

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

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

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41 Supramolecular chirality has received large attention along the last years in several research fields as
42 chiral catalysis, recognition and sensing or CPL emission¹ as well by its potentially different reactivity
43 in biological environments.² As a subfield, chiral self-assembled coordination compounds revealed to
44 be attractive in the study of transfer of chirality, chiroptical properties (often lanthanide complexes), or
45 magnetochemistry in close relationship to the search of chiral SMM or extended magnets.³ Employment
46 of enantiomerically pure ligands allow the direct syntheses of chiral coordination compounds that can be
47 useful in the search of multifunctional systems in which optical or emissive properties could be
48 combined with its magnetic response. Among them, Schiff bases constitute an appropriate family of
49 ligands to reach this target due to its ability to generate large nuclearity or high spin clusters and because
50 these ligands can be easily functionalized to incorporate chiral centres. In this communication we report
51 preliminary results from the employment of the R / S chiral Schiff base H2L obtained by condensation
52 of o-vanilline and R- or S-phenylglycinol in manganese chemistry and the characterization of
53 enantiomeric pairs of MnII Mn3 III NaI penta and the new MnII Mn6 III Na2 I nonanuclear complexes, in
54 which the dianionic form of H2L links three different cations, Scheme 1.

55 Reaction of R- or S-H2L with manganese bromide and sodium azide yields the pentanuclear complexes
56 $[\text{Mn}_4\text{NaOL3Br}_4] \cdot [\text{Mn}_4\text{NaOL3Br}_4(\text{H}_2\text{O})] \cdot [\text{Mn}_4\text{NaOL3Br}_3(\text{MeOH})(\text{MeCN})(\text{H}_2\text{O})] \cdot [\text{Mn}_4\text{NaOL3Br}_3(\text{MeOH})(\text{MeCN})_2]\text{Br}_2 \cdot 6\text{CH}_3\text{CN} \cdot 5\text{CH}_3\text{OH}$ (1R) and
57 $[\text{Mn}_4\text{NaOL3Br}_4(\text{H}_2\text{O})] \cdot [\text{Mn}_4\text{NaOL3Br}_3(\text{MeOH})(\text{H}_2\text{O})_2]\text{Br} \cdot 6\text{CH}_3\text{CN} \cdot \text{CH}_3\text{OH}$ (1S) which exhibit a
58 core similar to some previously reported systems with azido or other ligands instead of halides and
59 related Schiff bases.⁴ In contrast, the reaction in basic NaOH medium yields the nonanuclear clusters
60 $[\text{Mn}_7\text{Na}_2(\text{O})_2\text{L}_6\text{X}_6] \cdot \text{solvents}$ (X = Cl, 2R and 2S, X = Br 3R), that exhibit an unprecedented core,
61 (synthetic details in ESI). To our knowledge, the $\{(\mu_3\text{-O})\text{Mn}^{\text{III}}_3\text{-Mn}^{\text{II}}\text{-Mn}^{\text{III}}_3(\mu_3\text{-O})\}$ core has only
62 been reported as fragment of larger Mn¹⁹ clusters⁵ and in one Mn⁷ system built from salicyloximate
63 ligands.⁶ However, in this later case, the core was closer to two pseudocubanes sharing the central MnII
64 cation and becomes less comparable

65 The structures (ESI, Tables S1-S4) of 1R and 1S contain pentanuclear MnII Mn3 III NaI discrete units
66 linked by three L2-ligands. The metallic cations determine a trigonal bipyramidal arrangement with the
67 three MnIII ions in the equatorial plane and the MnII and NaI cations in the apical positions, Fig 1. The
68 O-phenoxide and O-methoxide donors form a octahedral cavity that holds the NaI cation, which is
69 bridged by means of the O-phenoxides to the MnIII cations whereas the O-alcoxide donors link the
70 MnIII cations with the MnII ions. An additional $\mu_3\text{-O}$ donor is placed in the centre of the triangle
71 determined by the trivalent manganese cations.

72 Noteworthy, the complicated structure of 1R contains four different clusters that differ in how the
73 coordination sphere of the MnII cation is fulfilled: three fac-coordination sites are occupied in all cases
74 by three O-alcoxide donors from the L2- ligands but the remaining positions can be occupied by one
75 bromide (tetracoordinated), three solvent molecules (hexacoordinated) or by one water molecule and
76 one bromo ligand (pentacoordinated). For 1S a similar fact was observed with the presence of two
77

78 independent units with the MnII cations in octahedral or pentacoordinated environments (ESI, Fig. S2).
79 The main structural consequence consists in the increase of the MnIII-O-MnII bond angles, which are
80 close to 122° (octahedral MnII), 118° (pentacoordinated MnII) and 111° (tetrahedral MnII). Remaining
81 angles or distances of the cluster core are similar in all units (ESI, Table S2).
82 The chirality transfer for complexes 1R and 1S can be observed at level of the inner NaI cations that
83 exhibit Λ (1R) or Π (1S) configuration or at the whole helical shape of the molecule due to the tilted
84 arrangement of the ligands with respect to the main axis of the molecule, Fig. 2.
85 The R and S pairs of enantiomers of 2 consist of two pentanuclear units (similar to those described for
86 1), sharing the MnII cation, resulting a nonanuclear MnIIMn6 IIIINa2I core, Fig. 3. The 22 positive
87 charges are balanced by the six dianionic Schiff bases, six halides and two μ -3-oxo donors. The L2-
88 ligands and the MnIII cations in each pentanuclear subunit are related by one C3 axis (R3 space group)
89 but the lack of symmetry between them determine different bond parameters around Mn3 in each
90 subunit: Mn2-O4-Mn3 bond angles takes a mean value of 125.8(3)° whereas Mn1-O1-Mn3 is 122.9(3)°.
91 Surprisingly, the helicity of each MnIIMn3IIINaI moiety turns in opposite sense and thus, the NaI
92 cations show also opposite Λ/Π configuration. Complex 3R, prepared to check if this structure can be
93 extended to other halides, exhibits the same core than 2R and with the logical exception of the larger
94 MnIII-Br bond distances, all bond parameters of the cluster core are very similar to 2 (ESI, Table S4).
95 Noteworthy, in all cases the oxo ligand is slightly displaced out of the MnIII3 plane towards the NaI
96 cation, with a Na-O distance of around 2.7 Å and thus, the coordination of the sodium ions can be
97 formally described as an apicated octahedron and the oxo donors can be assumed as μ -4-O ligands.
98 ECD spectra of the pairs of enantiomers 1R/1S and 2R/2S measured in solid phase and acetonitrile
99 solution show perfect mirror images of each other, which confirm the enantiomeric purity of samples,
100 Fig. 4. The spectra of the penta and nonanuclear complexes are closely related as can be expected for
101 systems in which the ECD spectrum is directed mainly by chirality of the chelating ligands. Comparison
102 between solid and solution spectra, in the 250-800 range suggest that the crystal structure is pretty close
103 to the predominant conformer(s) in acetonitrile solution.
104 As expected from the structural data the magnetic response for each kind of core is very similar and
105 independent of the enantiomer or the halide donors. Thus, we provide a general description of their
106 magnetic behaviour. The room temperature χ_{MT} value for the complexes with MnIIMn3 IIIINaI
107 core is close to 10.5 cm³·mol⁻¹·K, slightly lower than the expected value for three isolated MnIII and
108 one MnII cations (13.375 cm³·mol⁻¹·K) and this value decreases continuously on cooling down to a
109 plateau between 25 - 5 K, with a low T fall down to 6 cm³·mol⁻¹·K at 2K. In contrast, the complexes
110 with MnIIMn6 IIIINa2 I core exhibit a room temperature χ_{MT} value close to 19 cm³·mol⁻¹·K, also
111 lower than the expected value for six non-interacting MnIII and one MnII cations (22.375 cm³·mol⁻¹·
112 1·K). On cooling, χ_{MT} decreases down to a well defined minimum around 120 K with a further increase
113 up to a maximum value close to 28 cm³·mol⁻¹·K at 10-15 K with a final decrease below these
114 temperatures indicating a ferromagnetic response, Fig. 5.

115 Previously reported related systems with MnII-Mn3IIINaI core have different ligands in the elongated
116 coordination sites of the MnIII cations⁴ but in our case the clusters are close or possess an strict C₃
117 symmetry with halide donors in these positions, simplifying the coupling scheme. Fit of the
118 experimental data was performed with PHI program⁷ applying a 2-J model in which J₁ corresponds to
119 the interaction between the MnIII cations inside the triangular subunits and J₂ corresponds to the
120 MnIII···MnII interactions according the Hamiltonians and coupling scheme shown in Fig. S3.
121 Excellent fits were obtained with consistent FM coupling for the MnIII-MnIII interactions (J₁ in the
122 +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)
123 and g around 1.9.
124 Noteworthy, the new Mn₇ core of 2-3 is similar to the central fragment of the S = 83/2 ground state
125 supertetrahedral vertexsharing Mn₁₉ clusters, Fig. S4.5 In contrast with 2-3, the MnII-OMn III
126 interaction for Mn₁₉ was ferromagnetic contributing to reach the maximum spin. Close inspection of the
127 bond parameters for both systems show that the MnII-O-MnIII bond angle for 2-3 is much larger than
128 for Mn₁₉ (≈124° vs. ≈110°), and consequently the MnII···Ooxo distance increases by about 0.75 Å and
129 the MnII environment for 2-3 becomes closer to a regular octahedron instead of the pseudo
130 octacoordination observed in Mn₁₉, resulting in interactions of opposite sign. The easy axis of the MnIII
131 cations lies in the {μ₃O-Mn₃ III} plane directed towards the chloro ligands forming angles of around
132 60° between them. This easy axis arrangement is unfavourable to reach high anisotropy and, as was
133 experimentally checked, no out-of-phase response was found in AC experiments.
134 .

135 **CONCLUSIONS**

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137 Reaction of manganese halides with enantiomerically pure Schiff bases obtained from the condensation
138 of o-vanilline and (R) or (S)-phenilglycinol lead to the characterization of chiral penta and nonanuclear
139 complexes with Mn^{II}Mn³ III^{Na}I and the rare Mn^{II}Mn⁶ III^{Na}2 I cores. Current efforts to fully
140 characterize series of related complexes changing the NaI cations by other monovalent or divalent
141 cations, its role as oxygen evolving systems and a wide magnetostructural correlation are in due course
142 and will be reported in a forthcoming full paper.

143

144 **ACKNOWLEDGEMENTS**

145

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150 **REFERENCES**

151

152 1 M. Liu, L. Zhang and T. Wang, *Chem. Rev.* 2015, 115, 7304.

153 2 R. Carr, N. H. Evans and D. Parker, *Chem. Soc. Rev.*, 2012, 41, 7673.

154 3 J. Crassous, *Chem. Soc. Rev.*, 2009, 38, 830; b) H. Miyake, *Symmetry* 2014, 6, 880.

155 4 a) L.-L. Fan, F.-S. Guo, L. Yun, Z.-J. Lin, R. Herchel, J.-D. Leng, Y.-C. Ou and M.-L. Tong,
156 *Dalton Trans.*, 2010, 39, 1771; b) S. Nayak, H. P. Nayek, S. Dehnen, A. K. Powell and J.

157 *Reedijk*, *Dalton Trans.*, 2011, 40, 2699; c) P.-P. Yang, C.-Y. Shao, L.-L. Zhu and Y. Xu, *Eur. J.*

158 *Inorg. Chem.*, 2013, 5288; d) P.-P. Yang, L.-L. Zhu and Y. Xu, *Z. Anorg. Allg. Chem.*, 2013,

159 639, 1821; e) C. Ding, C. Gao, S. Ng, B. Wang and Y. Xie, *Chem. Eur. J.*, 2013, 19, 9961; L.

160 Cong, X. Qin, W. Sun, Y. Wang, S. Ding and Z. Liu, *New J. Chem.*, 2014, 38, 545; f) B. Gole,

161 K. C. Mondal and P. S. Mukherjee, *Inorg. Chim. Acta*, 2014, 415, 151; Y. Song, G. Zhang, X.

162 Qin, Y. Gao, S. Ding, Y. Wang, C. Du and Z. Liu, *Dalton Trans.*, 2014, 43, 3880.

163 5 a) A. M. Ako, I. J. Hewitt, V. Mereacre, R. Clerac, W. Wernsdorfer, C. E. Anson and A. K.

164 Powell, *Angew. Chem., Int. Ed.*, 2006, 45, 4926 ; b) S. Nayak, M. Evangelisti, A. K. Powell and

165 J. Reedijk, *Chem. Eur. J.*, 2010, 16, 12865; J.-L. Liu, J.-D. Leng, Z. Lin and M.-L. Tong, *Chem.*

166 *Asian J.*, 2011, 6, 1007; c) A. M. Ako, Y. Lan, O. Hampe, E. Cremades, E. Ruiz, C. E. Anson

167 and A. K. Powell, *Chem. Commun.*, 2014, 50, 5847.

168 6 C. J. Milios, I. A. Gass, A. Vinslava, L. Budd, S. Parsons, W. Wernsdorfer, S. P. Perlepes, G.

169 Christou and E. K. Brechin, *Inorg. Chem.*, 2007, 46, 6215.

170 7 N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, *J. Comput. Chem.*,

171 2013, 34, 1164

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174 **Legends to figures**

175

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

178

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

182

183 **Figure. 2** Left, a spacefill view of the two pentanuclear enantiomers of 1R and 1S showing the helical
184 arrangement of the ligands. Right, NaI environment for 1R (Λ) and 1S ($\bar{\Lambda}$) viewed along the O10-Na
185 direction.

186

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

189

190 **Figure. 4** Solid state (left) and acetonitrile solution (right) ECD spectra for the pair of enantiomers of
191 the MnIIMnIII 3NaI complexes 1 (S green line; R orange line) and MnIIMn6 IIIINa2 I complexes 2 (S
192 red line; R blue line, X10).

193

194 **Figure 5.** Plot of χ_{MT} product vs. T for one of the enantiomers of complexes 1S (diamonds, red axis),
195 2S and 3R (squares and circles, blue axis). Solid lines show the best fit of the data.

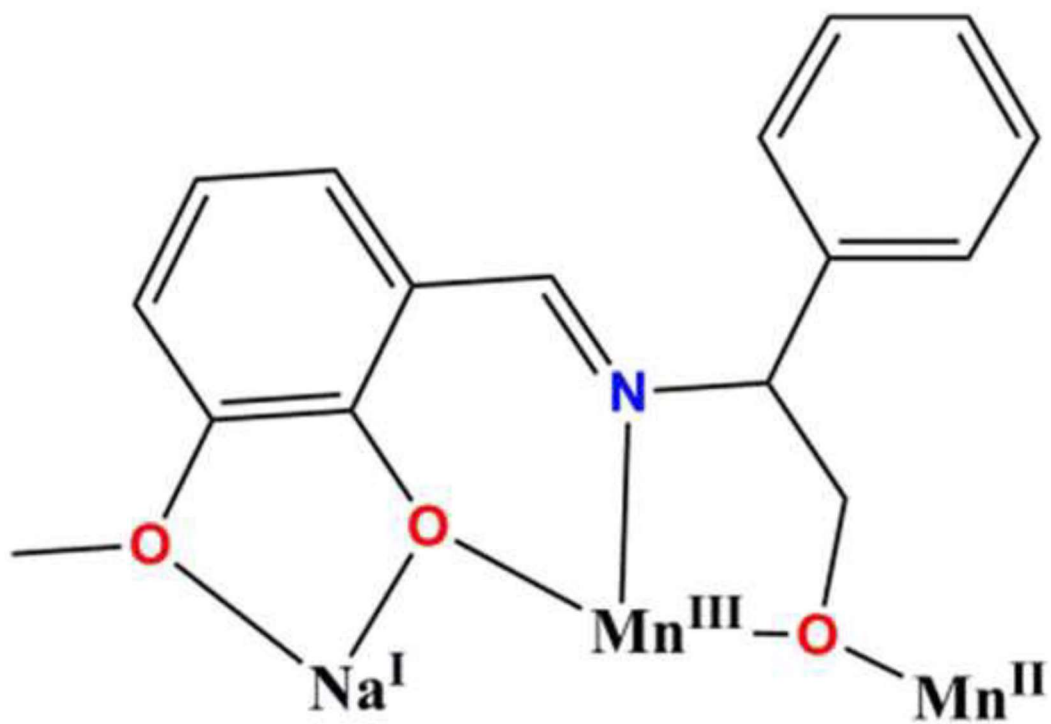
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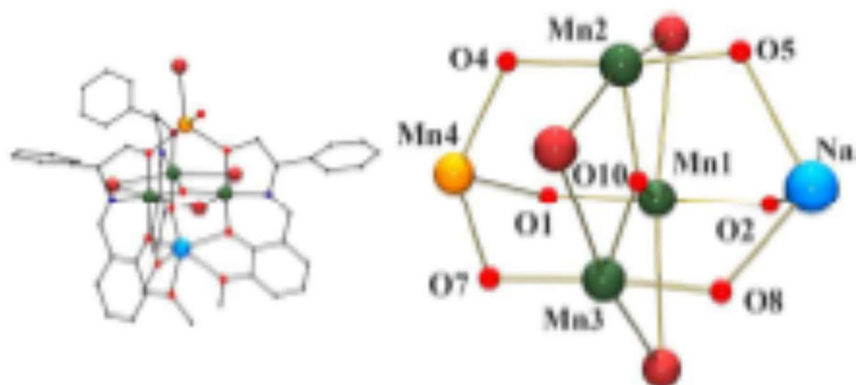
Scheme 1



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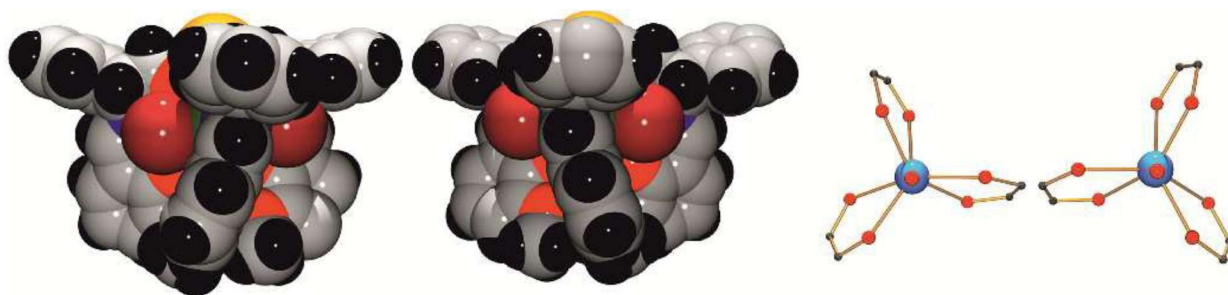
FIGURE 1



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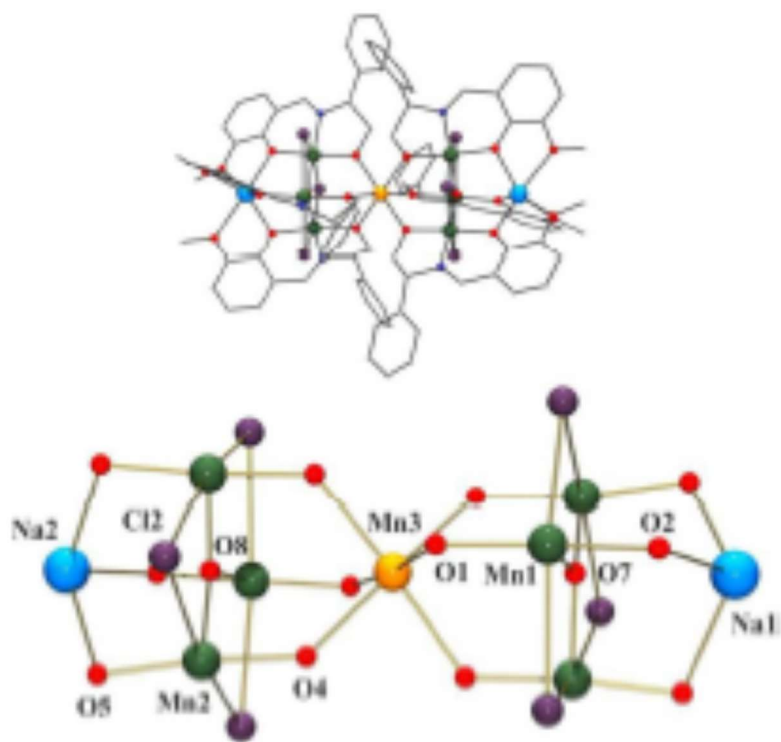
FIGURE 2



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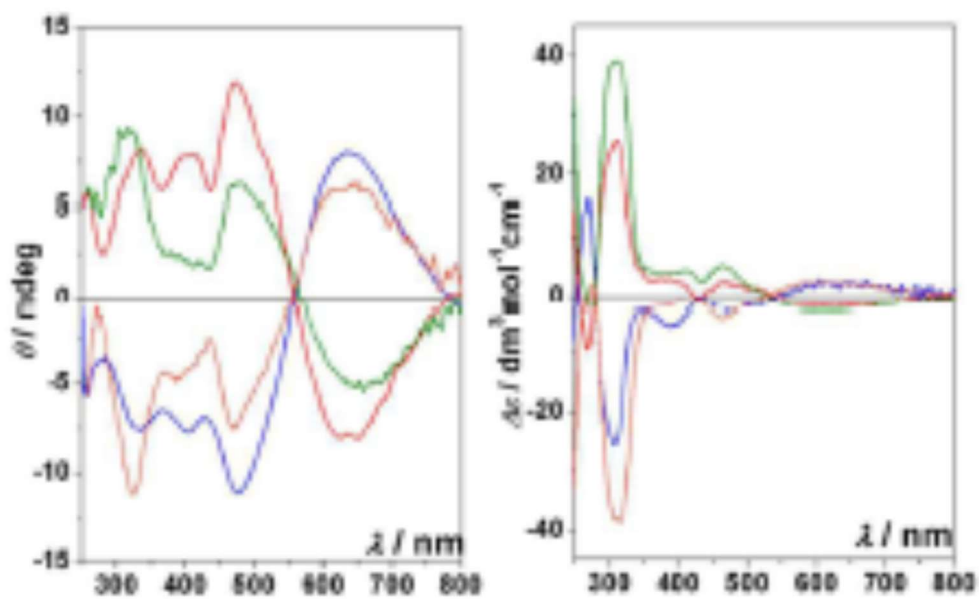
FIGURE 3



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FIGURE 4



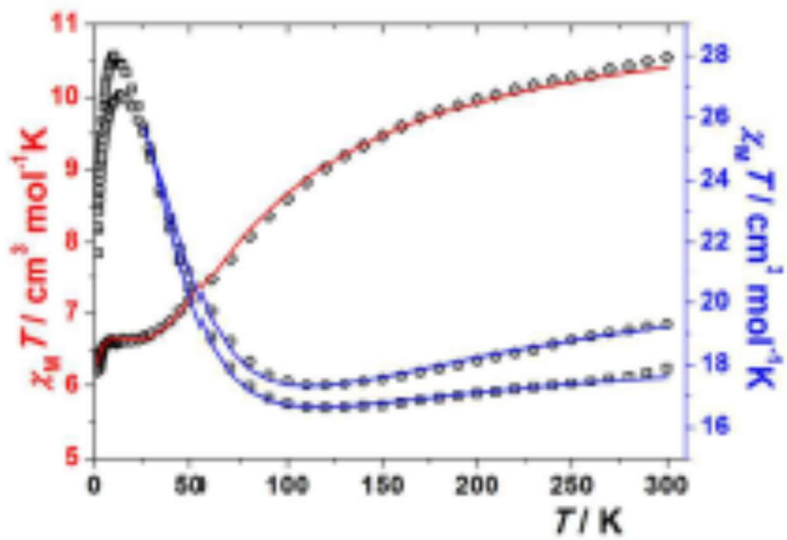
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FIGURE 5

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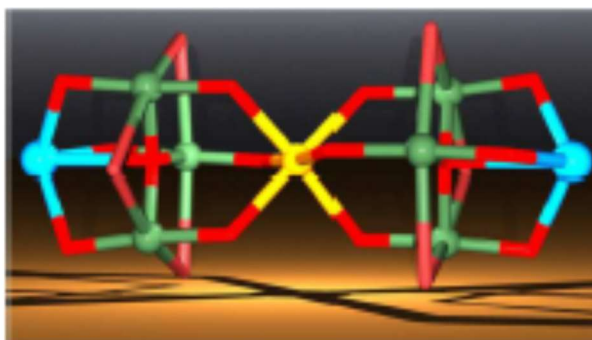
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230 Table of contents
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239 Enantiomeric pairs of clusters with $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_3\text{NaI}$ and the unprecedented $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_6\text{NaI}_2$ cores have
240 been synthesized employing enantiomerically pure Schiff bases.