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New insights into the comprehension of the magnetic properties of dinuclear Mn(III) compounds with general formula $[\{MnL(NN)\}_2(\mu\text{-}O)(\mu\text{-}n\text{-}RC_6H_4COO)_2]X_2$

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1. Synthesis

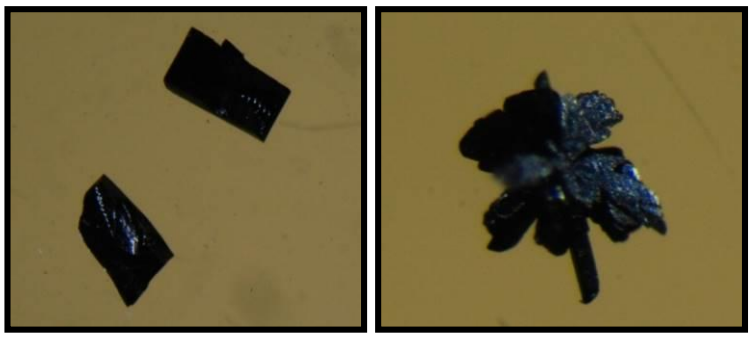

Figure S1. Photographs of crystals for compounds **3** (right) and **4** (left).

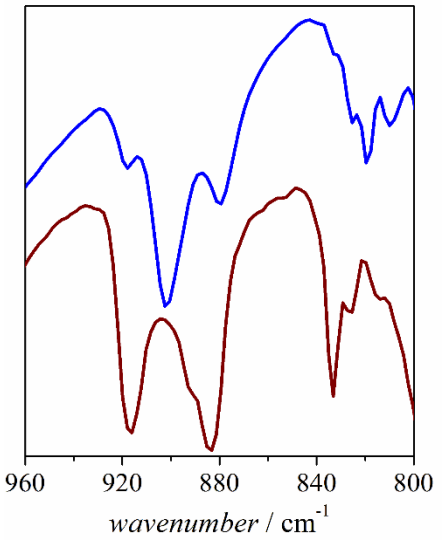

Figure S2. Transmittance infrared spectra (range 960–800 cm^{-1}) of compounds **3** (blue) and **4** (red).

2. Crystallography

Table S1. Crystal data and structure refinement for compounds **3**, **4**, **5**, **6** and **7**.

	3·2CH_3CN	**4**·1/2H_2O·1/2MeCN	**5**	**6**·1/3MeCN·1/3H_2O	**7**
Formula	$C_{40}H_{36}Mn_2N_8O_{13}$[a]	$C_{74}H_{69}Mn_4N_{13}O_{29}$[b]	$C_{36}H_{32}Cl_2Mn_2N_4O_{16}$	$C_{116}H_{113}Cl_6Mn_6N_{13}O_{49}$[c]	$C_{44}H_{47}Cl_2Mn_2N_4O_{14}$
Fw (g/mol)	946.65	1824.18	957.44	3015.53	1036.64
Crystal colour, habit	Dark green, prism	Green, needle	Green, prism	Brown, thin plate	Green, needle
T (K)	100(2)	100(2)	100(2)	293(2)	100(2)
λ (Mo-Kα) / Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal size (mm)	0.25 x 0.22 x 0.21	0.42 x 0.20 x 0.05	0.54 x 0.46 x 0.33	0.2 x 0.03 x 0.03	0.35 x 0.08 x 0.03
Crystal system	Monoclinic	Triclinic	Triclinic	Trigonal	Orthorhombic
Space group	*C*2/*c*	*P*-1	*P*-1	*R*-3	*Pca*2(1)
a / Å	24.3681(19)	9.8493(9)	10.0416(16)	25.409(7)	24.6687(18)
b / Å	13.7810(11)	14.2702(14)	14.598(3)	25.409(7)	13.5393(9)
c / Å	16.1592(13)	15.7977(16)	15.706(3)	35.1430(10)	28.996(2)
α / °	90	114.076(4)	114.091(6)	90	90
β / °	130.004(3)	97.913(4)	100.507(6)	90	90
γ / °	90	94.134(4)	91.521(6)	120	90
V / Å^3	4156.7(6)	1987.6(3)	2053.4(7)	19649(8)	9684.6(12)
Z	4	1	2	6	8
ρ_{calcd} / g·cm^{-3}	1.513	1.524	1.549	1.529	1.422
μ / mm^{-1}	0.683	0.713	0.821	0.777	0.699
F(000)	1944	936	976	9264	4280
θ range / °	2.18 to 24.70	2.32 to 26.52	2.08 to 35.98	1.48 to 32.38	2.17 to 22.98
Completeness (to θ / °)	91.4% (24.70)	98.7% (26.52)	100.0% (25.00)	99.8% (25.00)	99.7% (22.98)
Index ranges	h = -28 → 28	h = -12 → 12	h = -16 → 15	h = -38 → 19	h = -27 → 27
	k = -16 → 16	k = -17 → 17	k = -23 → 22	k = 0 → 38	k = -14 → 14
	l = -18 → 18	l = -19 → 19	l = -24 → 23	l = 0 → 52	l = -31 → 28
Data/restraints/parameters	3234 / 0 / 286	8150 / 63 / 556	16188 / 286 / 592	14081 / 38 / 591	12723 / 480 / 1244
GooF on F^2	1.091	1.158	1.023	0.881	1.030
R_1[d], ωR_2[e] [$I > 2\sigma(I)$]	0.0344, 0.0876	0.0842, 0.2440	0.0620, 0.1595	0.0470, 0.1094	0.0374, 0.0832
R_1[d], ωR_2[e] (all data)	0.0400, 0.0934	0.1058, 0.2564	0.0792, 0.1674	0.1303, 0.1287	0.0486, 0.0881

[a] **3**·2 CH_3CN. [b] 2eq. of **4**·1/2 H_2O·1/2 MeCN. [c] 3 eq. of **6**·1/3 MeCN·1/3 H_2O. [d] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. [e] $\omega R_1 = \{\sum[\omega(F_o^2 - F_c^2)^2] / \sum[\omega(F_o^2)^2]\}^{1/2}$, $\omega = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2] / 3$.

[{Mn(bpy)(NO_3)}$_2$(μ-3-$MeOC_6H_4CO_2$)$_2$(μ-O)]·2 MeCN (3·2 MeCN)

The crystal structure of compound **3** consists of a neutral complex and two molecules of acetonitrile. The most relevant distances and angles are listed in Table S3.

A parallel-displaced π-π interaction may be found between bipyridine ligands of adjacent complexes, whose planes are at 3.2 Å, generating a helicoidally organized chain (Figure S3).

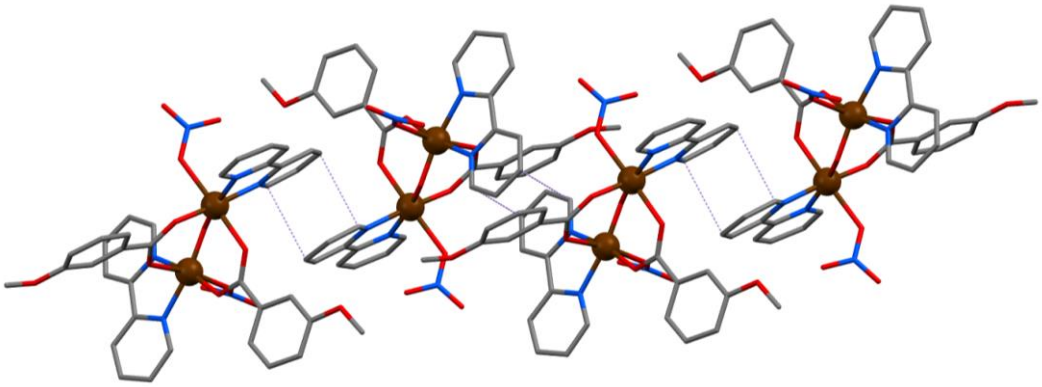

Figure S3. π-π interactions (purple lines) in the crystal structure of compound **3**. Hydrogen atoms have been omitted for clarity. Colour code: Mn^{III}, brown; O, red; C, dark grey; N, blue.

[{Mn(bpy)(H_2O)}(μ-3-$MeOC_6H_4CO_2$)$_2$(μ-O){Mn(bpy)(NO_3)}]NO_3·1/2 H_2O·1/2 MeCN (4·1/2 H_2O·1/2 MeCN)

The crystal structure of compound **4** consists of a cationic complex, a molecule of nitrate and two 50% occupancy molecules of water and acetonitrile. The most relevant distances and angles are listed in Table S3.

There are hydrogen bonds between the coordinated water molecule and the coordinated nitrate anion of the neighbour. Such interactions are extended along a longitudinal axis (Figure S4).

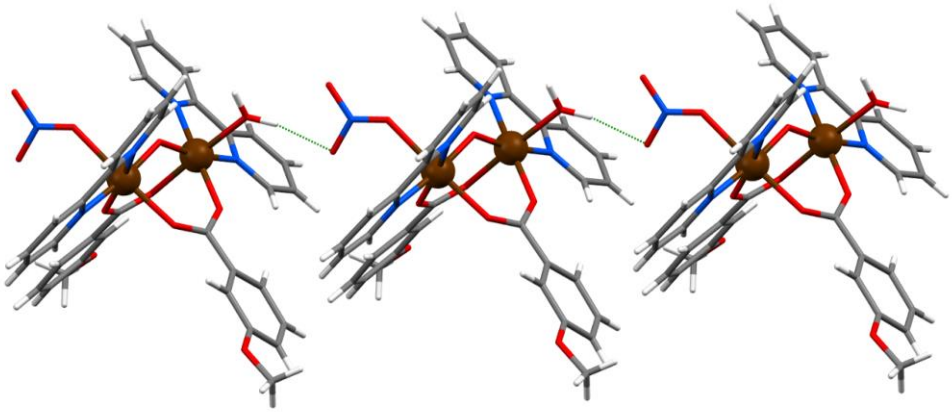

Figure S4. Hydrogen bonds (green lines) in the crystal structure of compound **4**. Colour code: Mn^{III}, brown; O, red; C, dark grey; N, blue; H, white.

[{Mn(bpy)(H_2O)}(μ-3-$MeOC_6H_4CO_2$)$_2$(μ-O){Mn(bpy)(ClO_4)}]ClO_4 (5).

Figure 1 shows the crystal structure of the cationic complex of compound **5**. The most relevant distances and angles are listed in Table S3.

As seen for compound **4**, hydrogen bonds are found between the coordinated water molecule and the coordinated perchlorate anion of the neighbour, generating a chain (Figure S5).

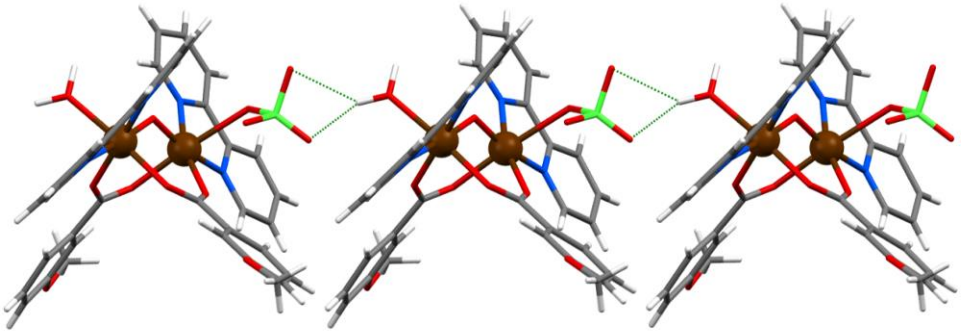

Figure S5. Hydrogen bonds (green lines) in the crystal structure of compound **5**. Colour code: Mn^{III}, brown; O, red; C, dark grey; N, blue; Cl, green; H, white.

[{Mn(bpy)(EtOH)}(μ-4-$MeOC_6H_4CO_2$)$_2$(μ-O){Mn(bpy)(ClO_4)}]ClO_4·1/3 MeCN·1/3 H_2O (6·1/3 MeCN·1/3 H_2O).

Figure 1 shows the crystal structure of the cationic complex of compound **6**. The most relevant distances and angles are listed in Table S3.

The complexes of compound **6** are situated around the 3-fold symmetry axis, leading to a three dimensional structure with channels that are filled with disordered solvent (Figure S6).

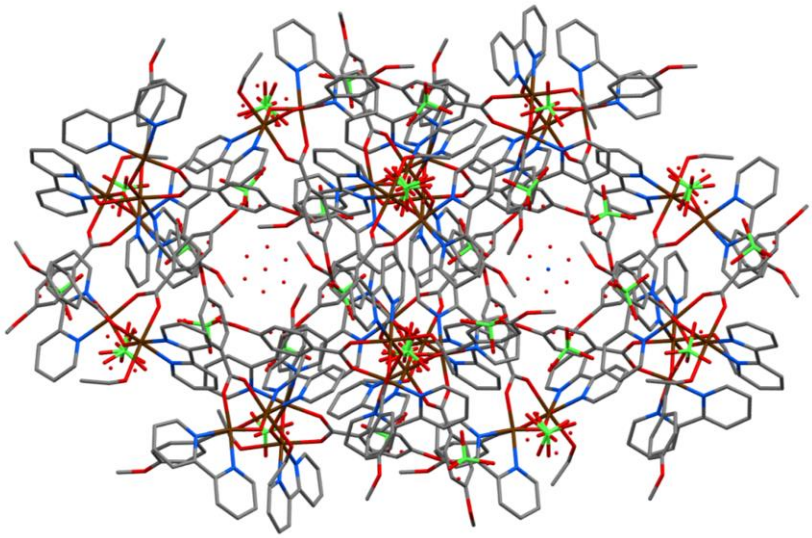

Figure S6. View from the c-axis of the packing of compound **6**. Hydrogen atoms have been omitted for clarity. Colour code: Mn^{III}, brown; O, red; C, dark grey; N, blue; Cl, green.

[{Mn(bpy)(EtOH)}(μ-4-^{t}BuC$_6$H$_4$CO$_2$)$_2$(μ-O){Mn(bpy)(ClO$_4$)}]ClO$_4$ (7).

The crystal structure of compound **7** consists of two different dinuclear complexes (shown in Figure 1) and two perchlorate anions. The most relevant distances and angles are listed in Table S6. The two complexes are conformational isomers, whose most remarkable difference is the relative orientation of the octahedra, being 79.9 and 67.5º for each complex.

Tables with interatomic distances and angles for compounds 3–7

Table S2. Selected interatomic distances (Å) and angles (deg) for compound **3** with standard deviations in parentheses.

Mn1–O1	1.7866(10)	O2–Mn1–N1	169.65(7)
Mn1–N2	2.0692(18)	O1–Mn1–N2	168.94(7)
Mn1–O2	1.9716(16)	O3–Mn1–O4	170.14(6)
Mn1–N1	2.0478(19)	O4–Mn1···Mn1'–O4'	117.24(8)
Mn1–O3	2.1799(17)	O3–C1'–C2'–C3'	16.9(4)
Mn1–O4	2.2456(19)		
Mn1···Mn1'	3.1628(7)		
Mn1–O1–Mn1'	124.54(12)		

Symmetry codes: (') -x,y,0.5-z

Table S3. Selected interatomic distances (Å) and angles (deg) for compounds **4**, **5** and **6** with standard deviations in parentheses.

	Compound 4	**Compound 5**	**Compound 6**
Mn1–O1	1.783(4)	1.7796(16)	1.7659(16)
Mn1–N2	2.058(5)	2.075(2)	2.055(2)
Mn1–O2	1.982(4)	1.9741(17)	1.9571(17)
Mn1–N1	2.081(6)	2.059(2)	2.063(2)
Mn1–O4	2.182(4)	2.1513(17)	2.1441(19)
Mn1–O6	2.171(5)	2.186(2)	2.2995(19)
Mn2–O1	1.779(4)	1.7856(16)	1.7873(16)
Mn2–N4	2.054(6)	2.055(2)	2.086(2)
Mn2–O5	1.964(4)	1.9587(17)	1.9227(18)
Mn2–N3	2.045(5)	2.0452(19)	2.0171(19)
Mn2–O3	2.189(4)	2.1234(17)	2.1218(17)
Mn2–O7	2.262(6)	2.4128(18)	2.483(2)
Mn1···Mn2	3.1555(12)	3.1457(6)	3.1301(6)
Mn1–O1–Mn2	124.7(2)	123.85(9)	123.50(9)
O1–Mn1–N2	169.2(2)	168.70(8)	169.79(8)
O2–Mn1–N1	169.0(2)	171.09(8)	168.09(8)
O6–Mn1–O4	173.36(18)	170.07(8)	172.42(7)
O1–Mn2–N4	168.4(2)	167.79(8)	169.77(8)
O5–Mn2–N3	168.4(2)	163.52(7)	165.92(8)
O3–Mn2–O7	175.09(18)	174.36(7)	166.11(7)
O6–Mn1···Mn2–O7	92.8(2)	102.25(9)	95.50(8)
O3–C1–C2–C3	16.8(9)	16.1(1)	16.8(4)
O4–C8–C9–C10	6.7(9)	5.3(3)	6.6(4)

Symmetry codes: (') x-1,y,z

Table S4. Selected interatomic distances (Å) and angles (º) for compound **7** with standard deviations in parentheses.

Mn1–O1	1.779(3)	Mn3–O15	1.785(3)
Mn1–N2	2.057(4)	Mn3–N6	2.055(4)
Mn1–O2	1.940(3)	Mn3–O16	1.935(3)
Mn1–N1	2.063(4)	Mn3–N5	2.064(4)
Mn1–O4	2.143(3)	Mn3–O18	2.150(3)
Mn1–O6	2.232(3)	Mn3–O20	2.223(3)
Mn2–O1	1.792(3)	Mn4–O15	1.788(3)
Mn2–N4	2.048(4)	Mn4–N8	2.050(4)
Mn2–O5	1.930(3)	Mn4–O19	1.944(3)
Mn2–N3	2.040(4)	Mn4–N7	2.062(4)
Mn2–O3	2.205(3)	Mn4–O17	2.186(3)
Mn2–O7	2.302(3)	Mn4–O21	2.286(3)
Mn1···Mn2	3.0990(9)	Mn3···Mn4	3.1130(9)
Mn1–O1–Mn2	120.39(14)	Mn3–O15–Mn4	121.24(15)
O1–Mn1–N2	172.44(14)	O16–Mn3–N5	168.80(15)
O2–Mn1–N1	166.70(13)	O15–Mn3–N6	171.38(14)
O4–Mn1–O6	173.00(13)	O18–Mn3–O20	169.39(13)
O1–Mn2–N4	170.79(15)	O15–Mn4–N8	170.78(15)
O5–Mn2–N3	171.24(14)	O19–Mn4–N7	170.04(14)
O3–Mn2–O7	162.62(12)	O17–Mn4–O21	174.97(13)
O6–Mn1···Mn2–O7	79.9(1)	O20–Mn3···Mn4–O21	67.5(1)
O3–C1–C2–C3	0.3(6)	O17–C45–C46–C47	5.7(6)
O4–C8–C9–C10	0.3(6)	O18–C52–C53–C54	8.8(6)

3. Magnetic properties

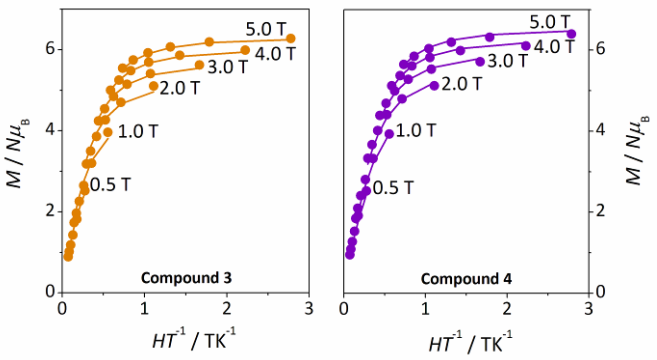

Figure S7. *M/Nμβ vs. HT*$^{-1}$ plots for compounds **3** and **4**. The solid lines are the best fits of the experimental data.