ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Title:

Singlet ground state in compounds with $[Mn^{III}_4O_2]^{8+}$ core due to broken degeneration

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Content:

Table S1. Crystal data and structure refinement details for compound **1**.

	1·1/2EtOH·5/4CH_3CN·1/4H_2O	**2**·2 CH_3CN*
Formula	$C_{167}H_{144.50}Cl_2Mn_8N_{10.50}O_{55.50}$ [a]	$C_{192}H_{210}Cl_4Mn_8N_{14}O_{46}$
Fw (g/mol)	3696.84	4031.05
Crystal color, habit	red, prism	Red, thin plate
***T* (K)**	100(2)	100
λ (Mo Kα) / Å	0.71073	0.71073
Crystal size (mm)	0.62 x 0.25 x 0.23	0.23 x 0.20 x 0.03
Crystal system	Triclinic	Monoclinic
Space group	*P*1	*P*21/*c*
***a* / Å**	16.254(3)	27.685(3)
***b* / Å**	16.408(3)	19.1531(18)
***c* / Å**	17.493(3)	18.3634(16)
α / °	111.443(6)	90
β / °	93.798(6)	91.828(3)
γ / °	103.048(6)	90
***V* / Å^3**	4172.9(13)	9732.3(16)
Z	1	2
ρ_{calcd} / g·cm^{-3}	1.471	1.376
μ / mm^{-1}	0.708	0.637
***F*(000)**	1897	4192
θ range / °	2.21 to 26.88	2.10 to 30.72
Completeness to θ_{max}	99.7%	98.0%
Index ranges	$h = -20 \rightarrow 20$	$h = -39 \rightarrow 39$
	$k = -20 \rightarrow 20$	$k = -23 \rightarrow 27$
	$l = -22 \rightarrow 22$	$l = -26 \rightarrow 24$
Data/restraints/parameters	34398/75/2243	29671 / 3 / 553
GooF on F^2	1.105	1.531
R_1[c], ωR_2[d] [$I > 2\sigma(I)$]	0.0397, 0.1060	0.1949, 0.4709
R_1[c], ωR_2[d] (all data)	0.0428, 0.1104	0.3236, 0.5161

[a] 2 eq. of **1**·1/2 EtOH·5/4 CH_3CN·1/4 H_2O; b 2 eq. of **2**·2 CH_3CN [c] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; [d] $\omega R_2 = \{\sum[\omega(F_o^2 - F_c^2)^2] / \sum[\omega(F_o^2)^2]\}^{1/2}$, $\omega = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2] / 3$. * NOTE: This structure was only isotropically refined. The crystal was poorly diffracting and could not be refined completely. Therefore, it was neither deposited in the CCDC database.

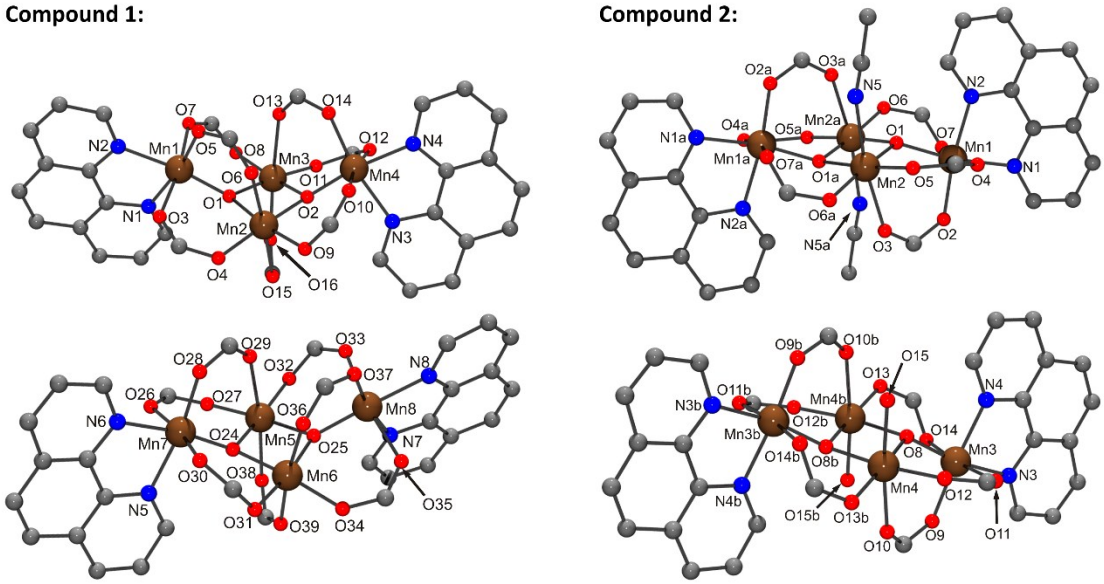

Figure S1. Crystal structure of the cationic complex of **1** and **2**. 4-RC_6H_4– groups and H atoms of phen ligands have been omitted for better clarity. Color code: Mn^{III}, brown; C, grey; N, blue; O, red. The Crystal structure of **2** could not be fully refined due to poor statistics of its measurement.

Table S2. Selected interatomic distances (Å) and angles (deg) for compound **1** with standard deviations in parentheses.

Mn1–O1	1.834(3)	Mn5–O27	1.944(3)
Mn1–O3	2.144(3)	Mn5–O24	1.901(3)
Mn1–O5	1.940(3)	Mn5–O25	1.904(3)
Mn1–O7	2.124(3)	Mn5–O38	2.110(4)
Mn1–N1	2.079(4)	Mn5–O29	2.174(4)
Mn1–N2	2.061(4)	Mn5–O32	1.928(3)
Mn2–O1	1.909(3)	Mn6–O24	1.898(3)
Mn2–O2	1.908(3)	Mn6–O34	1.932(3)
Mn2–O4	1.961(3)	Mn6–O25	1.901(3)
Mn2–O6	2.171(3)	Mn6–O31	1.968(3)
Mn2–O9	1.962(3)	Mn6–O36	2.204(3)
Mn2–O15	2.147(3)	Mn6–O39	2.246(3)
Mn3–O1	1.898(3)	Mn7–N5	2.083(3)
Mn3–O2	1.897(3)	Mn7–O24	1.834(3)
Mn3–O8	1.966(3)	Mn7–O26	2.194(3)
Mn3–O11	1.946(3)	Mn7–O28	1.939(3)
Mn3–O13	2.213(4)	Mn7–N6	2.064(4)
Mn3–O16	2.201(4)	Mn7–O30	2.141(3)
Mn4–O2	1.833(3)	Mn8–O33	2.181(3)
Mn4–O10	2.145(3)	Mn8–O35	2.178(3)
Mn4–O12	2.153(3)	Mn8–O37	1.911(3)
Mn4–O14	1.942(4)	Mn8–N7	2.070(5)
Mn4–N3	2.093(4)	Mn8–N8	2.076(3)
Mn4–N4	2.050(4)	Mn8–O25	1.846(3)
Mn2···Mn3	2.860(1)	Mn5···Mn6	2.839(1)
Mn1···Mn2	3.309(1)	Mn5···Mn7	3.284(1)
Mn1···Mn3	3.362(1)	Mn6···Mn7	3.409(1)
Mn2···Mn4	3.355(1)	Mn5···Mn8	3.381(1)
Mn3···Mn4	3.303(1)	Mn6···Mn8	3.332(1)
Mn1···Mn4	5.525(1)	Mn7···Mn8	5.693(1)
O1–Mn1–N2	170.47(17)	O24–Mn5–O32	171.56(14)
O3–Mn1–O7	172.02(13)	O25–Mn5–O27	173.00(15)
O5–Mn1–N1	169.47(14)	O29–Mn5–O38	173.55(13)
O6–Mn2–O15	176.65(13)	O25–Mn6–O31	170.50(15)
O1–Mn2–O9	172.63(14)	O36–Mn6–O39	172.72(12)
O2–Mn2–O4	176.14(15)	O24–Mn6–O34	175.16(15)
O1–Mn3–O11	174.01(15)	O24–Mn7–N6	168.55(17)
O2–Mn3–O8	171.57(15)	O26–Mn7–O30	170.92(13)
O13–Mn3–O16	176.46(13)	O28–Mn7–N5	170.84(14)
O2–Mn4–N4	170.18(17)	O33–Mn8–O35	170.25(13)
O10–Mn4–O12	170.43(13)	O37–Mn8–N7	169.13(17)
O14–Mn4–N3	168.83(14)	O25–Mn8–N8	171.81(15)
Mn1–O1–Mn3	128.51(18)	Mn6–O24–Mn7	132.00(18)
Mn1–O1–Mn2	124.17(16)	Mn5–O24–Mn7	123.10(18)
Mn2–O1–Mn3	97.38(14)	Mn5–O24–Mn6	96.77(14)
Mn2–O2–Mn3	97.47(14)	Mn5–O25–Mn6	96.55(14)
Mn2–O2–Mn4	127.50(17)	Mn5–O25–Mn8	128.76(19)
Mn3–O2–Mn4	124.63(19)	Mn6–O25–Mn8	125.58(17)
Mn2–O1–O2–Mn3	166.6(2)	Mn5–O25–O24–Mn6	169.2(2)
Mn1–Mn3···Mn2–O1	15.5(1)	Mn8···Mn6···Mn5–O25	14.7(1)
Mn4–Mn2···Mn3–O2	15.9(1)	Mn7···Mn5···Mn6–O24	13.9(1)
O15–Mn2···Mn1–O7	85.5(1)	O33–Mn8···Mn6–O39	89.8(1)
O16–Mn3···Mn4–O10	82.6(1)	O38–Mn5···Mn7–O30	91.7(1)

Table S3. Selected interatomic distances (Å) and angles (deg) for compound **2** with standard deviations in parentheses. ***NOTE***: The crystal structure of **2** could not be completely refined due to poor quality of the crystallographic data. The following structural parameters should **never** be used for magneto-structural correlations, neither as precise values.

Mn1–O1	1.870(6)	Mn3–N4	2.043(8)
Mn1–O2	1.912(6)	Mn3–O9	1.923(6)
Mn1–O4	2.142(7)	Mn3–O11	2.083(6)
Mn1–O7	2.208(6)	Mn3–O8	1.855(6)
Mn1–N1	2.039(8)	Mn3–N3	2.037(8)
Mn1–N2	2.036(8)	Mn3–O14	2.219(6)
Mn2–O1	1.860(6)	Mn4–O8b	1.919(6)
Mn2–O3	2.162(6)	Mn4–O15	2.216(6)
Mn2–O5	1.945(7)	Mn4–O12	1.936(6)
Mn2–N5	2.355(8)	Mn4–O8	1.890(6)
Mn2–O1a	1.919(6)	Mn4–O13b	1.935(6)
Mn2–O6a	1.913(6)	Mn4–O10	2.143(6)
O1–Mn1–N1	169.7(3)	O8–Mn3 –N3	168.6(3)
O4–Mn1–O7	168.0(3)	O9–Mn3 –N4	170.2(3)
O2–Mn1–N2	171.2(3)	O11–Mn3 –O14	170.9(2)
O1–Mn2–O6a	171.6(3)	O8–Mn4–O13b	171.7(2)
O3–Mn2–N5	169.5(3)	O10–Mn4–O15	171.2(2)
O1a–Mn2–O5	175.7(3)	O8b–Mn4–O12	173.2(2)
Mn1–O1–Mn2	122.0(3)	Mn3–O8–Mn4	120.4(3)
Mn1–O1–Mn2a	125.7(3)	Mn3–O8–Mn4b	125.9(3)
Mn2–O1–Mn2a	98.8(3)	Mn4–O8–Mn4b	98.7(3)
Mn2–O1–O1a–Mn2a	180	Mn4–O8–O8b–Mn4b	180
Mn1–Mn2–Mn2a–O1	18.9(3)	Mn3–Mn4–Mn4b–O8	19.8(3)
N5–Mn2–Mn1–O7	98.1(2)	O15–Mn4–Mn3–O14	97.5(2)

Symmetry codes: (a) 1 – x, 1 – y, –z; (b) –x, 1 – y, 1 – z.

Table S4 *x*, *y*, and *z* axes length and the elongated (Δ) and rhombic distortion (ρ) of each Mn ion for compounds **1** and **2**.

Compound	Mn centre	*x* / Å	*y* / Å	*z* / Å	Δ / %	ρ / %
1	Mn1	3.895	4.019	4.267	7.8	3.2
	Mn2	3.87	3.87	4.319	11.6	0.0
	Mn3	3.862	3.843	4.414	14.6	–0.5
	Mn4	3.883	4.035	4.297	8.5	3.9
	Mn5	3.827	3.846	4.283	11.6	0.5
	Mn6	3.83	3.868	4.449	15.6	1.0
	Mn7	3.898	4.021	4.334	9.5	3.2
	Mn8	3.923	3.98	4.36	10.3	1.5
2*	Mn1	~3.90	~3.95	~4.34	~11	~1
	Mn2	~3.78	~3.85	~4.50	~18	~2
	Mn3	~3.90	~3.96	~4.31	~10	~2
	Mn4	~3.83	~3.85	~4.36	~14	~1

$\Delta = (z - \bar{xy}) / \bar{xy}$, $\bar{xy} = (x + y)/2$; $\rho = (y - x) / x$. * The Crystal structure of **2** could not be fully refined due to poor statistics of its measurement.

		Constraints and restraints		
		Fit 1 $J_2 = J_3$ $D_{Mn} = 0$	Fit 2 $J_2 = J_3$ $D_{Mn} > -4.9$ cm^{-1}	Fit 3 $J_2 \neq J_3$ $D_{Mn} = 0$
Compound	Parameters			
1	$2J_1$ / cm^{-1}	–18.6	–18.2	–46.6
	$2J_2$ / cm^{-1}	–13.3	–13.4	–13.9
	$2J_3$ / cm^{-1}	–13.3	–13.4	–3.1
	D_{Mn} / cm^{-1}	0	–3.2	0
2	$2J_1$ / cm^{-1}	–17.9	–72.2	–50.1
	$2J_2$ / cm^{-1}	–11.5	–5.8	–13.3
	$2J_3$ / cm^{-1}	–11.5	–5.8	–6.3
	D_{Mn} / cm^{-1}	0	–4.9	0

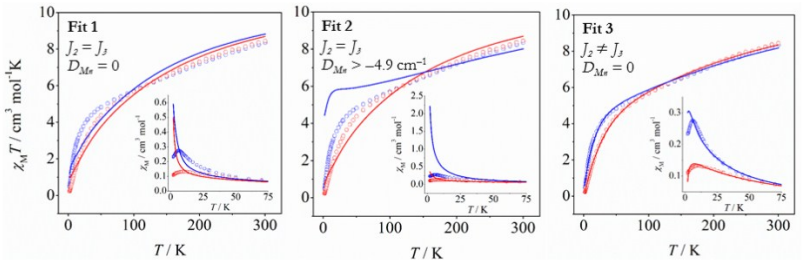

Figure S2. Results from different fits of the $\chi_M T$ versus T plots of compounds **1** (red) and **2** (blue). The solid lines correspond to the fit to the experimental data considering $J_2 = J_3$, omitting or including D_{Mn} (Fit 1 and 2, respectively), and considering $J_2 \neq J_3$ (Fit 3). The molecular weight of **2** was referred to one Mn_4 unit, considering an average formula between the two entities.

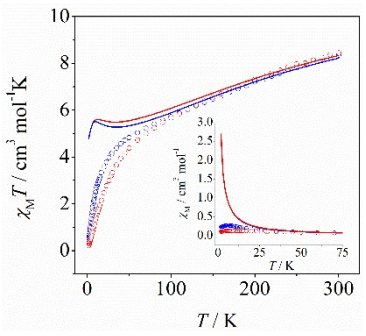

Figure S3. Experimental (open circles) and simulated (straight lines) $\chi_M T$ versus T and χ_M versus T (inset) plots for compounds **1** (red) and **2** (blue). The simulation was performed with $2J_1$ and D_{Mn} values obtained from the fit and with the average value between $2J_2$ and $2J_3$ (–9.7 cm^{-1} for **1** and –11.5 cm^{-1} for **2**). The molecular weight of **2** was referred to one Mn_4 unit, considering an average formula between the two entities.

Table S5. Comparison of the average core parameters, distances (Å) and angles (deg), for the $[Mn^{III}_2O_2]^{8+}$ subunits of the several $[Mn^{III}_4O_2]^{8+}$ compounds.

Compound	$Mn_c \cdots Mn_c$	$Mn_c–O_b–Mn_c$	$Mn_c–O_b–O_b–Mn_c$	$2J_1$ / cm^{-1}	*Ref.*
1	2.849	97.1	168	–45.5	This work
2*	~2.88	~99	180	–43.0	This work
$[Mn_4O_2(NO_3)(O_2CEt)_6(bpy)_2]^+$	2.847	97.2	169	–33.0	[1]
$[Mn_4O_2(O_2CEt)_7(bpya)_2]^+$	2.871	97.2	170	–51.4	[2]
$[Mn_4O_2(O_2CMe)_7(bpy)_2]^+$	2.848	96.3	167	–47.0	[3]
$[Mn_4O_2(O_2CMe)_7(pic)_2]^-$	2.842	96.6	165	–49.2	[4]
$[Mn_4O_2(py)_2(O_2CMe)_6(dbm)_2]$	2.875	99.1	180	–29.8	[5]
$[Mn_4O_2(O_2CPh)_6(dpm)_2]$	2.841	98.5	179	–55.0	[6]

Abbreviations: bpya = bis(2-pyridyl)amine, bpy = 2,2′-bipyridine, pic = picolinate, py = pyridine, dbmH = dibenzoylmethane, dpmH = dipivaloylmethane; see Eq. 1 and Figure 5 for the *J* assignment. * The crystal structure of **2** could not be fully refined due to poor statistics of its measurement.

Table S6. Comparison of the average core parameters, distances (Å) and angles (deg), for the $[Mn_2O(RCOO)_2]^{2+}$ subunits of the several $[Mn^{III}_4O_2]$ compounds.

Compound	$Mn_c\cdots Mn_t$	$Mn_c–O_b–Mn_t$	$L–Mn_c\cdots Mn_t–L$	$2J_2$ / cm^{-1}	*Ref.*
1	3.307	124.4	87.4	– 15.1/–4.4	This work
2*	~3.26	~121	~99	– 14.7/–8.2	This work
$[Mn_4O_2(NO_3)(O_2CEt)_6(bpy)_2]^+$	3.258	121.8	74.1	–3.4	[1]
$[Mn_4O_2(O_2CEt)_7(bpya)_2]^+$	3.307	126.1	92.6	–6.6	[2]
$[Mn_4O_2(O_2CMe)_7(bpy)_2]^+$	3.301	123.7	82.5	–15.6	[3]
$[Mn_4O_2(O_2CMe)_7(pic)_2]^-$	3.311	125.0	82.3	–10.6	[4]
$[Mn_4O_2(py)_2(O_2CMe)_6(dbm)_2]$	3.308	123.2	105.1	–10.0	[5]
$[Mn_4O_2(O_2CPh)_6(dpm)_2]$	3.255	120.1	70	–0.8	[6]

$L–Mn_c\cdots Mn_c–L$ = torsion angle between the two Jahn-Teller axes. Abbreviations: bpya = bis(2-pyridyl)amine, bpy = 2,2'-bipyridine, pic = picolinate, py = pyridine, dbmH = dibenzoylmethane, dpmH = dipivaloylmethane. See Eq. 1 and Figure 5 for the *J* assignment. * The crystal structure of **2** could not be fully refined due to poor statistics of its measurement.

Table S7. Comparison of the average core parameters, distances (Å) and angles (deg), for the $[Mn_2O(RCOO)]^{3+}$ unit of the several $[Mn^{III}_4O_2]$ complexes.

Compound	$Mn_c\cdots Mn_t$	$Mn_c–O_b–Mn_t$	$2J_3$ / cm^{-1}	*Ref.*
1	3.377	129.2	–15.1/–4.4	This work
2*	~3.37	~126	–14.7/–8.2	This work
$[Mn_4O_2(NO_3)(O_2CEt)_6(bpy)_2]^+$	3.34	126.4	–3.4	[1]
$[Mn_4O_2(O_2CEt)_7(bpya)_2]^+$	3.444	130.7	–6.6	[2]
$[Mn_4O_2(O_2CMe)_7(bpy)_2]^+$	3.378	130.2	–15.6	[3]
$[Mn_4O_2(O_2CMe)_7(pic)_2]^-$	3.396	129.7	–10.6	[4]
$[Mn_4O_2(py)_2(O_2CMe)_6(dbm)_2]$	3.398	128.6	–10.0	[5]
$[Mn_4O_2(O_2CPh)_6(dpm)_2]$	3.362	126.0	–0.8	[6]

Abbreviations: bpya = bis(2-pyridyl)amine, bpy = 2,2'-bipyridine, pic = picolinate, py = pyridine, dbmH = dibenzoylmethane, dpmH = dipivaloylmethane; see Eq. 1 and Figure 5 for the *J* assignment. * The crystal structure of **2** could not be fully refined due to poor statistics of its measurement.

References for tables S5, S6, and S7

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