# Chiral versus non-Chiral [Mn<sup>III</sup><sub>6</sub>Mn<sup>II</sup>Na<sup>I</sup>], [Mn<sup>III</sup><sub>6</sub>Mn<sup>II</sup><sub>2</sub>Na<sup>I</sup><sub>2</sub>] and [Mn<sup>III</sup><sub>3</sub>Mn<sup>II</sup>Na<sup>I</sup>] Clusters Derived from Schiff Bases or the Fight for Symmetry.

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**Abstract:** The reaction in basic media of manganese chloride with Schiff bases derived from the condensation of *o*-vanillin with different chiral/racemic aminoalcohols yielded in a family of complexes where the nuclearity, symmetry and magnetic behavior is controlled by changing the position of the chiral carbon. Chiral and racemic clusters with [Mn<sup>III</sup><sub>6</sub>Mn<sup>II</sup>Na<sup>I</sup>], [Mn<sup>III</sup><sub>6</sub>Mn<sup>II</sup><sub>2</sub>Na<sup>I</sup><sub>2</sub>] and [Mn<sup>III</sup><sub>3</sub>Mn<sup>II</sup>Na<sup>I</sup>] metallic core have been structurally and magnetically characterized. The racemic clusters with an odd number of chiral ligands exhibit the anomalous mixing of ligands with different conformation. Related racemic compounds have been reviewed.

## Introduction

Schiff bases are organic ligands formed by the condensation of a primary amine with a carbonyl group and are also known as imines or azomethines. This family of ligands has been extensively employed in coordination chemistry thanks to the enormous variety of possible precursors available for this condensation which yields in an almost endless number of Schiff bases, allowing the generation of a wide variety of structures with different nuclearity, geometries and coordination with 3d and/or 4f cations. These systems proved to be interesting in many fields of chemistry like catalysis,[1] luminescence[2] or pharmacy.<sup>[3]</sup> Thanks to the above mentioned large amount of synthetic possibilities, the use of Schiff bases as ligands increased exponentially during the past years, with an special use of o-vanillin, recently reviewed by Andruh.[4] The use of ovanillin, combined with some specific aminoalcohols allows the formation of polydentate two-pocket ligands with a O<sub>3</sub>N set of donors which helps in the stabilization of the resulting clusters. The aminoalcohols used for the syntheses of these two-pocket Schiff bases present some advantages in synthetic aspects, like its easy functionalization and the possibility of working with chiral/racemic ligands.

We have been working in recent years in  $Mn^{II,III}$ ,  $Ni^{II}$  and  $Fe^{III}$  chemistry<sup>[5-7]</sup> with the H<sub>2</sub>L1 and H<sub>2</sub>L2 Schiff bases derived from

o-vanillin, Scheme 1, exploring the effect of changing the substituents in the C-atom neighboring the nitrogen in the aminoalcohol. We have observed that this change, even sometimes is apparently small, has a non-innocent effect in the final shape and nuclearity of the clusters. Specifically, in manganese chemistry we realized that there is a characteristic group of Mn<sup>II,III</sup> penta, nona and decanuclear mixed-valent clusters depending on the nature of the substituents in the aminoalcohol and on the alkali or alkaline earth cation present in the reaction media from the salt used as a base for the deprotonation.<sup>[5]</sup> The structures derived from H<sub>2</sub>L1 and H<sub>2</sub>L2 ligands can be divided in four global types named I, II,III and IV (Figure 1).



**Scheme 1**. Ligands derived from the condensation of o-vanillin with different aminoalcohols employed in this work and its common coordination mode.

In all the cases, the clusters form a bipyramidal metallic core (or double bipyramidal for type I and II), with three Mn<sup>III</sup> cations in the equatorial plane and the apical sites occupied by one Mn<sup>II</sup> and one Na<sup>1</sup> cations or in some few cases by two divalent cations such two Mn<sup>II</sup> or one Mn<sup>II</sup> and one Ca<sup>II</sup> depending on the used base for the deprotonation, Figure 1. In all the clusters that we have reported until now the Mn<sup>III</sup> cations are bridged by one  $\mu_3$ -O ligand in the center of the equatorial plane and three  $\mu$ -Cl or µ-Br ligands coordinated in the elongated coordination sites of the trivalent manganese cations.<sup>[5]</sup> Each unit is assembled by ligands in its deprotonated dianionic form, linking the different cations in the coordination mode depicted in Scheme 1. In the case of types-I and II the clusters exhibit a  $C_3$  symmetry, for type-III the clusters are close to the three-fold symmetry while this symmetry is broken in the case of type IV structures because one of the ligands is reversed with respect to the other two (Figure 1). Several type-I and one type-IV systems with a variety of coligands (summarized in ref. 5c), have also been reported by other authors.

Noteworthy, for the enantiopure type I-IV clusters obtained from chiral Schiff bases<sup>[5,8]</sup> in which all the ligands in the molecule are (*R*) or (*S*), the chirality of the ligands is transferred to the metallic centers because all the ligands are tilted in the same direction with respect to the main axis of the molecule, and thus, the helical clusters turn in opposite sense for each enantiomer,  $\Delta$  for (*R*) and  $\Lambda$  for (*S*). This "*chiral at the metal*" transfer has been reported for many complexes in the literature and, even the control of the chirality is still under development, one can say that chirality transfer is the "common" behavior when using enantiopure organic ligands in coordination chemistry.<sup>[9]</sup> The comparison of the reactivity of the chiral *vs* the racemic ligands is uncommon but some few examples in the literature show that the final topology and the physical properties of the chiral *vs*. racemic form of the complexes can be substantially different.<sup>[10]</sup>



**Figure 1.** Representation of the four types of structures derived from H<sub>2</sub>L1 and H<sub>2</sub>L2. The blue bonds indicate the reversed ligands for type-IV.  $C_3$  symmetry axis are shown as green lines. Color key for all figures: Mn<sup>III</sup>, green; Mn<sup>II</sup>, orange; Na<sup>I</sup>, blue; CI, violet; O, red; N, blue; for type-IV divalent cations (Mn<sup>III</sup> or Ca<sup>III</sup>) firebrick.

In the present work, taking advantage of our previous experience with these type of ligands, we decided to play with the chirality of the aminoalcohol precursor by using two different strategies: on one side, we decided to change the position of the chiral carbon, from the carbon atom neighboring the N-donor to the carbon atom neighboring the O-donor to induce steric hindrance on the coordination sphere of the divalent manganese and, on the other hand, to compare the use of chiral ligands with its racemic form. To do this, we have prepared (or completed from our previous publications) series of the racemic (NRac) and chiral derivatives (NR / NS) of the ligands H<sub>2</sub>L1, H<sub>2</sub>L2, H<sub>2</sub>L3 and H<sub>2</sub>L4 (Scheme 1), resulting the complexes  $[Mn^{III}_{6}Mn^{II}Na^{I}_{2}(\mu_{3}-$ O)<sub>2</sub>Cl<sub>6</sub>(L1)<sub>6</sub>] (**1***Rac*), Na[Mn<sup>III</sup><sub>6</sub>Mn<sup>II</sup><sub>2</sub>Na<sup>I</sup><sub>2</sub>( $\mu_3$ -O)<sub>2</sub>( $\mu$ -Cl)<sub>3</sub>Cl<sub>6</sub>(L2)<sub>6</sub>] (2Rac),  $[Mn^{II}_{3}Mn^{II}Na^{I}(\mu_{3}-O)CI_{4}(L3)_{3}]$  (3Rac, 3R and 3S) and  $[Mn^{III}_{3}Mn^{II}Na^{I}(\mu_{3}-O)CI_{4}(L4)_{3}]$  (4Rac). 1R and 1S were previously reported<sup>[5a,c]</sup> and 2R and 2S were recently advanced as communication.[5d]

The reported systems afford the first structurally characterized coordination complexes derived from H<sub>2</sub>L4, the successful octahedral / tetrahedral tailoring of the coordination sphere around the apical Mn<sup>II</sup> cation and the unusual mix in the same cluster of an odd number of chiral ligands with different configuration. The magnetic properties for the new systems **3***Rac* and **4***Rac*, containing tetracoordinate Mn<sup>II</sup> cations, have been studied and correlated with the systems with octahedral Mn<sup>II</sup> environment.

## **Results and Discussion**

#### **Structural Description**

All the reported compounds present a common  $[Mn^{II}_{3}Mn^{II}Na^{I}]$  fragment in which the cations are placed in a trigonal bipyramidal arrangement of three  $Mn^{III}$  cations in the equatorial plane and the other two cations in the apical sites. To avoid repetitive text, the general trends of this unit will be described previously to the specific features of each compound that exhibit isolated  $[Mn^{III}_{3}Mn^{II}Na^{I}]$ , sharing vertex  $[Mn^{III}_{6}Mn^{II}_{2}Na^{I}_{2}]$  or double  $[Mn^{III}_{6}Mn^{II}_{2}Na^{I}_{2}]$  units.

[Mn<sup>III</sup><sub>3</sub>Mn<sup>II</sup>Na<sup>I</sup>(µ<sub>3</sub>-O)(CI)<sub>3</sub>(L)<sub>3</sub>] fragment. The pentanuclear unit is assembled by three Schiff bases in their deprotonated dianionic form linking three different cations (see Scheme 1). In all the cases, one  $\mu_3$ -O donor is placed in the center of the triangle formed for the three Mn<sup>III</sup> cations, slightly displaced from the center of the triangle towards the Na<sup>I</sup> cation. The Mn<sup>III</sup> cations show an axially elongated NO<sub>3</sub>Cl<sub>2</sub> octahedral environment. The elongated coordination sites of the Mn<sup>III</sup> cations lie in the  $\{Mn^{\parallel}_{3}(\mu_{3}-O)\}\$  plane and are occupied by three  $\mu$ -Cl bridges. The divalent manganese cation is fac-linked by the three O-alcoxo donors from the Schiff bases and can coordinate up to three additional ligands to reach hexacoordination. The linkage between the divalent and trivalent manganese ions is provided by three Mn<sup>II</sup>-O<sub>alcoxide</sub>-Mn<sup>III</sup> bridges with bond angles ranging ~115-125° as a function of the Mn<sup>II</sup> coordination. The sodium cation is coordinated by the bidentate fragment formed by the Ophenoxo and the O-methoxide donors in a cavity with intermediate octahedral-triangular prism shape, Table S1. The  $\mu_3$ -O donor weakly interact with the Na<sup>I</sup> cation (distance ~2.7 Å) and formally, the oxo donor could be formally assumed as  $\mu_4$ -O and the environment of the sodium ions as an apicated polyhedron. The L<sup>2-</sup> ligands are tilted with respect with the main axis of the bypiramid, resulting a propeller shape (helicate) that turns right or left as function of the chirality of the ligands. In the same way, the sodium cation exhibits  $\Delta$  or  $\Lambda$  chirality according to the helicity of the molecule. The oxidation state of the manganese cations has been assigned in basis of the bond distances of the coordination polyhedra and bond-valence sum (BVS) calculations, summarized in Table S2.

[Mn<sup>III</sup>6Mn<sup>II</sup>Na<sup>I</sup>2(µ3-O)2CI6(L1)6] (1*Rac*). The nonanuclear [Mn<sup>III</sup><sub>6</sub>Mn<sup>II</sup>Na<sup>I</sup><sub>2</sub>] core of the **1***R* and **1S** pair of enantiomers were included in our previous work,<sup>[5a,c]</sup> so, only the racemic form will be described. The main bond parameters are summarized in Table 1. The type-I 1Rac complex consists of two pentanuclear units sharing the Mn<sup>II</sup> cation which consequently, exhibits an octahedral environment, Figure 2. The 22 positive charges are balanced by the six dianionic Schiff bases, two oxo donors, and six µ-CI bridges linking the axial coordination sites of the Mn<sup>III</sup> cations. The L12- ligands and the MnIII cations in each pentanuclear unit are related by one  $C_3$  axis (*R*-3 space group). Each pentanuclear subunit links three (R)-L12- or three (S)-L12ligands ( $D_{3d}$  molecular symmetry) and are related by an inversion center placed on the Mn<sup>II</sup> cation. The helicity of these pentanuclear fragments turns in opposite sense, and consequently, the tris-bidentate environment of the Na1 and Na1? cations shows opposite  $\Delta$  and  $\Lambda$  configurations. The Mn<sup>III</sup>-O-Mn<sup>III</sup> bond angles are close to 120° and the Mn<sup>II</sup>-O-Mn<sup>III</sup> angles are 124.4(1)°. The  $\mu_3$ -O donors are slightly displaced (0.194 Å) from the center of the triangle towards the Na<sup>1</sup> cations that are placed in a distorted octahedral pocket defined by the O-phenoxide and O-methoxide donors.



racemic form will be presented. The type-II compound **2***Rac* consists of two trigonal-bypiramidal [Mn<sup>III</sup><sub>3</sub>Mn<sup>II</sup>Na<sup>I</sup>] units joined by a triple µ-Cl bridge that links the two Mn<sup>II</sup> cations, Figure 3. Selected bond parameters can be found in Table 1. The 25 negative charges (six dianionic Schiff bases, two oxo donors, six µ-Cl bridges linking the axial coordination sites of the Mn<sup>III</sup> cations and three µ-Cl bridging the Mn<sup>II</sup> cations) are balanced by the six Mn<sup>III</sup>, two Mn<sup>II</sup>, two Na<sup>I</sup> of the cluster and one ionic Na<sup>I</sup> cation. The L2<sup>2-</sup> ligands and the Mn<sup>III</sup> cations in each unit are related by one *C*<sub>3</sub> axis and both moieties of the cluster are related by one additional reflection plane, resulting a *C*<sub>3h</sub> molecular symmetry. As occurs for **1***Rac*, each subunit links three (*R*) or (*S*) ligands and its helicity turns in opposite sense and the Na1 and Na1' cations show opposite  $\Delta$  and  $\Lambda$  configurations.

The divalent manganese cations are placed in an *fac*-MnCl<sub>3</sub>O<sub>3</sub> octahedral environment, whereas the Mn<sup>III</sup> cations exhibit an axially elongated octahedral coordination.



**Figure 3**. Top, labelled core of complex **2***Rac*, bottom, view of the molecular structure, where can be appreciated that there are three (R) ligands in one side of the complex and three (S) ligands in the other side of the complex.

Table 1. Selected interatomic distances (Å) and angles (deg.) for compounds 1Rac and 2Rac

	1Rac	2Rac
Mn(1)-O(4)	1.8862(6)	1.881(2)
Mn(1)-O(1)	1.887(2)	1.897(5)
Mn(2)-O(1)	2.195(2)	2.095(6)
Mn(2)-Cl(2)		2.563(4)
Mn(1)-O(4)-Mn(1')	118.96(4)	118.81(7)
Mn(1)-O(1)-Mn(2)	124.4(1)	121.5(3)
Mn(2)-Cl(2)-Mn(2')		89.9(2)

Figure 2. Top, labelled core of complex 1*Rac*. Down, distribution of the ligands for 1*Rac*. Different colors of the ligands represent different enantiomers.

 $Na[Mn^{II}_{6}Mn^{II}_{2}Na^{I}_{2}(\mu_{3}-O)_{2}(\mu-CI)_{3}CI_{6}(L2)_{6}]$  (2*Rac*). The description of the corresponding chiral complexes 2*R* and 2*S* can be found in a previous communication<sup>[5d]</sup> and only the description of the

 $[Mn^{III}_{3}Mn^{II}Na^{I}(\mu_{3}-O)Cl_{4}(L3)_{3}]$  3*Rac* and 3*R*. Complexes 3*Rac* and 3*R* show similar structures that consist of discrete neutral pentanuclear units in which the 12 positive charges are balanced by three dianionic Schiff bases, one oxo ligans and

four coordinated chloride atoms. The molecular structure is shown in Figure 4 and the main bond parameters are summarized in Table 2.

The main feature of these structures is derived of the position of the chiral carbon, that is now just next to the Oalkoxo donor atom of the aminoalcohol. Due to the steric impediment promoted by the methyl group, the coordination environment around the Mn<sup>II</sup> cannot reach five or six coordination numbers like the previously reported complexes derived from H<sub>2</sub>L1 and H<sub>2</sub>L2<sup>5</sup> and, for a very first time, the environment around this Mn<sup>II</sup> cation is four coordinated. One of the methyl substituents is tilted to provide the adequate space for the chloro ligand that is displaced from the main axis of the molecule towards this extra space. This distortion from the ideal tetrahedron is larger for 3R than for **3***Rac*, and evaluated with SHAPE program<sup>[11]</sup> as  $S(T_d) = 1.05$ and 0.70 respectively. Consequently, the molecule becomes asymmetric and does not possess the usual  $C_3$  symmetry. The Mn<sup>II</sup> ion is linked to the three alcoxo arms of the ligands and one Cl<sup>-</sup> donor in apical position. The Mn<sup>II</sup>-O-Mn<sup>III</sup> bond angles and the Mn<sup>II</sup>-O bond distances are shorter than the systems in which the divalent manganese is hexacoordinated, Table 2.



**Figure 4**. Top, common labelled core for complexes **3***Rac* and **3***R* and the coordination arrangement around Mn(4) compared with the ideal polyhedron. Down, arrangement of the chiral ligands for complex **3***Rac*: (*R*)-L<sup>2</sup>· is plotted in green, (*S*)-L<sup>2</sup>· is plotted in yellow and the bonds depicted in black shows the disordered (*R*)-L<sup>2</sup>·(*S*)-L<sup>2</sup>· ligands.

Table 2. Selected interatomic distances (Å) and angles (deg.) for compounds 3Rac, 3R and 4Rac.

		3Rac	3R	4Rac
	Mn(1)-O(10)	1.899(3)	1.900(3)	1.884(3)
	Mn(2)-O(10)	1.893(3)	1.898(3)	1.889(3)
	Mn(3)-O(10)	1.906(3)	1.898(2)	1.905(3)
	Mn(1)-O(1)	1.910(3)	1.919(3)	1.910(3)
	Mn(2)-O(4)	1.899(3)	1.891(2)	1.903(3)
	Mn(3)-O(7)	1.904(3)	1.911(3)	1.928(3)
	Mn(4)-O(1)	2.051(3)	2.040(3)	2.083(3)
	Mn(4)-O(4)	2.047(4)	2.036(3)	2.081(3)
	Mn(4)-O(7)	2.052(3)	2.045(2)	2.088(3)
	Mn(4)-Cl(4)	2.308(2)	2.310(1)	2.312(1)
	Mn(1)-O(10)-Mn(2)	119.0(2)	118.2(1)	120.1(1)
4	Mn(1)-O(10)-Mn(3)	118.4(2)	118.981)	119.5(1)
	Mn(2)-O(10)-Mn(3)	121.8(2)	122.0(1)	120.2(1)
	Mn(1)-O(1)-Mn(4)	112.2(2)	112.9(1)	114.2(1)
	Mn(2)-O(4)-Mn(4)	113.2(2)	115.0(1)	114.3(1)
	Mn(3)-O(7)-Mn(4)	113.7(2)	114.1(1)	113.7(1)
	O(1)-Mn(4)-O(4)	107.8(1)	105.9(1)	108.1(1)
	O(1)-Mn(4)-O(7)	103.0(2)	102.9(1)	101.9(1)
	O(4)-Mn(4)-O(7)	106.9(2)	106.9(6)	102.0(1)
	O(1)-Mn(4)-Cl(4)	119.4(1)	122.66(8)	114.24(8)
	O(4)-Mn(4)-Cl(4)	108.6(1)	103.85(4)	103.63(9)
	O(7)-Mn(4)-Cl(4)	110.5(1)	113.62(8)	125.45(8)

The **3***Rac* complex shows a rare feature: one of the Schiff bases shows the (*R*)-L3<sup>2-</sup> configuration, one of the Schiff bases shows the (*S*)-L3<sup>2-</sup> configuration and the third one is disordered between the two configurations and then, the structure should contain an equivalent number of disordered (*RRS*) and (*SSR*) molecules. The lack of molecular symmetry combined with the 2:1 arrangement of chiral ligands excludes the inversion centers or reflection planes in the network and despite to be racemic, **3***Rac* crystallizes in the chiral P212121 group.

 $[Mn^{III}_{3}Mn^{II}Na^{I}(\mu_{3}-O)Cl_{4}(L4)_{3}]$  (4*Rac*). The structure of 4*Rac* contains the discrete pentanuclear  $[Mn^{III}_{3}Mn^{II}Na^{I}]$  core in a trigonal bipyramidal arrangement, Figure 5. The main bond parameters are summarized in Table 2. Charge balance, coordination sphere of the cations and bond parameters are similar to those found in complexes 3*Rac* and 3*R*.

The system shows also the mixing of (R) and (S) Schiff bases in the same molecule but in this case the two (RRS) and (SSR) enantiomers are well defined and related between them in the network by inversion centers (P-1 space group). One of the phenyl groups, (the (S) for (RRS) and the (R) for the (SSR) cluster) is tilted minimizing the repulsions with the chloro ligands which is displaced towards the extra space. The larger hindrance produced by the phenyl groups produces a larger distortion of the tetrahedral environment around Mn4, parametrized as  $S(T_d) = 1.30$ . The two chiral (*RRS*) and (*SSR*) molecules show a helical arrangement of the ligands, turning in opposite sense ( $\Delta$  or  $\Lambda$  respectively) and consequently the environment of the sodium cations becomes chiral centers with opposite conformation.



**Figure 5**. Top, a view of the molecular cluster and the core of **4***Rac*. Bottom, a view of both enantiomers found in the network.

Nuclearity vs. ligand. The studied H<sub>2</sub>L Schiff bases, reacting in the same conditions, give in all cases the [Mn<sup>III</sup><sub>3</sub>Mn<sup>II</sup>Na<sup>I</sup>] fragment, independently of the substituents attached on the Catoms of the aminoalcohol. However, these substituents are not innocent and determine the nuclearity of the final complexes, resulting in pentanuclear clusters for L3<sup>2-</sup> and L4<sup>2-</sup>, nonanuclear clusters for L1<sup>2-</sup> and decanuclear systems for L2<sup>2-</sup>. The Mn<sup>II</sup> cation is coordinated in fac- arrangement by three O-alcoxo donors from the three Schiff bases and the remainder coordination sites must be fulfilled by additional ligands. The possibilities reported until now have been to complete the coordination sphere with solvent molecules or counteranions, (resulting in discrete [Mn<sup>III</sup><sub>3</sub>Mn<sup>II</sup>Na<sup>I</sup>] clusters<sup>[5c]</sup> as occurs in type-III and -IV complexes), to reach an octahedral environment sharing the Mn<sup>II</sup> cation and coordinating six O-alcoxo donors from six Schiff bases (as occurs in type-I complexes) or sharing two units by means of triple bridges such  $\mu_{1,1}$ -N<sub>3</sub><sup>-</sup> or halides<sup>[5d,8b,12]</sup> (as occurs in type-II systems). In these cases, the open face of the coordination polyhedron of the Mn<sup>II</sup> cation tends to hexacoordination and lower coordination numbers are exceptional. The strategy to reach tetracoordination around the Mn<sup>II</sup> cation has been to employ spherical ligands with a relatively large radius such halides and to increase the steric hindrance with methyl or phenyl substituents placed on the carbon atom closer to the O-donor. By the other hand, the large hindrance promoted by the methyl or phenyl groups blocks the growing to

larger nuclearities sharing the divalent manganese, determining the lower [Mn<sup>III</sup><sub>3</sub>Mn<sup>II</sup>Na<sup>I</sup>] nuclearity for L3<sup>2-</sup> and L4<sup>2-</sup> ligands. The successful characterization of complexes **3** and **4** demonstrates that the coordination sphere of this cation can be tailored employing the adequate ligands.

Racemic vs. chiral ligands: chirality transfer. The syntheses of complexes employing a racemic mixture of chiral ligands usually produce the simultaneous coordination of both enantiomers to the same molecule related by inversion centers or reflection planes (implicitly, it means a pair number of ligands), the two enantiopure complexes in the network related by inversion centers or reflection planes or, in some less common cases, the spontaneous resolution of enantiomerically pure isomers in separate crystals. For an odd number of chiral centers, it is generally accepted that the mixing of different conformations is not adequate and thus, the possibilities are reduced to enantiopure complexes related in the network by symmetry or its spontaneous resolution. This paradigm is closely related to basic concepts such chiral recognition or enantioselectivity.<sup>[13]</sup> The configuration of enantiopure chiral clusters is determined usually by the conformation of the chiral ligands due to the well-known transference of chirality phenomenon. In fact, chirality is transferred from the chiral ligands to the coordination sphere of the cations, to the overall complex or the crystalline network. This "predetermined chirality" turns the structural or optical properties in opposite sense for each enantiomer, resulting in mirror image clusters or networks.<sup>[14]</sup>

In agreement with the usual features observed for the clusters obtained from racemic ligands such as **3***Rac* and **4***Rac*, it should be expected the presence of two (*RRR*) and (*SSS*) enantiomers in the network or its spontaneous resolution but surprisingly, the (*RRS*) and (*RRS*) enantiomers were characterized, both in the same unit cell. This feature is extremely rare because it means that the most stable conformation for the reported chiral clusters goes against the rules that usually control the arrangement of chiral centers.

The L3<sup>2-</sup> ligands are tilted respect to the main molecular Mn<sup>II</sup>-( $\mu_3$ -O)-Na<sup>I</sup> axis resulting in a propeller shape for the whole molecules, that can be properly described as helicates. As can be observed for the clearest example provided by **4***Rac*, the ligand in 2:1 ratio dominates the transference of chirality and thus, the (*RRS*) molecule turns  $\Delta$  whereas the (*SSR*) enantiomer turns  $\Lambda$ , Figures 5 and 6. As consequence of this arrangement the Na<sup>I</sup> cations become chiral centers with opposite  $\Delta/\Lambda$  configuration.

In light of the unusual configuration of complexes **3***Rac* and **4***Rac*, we have reviewed the configuration of related racemic type-III systems, reported in the CCDC database with the same topology and odd number of chiral Schiff bases. The first conclusion that can be extracted from the data summarized in Table 3 is that this phenomenon, despite that has not been pointed out until now, is more common that the expected.



Figure 6. Top, space-fill view showing the opposite helicity for 4RRS and 4SSR molecules in 4Rac. Down, arrangement of the bidentate fragments around the Na<sup>I</sup> cations.

In fact, only 5 over 15 of the complexes show the conventional (*RRR*) / (*SSS*) pair of pure enantiomers related by symmetry elements in the network with opposite  $\Delta/\Lambda$  helicity and chirality for the Na<sup>I</sup> cation, whereas the remainder complexes show the mixing of (*R*) / (*S*) Schiff bases. With the exception of the well-defined (*RRS*) / (*SSR*) complex SINDAW<sup>[20]</sup> obtained from H<sub>3</sub>L6 (Scheme 2), the most of the complexes show one (*R*), one (*S*)

and one disordered or crystallographically ambiguous Schiff base, resulting (*RS?*) / (*SR?*) or two ligands with the same configuration and the third one crystallographically undefined resulting (*RR?*) / (*SS?*). In one case (XIJLUZ),<sup>[17]</sup> all the ligands are not well defined, and the chiral C-atom appears crystallographically planar instead tetrahedral as consequence of the disorder.



Scheme 2. Chiral (\*) or pro-chiral (\*\*) ligands referenced in the chirality transfer section and key for the XYZ ligands summarized in Table 3.

CCDC Code	Metallic Core	Schiff base	Mn <sup>⊪</sup> Axial XYZ bridges	Configuration	Ref.
EQEWIH	Mn <sup>⊪</sup> ₃Ca <sup>⊪</sup> Na <sup>ı</sup>	H₃L7	(μ11-N3)2 / μ11-N3 / (μ13-N3)	(RRR) / (SSS)	16
XIJMIO	Mn <sup>⊪</sup> ₃Mn <sup>⊪</sup> Na <sup>i</sup>	H₃L7	H <sub>2</sub> O / H <sub>2</sub> O / PhCOO	(RRR) / (SSS)	17
RILYUI	Mn <sup>⊪</sup> ₃Mn <sup>⊪</sup> Na <sup>i</sup>	H₃L7	(μ11-N3)2 / μ11-N3 / (μ11-N3)	(RRR) / (SSS)	18
WIMZID	Mn <sup>⊪</sup> ₃Mn <sup>⊪</sup> Na <sup>i</sup>	H₃L7	SCN / SCN / SCN	(RRR) / (SSS)	19
SINDAW	Mn <sup>iii</sup> Ln <sup>iii</sup> Na <sup>i</sup>	H₃L6	(Me) <sub>3</sub> CCOO) <sub>2</sub> / (Me) <sub>3</sub> CCOO) <sub>2</sub> / $\mu_{11}$ -N <sub>3</sub>	(RRS) / (SSR)	20
LIQXOA	Mn <sup>⊪</sup> ₃Mn <sup>⊪</sup> Na <sup>i</sup>	H₃L7	CI / CI / CI	(RR?) / (SS?)	21
XIJMAG	Mn <sup>⊪</sup> ₃Mn <sup>⊪</sup> Na <sup>i</sup>	H <sub>3</sub> L7	(μ11-N3)2 / μ11-N3 / (μ13-N3)	(RR?) / (SS?)	17
RILZAP	Mn <sup>⊪</sup> ₃Mn <sup>⊪</sup> Na <sup>i</sup>	H <sub>3</sub> L7	(μ11-N3)2 / μ11-N3 / (μ13-N3)	(RR?) / (SS?)	18
RILZUJ	Mn <sup>⊪</sup> ₃Mn <sup>⊪</sup> Na <sup>i</sup>	H₃L7	$H_2O$ / $H_2O$ / PhCOO	(RR?) / (SS?)	18
MEJKAO	Mn <sup>⊪</sup> ₃Mn <sup>⊪</sup> Ca <sup>⊪</sup>	H <sub>2</sub> L3	CI / CI / MeCOO	(RS?) / (SR?)	22
MEJKES	Mn <sup>⊪</sup> ₃Mn <sup>⊪</sup> Na <sup>i</sup>	H <sub>2</sub> L3	( $\mu_{11}$ -N <sub>3</sub> ) <sub>2</sub> / $\mu_{11}$ -N <sub>3</sub> / MeCOO	(RS?) / (SR?)	23
WIMBIF	Mn <sup>⊪</sup> ₃Mn <sup>⊪</sup> Na <sup>i</sup>	H <sub>3</sub> L7	CI / CI / CI	(RS?) / (SR?)	19
EQEWED	Mn <sup>⊪</sup> ₃Mn <sup>⊪</sup> Na <sup>i</sup>	H <sub>3</sub> L7	CI / CI / $\mu_{11}\text{-}N_3$	(R??) / S??)	16
XIJLUZ	Mn <sup>⊪</sup> ₃Mn <sup>⊪</sup> Na <sup>i</sup>	H₃L7	MeCOO / MeCOO / MeCOO	??? / ???	17

The complexes type-I and II offer the possibility to check what it happens if the system has the option to be as symmetric as possible and thus we prepared the complexes 1Rac and 2Rac. In both cases the systems adopts the "conventional" (RRR) / (SSS) arrangement conformation with one inversion center on the Mn<sup>II</sup> cation for **1 Rac** or one reflection plane between the two pentanuclear subunits for 2Rac, Figures 2 and 3. It is very interesting the comparison with the corresponding enantiomerically pure 1R/1S or 2R/2S complexes in which the imposed absence of the inversion or reflection symmetry elements promotes a considerable asymmetrization of the molecules, with different bond parameters for each pentanuclear subunit and some degree of chirality transfer to the Mn<sup>II</sup> cations in the case of 1R/1S. However, the system analogous to 2Rac derived from H<sub>2</sub>L5 and  $\mu_{11}$ -N<sub>3</sub> bridges between the Mn<sup>II</sup> cations (PIZLAO)<sup>[12b]</sup> shows one (RRS) and one (SSR) moieties and the non-identical but close system with a pair number of H<sub>2</sub>L3 ligands BOGCUX.<sup>[15]</sup> formed by two pentanuclear units linked by two Mn<sup>II</sup>-( $\mu_{13}$ -N<sub>3</sub>)-Mn<sup>III</sup> bridges, shows one (*RRS*) and one (*SSR*)

the molecule. From this set of experimental data, some conclusions and unsolved questions emerge. On one side, the "anomalous" arrangement of chiral ligands in this kind of systems has been systematically found for the derivatives of H<sub>2</sub>L1 and H<sub>2</sub>L3. This feature could be attributed to the relative position of one of the Me- or Ph- substituents that helps to minimize the repulsions with the chloro ligand (Figures 4 and 5). In contrast, becomes hard to explain the random distribution of "normal" and "anomalous" configurations for the ligands with the chiral center closer to the N-atom, for which the steric hindrance becomes irrelevant. Other factors as could be differences derived from the strong distortions induced by the size and bite of the XYZ substituents, Scheme 2 and Table 3, do not seem relevant if we compare systems with the same Schiff base and XYZ ligands such EQEWIH-RILYUI vs. XIJMAG or XIJMIO vs. RILZUJ. In general, the nature tends to be symmetric in all the cases where this is possible, but sometimes, as has been shown in the present paper, the best way to reach stability is apparently being not symmetric.

moieties related by an inversion center placed in the center of

#### Electronic circular dichroism.

Complex 3R was structurally determined but adequate crystals were not obtained for its 3S enantiomer. However, ECD spectroscopy is an efficient technique to characterize pairs of enantiomers that must give mirror-image spectra in all the range of wavelengths. In fact, 3R exhibit positive Cotton effect at 249 nm, negative peaks at 225, 303 nm and broad minimums around 380 and 430 nm, vanishing the absorptions for larger wavelengths up to 800 nm and 3S shows exactly the reversed spectrum. The spectra of complexes 2R and 2S is very similar attending to the fact that ligands L22- and L32- have alkylic substituents that do not contribute to the  $\pi$  system of the ligands and thus do not modify the spectra in the high energy region, Figure 7. Comparison with the previously reported spectra for related complexes derived from H<sub>2</sub>L1 shows characteristic differences attributable to absorptions of the phenyl groups of the organic ligand at higher energies and similar transitions at lower energies related with the chiral cationic centers.[5c]



Figure 7. ECD spectra for the pair of enantiomers 2R / 2S and 3R / 3S.

#### **Magnetic properties**

The magnetic response for the type-I complexes **1** with S = 19/2 ground state was previously described and the reader can find a complete description in reference 5c.

 $\chi_M T$  vs. T plot for complexes **3Rac** and **4Rac** show room temperature  $\chi_M T$  values of 12.6 and 12.3 cm<sup>3</sup>·mol<sup>-1</sup>·K respectively, slightly lower than the expected values for three Mn<sup>III</sup> and one Mn<sup>II</sup> non-interacting cations (13.375 cm<sup>3</sup>·mol<sup>-1</sup>·K for g = 2.00). On cooling, complex **3***Rac* shows an almost constant value  $\chi_M T$  value in the 300-125 K range and for lower temperatures, it decreases continuously reaching a value of 4.94 cm<sup>3</sup>·mol<sup>-1</sup>·K at 2 K, whereas for **4Rac**  $\chi_M T$  increases up to a maximum value of 13.7 cm<sup>3</sup>·mol<sup>-1</sup>·K at 50 K followed by a continuous decrease down to a 6.45 cm<sup>3</sup>·mol<sup>-1</sup>·K at 2 K, Figure 8. The system is expected to be anisotropic due to the presence of Mn<sup>III</sup> cations and the low temperature region can be influenced by the axial zero field splitting effect (D) or intercluster interactions (z'J'). However, the D and z'J' parameters are strongly correlated and usually fits of the  $\chi_M T$  data give poorly reliable values of D in contrast with the reduced magnetization measurements which allow more precise information about the anisotropy of the ground state. On this basis, the coupling constants values have been obtained from the fit using the isotropic Hamiltonian of the experimental  $\chi_M T$  data in the range 300-20 K in order to minimize the D and intercluster effects and, after that, the D parameter has been calculated separately from magnetization measurements. A comparative different kind of fits and the corresponding Hamiltonian can be found in Table S3. In light of the similar bond parameters between the paramagnetic cations in the bridging region and according to Scheme 3, the derived two-J Hamiltonian, with a common Jconstant for each Mn<sup>III</sup>-O-Mn<sup>III</sup> or Mn<sup>III</sup>-O-Mn<sup>II</sup> pathways, is:

$$H = -2J_1(S_1 \cdot S_2 + S_2 \cdot S_3 + S_1 \cdot S_3) - 2J_2(S_1 \cdot S_4 + S_2 \cdot S_4 + S_3 \cdot S_4)$$

Fit of the experimental data in the 300-20 K range gave an excellent fit for the parameters  $J_1 = 3.70(1) \text{ cm}^{-1}$ ,  $J_2 = -2.36(1) \text{ cm}^{-1}$ , g = 1.937(1) for **3***Rac* and  $J_1 = 3.02(1) \text{ cm}^{-1}$ ,  $J_2 = -0.97(1) \text{ cm}^{-1}$ , g = 1.885(1) for **4***Rac*.

The calculated energy of the spin levels shows an isolated S = 7/2 ground state with a gap of 21 and 8.7 cm-1 to the first S = 9/2 excited state for **3***Rac* and **4***Rac* respectively. The 7/2 ground state is then the result of the antiferromagnetic interaction of the Mn<sup>II</sup> (S = 5/2) with the local S = 6 from the

ferromagnetic Mn<sup>III</sup><sub>3</sub> triangle. This value is confirmed by the magnetization measurement that tends to an non saturated values of 5.9 (3Rac) or 6.3 N $\mu_{B}$  (4Rac) under the maximum applied field of 5 T, in agreement with data reported for related  $[Mn^{III}_{3}Mn^{II}Na^{I}]$  systems with  $S_{T} = 7/2$ . These values are close to the expected ones for seven electrons assuming the g values around 1.90 calculated from the susceptibility measurements (~6.5 N $\mu_{B}$ ). The isotropic fit of the magnetization plots was not possible as can be expected for anisotropic systems and fit of the data as an isolated 7/2 spin was satisfactory for D values close to -0.5 cm<sup>-1</sup>. To have a more precise values, the reduced magnetization were measured for the two compounds, resulting D values of -0.58(2) and -0.72(3) cm<sup>-1</sup>, Figure S1. These D values allow to low DS2-1/4 possible barriers for the reversal of the magnetization around 7-8 cm<sup>-1</sup> and alternated current measurements do not show out-of-phase signals above 2 K, probably as a consequence of the unfavorable arrangement of easy the axis.



Figure 8.  $\chi_M T$  vs. T plot for complexes **2**R (diamonds), **3**Rac (circles) and **4**Rac (squares). Solid lines show the best fit of the experimental data

The representative  $\chi_M T$  vs. T plot for 2R show a room temperature value of 20.8 cm<sup>3</sup>·mol<sup>-1</sup>·K, lower than the expected value for six Mn<sup>III</sup> and two Mn<sup>II</sup> non interacting cations (26.75 cm<sup>3</sup>·mol<sup>-1</sup>·K for g = 2.00). On cooling, the  $\chi_M T$  value decreases continuously down to 3.60 cm<sup>3</sup>·mol<sup>-1</sup>·K at 2 K with a faster decrease below 25 K, Figure 8.

Fit of the experimental data was performed as two {Mn<sub>4</sub>} units, Scheme 3, with an additional  $J_3$  parameter to describe the interaction promoted by the Mn<sup>II</sup>-( $\mu$ -Cl)<sub>3</sub>-Mn<sup>II</sup> pathway, applying the Hamiltonian:

$$H = -2J_1(S_1 \cdot S_2 + S_2 \cdot S_3 + S_1 \cdot S_3 + S_5 \cdot S_6 + S_6 \cdot S_7 + S_5 \cdot S_7) - 2J_2(S_1 \cdot S_4 + S_2 \cdot S_4 + S_3 \cdot S_4 + S_5 \cdot S_8 + S_5 \cdot S_8 + S_6 \cdot S_8) - 2J_3(S_4 \cdot S_8)$$

The best fit values were  $J_1 = +1.0(2)$  cm<sup>-1</sup>,  $J_2 = -3.9(1)$  cm<sup>-1</sup>,  $J_3 = -1.3(2)$  cm<sup>-1</sup>, g = 1.91(1). These values show the usual ferromagnetic interaction inside the Mn<sup>III</sup> triangular units, the antiferromagnetic interaction between the Mn<sup>III</sup>...Mn<sup>III</sup> cations and a moderately weak antiferromagnetic interaction between the two units that is the responsible of the  $\chi_M T$  decay below 25 K and the resulting S = 0 ground state. In good agreement, the magnetization measurements show a continuous increase up to

an unsaturated value of 7.1 N $\mu_{\beta}$  under the maximum applied field of 5 T. Triple  $\mu$ -Cl bridges between divalent manganese cations are rare and magnetic measurements have only been reported for three chloro chains<sup>[23]</sup> and one dimer reported by Wieghardt et al.<sup>[24]</sup> The negative  $J_3$  value confirms the antiferromagnetic nature of the triple chloro bridge for comparable bond angles.

For this kind of complexes based on the  $[Mn^{III}_3Mn^{II}Na^{I}]$  core, the easy axis corresponding to the elongated bonds are always placed on the  $Mn^{III}_3$  plane and, its magnetic response can be ferro- or antiferromagnetic as a function of the ligands that link these positions bridging the  $Mn^{III}_3$  cations. As was previously described,<sup>[5c]</sup> any correlation can be found between the bond parameters inside the triangle and its magnetic response, indicating the relevant effect of the bridging ligands in that position. In contrast, all the reported systems with  $\mu$ -halides in these sites provide equilateral or quasi  $C_3$  triangles and they promote ferromagnetic interaction in all reported cases. The  $Mn^{II}$ -O-Mn<sup>III</sup> pathway is always antiferromagnetic<sup>[5c]</sup> and thus, this system becomes adequate to perform magnetic analysis with a simple and reliable two-*J* model.

In fact, due to the presence of one antiferromagnetic (AF) and one ferromagnetic (FM) interactions the  $J_2/J_1$  ratio determines the different shape of the  $\chi_M T$  plots for this kind of systems that, in spite to exhibit in all cases a S = 7/2 ground state, can be strongly different as function of the dominant interaction, showing a strong decay from room temperature for the systems dominated by  $J_2$  or increasing values for the systems dominated by  $J_1$ , Scheme 3 and Figure 9.



Scheme 3. Scheme of the {Mn4} core for complexes in which the Mn<sup>II</sup> cation exhibits tetrahedral or octahedral environment. Right, coupling scheme for complexes 2*R* (botom), 3*Rac* and 4*Rac* (top).



**Figure 9**. Simulated  $\chi_M T$  vs. *T* response for type-III complexes as function of the  $J_2/J_1$  ratio. Dotted and dashed lines show the position of **3***Rac* (ratio -0.64) and **4***Rac* (ratio -0.32) respectively

In contrast with 2R or the examples reported in the literature, [5c] complexes 3Rac and 4Rac show very weak antiferromagnetic coupling for the Mn<sup>II</sup>...Mn<sup>III</sup> interactions mediated by one Mn<sup>II</sup>-O-Mn<sup>III</sup> superexchange pathway. The previously studied complexes with [Mn<sup>III</sup><sub>3</sub>Mn<sup>II</sup>Na<sup>I</sup>] core have typically hexacoordinated cations but for 3Rac and 4Rac the divalent manganese cation is placed in a tetrahedral environment. This different coordination implies that the O-Mn<sup>II</sup>-O bond angles ( $\alpha$ , Scheme 3) are larger in the latter case and its increase implies shorter Mn<sup>II</sup>-O-Mn<sup>III</sup> bond angles ( $\beta$ , Scheme 3). This reduction is close or even larger than 10°, for the Mn<sup>II</sup>-O-Mn<sup>III</sup> bond angles that takes values typically around 125° for the octahedrically coordinated cations or values lower than 115° for the tetrahedral ones. The dependence of the antiferromagnetic interaction with the bond angles for O-bridges (hydroxo, alkoxo, phenoxo) is a general trend in 3d cluster chemistry, increasing the antiferromagnetic interaction when increasing bond angles. In agreement with this general trend, lower Mn<sup>II</sup>-O-Mn<sup>III</sup> antiferromagnetic interactions should be expected for the new kind of systems with Mn<sup>II</sup> tetrahedral environment.

## Conclusion

Playing with the substituents on the aminoalcohol fragment of the Schiff bases obtained by condensation with *o*-vanillin, the work describes the first derivatives of the H<sub>2</sub>L4 base, the second example of the Mn<sup>II</sup>-( $\mu$ -CI)<sub>3</sub>-Mn<sup>II</sup> bridge in molecular systems and the first examples of well-defined tetrahedral MnO<sub>3</sub>Cl environment for the [Mn<sup>III</sup><sub>3</sub>Mn<sup>II</sup>Na<sup>I</sup>] class of clusters. The employment of bulky substituents on the C-atom neighboring the O-donor allows the tailoring of the divalent manganese coordination sphere. The magnetic properties of these systems have been studied and correlated with the previous systems reported in the literature with the divalent manganese in octahedral environment as well the magnetic response of the triple chloro bridge.

Noteworthy, the reported clusters and the bibliographic review of related systems with an odd number of chiral Schiff bases evidences that the unexpected mix of ligands with different (*R*) / (*S*) configuration is not so exceptional in contrast with the usually accepted paradigm and that the majority configuration dominates the chirality transfer to the cations and the helical clusters. We have pointed out for the very first time the process equivalent to the spontaneous racemization, that goes against the usual rules.

## **Experimental Section**

**Materials and Methods.** Variable-temperature magnetic studies were performed using a MPMS5 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 constants. Fit of the experimental data was performed with PHI program.<sup>[25]</sup> Electronic Circular Dichroism (ECD) spectra were recorded in methanolic solution in a Jasco-815 spectropolarimeter. Instrumental measurements were performed on the crystalline fraction of the corresponding complex.

X-ray crystallography. Details of crystal data, data collection and refinement for complexes 1Rac, 2Rac, 3Rac, 3R and 4Rac are

summarized in Table S4. Collection data were made on a Bruker D8 Venture system equipped with a multilayer monochromator and a Mo microfocus ( $\lambda$ = 0.71073 Å). All structures were solved using the Brucker SHELXTL software package and refined with SHELXL computer program.<sup>[26]</sup> Data were corrected for absorption effects using the multi-scan method (SADABS). Plots for publication were generated with ORTEP3 for Windows<sup>[27]</sup> and plotted with Pov-Ray programs.

All data can be found in the supplementary crystallographic data for this paper in cif format with CCDC numbers 1977691-1977695. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data\_request/cif</u>.

#### Synthetic Procedure

The chiral aminoalcohols and o-vanillin (TCI Europe) and solvents reagent grade (Aldrich) were employed as received.

H<sub>2</sub>L Schiff bases: The (*R*)-, (*S*)-enantiomer or the racemic mixture of 0.5 mmol of the corresponding aminoalcohol and 2-hydroxy-3-methoxybenzaldehyde (0.5 mmol, 0.076 g) were dissolved in 15 mL of methanol and the solution was refluxed for 1 h. Alternatively, the ligands can be prepared in a microwave furnace heating 20 minutes at 80°. The resulting yellow solutions of the H<sub>2</sub>L ligands were employed directly in the synthesis of the derived complexes without a previous isolation of the ligand.

**Manganese clusters.** All the reported complexes were prepared following the same procedure:  $MnCl_2 \cdot 4H_2O$  (0.099 g, 0.5 mmol) and NaOH (0.020 g, 0.5 mmol) were stirred for 5 min in acetonitrile (15 mL). After that, the previously prepared solution of the corresponding H<sub>2</sub>L ligand (0.5 mmol) was added. The color of the resulting mixture immediately changed to very dark brown and was stirred at open air at room temperature for 3 h and filtered. Dark-brown crystals were obtained after a few days by vapor diffusion or layering the resulting solutions with diethyl ether. The chiral systems **3***R*/**3***S* were also obtained by slow evaporation. Crystals suitable for single crystal X-Ray determination were not obtained for the chiral derivatives of H<sub>2</sub>L4. Anal. calculated/found (%) for complex **1***Rac*, C, 49.33/48.9; H 4.63/4.8; N 3.38/3.5; **2***Rac*, C, 40.47/40.3; H 4.21/4.5; N 3.78/3.8; **3***Rac*, C, 38.77/38.8; H 3.85/4.2; N 4.11/4.2; **3***R*, C,38.77/38.5; H 3.85/4.2; N 4.119/4.3. **3***S*, C,38.77/38.2; H 3.85/4.1; N 4.11/4.1. **4***Rac*, C,47.69/47.0; H 4.01/4.4; N 4.01/3.9.

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# **Entry for the Table of Contents**



Chiral and racemic clusters with  $[Mn^{III}_{6}Mn^{II}Na^{I}]$ ,  $[Mn^{III}_{6}Mn^{II}_{2}Na^{I}_{2}]$  and  $[Mn^{III}_{3}Mn^{II}Na^{I}]$  metallic core obtained from tridentate Schiff bases exhibit unusual spontaneous racemization with (*RRS/SSR*) mix of chiral centers.