Na2MnIII 6 LnIII clusters with a non-equivalent core: chiral vs. meso isomerism†

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A wide family of clusters with the Na2MnIII 6 LnIII core derived from an enantiomerically pure or a racemic mixture of Schiff bases lead to the characterization of a unique case of chiral/meso isomers with C3/D3d symmetry respectively, involving the rearrangement of the cluster bond parameters and the change from hepta- to hexacoordination of the central LnIII cation.

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Supramolecular chemistry is defined as the chemistry of molecular assemblies and of the intermolecular bond,[1] based on the key molecular recognition concept. Supramolecular chirality[2] is an emerging subfield that focuses its attention on selfassembled entities built from chiral components. Employment of chiral ligands in coordination chemistry induces the phenomenon of chirality transfer that produces clusters with predetermined chirality at several hierarchical levels, from the ligand to the coordination sphere of the cations, to the molecule or the whole network.[3,4]

On one hand, the comparison between clusters synthesized from a chiral or racemic mixture of ligands is rarely performed because interest in these complexes is directly related to chirality and associated properties (stereoselective catalysis, sensing, chiroptical effects, etc.) and on the other hand, because it is generally assumed that the systems obtained from the racemic ligands will be a symmetric meso form or a simple mixture of both enantiomers, related by inversion centers or reflection planes in the network, maintaining the molecular core and very similar bond parameters. Nevertheless, this assumption is not a rule and in some cases radical differences have been found as was reported for the case of centrosymmetric meso [Ni2Fe2] or [Cu2Ln2] rings obtained from a racemic mixture of chiral organic ligands and (R)- or (S)-[Ni2Fe2]n or [Cu2Ln2]n chiral chains obtained from enantiomerically pure organic ligands.[5,6]

Noteworthily, in these cases the different dimensionality is based on how the building blocks are spatially arranged but always the inner structure and the connectivity between them are maintained. Interestingly, the differences between the meso and chiral forms in these examples go beyond structural and symmetric considerations and are also reflected in their magnetic response, because of the different dimensionality: single molecule magnet (SMM) behavior for discrete clusters and single chain magnet (SCM) response for 1D systems.[5,6]

Following our work on the properties of ligands involving chirality[7–9] and selecting the (Rac)-, (R)- or (S)-H2L Schiff base obtained from the condensation of o-vanilline and the enantiomerically pure (S)-, (R)- or (Rac)-phenylglycinol precursor, Scheme 1, we report in this communication the characterization of nonanuclear clusters [Na2MnIII 6 TbIII(Cl)6(L)6(μ_4-O)2] (OH) (1Rac), (1R), (1S), [Na2MnIII 6 TbIII(Br)6(R-L)6(μ_4-O)2]Br (2S) and [Na2MnIII 6 GdIII(Cl)6(L)6(μ_4-O)2](OH) (3Rac) and (3S) in which L2− is the dianionic form of H2L (synthetic details in ESI†).

The reported complexes provide unprecedented and unexpected examples of the relationship between chiral and meso isomerism, which, among others, involves changes in the coordination number of the lanthanide cation and does not fit with the conventional definitions of isomerism.

The centrosymmetric complex 1Rac can be envisaged as two heterometallic [NaMnIII 3 TbIII] trigonal bipyramidal subunits sharing the TbIII cation which is placed in one of the apical sites, resulting in nonanuclear [NaI 2MnIII 6 TbIII] cluster with D3d symmetry, Fig. 1, and ESI, Tables S1 and S3.† The L2−ligand links the lanthanide, manganese and sodium cations and the inversion center present on the TbIII ion relates three (R)-L2− and three (S)-L2− ligands linked to each pentanuclear subunit. The MnIII

72 cations are related by a C3 axis and thus become equivalent inside each subunit. One oxo donor is placed

73 in the center of the equilateral triangular arrangement of MnIII cations with Mn1–O–Mn1′ bond angles

74 very close to 120°.

75   The MnIII cations are coordinated by the oxo donor, the iminic nitrogen from one L2− ligand,

76 one O-alkoxo donor that links each manganese atom with the lanthanide ion, one O-phenoxo atom that

77 bridges with the sodium cation and two μ-Cl bridges with the neighboring MnIII cations, resulting in an

78 octahedral coordination with the Jahn–Teller elongation axis directed towards the trans-chloro donors.

79 The coordination polyhedron around the hexacoordinated TbIII ion consists of an octahedron compressed

80 along the C3 axis, with an O1–Tb–O1′ bond angle of 97.65(9)°, Fig. 2 and ESI, Table S3.† All Mn1–O1–

81 Tb bond angles are identical, 117.5(1)°, and the TbIII cation is equidistant to O4 and O4′ with a non-

82 contact distance of 2.988 Å. Each subunit shows a propeller shape (helicate) that turns in opposite sense

83 and, consequently, the NaI cations show the opposite Δ/Λ configuration. Complex 3Rac is isostructural

84 to 1Rac with practically identical structural parameters (ESI, Tables S1 and S3†).

85   The structure of the 1R complex is similar to 1Rac in its general aspects but the lack of inversion

86 center reduces its symmetry to C3. The main consequences of this fact are related to the coordination

87 environment around the TbIII cation that becomes heptacoordinated with six shorter Tb–O bond distances

88 to the six O-alkoxo donors (Tb–O1 2.310(6) Å, Tb–O4 2.282(6) Å) and one larger Tb–O8 distance of

89 2.688(11) Å to one of the μ4-oxo ligands, resulting in one apicated octahedron, Fig. 2. This distance is

90 shorter than the Tb⋯O7 distance of 3.281 Å, showing the clear displacement of the TbIII cation from the

91 centre of the complex towards the μ4-O oxo donor O8, resulting in an asymmetrization of 0.593 Å.

92   The core bond parameters show several distortions to facilitate the coordination of the μ4-O donor

93 to the TbIII cation: the O4–Tb–O4′ bond angle increases up to 103.2(2)°, larger than O1–Tb–O1′ which

94 reduces to 91.0(2)°, the Mn2–O4–Tb bond angle becomes shorter than Mn1–O1–Tb (111.0(3)° vs. 124.0

95 (3)°) and the O8 oxo donor is displaced 0.187 Å out of the plane defined by the three Mn(2) cations

96 towards the lanthanide cation, Fig. 2, whereas on the other side of the molecule, O7 is placed 0.076 Å out

97 of the plane defined by the three Mn cations towards the Na(1) cation (Na1–O8 2.811() Å) and can be

98 assumed as heptacoordinated, whereas Na(2) remains hexacoordinated (Na2⋯O8 3.104 Å).

99   Complexes 1R, 1S, 2S and 3S, in which we have modified selectively the L2− enantiomer (R or

100 S), the LnIII cation (TbIII or GdIII) or the axial co-ligand (Cl− or Br−), show a similar core, confirming

101 that these features are common to a large series of complexes (ESI, Tables S2 and S4†).

102   The complexes obtained from the racemic mixtures could yield three kinds of products: the meso

103 form in which the different conformations of the ligands are related by Sn symmetry elements placed in

104 the molecule, a pair of enantiopure isomers in the same crystal related by symmetry in the network or

105 more rarely, the enantiomeric resolution in separate crystals. Among them, experimental structural data

106 show that the meso form is the preferred option for 1Rac and 3Rac. On the other hand, reproducing the

107 synthesis with a mixture containing an enantiomeric excess of (S)-H2L providing adequate stoichiometry

108 to equally crystallize the meso or the chiral cluster yielded the centrosymmetric form (synthetic details in

109 ESI†), showing that, in this case, the meso isomer is preferred to the chiral cluster. This feature could be

110 related to the relative rotation of both subunits which minimizes the repulsion between them for the meso

111 form, Fig. 1. Noteworthily, previously reported related systems obtained from achiral ligands have also

112 been shown to be centrosymmetric.[10]

113   Modification of the substituents on the ligands is a usual synthetic tool to obtain different products

114 on the basis of the involved packing forces, solubility or intermolecular interactions. From this point of

115 view, the reported examples of meso/chiral isomerism could be assumed as a subtle but similar effect.

116 However, the features observed for the [Na2MnIII 6 LnIII] family of clusters are completely new because

117 the packing of the meso or chiral clusters is identical even at the level of the torsion angles of the pendant

118 phenyl groups (ESI, Fig. S2†) and the only difference is the symmetry centre (R3 vs. R3¯ space group)

119 and thus, the phenomenon appears to be strictly intramolecular and symmetry dependent. From the host–

120 guest point of view the size of the central cation is a determinant: an analogous chiral [NaMnIII 6 MnII]

121 system with one smaller MnII cation instead of the LnIII ion exhibits an MnIIO6 octahedral

122 environment,[7,8] whereas the lanthanides are large enough to establish contact with the seventh O-donor

123 at distances of around 2.7 Å. It becomes crucial to note that this arrangement is the consequence of the

124 possibility of being centrosymmetric but not due to the alternative arrangement in the network of S and R

125 clusters related by inversion centres and that retaining the most usual heptacoordination of the LnIII cation

126 could be equally possible (or even more probable a priori), in light of the structures of the chiral clusters

127 and the flexibility of L2−.

128   O-centred MnIII 3 triangles with axial bridging chloro ligands are scarce and have been revealed

129 to show typical ferromagnetic coupling.[7,11,12] Susceptibility measurements in the 2–300 K range of

130 temperatures were performed for the reported complexes. In all cases the χMT plots show a continuous

131 increase from room temperature up to a maximum of χMT around ∼20 K followed by a strong decrease

132 at low temperature. The room temperature values agree with the expected ones for six S = 2 and one TbIII

133 cation (29.8 cm3 mol−1 K) or one GdIII cation (25.6 cm3 mol−1 K) with g values slightly lower than

134 2.00.

135   Isotropic fit of the GdIII complexes up to the χMT maximum with the two-J Hamiltonian derived

136 from the scheme shown in the Fig. 3 inset yields the best values J1 = +2.3 cm−1, J2 = −0.11 cm−1 and g

137 = 1.89 for 3Rac and J1 = +3.4 cm−1 J2 = −0.20 cm−1 and g = 1.89 for 3S (PHI program,[13] 2J convention).

138   As can be expected from the structural information the chiral and meso clusters exhibit a similar

139 but not identical magnetic response. The fit confirms the ferromagnetic interaction inside the triangular

140 MnIII 3 fragments and suggests weak antiferromagnetic interactions between the ferromagnetic MnIII 3

141 units and the central lanthanide. However, the strong decay at lower temperatures indicates a moderately

142 strong anisotropy that is evidenced in the magnetization measurements, reaching values clearly lower than

143 that expected for an isotropic system, (ESI†). The TbIII complexes follow a similar pattern to that of the

144 GdIII ones.

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CONCLUSIONS

In conclusion, a unique case of strictly intramolecular meso/chiral isomerism has been found, in which, in addition to the conventional supramolecular recognition tools such as the size and spatial distribution of O-donors, also the symmetry is involved. The most interesting feature of the reported systems is that for the very first time we report a symmetry-dependent case of intramolecular meso–chiral isomerism that does not fit with the conventional nomenclature (the same shape and dimensionality but different connectivity), involving the full rearrangement of the bond parameters and the change in the coordination numbers of the cations. The employment of symmetry elements to modify the dimensionality or the coordination sphere of the cations is an emerging supramolecular tool that is demonstrated to be useful for the rational design of unusual isomers with coordination environments such as LnIII cations or d-cations with tunable coordination spheres. In a further paper the complete series of [Na2MnIII 6 LnIII] complexes from CeIII to YbIII central cations will be explored to determine the size effect of the cation along the f-block.

161 **ACKNOWLEDGEMENTS**

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REFERENCES

1.   J. M. Lehn, Supramolecular Chemistry, VCH-Weinheim, 1995.

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

3.   H. Miyake, Symmetry, 2014, **6**, 880.

4.   J. Crassous, Chem. Soc. Rev., 2009, **38**, 830.

5.   N. Hoshino, Y. Sekine, M. Nihei and H. Oshio, Chem. Commun., 2010, **46**, 6117.

6.   T. Ueno, T. Fujinami, N. Matsumoto, M. Furusawa, R. Irie, N. Re, T. Kanetomo, T. Ishida and Y. Sunatsuki, Inorg. Chem., 2017, **56**, 1679.

7.   A. Escuer, J. Mayans, M. Font-Bardia, M. Górecki and L. Di Bari, Dalton Trans., 2017, **46**, 6514.

8.   J. Mayans, M. Font-Bardia, L. Di Bari and A. Escuer, Chem. – Eur. J., 2018, **24**, 18705.

9.   J. Mayans, M. Font-Bardia and A. Escuer, Inorg. Chem., 2018, **57**, 926.

10.   P.-P. Yang, X.-L. Wang, L.-C. Li and D.-Z. Liao, Dalton Trans., 2011, **40**, 4155.

11.   C. Ding, C. Gao, S. Ng, B. Wang and Y. Xie, Chem. – Eur. J., 2013, **19**, 9961.

12.   P.-P. Yang, L.-L. Zhu, Y. Xu and C.-Y. Shao, Z. Anorg. Allg. Chem., 2013, **639**, 1821.

13.   N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, J. Comput. Chem., 2013, **34**, 1164.

184   **Legends to figures**

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186   **Scheme 1** Coordination to one MnIII, one LnIII and one Na cations for

187   the L2− ligand employed in this work. The asterisk denotes the chiral

188   carbon.

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190   **Figure. 1** Top, view of the molecular structure of 1Rac. Down, axial view of

191   1Rac (left) and 1R (right) showing the rotation between subunits and the

192   distances between centroids. Color code: MnIII, dark green; GdIII, light

193   blue; Na, orange; N, navy; O red; Cl, violet.

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195   **Figure 2**. Top, labelled view of the common core of clusters 1R, 1S, 2S and

196   3S. Middle, labelled common core of complexes 1Rac and 3Rac. Down,

197   Coordination environment of the chiral and meso isomers of complexes

198   1–3.

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200   **Figure 3.** Plot of $\chi_M T$ product vs. T for 1R (diamonds), 2S (triangles), 3Rac

201   (blue) and 3S (red). Inset, the coupling scheme for compounds 3. Solid

202   lines show the best fit of the experimental data in the 20–300 K range

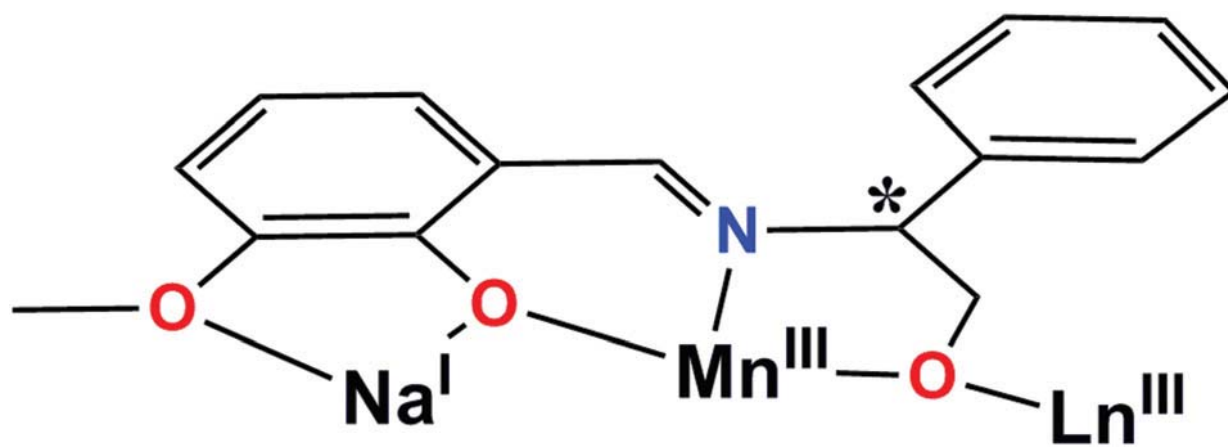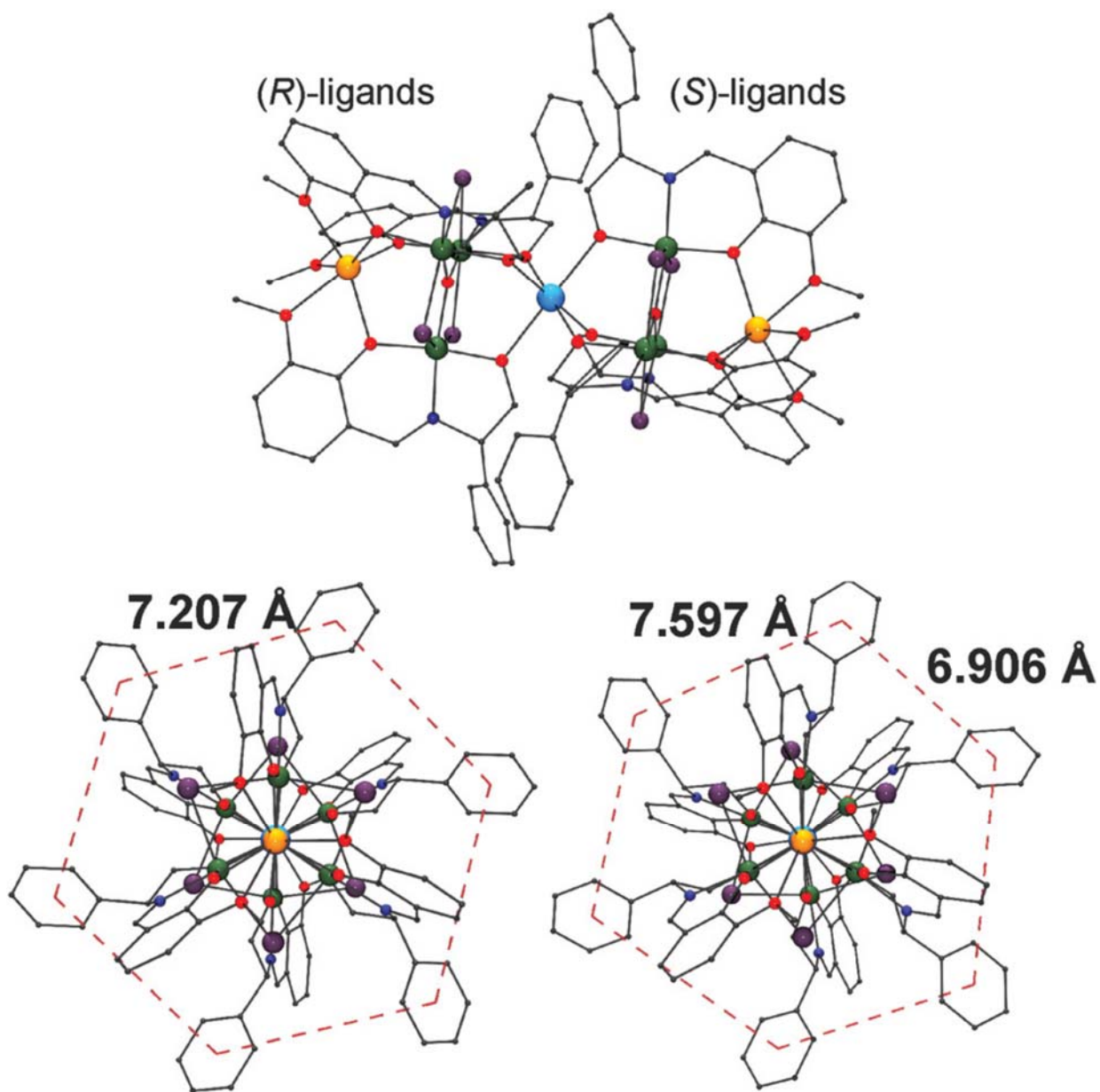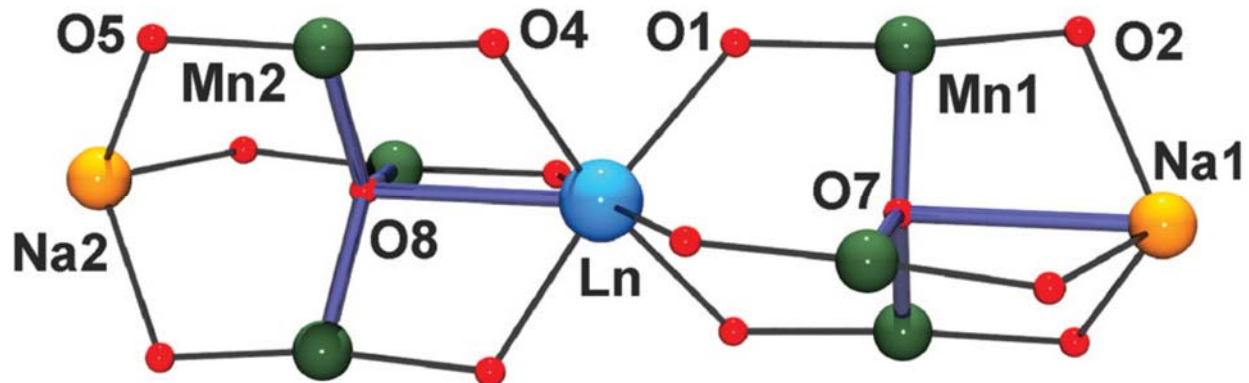203   of temperatures.

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SCHEME 1

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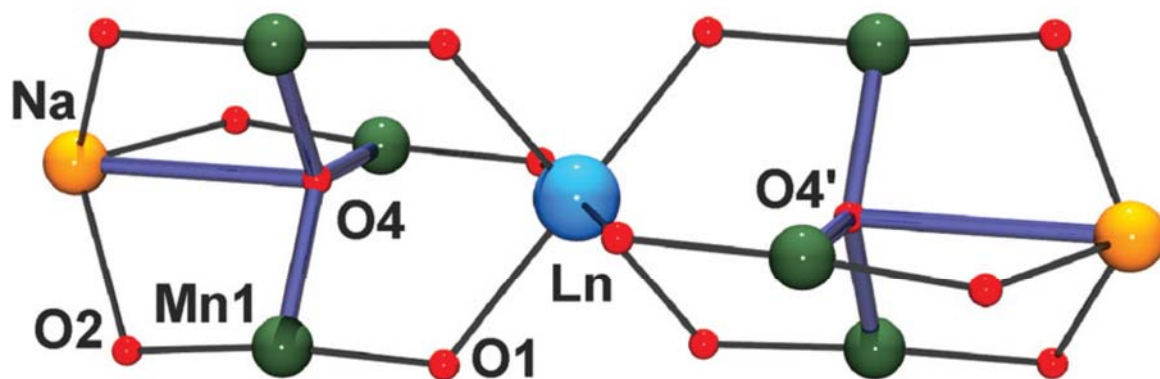213
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FIGURE 1

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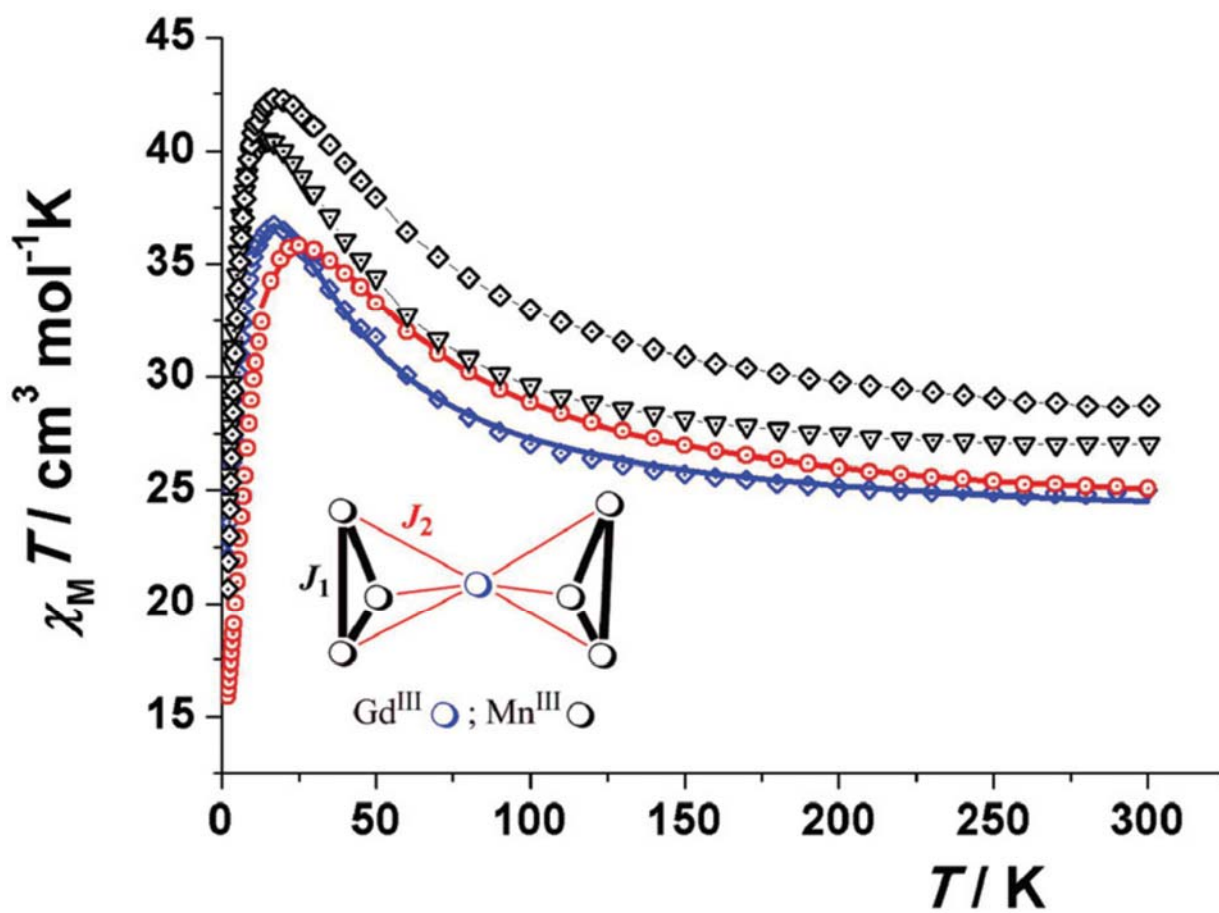

(R)-ligands   (S)-ligands

7.207 Å   7.597 Å

6.906 Å
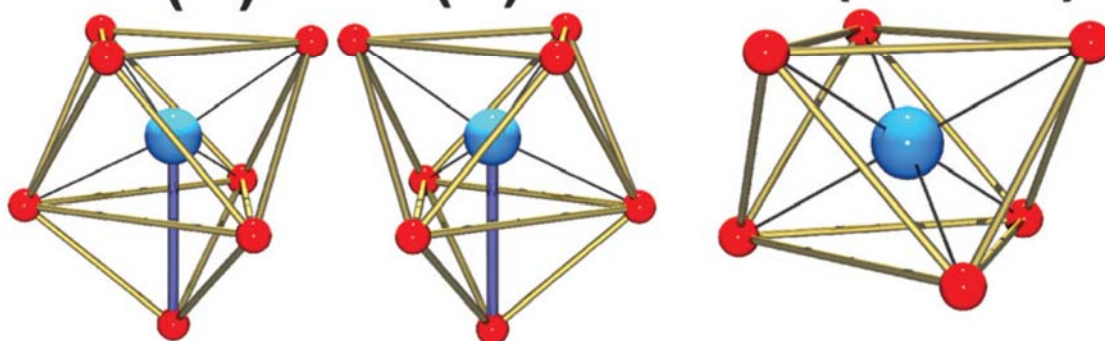
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FIGURE 2

Δ (Ln-O8)-(Ln···O7) = 0.593 Å

D (Ln···O4)-(Ln···O4') = 0.0 Å

(R)   *(S)*   (meso)

FIGURE 3