de Ruiter, Stefania Tanase, Jan M. M. Smits, René de Gelder, Ilpo Mutikainen, Urho Turpeinen, L. Jos de Jongh and Jan Reedijk

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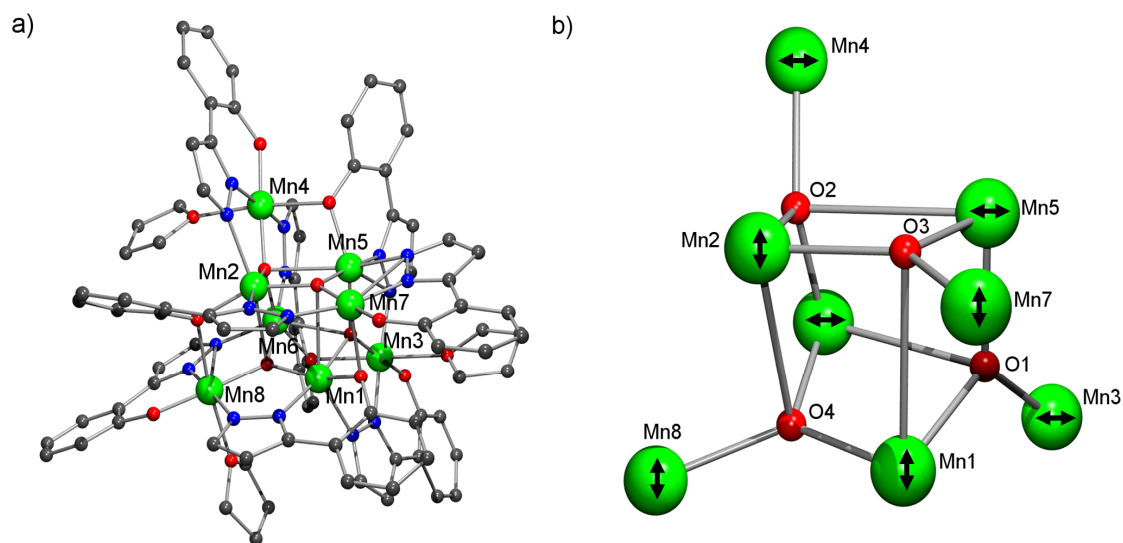


Fig. S1 a) Pluton projection of the compound $[\text{Mn}_8(\mu_4\text{-O})_4(\text{phpzH})_8(\text{thf})_3]$ (**1a**). b) The $[\text{Mn}_8(\mu_4\text{-O})_4]^{16+}$ core showing the orientation of the Jahn-Teller axes (↔). Hydrogen atoms are omitted for clarity. Colour code: green, manganese; blue, nitrogen; red, oxygen; grey, carbon.

Table B1 Crystal data and structure refinements for $[\text{Mn}_8(\mu_4\text{-O})_4(\text{phpzH})_8(\text{thf})_3]$ (**1a**).

	1
Formula	$\text{C}_{84}\text{H}_{72}\text{Mn}_8\text{N}_{16}\text{O}_{15}$
Formula mass [g mol^{-1}]	1985.10
Crystal system	Triclinic
Space group	P-1
a [Å]	14.139(6)
b [Å]	15.162(5)
c [Å]	20.726(5)
α [°]	78.212(18)
β [°]	86.77(2)
γ [°]	70.32(3)
V [Å ³]	4095(2)
Z	2
D_{calc} [g cm^{-3}]	1.610
Crystal size	0.28×0.06×0.04
Number of collected reflections(unique)	70380(14388)
Number of observed reflections ($I_o > 2\sigma(I_o)$)	6952
Internal R factor	0.1847
Number of parameters	1108
Goodness-of-fit S on F^2	1.066
μ [mm^{-1}]	1.268
$R_1^{[a]}$ [$I > 2.0\sigma(I)$]	0.1161
$wR_2^{[b]}$ [all data]	0.2332
T [K]	208
^[a] $R_1 = \sum F_o - F_c / \sum F_o $. ^[b] $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$.	

Table S2 Selected bonds lengths [Å] and angles [°] for the compound [Mn₈(μ₄-O)₄(phpzH)₈(thf)₃] (**1a**).

Bond Lengths					
Mn(1)–O(1)	1.938(7)	Mn(1)–O(161)	1.924(7)	Mn(1)–O(4)	1.889(7)
Mn(1)–N(152)	1.977(8)	Mn(1)–N(11)	2.115(10)	Mn(2)–O(2)	1.913(7)
Mn(2)–O(3)	1.895(7)	Mn(2)–O(141)	1.922(7)	Mn(2)–N(31)	2.155(10)
Mn(2)–N(132)	1.938(9)	Mn(3)–O(1)	1.891(7)	Mn(3)–O(1A)	2.286(8)
Mn(3)–O(21)	1.825(7)	Mn(3)–O(121)	2.302(8)	Mn(3)–N(12)	1.935(9)
Mn(3)–N(91)	1.990(9)	Mn(4)–O(1B)	2.272(8)	Mn(4)–O(2)	1.914(7)
Mn(4)–O(41)	1.856(8)	Mn(4)–O(101)	2.299(8)	Mn(4)–N(32)	1.936(9)
Mn(4)–N(111)	1.974(9)	Mn(5)–O(1)	1.924(7)	Mn(5)–O(3)	1.910(6)
Mn(5)–O(101)	1.921(8)	Mn(5)–N(51)	2.145(9)	Mn(5)–N(92)	1.941(8)
Mn(6)–O(2)	1.911(7)	Mn(6)–O(4)	1.910(7)	Mn(6)–O(121)	1.917(7)
Mn(6)–N(71)	2.152(10)	Mn(6)–N(112)	1.965(9)	Mn(7)–O(3)	1.886(7)
Mn(7)–O(61)	1.820(9)	Mn(7)–O(161)	2.193(8)	Mn(7)–N(52)	1.931(10)
Mn(7)–N(131)	1.999(11)	Mn(8)–O(1C)	2.294(9)	Mn(8)–O(4)	1.907(7)
Mn(8)–O(81)	1.842(8)	Mn(8)–O(141)	2.271(8)	Mn(8)–N(72)	1.934(10)
Mn(8)–N(151)	1.982(9)				
Bond Angles					
O(1)–Mn(1)–O(3)	66.6(3)	O(1)–Mn(1)–O(4)	87.9(3)	O(1)–Mn(1)–O(161)	96.7(3)
O(1)–Mn(1)–N(11)	88.5(3)	O(1)–Mn(1)–N(152)	171.0(4)	O(2)–Mn(2)–O(3)	88.9(3)
O(2)–Mn(2)–O(4)	67.6(3)	O(2)–Mn(2)–O(141)	97.7(3)	O(2)–Mn(2)–N(31)	88.6(3)
O(2)–Mn(2)–N(132)	173.6(4)	O(1)–Mn(3)–O(1A)	92.6(3)	O(1)–Mn(3)–O(21)	175.8(3)
O(1)–Mn(3)–O(121)	82.5(3)	O(1)–Mn(3)–N(12)	93.1(4)	O(1)–Mn(3)–N(91)	87.0(3)
O(2)–Mn(4)–N(32)	93.1(4)	O(2)–Mn(4)–O(41)	176.5(4)	O(2)–Mn(4)–O(101)	80.7(3)
O(2)–Mn(4)–N(111)	87.4(4)	O(1)–Mn(5)–O(2)	87.3(3)	O(1)–Mn(5)–O(3)	87.4(3)
O(1)–Mn(5)–O(101)	156.5(3)	O(1)–Mn(5)–N(51)	105.4(3)	O(1)–Mn(5)–N(92)	88.0(3)
O(1)–Mn(6)–O(2)	86.7(3)	O(1)–Mn(6)–O(4)	69.3(3)	O(1)–Mn(6)–O(121)	73.3(3)
O(1)–Mn(6)–N(71)	151.8(3)	O(1)–Mn(6)–N(112)	108.9(3)	O(3)–Mn(7)–O(61)	173.9(4)
O(3)–Mn(7)–O(161)	89.3(3)	O(3)–Mn(7)–N(52)	93.0(3)	O(3)–Mn(7)–N(131)	85.6(4)
O(4)–Mn(8)–O(81)	175.5(3)	O(4)–Mn(8)–O(141)	82.8(3)	O(4)–Mn(8)–N(72)	93.3(4)
O(4)–Mn(8)–N(151)	86.6(3)	O(4)–Mn(8)–O(1C)	91.0(3)		

Table S3 Selected bond lengths (Å) and angles (°) for the compound
 $[\text{Mn}_8(\mu_4\text{-O})_4(\text{phpzH})_4(\text{EtOH})_4]\cdot 2\text{EtOH}$ (**2**).

Bond Lengths					
Mn(1)–O(1)	1.909(3)	Mn(1)–O(101)	2.347(3)	Mn(1)–O(312)	2.343(3)
Mn(1)–O(412)	1.849(3)	Mn(1)–N(41)	1.947(3)	Mn(1)–N(52)	1.992(3)
Mn(2)–O(1)	1.917(3)	Mn(2)–O(2)	2.709(3)	Mn(2)–O(4)	1.919(2)
Mn(2)–O(512)	1.911(3)	Mn(2)–N(51)	1.955(3)	Mn(2)–N(62)	2.171(3)
Mn(3)–O(1)	1.915(3)	Mn(3)–O(3)	1.916(3)	Mn(3)–O(4)	2.690(3)
Mn(3)–O(112)	1.906(3)	Mn(3)–N(11)	1.945(3)	Mn(3)–N(42)	2.155(3)
Mn(4)–O(1)	2.669(3)	Mn(4)–O(2)	1.926(3)	Mn(4)–O(3)	1.913(3)
Mn(4)–O(312)	1.939(3)	Mn(4)–N(22)	2.141(3)	Mn(4)–N(31)	1.958(3)
Mn(5)–O(3)	1.907(3)	Mn(5)–O(212)	1.843(3)	Mn(5)–>O(401)	2.39(2)
Mn(5)–O(712)	2.336(3)	Mn(5)–N(12)	2.001(3)	Mn(5)–N(21)	1.958(3)
Mn(5)–<O(41A)	2.29(3)	Mn(6)–O(4)	1.918(2)	Mn(6)–O(112)	2.353(3)
Mn(6)–O(201)	2.273(3)	Mn(6)–O(612)	1.862(3)	Mn(6)–N(61)	1.952(3)
Mn(6)–N(72)	1.990(3)	Mn(7)–O(2)	1.900(3)	Mn(7)–O(301)	2.3065
Mn(7)–O(512)	2.386(3)	Mn(7)–O(812)	1.850(3)	Mn(7)–N(32)	1.995(3)
Mn(7)–N(81)	1.955(3)	Mn(8)–O(2)	1.936(3)	Mn(8)–O(3)	2.665(3)
Mn(8)–O(4)	1.915(2)	Mn(8)–O(712)	1.926(3)	Mn(8)–N(71)	1.971(3)
Mn(8)–N(82)	2.157(3)				
Bond Angles					
O(1)–Mn(1)–O(101)	84.35(11)	O(1)–Mn(1)–O(312)	80.80(10)	O(1)–Mn(1)–O(412)	175.83(13)
O(1)–Mn(1)–N(41)	94.60(13)	O(1)–Mn(1)–N(52)	86.30(13)	O(1)–Mn(2)–O(2)	87.65(10)
O(1)–Mn(2)–O(4)	88.54(12)	O(1)–Mn(2)–O(512)	156.15(12)	O(1)–Mn(2)–N(51)	86.40(13)
O(1)–Mn(2)–N(62)	102.80(12)	O(1)–Mn(3)–O(3)	87.66(11)	O(1)–Mn(3)–O(4)	68.74(10)
O(1)–Mn(3)–O(112)	95.74(11)	O(1)–Mn(3)–N(11)	175.04(12)	O(1)–Mn(3)–N(42)	89.65(12)
O(1)–Mn(4)–O(2)	88.65(10)	O(1)–Mn(4)–O(3)	68.51(10)	O(1)–Mn(4)–O(312)	72.12(10)
O(1)–Mn(4)–N(22)	153.81(11)	O(1)–Mn(4)–N(31)	108.60(11)	O(3)–Mn(5)–O(212)	176.91(12)
O(3)–Mn(5)–>O(401)	86.0(6)	O(3)–Mn(5)–O(712)	81.60(11)	O(3)–Mn(5)–N(12)	87.17(12)
O(3)–Mn(5)–N(21)	92.90(13)	O(3)–Mn(5)–<O(41A)	85.0(7)	O(4)–Mn(6)–O(112)	82.36(11)
O(4)–Mn(6)–O(201)	93.27(12)	O(4)–Mn(6)–O(612)	175.24(13)	O(4)–Mn(6)–N(61)	93.40(12)
O(4)–Mn(6)–N(72)	87.21(12)	O(2)–Mn(7)–O(301)	95.76	O(2)–Mn(7)–O(512)	81.43(11)
O(2)–Mn(7)–O(812)	174.56(13)	O(2)–Mn(7)–N(32)	87.84(13)	O(2)–Mn(7)–N(81)	92.62(13)
O(2)–Mn(8)–O(3)	68.06(10)	O(2)–Mn(8)–O(4)	89.01(11)	O(2)–Mn(8)–O(712)	97.39(11)
O(2)–Mn(8)–N(71)	174.56(12)	O(2)–Mn(8)–N(82)	87.87(12)		

Table S4 Hydrogen bond details (distances [Å] and angles [°]) for $[\text{Mn}_8(\mu_4\text{-O})_4(\text{phpzH})_4(\text{EtOH})_4]\cdot 2\text{EtOH}$ (2).

Donor–H···Acceptor	D–H	H···A	D···A	D–H···A
O(501)–H(50A)···O(201)	0.8399	2.0174	2.727(6)	141.71
O(601)–H(60A)···O(301)	0.8404	2.1723	2.8245	134.36

Table S5 Selected bond lengths (Å) and angles (°) for [Mn₆(μ₃-O)₄(μ₃-Br)₂(HphpzEt)₆(phpzEt)] (**3**).

Bond Lengths					
Mn(1)–O(112)	1.874(4)	Mn(3)–Br(2)	2.7353(11)	Mn(6)–O(2)	1.910(3)
Mn(1)–O(2)	1.876(3)	Mn(3)–O(612)	2.577(3)	Mn(6)–O(4)	1.916(3)
Mn(1)–O(1)	1.901(3)	Mn(4)–O(1)	1.898(3)	Mn(6)–N(71)	1.978(4)
Mn(1)–N(11)	1.989(5)	Mn(4)–O(4)	1.903(3)	Mn(6)–Br(1)	2.8517(11)
Mn(1)–Br(1)	2.7488(10)	Mn(4)–O(412)	1.908(4)	Mn(6)–O(612)	2.294(3)
Mn(1)–Br(2)	3.0076(10)	Mn(4)–N(41)	2.000(5)	Mn(1)⋯Mn(2)	3.250
Mn(2)–O(3)	1.878(3)	Mn(4)–N(52)	2.260(4)	Mn(1)⋯Mn(4)	3.239
Mn(2)–O(212)	1.888(3)	Mn(4)–Br(1)	2.9014(11)	Mn(1)⋯Mn(6)	3.228
Mn(2)–O(1)	1.924(3)	Mn(5)–O(4)	1.901(3)	Mn(2)⋯Mn(3)	3.171
Mn(2)–N(21)	1.987(4)	Mn(5)–O(512)	1.923(3)	Mn(2)⋯Mn(4)	3.225
Mn(2)–Br(2)	2.7305(11)	Mn(5)–N(51)	1.975(4)	Mn(2)⋯Mn(5)	3.470
Mn(3)–O(3)	1.863(3)	Mn(5)–O(612)	1.994(3)	Mn(3)⋯Mn(5)	3.288
Mn(3)–O(2)	1.905(3)	Mn(5)–O(3)	2.158(3)	Mn(3)⋯Mn(6)	3.221
Mn(3)–O(312)	1.904(3)	Mn(5)–N(61)	2.221(4)	Mn(5)⋯Mn(6)	3.057
Mn(3)–N(31)	2.035(4)	Mn(6)–O(712)	1.875(4)		
Bond Angles					
Br(1)–Mn(1)–Br(2)	165.11(4)	Br(1)–Mn(1)–O(1)	87.75(10)	Br(1)–Mn(1)–O(2)	87.02(10)
Br(1)–Mn(1)–O(112)	95.05(12)	Br(1)–Mn(1)–N(11)	93.32(13)	Br(2)–Mn(2)–O(1)	90.05(10)
Br(2)–Mn(2)–O(3)	84.08(11)	Br(2)–Mn(2)–O(212)	96.70(11)	Br(2)–Mn(2)–N(21)	107.47(13)
Br(2)–Mn(2)–N(52)	161.42(9)	Br(2)–Mn(3)–O(2)	89.58(10)	Br(2)–Mn(3)–O(3)	84.22(10)
Br(2)–Mn(3)–O(312)	92.19(11)	Br(2)–Mn(3)–O(612)	154.42(8)	Br(2)–Mn(3)–N(31)	109.84(12)
Br(1)–Mn(4)–O(1)	83.42(10)	Br(1)–Mn(4)–O(4)	82.61(10)	Br(1)–Mn(4)–O(412)	93.88(11)
Br(1)–Mn(4)–N(41)	93.14(13)	Br(1)–Mn(4)–N(52)	167.87(12)	O(3)–Mn(5)–O(4)	91.88(13)
O(3)–Mn(5)–O(512)	87.19(13)	O(3)–Mn(5)–O(612)	83.42(13)	O(3)–Mn(5)–N(51)	88.99(15)
O(3)–Mn(5)–N(61)	165.68(15)	Br(1)–Mn(6)–O(2)	83.47(10)	Br(1)–Mn(6)–O(4)	83.79(10)
Br(1)–Mn(6)–O(612)	156.82(9)	Br(1)–Mn(6)–O(712)	104.05(13)	Br(1)–Mn(6)–N(71)	91.33(13)
Mn(1)–Br(1)–Mn(4)	69.90(3)	Mn(1)–Br(1)–Mn(6)	70.37(3)	Mn(4)–Br(1)–Mn(6)	70.13(3)
Mn(2)–Br(2)–Mn(3)	70.92(3)	Mn(1)–O(1)–Mn(2)	116.37(16)	Mn(1)–O(1)–Mn(4)	117.01(16)
Mn(2)–O(1)–Mn(4)	115.07(17)	Mn(1)–O(2)–Mn(3)	118.19(17)	Mn(1)–O(2)–Mn(6)	117.01(16)
Mn(3)–O(2)–Mn(6)	115.21(17)	Mn(2)–O(3)–Mn(3)	115.89(18)	Mn(2)–O(3)–Mn(5)	118.40(16)
Mn(3)–O(3)–Mn(5)	109.49(15)	Mn(4)–O(4)–Mn(5)	122.04(17)	Mn(4)–O(4)–Mn(6)	119.87(18)
Mn(5)–O(4)–Mn(6)	106.46(15)				