Syntheses, structures, chiroptical and magnetic properties of chiral clusters built from Schiff bases: a novel [MnIIMnIII 6NaI 2] core

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Chiral clusters with MnIIMnIII 3NaI and the new MnIIMnIII 6NaI 2 cores have been synthesised employing enantiomerically pure Schiff bases and halide ligands. The new compounds have been characterized by electronic circular dichroism (ECD) and magnetic susceptibility.

Supramolecular chirality has received large attention along the last years in several research fields as chiral catalysis, recognition and sensing or CPL emission1 as well by its potentially different reactivity in biological environments.2 As a subfield, chiral self-assembled coordination compounds revealed to be attractive in the study of transfer of chirality, chiroptical properties (often lanthanide complexes), or magnetochemistry in close relationship to the search of chiral SMM or extended magnets.3 Employment of enantiomerically pure ligands allow the direct syntheses of chiral coordination compounds that can be useful in the search of multifunctional systems in which optical or emissive properties could be combined with its magnetic response. Among them, Schiff bases constitute an appropriate family of ligands to reach this target due to its ability to generate large nuclearity or high spin clusters and because these ligands can be easily functionalized to incorporate chiral centres. In this communication we report preliminary results from the employment of the R / S chiral Schiff base H2L obtained by condensation of o-vanilline and R- or S-phenylglycinol in manganese chemistry and the characterization of enantiomeric pairs of MnIIMn3 IIINaI penta and the new MnIIMn6 IIINa2 I nonanuclear complexes, in which the dianionic form of H2L links three different cations, Scheme 1.

Reaction of R- or S-H2L with manganese bromide and sodium azide yields the pentanuclear complexes [Mn4NaOL3Br4]·[Mn4NaOL3Br4(H2O)]·[Mn4NaOL3Br3(MeOH)(MeCN)(H2O)]·[Mn4NaOL3Br3(MeOH)(MeCN)2]Br2·6CH3CN·5CH3OH (1R) and [Mn4NaOL3Br4(H2O)]·[Mn4NaOL3Br3(MeOH)(H2O)2]Br·6CH3CN·CH3OH (1S) which exhibit a core similar to some previously reported systems with azido or other ligands instead of halides and related Schiff bases.4 In contrast, the reaction in basic NaOH medium yields the nonanuclear clusters [Mn7Na2(O)2L6X6]·solvents (X = Cl, 2R and 2S, X = Br 3R), that exhibit an unprecedented core, (synthetic details in ESI). To our knowledge, the {(μ3-O)MnIII3-MnII-MnIII3(μ3-O)} core has only been reported as fragment of larger Mn19 clusters5 and in one Mn7 system built from salicyloximate ligands.6 However, in this later case, the core was closer to two pseudocubanes sharing the central MnII cation and becomes less comparable

The structures (ESI, Tables S1-S4) of 1R and 1S contain pentanuclear MnIIMn3IIINaI discrete units linked by three L2-ligands. The metallic cations determine a trigonal bipyramidal arrangement with the three MnIII ions in the equatorial plane and the MnII and NaI cations in the apical positions, Fig 1. The O-phenoxide and O-methoxide donors form a octahedral cavity that holds the NaI cation, which is bridged by means of the O-phenoxides to the MnIII cations whereas the O-alcoxide donors link the MnIII cations with the MnII ions. An additional μ3-O donor is placed in the centre of the triangle determined by the trivalent manganese cations.

Noteworthy, the complicated structure of 1R contains four different clusters that differ in how the coordination sphere of the MnII cation is fulfilled: three fac-coordination sites are occupied in all cases by three O-alcoxide donors from the L2- ligands but the remaining positions can be occupied by one bromide (tetracoordinated), three solvent molecules (hexacoordinated) or by one water molecule and one bromo ligand (pentacoordinated). For 1S a similar fact was observed with the presence of two independent units with the MnII cations in octahedral or pentacoordinated environments (ESI, Fig. S2). The main structural consequence consists in the increase of the MnIII-O-MnII bond angles, which are close to 122º (octahedral MnII), 118º (pentacoordinated MnII) and 111º (tetrahedral MnII). Remaining angles or distances of the cluster core are similar in all units (ESI, Table S2).

The chirality transfer for complexes 1R and 1S can be observed at level of the inner NaI cations that exhibit Λ (1R) or Δ (1S) configuration or at the whole helical shape of the molecule due to the tilted arrangement of the ligands with respect to the main axis of the molecule, Fig. 2.

The R and S pairs of enantiomers of 2 consist of two pentanuclear units (similar to those described for 1), sharing the MnII cation, resulting a nonanuclear MnIIMn6 IIINa2I core, Fig. 3. The 22 positive charges are balanced by the six dianionic Schiff bases, six halides and two μ3-oxo donors. The L2- ligands and the MnIII cations in each pentanuclear subunit are related by one C3 axis (R3 space group) but the lack of symmetry between them determine different bond parameters around Mn3 in each subunit: Mn2-O4-Mn3 bond angles takes a mean value of 125.8(3)º whereas Mn1-O1-Mn3 is 122.9(3)º. Surprisingly, the helicity of each MnIIMn3IIINaI moiety turns in opposite sense and thus, the NaI cations show also opposite Λ/Δ configuration. Complex 3R, prepared to check if this structure can be extended to other halides, exhibits the same core than 2R and with the logical exception of the larger MnIII-Br bond distances, all bond parameters of the cluster core are very similar to 2 (ESI, Table S4). Noteworthy, in all cases the oxo ligand is slightly displaced out of the MnIII3 plane towards the NaI cation, with a Na-O distance of around 2.7 Å and thus, the coordination of the sodium ions can be formally described as an apicated octahedron and the oxo donors can be assumed as μ4-O ligands.

ECD spectra of the pairs of enantiomers 1R/1S and 2R/2S measured in solid phase and acetonitrile solution show perfect mirror images of each other, which confirm the enantiomeric purity of samples, Fig. 4. The spectra of the penta and nonanuclear complexes are closely related as can be expected for systems in which the ECD spectrum is directed mainly by chirality of the chelating ligands. Comparison between solid and solution spectra, in the 250-800 range suggest that the crystal structure is pretty close to the predominant conformer(s) in acetonitrile solution.

As expected from the structural data the magnetic response for each kind of core is very similar and independent of the enantiomer or the halide donors. Thus, we provide a general description of their magnetic behaviour. The room temperature χMT value for the complexes with MnIIMn3 IIINaI core is close to 10.5 cm3·mol-1·K, slightly lower than the expected value for three isolated MnIII and one MnII cations (13.375 cm3·mol-1·K) and this value decreases continuously on cooling down to a plateau between 25 - 5 K, with a low T fall down to 6 cm3·mol-1·K at 2K. In contrast, the complexes with MnIIMn6 IIINa2 I core exhibit a room temperature χMT value close to 19 cm3·mol-1·K, also lower than the expected value for six non-interacting MnIII and one MnII cations (22.375 cm3·mol-1·K). On cooling, χMT decreases down to a well defined minimum around 120 K with a further increase up to a maximum value close to 28 cm3·mol-1·K at 10-15 K with a final decrease below these temperatures indicating a ferromagnetic response, Fig. 5.

Previously reported related systems with MnIIMn3IIINaI core have different ligands in the elongated coordination sites of the MnIII cations4 but in our case the clusters are close or possess an strict C3 symmetry with halide donors in these positions, simplifying the coupling scheme. Fit of the experimental data was performed with PHI program7 applying a 2-J model in which J1 corresponds to the interaction between the MnIII cations inside the triangular subunits and J2 corresponds to the MnIII···MnII interactions according the Hamiltonians and coupling scheme shown in Fig. S3.

Excellent fits were obtained with consistent FM coupling for the MnIII-MnIII interactions (J1 in the +0.8/+0.9 cm-1 range) and AF coupling for the MnII-MnIII interactions (J2 in the -2.3/-3.7 cm-1 range) and g around 1.9.

Noteworthy, the new Mn7 core of 2-3 is similar to the central fragment of the S = 83/2 ground state supertetrahedral vertexsharing Mn19 clusters, Fig. S4.5 In contrast with 2-3, the MnII-OMn III interaction for Mn19 was ferromagnetic contributing to reach the maximum spin. Close inspection of the bond parameters for both systems show that the MnII-O-MnIII bond angle for 2-3 is much larger than for Mn19 (≈124º vs. ≈110º), and consequently the MnII···Ooxo distance increases by about 0.75 Å and the MnII environment for 2-3 becomes closer to a regular octahedron instead of the pseudo octacoordination observed in Mn19, resulting in interactions of opposite sign. The easy axis of the MnIII cations lies in the {μ3O-Mn3 III} plane directed towards the chloro ligands forming angles of around 60º between them. This easy axis arrangement is unfavourable to reach high anisotropy and, as was experimentally checked, no out-of-phase response was found in AC experiments.

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CONCLUSIONS

Reaction of manganese halides with enantiomerically pure Schiff bases obtained from the condensation of o-vanilline and (R) or (S)-phenilglycinol lead to the characterization of chiral penta and nonanuclear complexes with MnIIMn3 IIINaI and the rare MnIIMn6 IIINa2 I cores. Current efforts to fully characterize series of related complexes changing the NaI cations by other monovalent or divalent cations, its role as oxygen evolving systems and a wide magnetostructural correlation are in due course and will be reported in a forthcoming full paper.

ACKNOWLEDGEMENTS

Founds from Ministerio de Economía y Competitividad, Project CTQ2015-63614-P are acknowledged. MG thanks for support from the Polish Ministry of Science and Higher Education ("Mobilnosc Plus" grant no. 1286/MOB/IV/2015/0).

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Legends to figures

Scheme 1 Coordination to one MnIII, one MnII and one NaI cations found in complexes 1- 3 for the L2- ligand employed in this work.

Figure. 1 Left, view of one of the non equivalent clusters of 1R. Right, partially labelled common core of complexes 1R and 1S. Color code: MnIII, dark green; MnII, orange; NaI, light blue; N, navy; O red; Br, firebrick..

Figure. 2 Left, a spacefill view of the two pentanuclear enantiomers of 1R and 1S showing the helical arrangement of the ligands. Right, NaI environment for 1R (Λ) and 1S ( ) viewed along the O10-Na direction.

Figure. 3 Top, a view of cluster 2. Bottom, partially labelled common core of complexes 2R, 2S. Color code: as Fig.1; Cl, violet.

Figure. 4 Solid state (left) and acetonitrile solution (right) ECD spectra for the pair of enantiomers of the MnIIMnIII 3NaI complexes 1 (S green line; R orange line) and MnIIMn6 IIINa2 I complexes 2 (S red line; R blue line, X10).

Figure 5. Plot of χMT product vs. T for one of the enantiomers of complexes 1S (diamonds, red axis), 2S and 3R (squares and circles, blue axis). Solid lines show the best fit of the data.

SCHEME 1

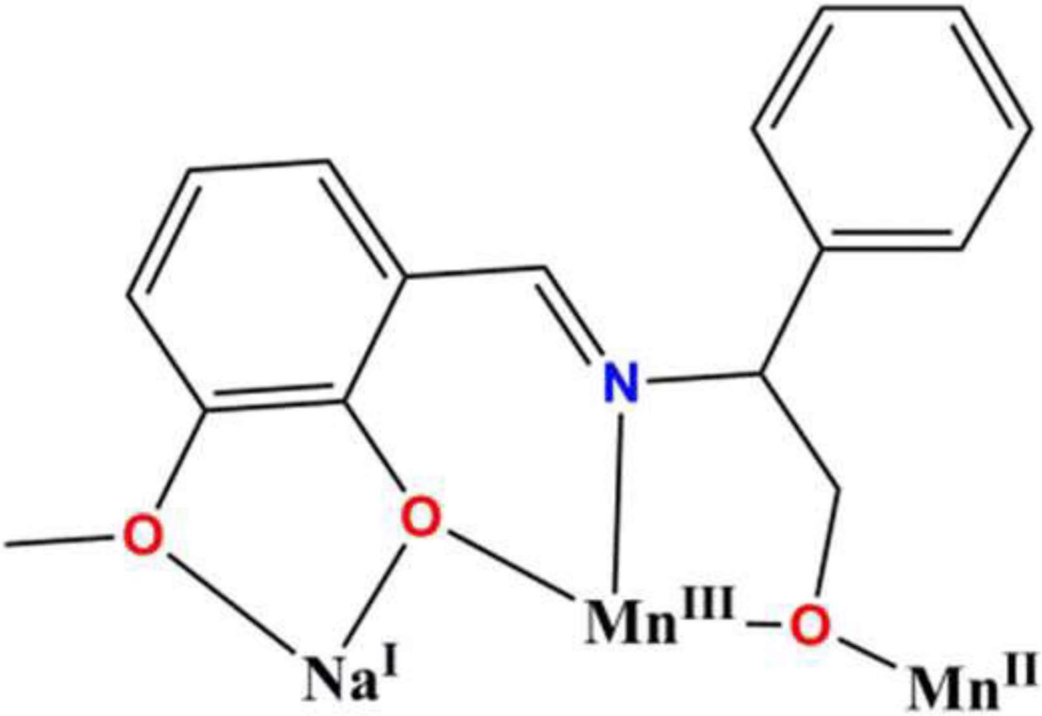


FIGURE 1

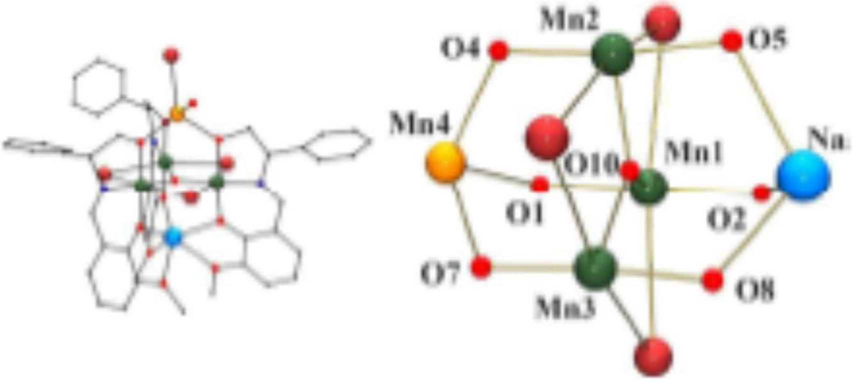
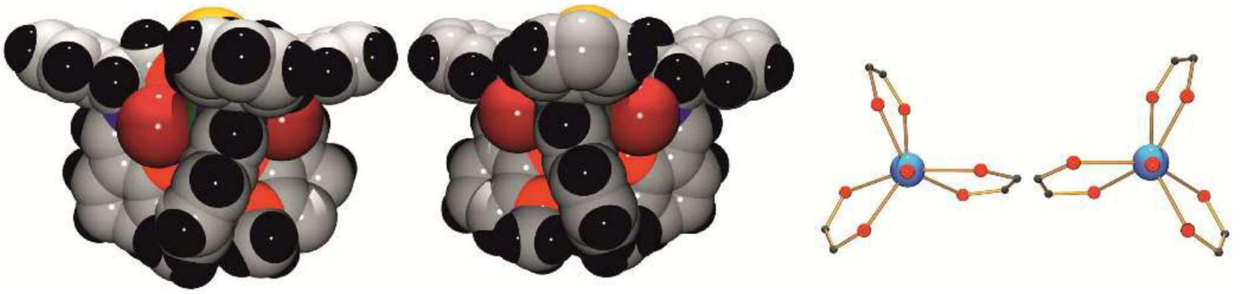


FIGURE 2



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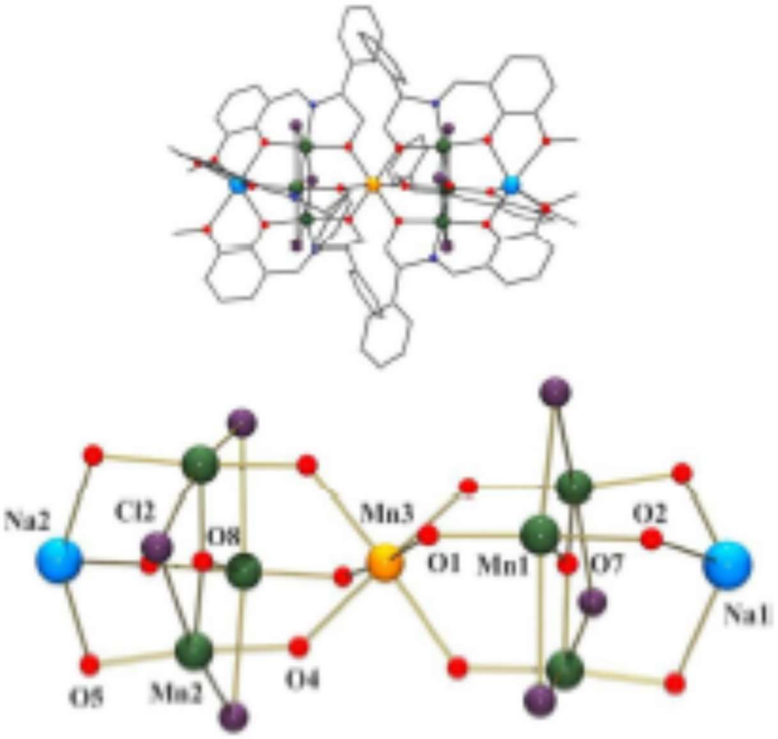

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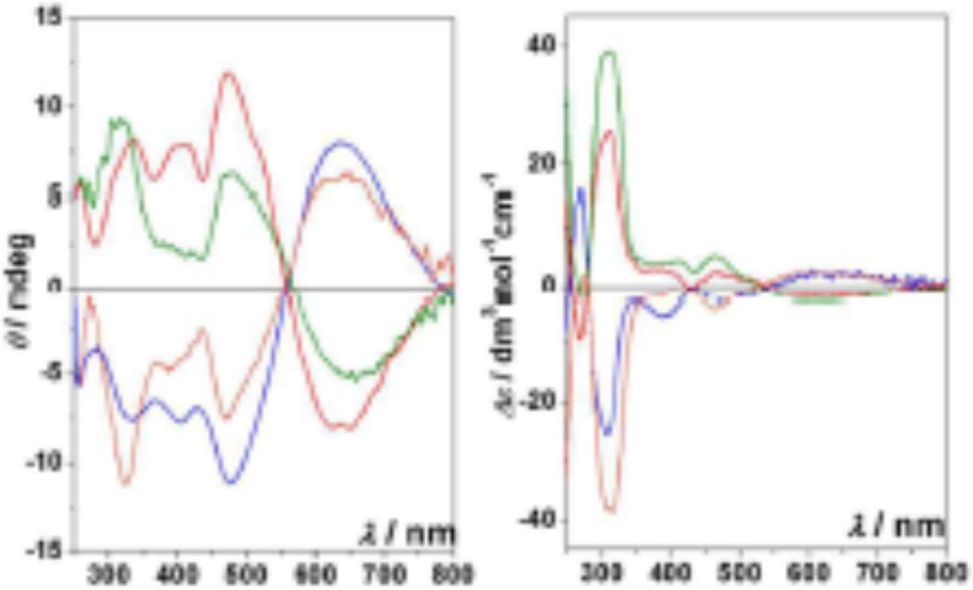
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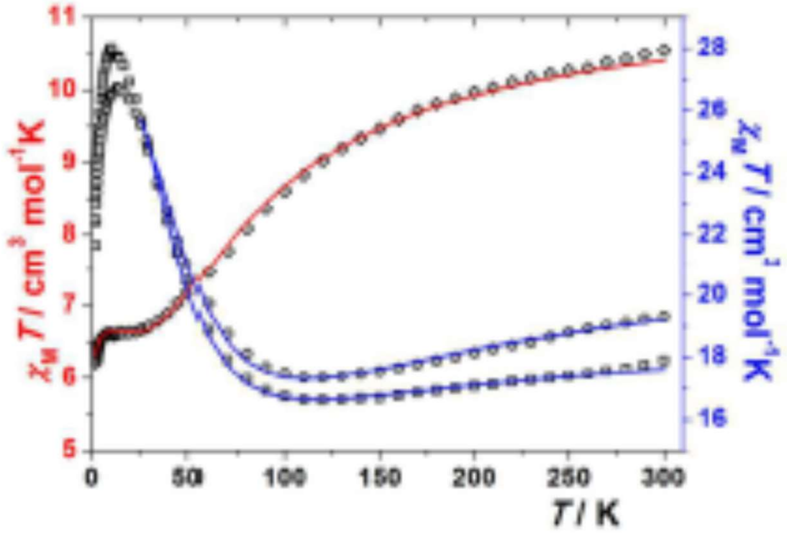
FIGURE 5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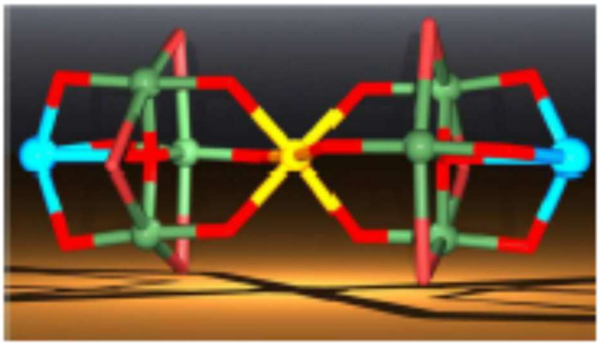

Enantiomeric pairs of clusters with MnIIMnIII3NaI and the unprecedented MnIIMnIII6NaI 2 cores have been synthesized employing enantiomerically pure Schiff bases.