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Electronic Supplementary Material (ESI) for

$Na_2Mn^{III}{}_6Ln^{III}$ clusters with non-equivalent core: chiral vs. meso isomerism.

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Syntheses and methods.

H_2L ligand: A solution 0.073 M of the ligand was previously prepared following the procedure: 3.64 mmols (0.5 g) of (*R*, *S* or Rac)-2-phenylglycinol and 3.64 mmols (0.55g) of 2-hydroxy-3-methoxybenzaldehyd in 20 mL of methanol. The yellow mixture was refluxed for 1 h and flushed to 50 mL with methanol.

{Na_2Mn_6Ln} clusters: All complexes can be prepared following the same method. $LnCl_3 \cdot xH_2O$ (0.243 mmols) and $MnCl_2 \cdot 4H_2O$ (0.243 mmols, 0.048g) were dissolved in 20 mL of acetonitrile and stirred for 15 minutes. After that, 10 mL of the ligand solution (0.73 mmols) and NaOH (0.365 mmols, 0.015 g) were added. The resulting mixture was stirred at room temperature for 24 hours and filtered. The resulting solution was layered with diethyl ether and dark brown crystals were obtained after a few days.

Meso clusters shown to be more soluble than the chiral ones and give in all cases smaller crystals.

Anal. Calc/found: 1Rac, C46.39/46.9; N 3.28/3.36; H 4.33/4.1. 1R, C45.73/45.1; N 3.33/3.24; H 4.16/4.32. 1S, C45.59/46.2; N 3.22/3.12; H 4.44/4.13. 2S, C41.38/42.1; N 2.95/2.88; H 4.39/4.47. 3Rac, C47.23/46.9; N 3.29/3.41; H 4.34/4.40. 3S, C46.18/46.8; N 3.33/3.43; H 4.36/4.20.

An experiment with an excess of one the enantiomers was performed to check the if the chiral or the centrosymmetric cluster is preferred by the system. A mixture with ratio (*Rac*)-H_2L : (*S*)-

H_2L: $MnCl_2$: $Gd(NO_3)_3$: NaOH of 4:1:3:3:5 yields small crystals that crystallographically proved to be the **3*Rac*** complex. (*R*-3 space group, cell parameters 19.354(1); 19.354(1);28.443(2) Å)

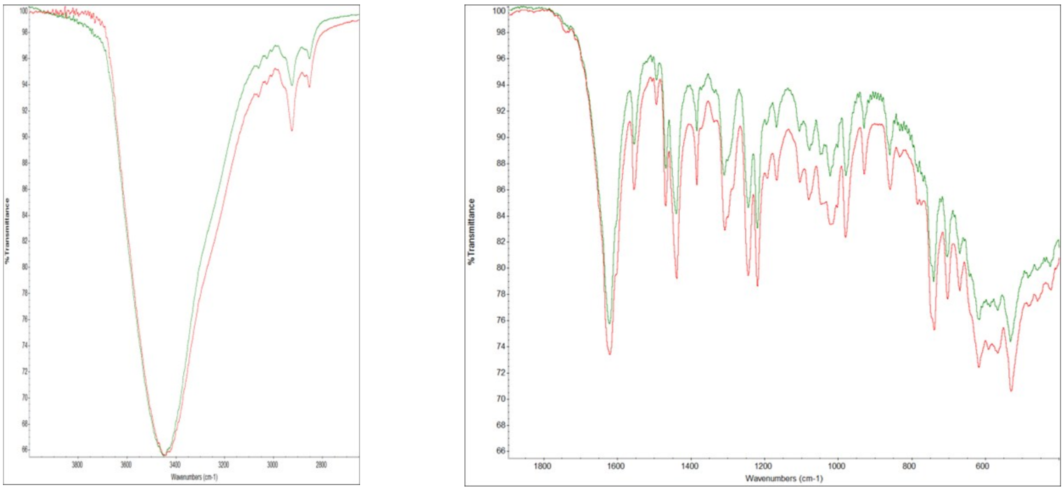

Fig. S1. As can be expected from the similar subunits and analogous coordination of the Schiff base, the IR spectra of the whole series of complexes do not show differences between them. As representative spectra, **3*S*** (red) and **3*Rac*** (green) are shown.

Instrumental measurements

IR spectra (4000-400 cm-1) were recorded using a Bruker IFS-125 FT-IR spectrometer with samples prepared as KBr pellets. Variable-temperature magnetic studies were performed using a MPMS-5 Quantum Design magnetometer operating at 0.03 T in the 300-2.0 K range. Diamagnetic corrections were applied to the observed paramagnetic susceptibility using Pascal's constants. Analysis of the magnetic data was performed with PHI program. The X-ray intensity data were measured on a D8-Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The final cell constants were based upon the refinement of the XYZ-centroids of reflections above 20 σ(I). Data were corrected for absorption effects using the multi-scan method (SADABS). The structures were solved using the Bruker SHELXTL Software Package, and refined using SHELXL.

Table S1. Crystal data and structure refinement for the *meso* compounds **1*Rac*** and **3*Rac***.

	1*Rac*	**3*Rac***
Formula	$C_{96}H_{110}Cl_6Mn_6N_6Na_2O_{27}Tb$	$C_{100.5}H_{110}Cl_6GdMn_6N_6Na_2O_{25.5}$
FW	2563.16	2555.51
System	Trigonal	Trigonal
Space group	R-3	R -3
a/Å	19.4240(8)	19.4486(6)
b/Å	19.4240(8)	19.4486(6)
c/Å	28.592(1)	28.7046(9)
α/deg.	90	90
β/deg.	90	90
γ/deg.	120	120
V/ Å^3	9342.4(8)	9402.8(7)
Z	3	3
T, K	100(2)	100(2)
λ(MoKα), Å	0.71073	0.71073
ρ_{calc}, g·cm^{-3}	1.367	1.354
μ(MoK$_\alpha$), mm^{-1}	1.349	1.305
R	0.0465	0.0692
ωR^2	0.1229	0.2011

Table S2. Crystal data and structure refinement for the chiral compounds **1*R***, **1*S***, **2*S***, and **3*S***.

	1*R*	**1*S***	**2*S***	**3*S***
Formula	$C_{96}H_{104}Cl_6Mn_6N_6Na_2O_{27}Tb$	$C_{96}H_{115}Cl_6Mn_6N_6Na_2O_{29.5}Tb$	$C_{96}H_{99}Br_6Mn_6N_6Na_2O_{23}Tb$	$C_{96}H_{103}Cl_6GdMn_6N_6Na_2O_{25}$
FW	2521.09	2608.20	2798.72	2486.41
System	Trigonal	Trigonal	Trigonal	Trigonal
Space group	R3	R3	R3	R3
a/Å	19.585(1)	19.5945(5)	19.9312(3)	19.6406(6)
b/Å	19.585(1)	19.5945(5)	19.9312(3)	19.6406(6)
c/Å	28.518(2)	28.3967(7)	28.8052(8)	28.447(1)
α/deg.	90	90	90	90
β/deg.	90	90	90	90
γ/deg.	120	120	120	120
V/ Å^3	9473(1)	9442.1(5)	9909.9(4)	9503.4(7)
Z	3	3	3	3
T, K	100(2)	100(2)	100(2)	100(2)
λ(MoKα), Å	0.71073	0.71073	0.71073	0.71073
ρ_{calc}, g·cm^{-3}	1.326	1.376	1.407	1.303
μ(MoK$_\alpha$), mm^{-1}	1.329	1.338	3.263	1.289
Flack param.	0.06(2)	0.02(2)	0.011(8)	0.02(2)
R	0.0625	0.0477	0.0363	0.0329
ωR^2	0.1844	0.1355	0.0869	0.0904

Table S3. Selected bond distances (Å) and angles (°) for the centrosymmetric compounds **1*Rac*** and **3*Rac***.

	1*Rac* (Ln = Tb^{III})	**3*Rac*** (Ln = Gd^{III})
Ln(1)-O(1)	2.271(3)	2.287(4)
Ln(1)···O(4)		
Ln(1)···O(4)'		
Mn(1)-O(1)	1.899(3)	1.893(4)
Mn(1)-O(2)	1.892(3)	1.893(5)
Mn(1)-O(4)	1.9068(6)	1.9093(9)
Mn(1)-N(1)	1.986(4)	1.982(6)
Mn(1)-Cl(1)	2.601(1)	2.603(2)
Mn(1)-Cl(1)#1	2.695(1)	2.687(2)
Na(1)-O(2)	2.301(3)	2.306(5)
Na(1)-O(3)	2.354(3)	2.378(5)
Na(1)-O(4)	2.912(5)	2.928(9)
Na(1)'-O(4)'	2.912(5)	2.928(9)
O(1)-Ln(1)-O(1)#1	82.36(9)	82.8(1)
O(1)-Ln(1)-O(1)#2	97.65(9)	97.2(1)
Mn(1)-O(1)-Ln(1)	117.5(1)	117.7(2)
Mn(1)'-O(1)'-Ln(1)	117.5(1)	117.7(2)
Mn(1)-O(4)-Mn(1)'	119.975(8)	119.96(2)
Mn(1)-O(2)-Na(1)	110.6(1)	110.8(2)

Table S4. Selected bond distances (Å) and angles (°) for the *meso* clusters **1*R***, **1*S***, **2*S*** and **3*S***.

	1*R* (Ln = Tb^{III}, X = Cl)	**1*S*** (Ln = Tb^{III}, X = Cl)	**2*S*** (Ln = Tb^{III}, X = Br)	**3*S*** (Ln = Gd^{III}, X = Cl)
Ln(1)-O(1)	2.327(8)	2.310(6)	2.320(5)	2.322(6)
Ln(1)-O(4)	2.264(7)	2.282(6)	2.262(5)	2.277(6)
Ln(1)-O(8)	2.738(16)	2.688(11)	2.798(10)	2.694(11)
Ln(1)····O(7)	3.29(1)	3.28(1)	3.33(1)	3.30(1)
Mn(1)-O(1)	1.878(8)	1.901(6)	1.880(5)	1.900(6)
Mn(1)-O(2)	1.871(8)	1.901(6)	1.898(6)	1.902(6)
Mn(1)-O(7)	1.891(1)	1.891(1)	1.893(1)	1.888(1)
Mn(1)-N(1)	1.985(9)	1.987(7)	1.969(6)	1.997(7)
Mn(1)-X(1)	2.685(3)	2.670(3)	2.788(2)	2.673(3)
Mn(1)-X(1)#1	2.645(3)	2.644(3)	2.833(2)	2.648(3)
Mn(2)-O(4)	1.903(8)	1.908(6)	1.909(6)	1.906(6)
Mn(2)-O(5)	1.886(8)	1.890(7)	1.873(6)	1.907(6)
Mn(2)-O(8)	1.926(2)	1.934(1)	1.929(1)	1.936(2)
Mn(2)-N(2)	1.982(9)	1.979(7)	1.970(6)	1.994(6)
Mn(2)-X(2)	2.649(3)	2.639(3)	2.714(2)	2.641(3)
Mn(2)-X(2)#1	2.590(3)	2.594(3)	2.761(2)	2.602(3)
Na(1)-O(5)	2.329(9)	2.311(7)	2.329(6)	2.317(6)
Na(1)-O(6)	2.373(10)	2.362(8)	2.375(8)	2.369(7)
Na(2)-O(2)	2.320(9)	2.313(7)	2.317(6)	2.322(7)
Na(2)-O(3)	2.376(10)	2.383(8)	2.385(7)	2.322(7)
Na(2)-O(7)	2.806(16)	2.812(12)	2.786(10)	2.810(12)
Na(1)···O(8)	3.06(1)	3.10(1)	3.04(1)	3.11(1)
O(4)-Ln(1)-O(4) #1	102.9(2)	103.2(2)	101.2(2)	102.9(2)
O(1)-Ln(1)-O(1)#1	90.6(2)	91.0(2)	89.5(2)	90.6(2)
O(1)-Ln(1)-O(4)	79.8(2)	80.0(2)	80.5(2)	79.8(2)
Mn(1)-O(1)-Ln(1)	124.1(3)	124.0(3)	125.6(2)	124.1(3)
Mn(2)-O(4)-Ln(1)	112.0(4)	111.0(3)	114.0(3)	111.5(3)
Mn(1)-O(7)-Mn(1) #1	119.83(7)	119.85(4)	119.72(5)	119.84(4)
Mn(2)-O(8)-Mn(2) #1	119.5(1)	119.1(1)	119.56(7)	119.1(1)
Mn(1)-O(2)-Na(2)	110.3(4)	109.5(3)	109.4(3)	109.1(3)
Mn(2)-O(5)-Na(1)	111.6(4)	112.2(3)	111.8(3)	111.6(3)

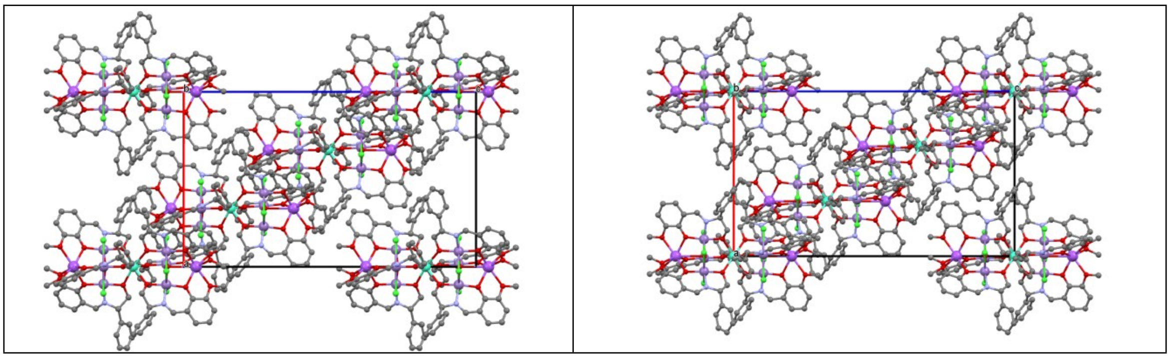

Fig. S2 View along *b* axis of the cell for compounds **3*S*** (left) and **3*Rac*** (right) showing the identical packing of the chiral and racemic isomers.

Magnetic data and fit procedure

The favourable C_3 axis that reduces the number of J constants to only two, allowing reliable fits without overparametrization. However, the anisotropy of the Mn_3 triangles (with slightly different bond parameters for the chiral systems) plays an important role at low temperature that can not be simulated due to the size of the calculations.

The isotropic Hamiltonian derived from the coupling scheme shown in the main text, Fig. 3-inset is :

$$H = -2J_1(S_1{\cdot}S_2 + S_1{\cdot}S_3 + S_2{\cdot}S_3 + S_4{\cdot}S_5 + S_4{\cdot}S_6 + S_5{\cdot}S_6) -2J_2(S_1{\cdot}S_7 + S_2{\cdot}S_7 + S_3{\cdot}S_7 + S_4{\cdot}S_7 + S_5{\cdot}S_7 + S_6{\cdot}S_7)$$

Isotropic fit of the experimental $\chi_M T$ data for the Gd^{III} compounds **3*S*** and **3*Rac*** was performed with PHI program in the 12-300 K range of temperature in order to avoid the low T effects (D, intercluster interactions). Best fit J values were J_1 = 3.4 cm^{-1}, J_2 = -0.19 cm^{-1} for **3*S*** and J_1 = 2.3 cm^{-1}, J_2 = -0.11 cm^{-1} for **3*Rac***. AC measurements do not show out-of-phase signals.

The effect of the anisotropy of the systems is reflected in the magnetization measurements that clearly gives a lower value than the expected for isotropic ions. According the susceptibility measurement, the ground state is formally S = [6-7/2+6] = 17/2. However, the very low Gd···Mn interaction is very low (0.1-0.2 cm^{-1}) and there are a large number of states close to the ground state and thus the fit of the magnetization or reduced magnetization becomes non reliable.

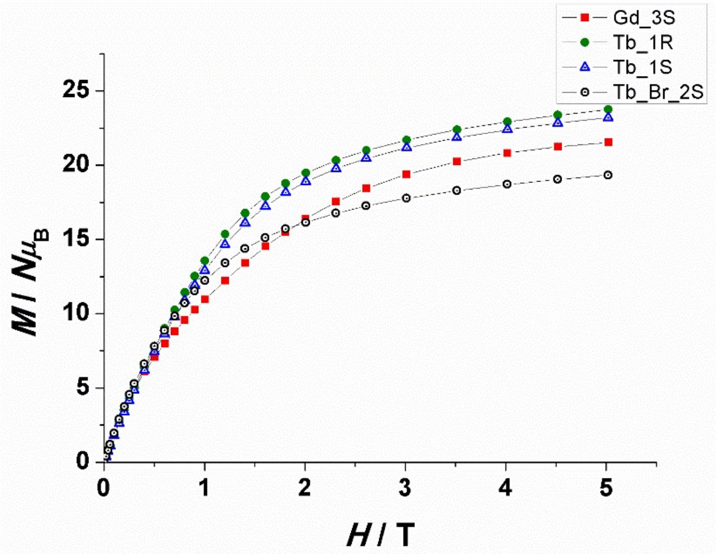

Fig. S3 Magnetization measurements for complexes **1**-**3**.