Supplementary Material (ESI) for New Journal of Chemistry

SUPPORTING INFORMATION FOR

Synthesis, crystal structure and magnetic properties of a new mixed-valence [$Mn^{III}_4Mn^{II}$] pentanuclear complex

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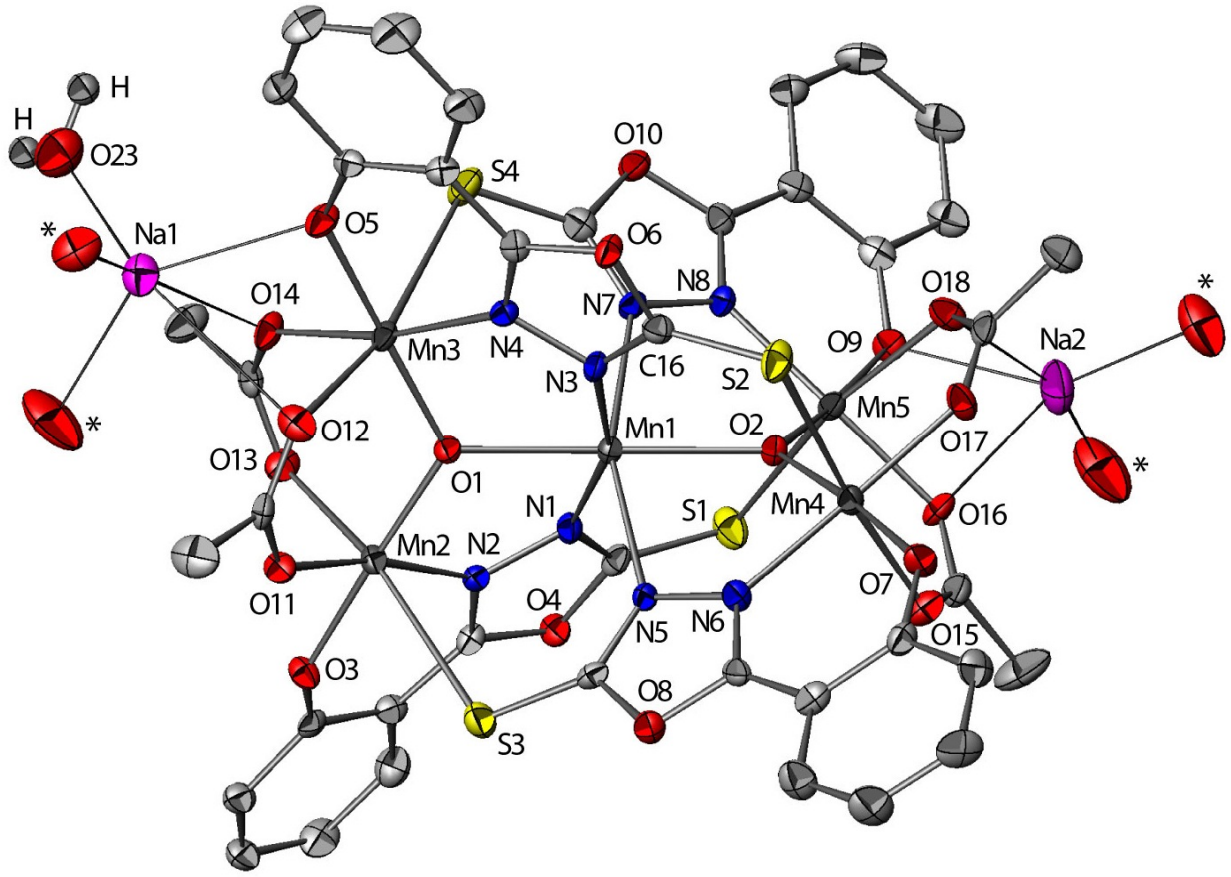

Figure S1: *ORTEP view of the pentanuclear $Mn^{III}_4Mn^{II}$ complex with partial labelling sheme. The ellipsoids enclose 50% of the electronic density. The hydrogen atoms and solvent molecules have been omitted for clarity. * Indicates oxygen atoms from DMF.*

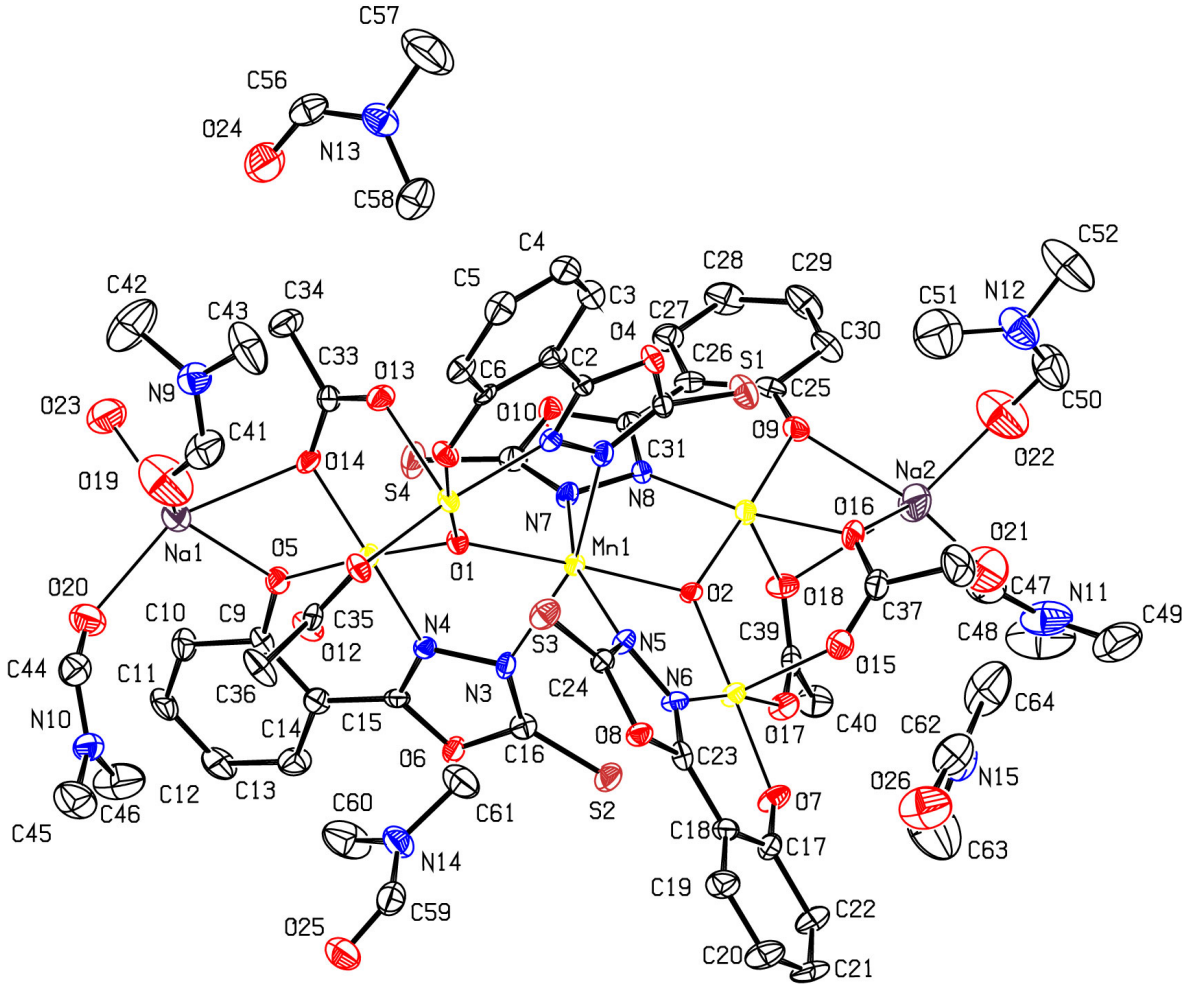

Figure S2: *Full ORTEP view of the pentanuclear $Mn^{III}_4Mn^{II}$ complex with labelling sheme. The hydrogen atoms have been omitted for clarity. The ellipsoids enclose 50% of the electronic density.*

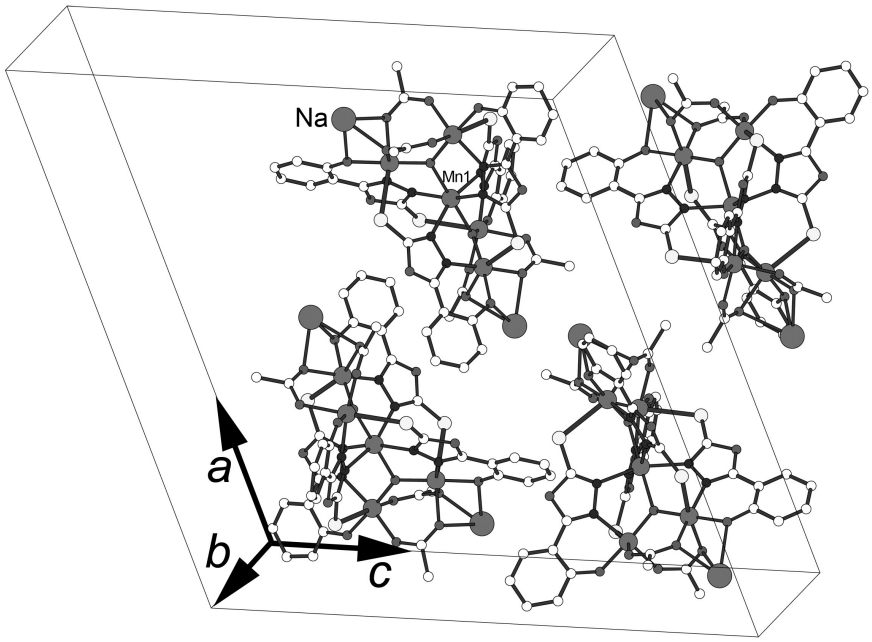

Figure S3: *Packing diagram of the pentanuclear complex. The hydrogen atoms, solvent molecules and DMF terminal groups have been omitted for clarity.*

Table S1: *Crystal data and refinements details for the* $[Mn_5Na_2O_2(O_2CMe)_4(L')_4(DMF)_4(H_2O)]\cdot 3DMF$ *compound.*

Formula	$C_{61}H_{79}Mn_5N_{15}Na_2O_{26}S_4$
Formula weight ($g.mol^{-1}$)	1887.31
Crystal system	monoclinic
Space group	P 21/c
a (Å)	26.349(5)
b (Å)	12.877(3)
c (Å)	25.364(5)
alpha (°)	90.00
Beta (°)	111.33(5)
gamma (°)	90.00
V (A^3)	8016(3)
Z	4
Density ($g.cm^{-3}$)	1.564
mu (Mo Kalpha) (mm^{-1})	0.966
F(000)	3876
Data collection	
Temperature (K)	173(2)
Theta min - max	1.62 - 27.10
Dataset[h, k, l]	-33/33, -16/16, -28/32
Tot., Uniq. Data, R(int)	17702, 11362, 0.1032
Observed data	>2sigma(I)
Refinement	
Nreflections, Nparameters	17702, 1063
R1, R2	0.0847, 0.1530
wR1, wR2	0.1264, 0.1569
Goof	1.114
Max. and Av. Shift/Error	0.001, 0.000
Min, Max. Resd Dens. ($e.A^{-3}$)	-1.056, 0.651

Table S2: *Main hydrogen bonds occurring in the [$Mn_5Na_2O_2(O_2CMe)_4(L')_4(DMF)_4(H_2O)]\cdot 3DMF$ complex in the crystalline solid state determined by the PLATON software.*[1]

Donor	*H*	*Acceptor*	*D-H (Å)*	*H-A (Å)*	*D-A (Å)*	*D-H-A (Å)*
O(23)	H(1O)	O(26)_$5	0.90(5)	1.82(5)	2.710(7)	176(9)
O(23)	H(2O)	O(25)_$4	0.89(5)	1.99(5)	2.886(6)	176(9)
C(4)	H(4)	O(25)_$7	0.95	2.57	3.475(7)	158
C(27)	H(27)	O(18)_$2	0.95	2.41	3.205(6)	141
C(40)	H(40C)	S(2)_$2	0.98	2.85	3.659(6)	140
C(52)	H(52C)	O(17)_$6	0.98	2.51	3.157(19)	123
C(34)	H(34A)	O(24)	0.98	2.41	3.328(7)	156
C(41)	H(41)	O(11)	0.95	2.43	3.254(7)	144
C(42)	H(42C)	O(19)	0.98	2.41	2.806(10)	104
C(49)	H(49A)	O(21)	0.98	2.36	2.764(10)	104
C(58)	H(58C)	O(24)	0.98	2.41	2.811(9)	104
C(60)	H(60A)	O(25)	0.98	2.39	2.797(9)	104
C(63)	H(63A)	O(26)	0.98	2.38	2.791(10)	104

Translation to Equivalent Position Code are given below : $1 = 1-x,1-y,-z; $2 = 1-x,-y,-z; $3 = 2-x,-y,-z; $4 = x,-1+y,z; $5 = x,1/2-y,-1/2+z; $6 = 1-x,-1/2+y,1/2-z; $7 = x,1/2-y,1/2+z

Table S3: *Bond lengths in[$Mn_5Na_2O_2(O_2CMe)_4(L')_4(DMF)_4(H_2O)]\cdot 3DMF$.*

Mn1	-O1	2.155(4)	/	S3	-C24	1.661(6)
Mn1	-O2	2.172(4)	/	S4	-C32	1.676(6)
Mn1	-N1	2.225(4)	/	Na1	-O5	2.551(5)
Mn1	-N3	2.246(4)	/	Na1	-O14	2.403(4)
Mn1	-N5	2.218(4)	/	Na1	-O19	2.291(5)
Mn1	-N7	2.212(4)	/	Na1	-O20	2.274(5)
Mn2	-O1	1.844(3)	/	Na1	-O23	2.303(6)
Mn2	-O3	1.893(3)	/	Na2	-O9	2.358(5)
Mn2	-O11	1.962(4)	/	Na2	-O16	2.388(5)
Mn2	-O13	2.166(4)	/	Na2	-O18	2.630(5)
Mn2	-N2	2.011(4)	/	Na2	-O21	2.190(6)
Mn3	-O1	1.839(3)	/	Na2	-O22	2.225(6)
Mn3	-O5	1.919(4)	/	O3	-C1	1.324(6)
Mn3	-O12	2.164(4)	/	O4	-C7	1.352(7)
Mn3	-O14	1.952(4)	/	O4	-C8	1.396(6)
Mn3	-N4	1.997(4)	/	O5	-C9	1.328(6)
Mn4	-O2	1.853(3)	/	O6	-C15	1.348(7)
Mn4	-O7	1.900(4)	/	O6	-C16	1.403(6)
Mn4	-O15	2.180(4)	/	O7	-C17	1.315(7)
Mn4	-O17	1.959(4)	/	O8	-C23	1.361(6)
Mn4	-N6	2.004(4)	/	O8	-C24	1.413(6)
Mn5	-O2	1.825(3)	/	O9	-C25	1.332(6)
Mn5	-O9	1.922(4)	/	O10	-C31	1.350(6)
Mn5	-O16	1.970(4)	/	O10	-C32	1.412(7)
Mn5	-O18	2.185(4)	/	O11	-C35	1.265(6)
Mn5	-N8	2.001(4)	/	O12	-C35	1.252(6)
S1	-C8	1.681(6)	/	O13	-C33	1.242(6)
S2	-C16	1.672(6)	/	O14	-C33	1.285(6)
O15	-C37	1.230(7)	/	N9	-C43	1.446(9)
O16	-C37	1.282(6)	/	N10	-C45	1.440(9)
O17	-C39	1.261(6)	/	N10	-C46	1.459(9)
O18	-C39	1.256(6)	/	N10	-C44	1.317(8)
O19	-C41	1.216(9)	/	N11	-C47	1.313(10)
O20	-C44	1.230(7)	/	N11	-C49	1.445(11)

O21	-C47	1.229(9)	/	N11	-C48	1.457(12)
O22	-C50	1.322(15)	/	N12	-C51	1.403(18)
O22	-C50A	1.283(15)	/	N12	-C52A	1.44(2)
O23	-H2O	0.89(5)	/	N12	-C50A	1.369(13)
O23	-H1O	0.90(4)	/	N12	-C50	1.342(15)
O24	-C56	1.210(8)	/	N12	-C52	1.502(16)
O25	-C59	1.226(7)	/	N12	-C51A	1.42(2)
O26	-C62	1.225(10)	/	N13	-C57	1.452(11)
N1	-C8	1.307(7)	/	N13	-C56	1.321(8)
N1	-N2	1.399(6)	/	N13	-C58	1.448(8)
N2	-C7	1.304(6)	/	N14	-C59	1.318(8)
N3	-N4	1.398(6)	/	N14	-C60	1.444(8)
N3	-C16	1.307(6)	/	N14	-C61	1.455(9)
N4	-C15	1.296(6)	/	N15	-C64	1.453(10)
N5	-C24	1.305(7)	/	N15	-C63	1.457(10)
N5	-N6	1.396(6)	/	N15	-C62	1.321(9)
N6	-C23	1.295(7)	/	C1	-C6	1.398(7)
N7	-C32	1.298(6)	/	C1	-C2	1.416(8)
N7	-N8	1.394(6)	/	C2	-C3	1.398(7)
N8	-C31	1.295(6)	/	C2	-C7	1.428(7)
N9	-C42	1.453(10)	/	C3	-C4	1.365(7)
N9	-C41	1.309(8)	/	C4	-C5	1.390(8)
C5	-C6	1.376(7)	/	C50A	-C51	1.47(2)
C9	-C10	1.422(7)	/	C51	-C51A	1.33(2)
C9	-C14	1.413(7)	/	C51A	-C52	1.47(3)
C10	-C11	1.369(7)	/	C52	-C52A	1.56(2)
C11	-C12	1.393(9)				
C12	-C13	1.374(8)				
C13	-C14	1.401(7)				
C14	-C15	1.444(7)				
C17	-C18	1.415(8)				
C17	-C22	1.417(7)				
C18	-C23	1.435(7)				
C18	-C19	1.395(7)				
C19	-C20	1.370(7)				
C20	-C21	1.389(8)				
C21	-C22	1.360(7)				
C25	-C26	1.413(7)				
C25	-C30	1.396(8)				
C26	-C31	1.441(8)				
C26	-C27	1.402(7)				
C27	-C28	1.368(8)				
C28	-C29	1.385(8)				
C29	-C30	1.384(8)				
C33	-C34	1.489(7)				
C35	-C36	1.518(8)				
C37	-C38	1.528(9)				
C39	-C40	1.512(7)				
C50	-C50A	1.39(2)				
C50	-C52A	1.35(2)				

*** Sodium salt of benzoic-2-hydroxy-2(dithiocarboxy)hydrazidacid (H_3L^-, Na^+) : synthesis details.**

This ligand was prepared according to the reported method[2] with a few modifications as indicated below : CS_2 (1ml ; 16.6 mmol) was added dropwise to a stirred solution of salicylhydrazide (2.52 g ; 16.6 mmol) and NaOH (0.66 g ; 8.3 mmol) in 40 ml of absolute ethanol, at room temperature. Stirring was continued for 12 h. After that, cold diethyl ether (120 ml) is added. The formed precipitate was then filtrated and rinsed with diethyl ether and dried at 65°C under vacuum (80% yield).

Supplementary Material (ESI) for New Journal of Chemistry

1 A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7-13.
2 K. Colanceska-Ragenovic, V. Dimova, V. Kakurinov, D. G. Molnar and A. Buzarovska, *Molecules*, 2001, **6**, 815.