Molecular Self-recognition: A Chiral [Mn(II)$_6$] Wheel *via* Donor-Acceptor π···π Contacts and H-Bonds

L. A. Barrios,[a] J. Salinas-Uber, O. Roubeau,[b] S. J. Teat[c] and G. Aromí[a,]*

SUPPORTING INFORMATION

Synthesis.

2,6-bis-(5-(naphth-2-yl)-pyrazol-3-yl)pyridine (H_2L). This ligand was prepared by reaction with hydrazine of the corresponding bis-β-diketone precursor.[1] The latter was obtained through the usual Claisen condensation[2] of 2-acetonaphtone and dimethyl 2,6-pyridinedicarboxylate. The details of this preparation will be published elsewhere.

[$Mn_3(OAc)_4(HL)_2$] (**1**). H_2L2 (50 mg, 0.11 mmol) was suspended in 10 mL of THF. This suspension was added drop-wise onto a dark mixture of $Mn(OAc)_2.4H_2O$ (50 mg, 0.2 mmol) and freshly prepared $TBAMnO_4$[3] (10 mg, 0.03 mmol) in 10 mL of THF under stirring. The resulting brown suspension was stirred 1 hour at room temperature and then filtered. The dark filtrate was layered with ether. Yellow pale crystals suitable to X-ray diffraction were obtained after 2 weeks. Anal. Calcd. (Found) for **1**·$2.5H_2O$·0.75THF: C, 61.76 (61.56); H, 4.43 (4.42); N, 9.77 (9.54).

The same procedure was repeated using acetone as a solvent and produced essentially analogous results.

Physical Measurements

Variable-temperature magnetic susceptibility data were obtained with a Quantum Design MPMS5 SQUID magnetometer. Pascal's constants were used to estimate diamagnetic corrections to the molar paramagnetic susceptibility. The elemental analysis was performed with an Elemental Microanalizer (A5), model Flash 1112 at the Servei de Microanàlisi of CSIC, Barcelona, Spain. IR spectra were recorded as KBr pellet samples on a Nicolet AVATAR 330 FTIR spectrometer. Fluorescence emission spectra were carried out in DMF ($c = 1x10^{-6}$ M) using Horiba Jobin–Yvon SPEX Nanolog-TM and Cary Eclipse spectrofluorimeters.

X-ray crystallography.

Data for the crystal with composition **[H_2L•$(Bu_4N)(AcO)$•H_2O]** were collected on a colorless parallelepiped at 100 K on a Bruker APEX II CCD diffractometer on Advanced Light Source beam-line 11.3.1 at Lawrence Berkeley National Laboratory, from a silicon 111 monochromator ($\lambda = 0.7749$ Å). Data reduction and absorption corrections were performed with SAINT and SADABS[4], respectively. The structure was solved and refined on F^2 with SHELXTL-2013 suite [5,6]. Hydrogens on the lattice water molecule O1W as well as those on the pyrazole nitrogens N2 and N4 were found in a difference Fourier map and refined freely with their Ueq 1.5 times that of their carrier atom. The rest of hydrogens were placed on their carrier atom geometrically and refined with a riding model.

Data for compound **1** were collected on a colorless lozenge plate at 100 K on a Bruker APEX II CCD diffractometer on Advanced Light Source beam-line 11.3.1 at Lawrence Berkeley National Laboratory, from a silicon 111 monochromator (λ = 0.7749 Å). Data reduction and absorption corrections were performed with SAINT and SADABS[4], respectively. The structure was solved and refined on F^2 with SHELXTL-2013 suite [5,6]. Systematically on several crystals, significant diffraction was only observed for resolutions better than ca. 0.85 Å, likely due to the presence of diffuse solvent areas in the structure. The present data were cut at 0.85 Å for this reason. One of the naphthyl groups was refined disordered over two positions of the external ring, with relative occupancies of 0.53:0.47. The rest of naphthyl groups also showed some thermal disorder but splitting them did not converge. All were refined with displacement parameters restraints, as well as the lattice THF molecules. Hydrogens were placed on their carrier atom geometrically and refined with a riding model. At the end of the refinement there remained areas in the cell with only weak electron density peaks that could not be modeled as lattice solvent molecules. This was analyzed and taken into account with SQUEEZE as implemented in the PLATON package.[7,8] A total of 86 electrons per cell were recovered over mostly 2 large voids of 725 cubic angstroms and 4 voids of 165 cubic angstroms. At the most these figures would agree with two diffuse lattice THF molecules per cell, e.g. half a THF molecule per formula unit or less. It was thus not included in the formula.

All details can be found in CCDC-1022213 (**1**) and -1022214 (**$[H_2L•(Bu_4N)(AcO)•H_2O]$**) that contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic and refinement parameters are summarized in Table S1. Selected bond lengths and angles are given in Tables S2, S3 and S4.

Table S1. Crystal data for compounds **1** and **[H_2L•(Bu_4N)(AcO)•H_2O]**.

	1	**[H_2L•(Bu_4N)(AcO)•H_2O]**
formula	$C_{148}H_{96}Mn_6N_{20}O_{18}$	$C_{49}H_{62}N_6O_3$
fw, g/mol	2772.08	783.04
λ (Å)	0.7749	0.7749
crystal system	monoclinic	monoclinic
space group	$P2_1$/c	$P2_1$/n
a, Å	27.159(4)	14.623(3)
b, Å	13.925(2)	16.641(4)
c, Å	41.043(5)	18.326(4)
β, deg	112.375(8)	101.777(3)
V, Å^3	14353(4)	4365.6(17)
Z	4	4
ρ_{calc}, g/cm^3	1.283	1.191
μ, mm^{-1}	0.730	0.089
T, K	100	100
transmission range	0.55-0.74	0.56-0.75
unique reflections	24403	9930
parameters/restrains	1785/433	540/0
wR2 (all data)	0.2829	0.1323
R1 [$I > 2\sigma(I)$]	0.1132	0.0483
S (all data)	1.100	1.034

Table S2. Hydrogen bonding in the structure of compound **[H_2L•(Bu_4N)(AcO)•H_2O]**.

D–H···A	D–H (Å)	H···A (Å)	D–A (Å)	D–H···A (º)
N2–H2···O1	0.990(18)	1.824(18)	2.8127(16)	176.2(16)
N4–H4···O1	0.94(2)	1.86(2)	2.7934(17)	171.8(17)
O1W–H1W···N1	0.84(2)	2.08(2)	2.9038(17)	163(2)
O1W–H2W···O2	0.93(2)	1.80(2)	2.7120(18)	169.6(19)

Table S3. Selected bond distances (Å) and angles (º) in the structure of compound **1**.

Mn1–O3	2.064(5)	O3–Mn1–N4	102.5(2)	O2–Mn2N6	173.1(2)
Mn1–N4	2.200(6)	O3–Mn1–O1	130.7(2)	O7–Mn2–N6	88.85(18)
Mn1–O1	2.209(5)	N4–Mn1–O1	107.5(2)	O5–Mn2–N5	93.5(2)
Mn1–N3	2.239(6)	O3–Mn1–N3	113.1(2)	O4–Mn2–N5	95.8(2)
Mn1–N2	2.282(5)	N4–Mn1–N3	72.0(2)	O2–Mn2–N5	87.8(2)
Mn1–O2	2.404(5)	O1–Mn1–N3	112.9(2)	O7–Mn2–N5	173.0(2)
Mn2–O5	2.162(6)	O3–Mn1–N2	94.7(2)	N6–Mn2–N5	98.0(2)
Mn2–O4	2.185(5)	N4–Mn1–N2	142.2(2)	O6–Mn3–N7	101.2(2)
Mn2–O2	2.224(5)	O1–Mn1–N2	84.84(18)	O6–Mn3–N8	108.5(2)
Mn2–O7	2.233(4)	N3–Mn1–N2	70.3(2)	N7–Mn3–N8	72.3(2)
Mn2–N6	2.257(6)	O3–Mn1–O2	92.79(18)	O6–Mn3–O8	139.0(2)
Mn2–N5	2.263(6)	N4–Mn1–O2	80.8(2)	N7–Mn3–O8	101.8(2)
Mn3–O6	2.087(5)	O1–Mn1–O2	55.78(16)	N8–Mn3–O8	110.6(2)
Mn3–N7	2.171(6)	N3–Mn1 O2	145.6(2)	O6–Mn3–N9	96.4(2)
Mn3–N8	2.251(5)	N2–Mn1–O2	132.16(19)	N7–Mn3–N9	142.7(2)
Mn3–O8	2.253(5)	O5–Mn2–O4	168.7(2)	N8–Mn3–N9	71.1(2)
Mn3–N9	2.274(6)	O5–Mn2–O2	88.7(2)	O8–Mn3–N9	85.1(2)
Mn3–O7	2.280(4)	O4–Mn2–O2	85.29(18)	O6–Mn3–O7	91.84(18)
Mn1⋯Mn2	3.676(4)	O5–Mn2–O7	84.4(2)	N7–Mn3–O7	84.16(18)
Mn1⋯Mn3	7.024(5)	O4–Mn2–O7	85.59(17)	N8–Mn3–O7	151.2(2)
Mn2⋯Mn3	3.607(4)	O2–Mn2–O7	85.46(17)	O8–Mn3–O7	57.55(17)
Mn2–O2–Mn1	105.1(2)	O5–Mn2–N6	94.5(2)	N9–Mn3–O7	128.00(19)
Mn2–O7–Mn3	106.12(18)	O4–Mn2–N6	90.5(2)	Mn1–Mn2–Mn3	149.28(18)
Mn4–O11	2.077(6)	O11–Mn4–N14	100.9(2)	N16–Mn5–O15	85.5(2)
Mn4–N14	2.184(6)	O11–Mn4–N13	110.0(2)	O10–Mn5–O15	86.68(18)
Mn4–N13	2.233(6)	N14–Mn4–N13	72.4(2)	O13–Mn5–N15	90.6(2)
Mn4–O9	2.266(6)	O11–Mn4–O9	137.4(2)	O12–Mn5–N15	95.6(2)
Mn4–O10	2.281(5)	N14–Mn4–O9	105.2(2)	N16–Mn5–N15	98.6(2)
Mn4–N12	2.284(6)	N13–Mn4–O9	109.7(2)	O10–Mn5–N15	89.1(2)
Mn5–O13	2.168(6)	O11–Mn4–O10	93.4(2)	O15–Mn5–N15	175.6(2)
Mn5–O12	2.180(6)	N14–Mn4–O10	84.9(2)	O14–Mn6–N17	99.5(2)
Mn5–N16	2.228(7)	N13–Mn4–O10	149.8(2)	O14–Mn6–O16	137.8(2)
Mn5–O10	2.245(5)	O9–Mn4–O10	56.86(19)	N17–Mn6–O16	104.6(2)
Mn5–O15	2.288(5)	O11–Mn4–N12	94.1(2)	O14–Mn6–N18	111.2(2)
Mn5–N15	2.300(6)	N14–Mn4–N12	143.0(2)	N17–Mn6–N18	71.9(2)
Mn6–O14	2.066(5)	N13–Mn4–N12	70.7(2)	O16–Mn6–N18	109.0(2)
Mn6–N17	2.190(7)	O9–Mn4–N12	84.8(2)	O14–Mn6–N19	96.7(2)
Mn6–O16	2.202(5)	O10–Mn4–N12	128.0(2)	N17–Mn6–N19	142.6(2)
Mn6–N18	2.244(6)	O13–Mn5–O12	167.5(2)	O16–Mn6–N19	84.6(2)
Mn6–N19	2.276(6)	O13–Mn5–N16	92.9(2)	N18–Mn6–N19	70.8(2)
Mn6–O15	2.357(4)	O12–Mn5–N16	96.8(2)	O14–Mn6–O15	93.54(18)
Mn4⋯Mn5	3.621(4)	O13–Mn5–O10	86.5(2)	N17–Mn6–O15	81.5(2)
Mn4⋯Mn6	7.025(5)	O12–Mn5–O10	82.7(2)	O16–Mn6–O15	57.37(16)
Mn5⋯Mn6	3.693(4)	N16–Mn5–O10	172.2(2)	N18–Mn6–O15	146.0(2)
Mn5–O10–Mn4	106.2(2)	O13–Mn5–O15	87.87(19)	N19–Mn6–O15	130.9(2)
Mn5–O15–Mn6	105.33(19)	O12–Mn5–O15	85.1(2)	Mn4–Mn5–Mn6	147.68(18)

Table S4. Hydrogen bonding between $[Mn_3]_2$ pairs in the structure of **1**.

D–H···A	D–H (Å)	H···A (Å)	D–A (Å)	D–H···A (º)
N1–H1B···O16	0.88	1.97	2.834(7)	166.0
N10–H10A···O9	0.88	1.93	2.781(8)	161.1
N11–H11C···O8	0.88	1.88	2.716(7)	158.6
N20–H20B···O1	0.88	1.93	2.782(8)	161.9

Table S5. Inter-centroid distances of the eight main donor/acceptor π···π interactions within the $[Mn_3]_2$ pairs in the structure of **1** together with the closest interatomic distances between the rings of interest. See Figure S2 for labelled centroids.

(*Cd,Cd’*)	*Cd*···*Cd* (Å)	C/N···C/N	C/N···C/N (Å)
Cd9···Cd10	4.363	C81···C58	3.459
Cd7···Cd8	3.934	C65···C98	3.353
Cd5···Cd6	4.460	C121···N15	3.501
Cd3···Cd4	4.340	C131···C103	3.299
Cd1···Cd2	3.702	C7···C134	3.278
Cd15···Cd16	3.686	C18···C145	3.275
Cd13···Cd14	4.077	C49···C21	3.236
Cd11···Cd12	4.191	C51···C23	3.260

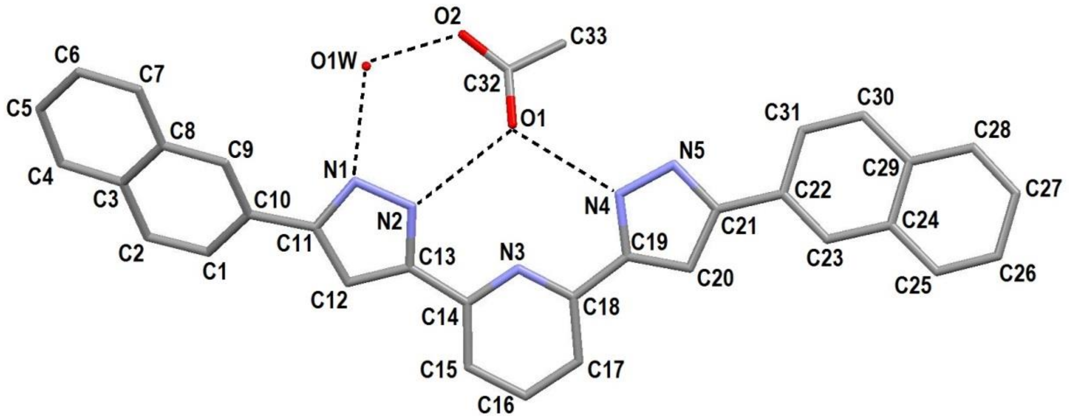

Figure S1. Labelled representation of the AcO^{-}, H_2O and H_2L components of the compound $[H_2L\bullet(Bu_4N)(AcO)\bullet H_2O]$, emphasizing the H-bonding interactions as dashed lines. Hydrogen atoms are not shown.

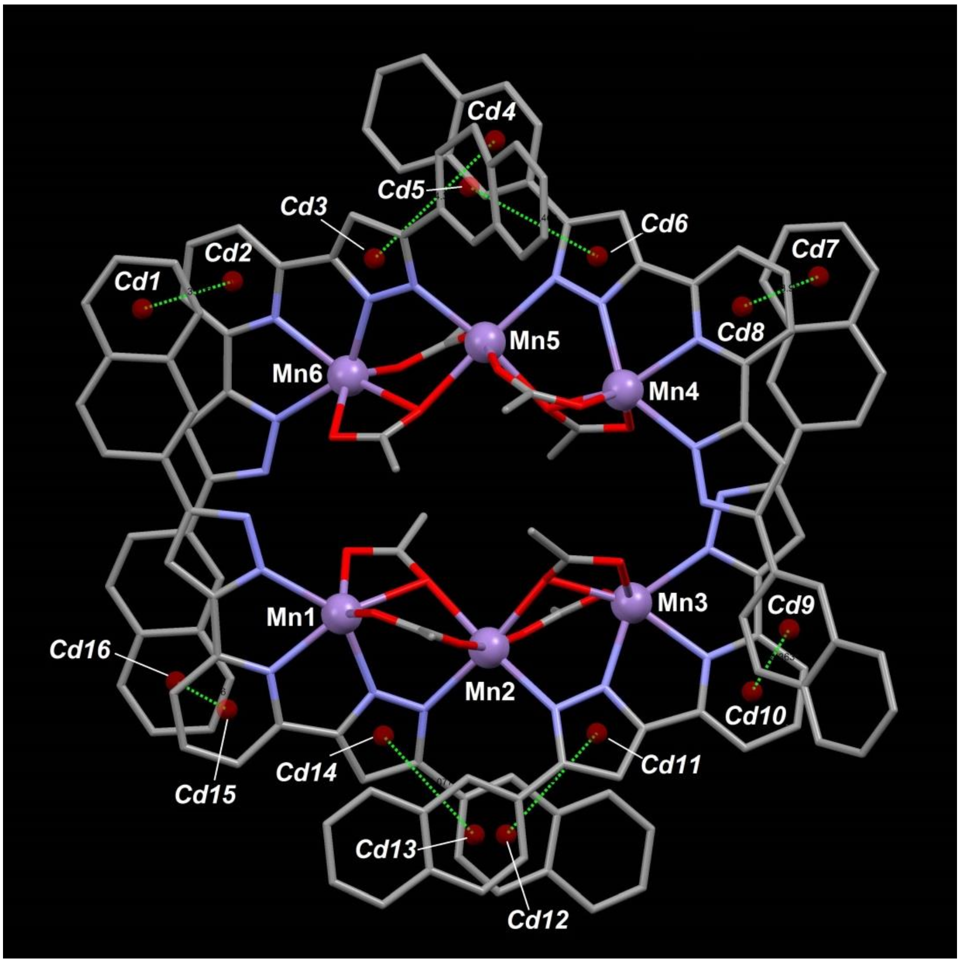

Figure S2. Representation of two linked molecules of [$Mn_3(AcO)_4(HL)_2$] (**1**), emphasizing the eight most important donor/acceptor intermolecular π···π interactions. Only centroids and metal atoms are labelled (See Table S4 for inter-centroid distances). Oxygen is in red, nitrogen is purple, carbon is grey and hydrogen atoms are not shown.

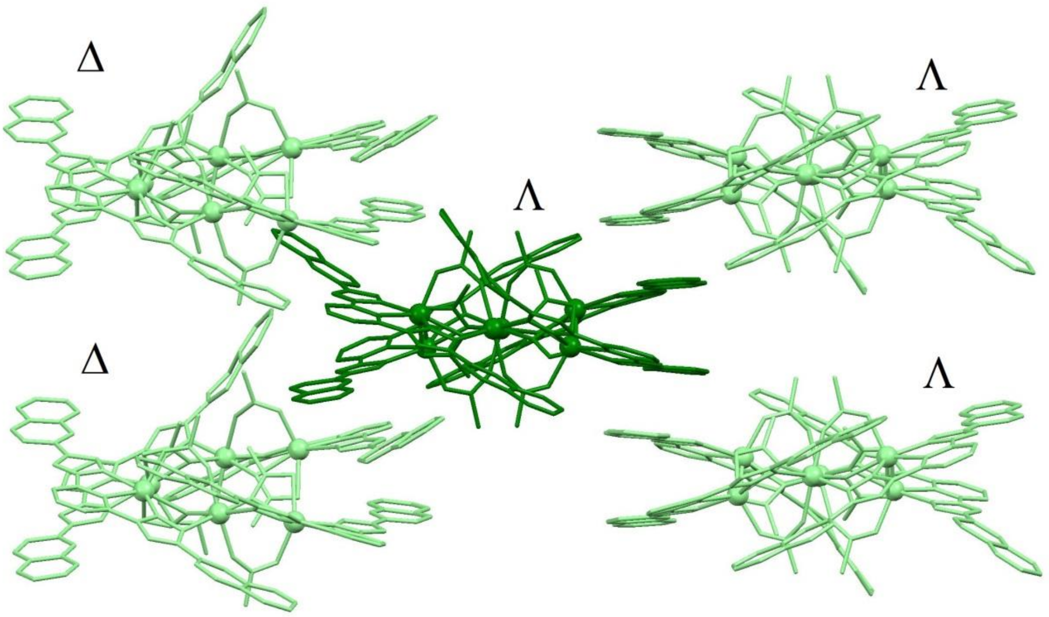

Figure S3. Representation of the intermolecular interactions established between each $[Mn_3]_2$ dimers of **1** and its four first-neighbors, showing that each dimeric assembly interacts with two such entities of the same chirality on one side and with two of opposite chirality on the opposite side. This view shows that the interaction between species of the same chirality is more efficient than the contacts between systems of opposite chirality.

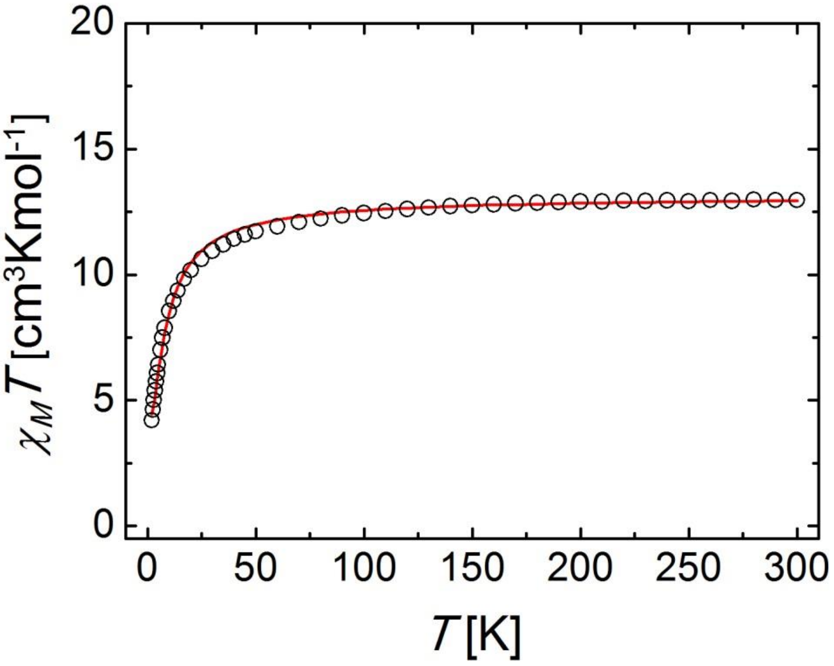

Figure S4 Plot of χT *vs* T for per mole of **1**. The solid line is a fit to the experimental data using the Van Vleck equation (see text). The data have been previously corrected for diamagnetic contributions and temperature independent paramagnetism.

[1] R. W. Saalfrank, V. Seitz, F. W. Heinemann, C. Gobel and R. Herbst-Irmer, *J. Chem. Soc., Dalton Trans.*, 2001, 599-603.
[2] D. Aguilà, L. A. Barrios, F. Luis, A. Repollés, O. Roubeau, S. J. Teat, G. Aromí, *Inorg. Chem*., 2010, 49, 6784-6786.
[3] J. B. Vincent, K. Folting, J. C. Huffman, G. Christou, *Inorg. Chem*., 1986, 25, 996 –999.
[4] SAINT and SADABS, Bruker AXS Inc., Madison, Wisconsin, USA
[5] G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2008, 64, 112–122.
[6] G. M. Sheldrick, SHELXTL, Bruker AXS Inc., Madison, Wisconsin, USA
[7] A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands), 2008.
[8] A. L. Spek, *J. Appl. Crystallogr.* 2003, 36, 7–13