New members of the \([\text{Mn6/oxime}]\) family and analogues with converging \([\text{Mn3}]\) planes

Citation for published version:

Digital Object Identifier (DOI):
10.1080/00958972.2016.1152359

Link: Link to publication record in Edinburgh Research Explorer

Document Version: Peer reviewed version

Published In: Journal of coordination chemistry

General rights
Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy
The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

ANDREAS G. FLAMOURAKIS †, DIMITRIS A. KALOFOLIAS †, MILOSZ SICZEK ‡, TADEUSZ LIS ‡, EUAN K. BRECHIN*§ and CONSTANTINOS J. MILIOS*†

† Department of Chemistry, University of Crete, Voutes 71003, Herakleion, Greece.
‡ Faculty of Chemistry, University of Wroclaw, Joliot-Curie 14, Wroclaw 50-383, Poland.
§ EaStCHEM School of Chemistry, The University of Edinburgh, David Brewster Road, Edinburgh, EH9 3FJ, UK.

*Corresponding authors: E-mail: komil@chemistry.uoc.gr (C. J. Milios).
 ebrechin@ed.ac.uk (E. K. Brechin)
Abstract

The synthesis, structural and magnetic characterization of five new members of the hexanuclear oximate [Mn\textsuperscript{III}6] family is reported. All five clusters can be described with the general formula [Mn\textsuperscript{III}6O2(R-sao)6(R’-CO2)2(sol)\textsubscript{x}H\textsubscript{2}O\textsubscript{y}] (where R-sao\textsubscript{2} = salicylaldoxime substituted at the oximic carbon atom with R = H, Me and Et; R’ = 1-naphthalene, 2-naphthalene and 1-pyrene; sol = MeOH, EtOH or MeCN; x = 0-4 and y = 0-4). More specifically, the reaction of Mn(ClO\textsubscript{4})\textsubscript{2}.6H\textsubscript{2}O with salicylaldoxime-like ligands and the appropriate carboxylic acid in alcoholic or MeCN solutions in the presence of base afforded complexes 1-5: [Mn\textsubscript{6}O\textsubscript{2}(Me-sao)\textsubscript{6}(1-naphth-CO\textsubscript{2})\textsubscript{2}(H\textsubscript{2}O)(MeCN)]4MeCN (1-4MeCN); [Mn\textsubscript{6}O\textsubscript{2}(Me-sao)\textsubscript{6}(2-naphth-CO\textsubscript{2})\textsubscript{2}(H\textsubscript{2}O)(MeCN)]3MeCN0.1H\textsubscript{2}O (2-3MeCN0.1H\textsubscript{2}O); [Mn\textsubscript{6}O\textsubscript{2}(Et-sao)\textsubscript{6}(2-naphth-CO\textsubscript{2})\textsubscript{2}(EtOH)\textsubscript{4}(H\textsubscript{2}O)\textsubscript{2}] (3); [Mn\textsubscript{6}O\textsubscript{2}(Et-sao)\textsubscript{6}(2-naphth-CO\textsubscript{2})\textsubscript{2}(MeOH)\textsubscript{6}] (4) and [Mn\textsubscript{6}O\textsubscript{2}(sao)\textsubscript{6}(1-pyrene-CO\textsubscript{2})\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}(EtOH)\textsubscript{2}]6EtOH (5-6EtOH). Clusters 3, 4 and 5 display the usual [Mn\textsubscript{6}/oximate] structural motif consisting of two [Mn\textsubscript{3}] sub-units bridged by two O\textsubscript{oximate} atoms from two R-sao\textsuperscript{2}- ligands to form the hexanuclear complex in which the two triangular [Mn\textsubscript{3}] units are parallel to each other. On the contrary, clusters 1 and 2 display a highly distorted stacking arrangement of the two [Mn\textsubscript{3}] sub-units resulting in two converging planes, thus forming a novel motif in the [Mn\textsubscript{6}] family. Investigation of the magnetic properties for all complexes reveal dominant antiferromagnetic interactions for complexes 1, 2 and 5, while complexes 3 and 4 display dominant ferromagnetic interactions with a ground state of S = 12 for both clusters. Finally, complexes 3 and 4 display Single-Molecule Magnet behaviour with $U_{\text{eff}} = 63$ K and 36 K, respectively.

Keywords: Mn(III) oximate complexes; Converging [Mn\textsubscript{3}] planes; Magnetic properties; Single-Molecule Magnets.
Figure for the table of contents
1. Introduction

Since the discovery of the Single Molecule Magnetism (SMM) phenomenon in the mixed-valence dodedanuclear manganese cluster \([\text{Mn}^{IV}_4\text{Mn}^{III}_8\text{O}_{12} (\text{MeCO}_2)_6(\text{H}_2\text{O})_4]\) \(2\text{MeCO}_2\text{H}_4\text{H}_2\text{O}\) [1-5], numerous paramagnetic polymetallic clusters that can retain their magnetization at low temperatures once magnetized upon removal of the external stimuli have been reported [6-22]. This unique magnetic behaviour results from the combination of a large spin ground state, and a relatively large and negative magnetoanisotropy, \(D\), which creates a significant energy barrier to magnetization reversal, \(U\), whose upper limit is given by \(U= S^2 \mid D \mid \) for integer spin, and \(U= (S^2-1/4) \mid D \mid \) for half-integer spin ground states. Besides the scientific interest that such molecules possess, it has been proposed that they may be used in various technological applications, such as in computer magnetic storage, in magnetic resonance imaging as contrast agents, and in cooling processes [23, 24]. Manganese oximate cluster chemistry has afforded a large family of compounds that function as SMMs; a series of complexes with general formulae \([\text{Mn}^{III}_x\text{O}_2(\text{R-sao})_x(\text{O}_2\text{CR})_{1-2}(\text{L})_{4-6}]\) (R= H, Me, Et, Ph, etc; L= solvent and \(x = 3\) or 6) were synthesized and characterized [25-39], with two representative members of this family that function as SMMs being \([\text{Mn}^{III}_6\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{CPh})_2(\text{EtOH})_4(\text{H}_2\text{O})_2]\) [40] and \([\text{Mn}^{III}_6\text{O}_2(\text{Et-sao})_6(\text{O}_2\text{CPh}(\text{Me})_2)_2(\text{EtOH})_6]\) [41]. A magneto-structural correlation was developed for this family of complexes in order to explain the “switch” from antiferromagnetic (AF) to ferromagnetic (F) exchange between neighbouring Mn centres, with the governing factor being the Mn-N-O-Mn torsion angle, \(\tau\) [30]. According to this magnetostructural correlation there is a “magic area” of \(\sim 30.4-31.3^\circ\); \(\tau\) angles of \(<30.4^\circ\) lead to an AF \((J<0)\) nearest-neighbour interaction, while for \(\tau > 31.3^\circ\) a F \((J>0)\) interaction is achieved. The Mn-N-O-Mn torsion angle is affected both by the steric bulk of substituents of the oxime and carboxylate ligands, and as such, different combinations of R-saoH\(_2\) and carboxylate ligands afford species with different torsion angles, and thus different magnetic properties.

In this contribution, we report seven new \([\text{Mn}^{III}_6/\text{oxime}]\) compounds from the use of R-saoH\(_2\) \((R = H, \text{Me, Et})\) and various carboxylic acids in Mn(III) chemistry. Two clusters of the family display a novel arrangement of the metallic core, in which the two \([\text{Mn}_3\text{O}]\) sub-units that form the hexanuclear core are positioned in a non-parallel fashion, while
in addition one \( \mu_4 \)-oxo group is present, in contrast with all other \([\text{Mn}_6]\) complexes reported so far.

Scheme 1. Ligands discussed in the text; Top-left to bottom-right: \text{saoH}_2, \text{Me-saoH}_2, \text{Et-saoH}_2, 1-naphthoic acid, 2-naphthoic acid and 1-pyrene carboxylic acid.

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions, using materials as received. \text{Me-saoH}_2, \text{Et-saoH}_2 and \text{saoH}_2 were synthesized by the reaction of the appropriate precursor aldehyde with hydroxylamine and sodium acetate in EtOH, as described in literature [42]. Elemental analyses (C, H, N) were performed by the University of Ioannina microanalysis service. Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 5 K were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T dc magnet at UoC. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal’s constants.

2.2. Compound preparation

2.2.1. General synthetic strategy for 3, 4 and 5.

To pale pink solutions of \( \text{Mn(ClO}_4\text{)}_2 \cdot 6\text{H}_2\text{O} \) in MeOH (or EtOH) were added equimolar amounts of the corresponding oxime and carboxylic acid ligands, in the presence of
excess base, NEt₃. The solutions were left stirring for ~30 min, filtered and then left to slowly evaporate. In each case suitable single-crystals grew after a period of 3-5 days. Anal. Calcd. [Mn₆O₂(Et-sao)₆(2-naphthoic)₂(EtOH)₄(H₂O)₂] (3) (C₈₄H₇₆Mn₆N₂O₂₄): C 53.01, H 5.08, N 4.42 %. Found C 52.92, H 4.88, N 4.29 %. Anal. Calcd for [Mn₆O₂(Et-sao)₆(2-naphthoic)₂(EtOH)₆] (4) (C₈₂H₉₂Mn₆N₂O₂₄): C 52.52, H 4.94, N 4.48 %. Found C 52.45, H 4.81, N 4.32 %. Anal. Calcd. for [Mn₆O₂(sao)₆(1-pyrene)₂(H₂O)₂(EtOH)₂]6EtOH (5 6EtOH) (C₉₂H₉₄Mn₆N₂O₂₈): C 53.60, H 4.60, N 4.08 %. Found C 53.48, H 4.37, N 3.95 %.

2.2.2. General synthetic strategy for 1 and 2.

To pale pink solutions of Mn(ClO₄)₂·6H₂O in MeCN were added equimolar amounts of the derivitized oximes, the corresponding carboxylic acid and CH₃ONa. The solutions were left stirring for ~45 min, filtered and then left to slowly evaporate. In each case suitable crystals grew after a period of 3-5 days. Anal. Calcd. for [Mn₆O₂(Me-sao)₆(1-naphthoic)₂(H₂O)(MeCN)]4MeCN (1·4MeCN) (C₈₀H₇₃Mn₆N₁₁O₁₉): C 52.73, H 4.04, N 8.46%. Found C 52.60, H 3.82, N 8.29 %. Anal. Calcd. for [Mn₆O₂(Me-sao)₆(2-naphthoic)₂(H₂O)(MeCN)]3MeCN·0.1H₂O (2·3MeCN·0.1H₂O) (C₇₈H₇₀Mn₆N₁₀O₁₉): C 52.60, H 3.96, N 7.86%. Found C 52.49, H 3.92, N 7.80 %.

2.3. Single-crystal X-ray crystallography

Diffraction data for 1·4.4H₂O·1.6EtOH, 2·6EtOH and 3·6EtOH were collected at 100 K on an Xcalibur PX diffractometer. All structures were refined by full-matrix least-squares techniques on F² with SHELXL [43]. Data collection parameters and structure solution and refinement details are listed in Table 1.
# Table 1

Crystal and structure refinement data for complexes 1 – 5

<table>
<thead>
<tr>
<th>Compound reference</th>
<th>Chemical formula</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula Mass</td>
<td>C\textsubscript{80}H\textsubscript{73}Mn\textsubscript{6}N\textsubscript{11}O\textsubscript{19}</td>
<td>1822.13</td>
<td>1782.88</td>
<td>1903.31</td>
<td>1875.26</td>
<td>2061.37</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
<td>Monoclinic</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>a/Å</td>
<td>15.080 (4)</td>
<td>14.435 (4)</td>
<td>15.999 (4)</td>
<td>11.650 (3)</td>
<td>12.123 (4)</td>
<td></td>
</tr>
<tr>
<td>b/Å</td>
<td>15.886 (5)</td>
<td>15.562 (5)</td>
<td>19.739 (5)</td>
<td>13.763 (4)</td>
<td>13.349 (4)</td>
<td></td>
</tr>
<tr>
<td>α/°</td>
<td>101.71 (3)</td>
<td>104.56 (3)</td>
<td>94.44 (3)</td>
<td>101.67 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β/°</td>
<td>109.29 (3)</td>
<td>107.50 (3)</td>
<td>112.83 (3)</td>
<td>111.22 (3)</td>
<td>110.49 (4)</td>
<td></td>
</tr>
<tr>
<td>γ/°</td>
<td>106.55 (3)</td>
<td>100.31 (3)</td>
<td>113.36 (3)</td>
<td>105.99 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unit cell volume/Å(^3)</td>
<td>3790 (2)</td>
<td>3787 (2)</td>
<td>4216 (2)</td>
<td>2032.1 (13)</td>
<td>2278.7 (17)</td>
<td></td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
<td>P-1</td>
<td>P-1/c</td>
<td>P-1</td>
<td>P-1</td>
<td></td>
</tr>
<tr>
<td>No. of formula units per unit cell, Z</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Radiation type</td>
<td>Mo-Kα</td>
<td>Mo-Kα</td>
<td>Mo-Kα</td>
<td>Mo-Kα</td>
<td>Mo-Kα</td>
<td></td>
</tr>
<tr>
<td>Absorption coefficient, μ/mm(^{-1})</td>
<td>1.05</td>
<td>1.05</td>
<td>0.95</td>
<td>0.99</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>No. of reflections measured</td>
<td>52489</td>
<td>45700</td>
<td>17846</td>
<td>26840</td>
<td>16434</td>
<td></td>
</tr>
<tr>
<td>No. of independent reflections</td>
<td>28759</td>
<td>25977</td>
<td>11086</td>
<td>15085</td>
<td>12119</td>
<td></td>
</tr>
<tr>
<td>R(_{int})</td>
<td>0.024</td>
<td>0.029</td>
<td>0.024</td>
<td>0.022</td>
<td>0.037</td>
<td></td>
</tr>
<tr>
<td>Final R(_{1}) values (I &gt; 2σ(I))</td>
<td>0.034</td>
<td>0.043</td>
<td>0.044</td>
<td>0.032</td>
<td>0.056</td>
<td></td>
</tr>
<tr>
<td>Final wR(^2) values (all data)</td>
<td>0.083</td>
<td>0.085</td>
<td>0.0621</td>
<td>0.0501</td>
<td>0.1052</td>
<td></td>
</tr>
<tr>
<td>Final wR(^2) values (all data)</td>
<td>0.082</td>
<td>0.090</td>
<td>0.116</td>
<td>0.080</td>
<td>0.135</td>
<td></td>
</tr>
<tr>
<td>Goodness of fit on R(^2)</td>
<td>1.01</td>
<td>1.00</td>
<td>1.04</td>
<td>1.00</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>CCDC</td>
<td>XXX</td>
<td>XXX</td>
<td>XXX</td>
<td>XXX</td>
<td>XXX</td>
<td></td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Syntheses

The reaction between Mn(ClO$_4$)$_2$·6H$_2$O, salicylaldoxime-like ligands and various carboxylic acids in a 1:1:1 molar ratio in basic alcoholic or acetonitrile solutions afforded hexanuclear species of general formula [Mn$^{III}$$_2$O$_2$(R-sao)$_6$(R’-CO$_2$)$_2$(sol)$_x$(H$_2$O)$_y$] (R = H, Me and Et; R’ = 1-naphthalene, 2-naphthalene and 1-pyrene; sol = MeOH, EtOH or MeCN; x = 0-4 and y = 0-4). In all five clusters, the manganese centres were found to be in the 3+ oxidation state due to the facile oxidation of Mn$^{2+}$ to Mn$^{3+}$ under standard aerobic conditions. Upon changing the nature of the base from NEt$_3$ or CH$_3$ONa to either NMe$_4$OH or NEt$_4$OH we did not manage to isolate any different products, as verified by pXRD measurements. Finally, repeating the same reactions under solvothermal conditions yielded an amorphous yellow precipitate in each case, which could not be further characterized and identified.

3.2. Description of structures

All five clusters (Figures 1-3) display similar but not identical structures; two [Mn$_3$O(R-sao)$_3$]$^+$ sub-units are linked together to form the final hexametallic core. Yet, there are significant differences between the seven structures. More specifically, the seven complexes may be divided in three distinct types:

**Type I**: complex 5 displays the “prototype” [Mn$_6$/oxime] structural pattern [26]. The cluster crystallizes in the triclinic P-1 space group. Its structure (Figure 1) consist of two off-set triangular [Mn$_3$(μ$_3$-O)(sao)$_3$]$^+$ sub-units, which are linked via two O$_{ox}$ atoms, to form a [Mn$_6$(μ$_3$-O)$_2$(sao)$_6$]$^{2+}$ metallic core with a central {Mn-O$_{ox}$-Mn-O$_{ox}$} rhomb between the two triangular units. The edges of each triangular sub-unit consist of –N$_{ox}$–O$_{ox}$– bridges, forming a {Mn-N$_{ox}$-O$_{ox}$}$_3$ ring, while the charge of the hexametallic core is counterbalanced by the presence of two syn, syn- η$^1$: η$^1$: μ carboxylates, with each one capping a triangular unit. The oximate ligands adopt two different coordination modes: four are found in an η$^1$: η$^1$: η$^1$: μ fashion, while the remaining two, responsible for the inter-triangular linkage, adopt an η$^2$: η$^1$: η$^1$: μ$_3$ coordination mode. The coordination environment of the metallic centres is completed by four terminal solvent/water molecules. Four of the six manganese centres are six-coordinate adopting
Jahn-Teller distorted octahedral geometry, while the remaining two are five-coordinate adopting square-pyramidal geometry. Finally, the two trimetallic planes, [Mn$_3$] and thus the JT axes, are parallel to each other.

Figure 1. The molecular structure of Type I cluster 5.

**Type II:** clusters 3 and 4 (Figure 2) display a slightly different structural motif than Type I clusters. The two main structural ingredients, the [Mn$_3$(μ$_3$-O)(R-saO)$_3$]$^+$ sub-units, are still retained, but now two extra bridges are present arising from two O$_R$ alkoxide groups belonging to two oximate ligands, each on a [Mn$_3$(μ$_3$-O)(R-sao)$_3$]$^+$ unit. Therefore, in Type II clusters the inter-triangular linkage takes place via four bridges vs. two in Type I complexes, forming two {Mn-O$_R$-Mn-N$_{ox}$-O$_{ox}$} and one {Mn-O$_{ox}$-Mn-O$_{ox}$} rhombs. Furthermore, the two carboxylate ligands found in the structures are in terminal mode (vs. bridging in Type I clusters). In addition, all manganese centres are six-coordinate, with JT elongated octahedral geometry. The two [Mn$_3$] planes are still retained parallel to each other, as in Type I clusters.

**Type III:** clusters 1 and 2 (Figure 3) present highly distorted intermediates between Type I and II complexes. Both clusters crystallize in the triclinic P-1 space group. Again, as in Type I/II clusters, the main structural ingredients, the [Mn$_3$(μ$_3$-O)(saO)$_3$]$^+$ units, are still present, but now the trimetallic planes are converging, deviating from parallel by 21.58° and 27.55° for 1 and 2, respectively. As a result of this distortion, three main structural consequences unfold: i) a central oxo group of one triangular sub-unit is now
$\mu_4$-O$^{2-}$, further bridging a manganese ion in the other [Mn$_3$] unit, ii) there is only one O$_R$ alkoxide bridge from one aromatic group of an oximate ligands vs. two in Type II clusters, and iii) two long inter-triangular Mn-O$_{ox}$ bonds are formed (~ 2.6 Å). Therefore, the bridging between the two triangular units occurs via five bridges vs. four bridges in Type II and two bridges in Type I complexes. Finally, the two carboxylate ligands are found to bond in a syn,syn-$\eta^1$: $\eta^1$: $\mu$ fashion. Here, we note that a similar type of complex was reported recently by Poole et al. [35], with the main difference in the latter complex being the presence of two $\mu_4$-O$^{2-}$ groups (vs. one in clusters 1 and 2).

Figure 2. The molecular structures of Type II complexes 3 (left) and 4 (right).

Figure 3. The molecular structures of Type III complexes 1 (left) and 2 (right).

In Figure 4, the metallic cores of all three types of clusters are given, and it becomes apparent that Type I and Type II complexes are closely related, while Type III clusters
are so distorted that the connectivity between the two triangular units is completely different.

Figure 4. The metallic core of Type I (left), Type II (centre) and Type III (right) complexes, highlighting their main differences (dotted lines).

In the crystal the packing of Type I complex 5 shows six intermolecular H-bonds to the co-crystallized solvent molecules, creating chains of $[\text{Mn}_6]$ units running along the $b$ axis of the unit cell (Figure 5).

Figure 5. Crystal packing for Type I complex 5, showing the inter-molecular H-bonds (dotted lines).

In the extended structures of Type II clusters 3 and 4 the Mn6 units stack directly upon each other forming sheets of molecules (Figure 6), while Type III complex 1 exhibits four inter-molecular H-bonds, creating isolated $\{[\text{Mn}_6]-[\text{Mn}_6]\}$ dimers (Figure 7).
3.3. Magnetic properties
Dc magnetic susceptibility measurements were performed for all compounds in the 5-300 K temperature range under an applied field of 0.1 T. The results are shown as $\chi M T$ vs. $T$ plots in Figure 8.

Complexes 1 and 2 display similar behaviour; the value of $\chi M T$ decreases upon cooling suggesting the presence of dominant antiferromagnetic interactions, while in complexes 3 and 4 $\chi M T$ increases upon cooling suggesting dominant ferromagnetic interactions. Finally, for cluster 5 the $\chi M T$ product decreases upon cooling until ~25 K, before it increases upon further cooling. More specifically, for complexes 1 and 2, the room temperature $\chi M T$ values of 18.14 cm$^3$mol$^{-1}$K and 18.26 cm$^3$mol$^{-1}$K, respectively, are very close to the spin-only value of 18 cm$^3$mol$^{-1}$K expected for six non-interacting
Mn$^{III}$ ions ($g$=2.00). Upon cooling the $\chi_M T$ value remains almost constant until ~120 K, below which it gradually decreases to reach minimum values of 8.42 cm$^3$mol$^{-1}$K and 8.35 cm$^3$mol$^{-1}$K, for 1 and 2, respectively. For complex 3, the room temperature $\chi_M T$ value of 18.43 cm$^3$mol$^{-1}$K slightly increases to 20.86 cm$^3$mol$^{-1}$K upon cooling until ~150 K, while upon further cooling it reaches its maximum value of 77.40 cm$^3$mol$^{-1}$K. For complex 4, the room temperature $\chi_M T$ value of 20.40 cm$^3$mol$^{-1}$K slightly increases upon cooling to 22.58 cm$^3$mol$^{-1}$K at ~150 K, before it reaches a maximum value of 58.00 cm$^3$mol$^{-1}$K at 5 K. Finally, for complex 5 the room temperature $\chi_M T$ value of 16.47 cm$^3$mol$^{-1}$K, is smaller than the theoretical value expected for six non-interacting Mn$^{III}$ centres ($g$ = 2.00), indicating moderately strong antiferromagnetic interactions. Upon cooling the $\chi_M T$ value reaches its minimum value of 8.30 cm$^3$mol$^{-1}$K at ~20 K, before it increases to a final value of 12.94 cm$^3$mol$^{-1}$K at ~5 K.

We were able to successfully simulate the magnetic susceptibility data for all complexes, adopting two general exchange coupling schemes: i) For clusters 3, 4 and 5 we used a scheme based on the well-established torsion angles rule, with the main parameter governing the number of $J$ values employed in each case being the magnitude and size of the Mn-N-O-Mn torsion angle, $\tau$ (Table 3). Therefore, for cluster 5 we adopted a 2-$J$ model (Figure 6, left). Employment of [isotropic] spin-Hamiltonian (1),

$$\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_3') -2J_2(\hat{S}_1\hat{S}_2' + \hat{S}_2\hat{S}_3' + \hat{S}_1\hat{S}_3')$$ (1)

and using program MAGPACK [44], yielded $J_1$ = -7.95 cm$^{-1}$, $J_2$ = +13.80 cm$^{-1}$ and $g$ = 2.00. These parameters lead to a spin ground state of $S$ = 4 for cluster 5.

For clusters 3 and 4 we adopted a 1-$J$ model (Figure 6, right) and spin-Hamiltonian (2),

$$\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_1\hat{S}_3 + \hat{S}_1\hat{S}_3') -2J_2(\hat{S}_1\hat{S}_2' + \hat{S}_2\hat{S}_3' + \hat{S}_1\hat{S}_3')$$ (2)

which afforded $J_1$ = +1.35 cm$^{-1}$ and $g$ = 2.00 for complex 3, and $J_1$ = +0.82 cm$^{-1}$ and $g$ = 2.00 for complex 4. These parameters lead to a spin ground state of $S$ = 12 for both complexes.

ii) For complexes 1 and 2, which are non-classical examples of [Mn$_6$/oximate] clusters since they present an extra bridge through the $\mu_4$-oxo ion, we modified the exchange coupling scheme by adding this extra feature. More specifically, for complex 1 we adopted a 3-$J$ model (Figure 7) assuming one $J_1$ interaction between a) Mn1-Mn2 and
Mn2-Mn3 mediated by an \( \mu_4 \)-oxo bridge and an oximate ligand with Mn-N-O-Mn torsion angles of 15.95° and 17.73° respectively, b) Mn4-Mn5 and Mn5-Mn6 mediated by an \( \mu_3 \)-oxo bridge and an oximate ligand with torsion angles of 21.25° and -19.69° respectively, and c) Mn2-Mn6 mediated by two monoatomic \( \text{O}_{\text{oxim}} \) bridges (Mn-\( \text{O}_{\text{oxim}} \)-Mn: 95.0° and 98.3°); one \( J_2 \) interaction between a) Mn1-Mn3 and Mn4-Mn6 mediated by an \( \mu_3 \)-oxo bridge and an oximate ligand with Mn-N-O-Mn torsion angles of -33.96° and 39.56° respectively, and b) Mn1-Mn5 mediated by an oximate ligand with torsion angle of -88.13° (inter-triangular linkage), and one \( J_3 \) interaction between a) Mn1-Mn4 and Mn2-Mn4 mediated by an \( \mu_4 \)-oxo bridge and an \( \text{O}_{\text{oxim}} \) bridge, and b) Mn3-Mn4 mediated by an \( \mu_4 \)-oxo bridge and an alkoxo group of the oximate ligand. Using the program MAGPACK and spin-Hamiltonian (3),

\[
\hat{H} = -2J_1(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_4\hat{S}_5 + \hat{S}_5\hat{S}_6 + \hat{S}_3\hat{S}_6 + \hat{S}_3\hat{S}_5) -2J_2(\hat{S}_1\hat{S}_3 + \hat{S}_4\hat{S}_6 + \hat{S}_3\hat{S}_5) -2J_3(\hat{S}_1\hat{S}_4 + \hat{S}_2\hat{S}_4 + \hat{S}_3\hat{S}_4) (3)
\]

afforded the parameters \( J_1 = -1.25 \text{ cm}^{-1}, J_2 = +3.70 \text{ cm}^{-1}, J_3 = -1.00 \text{ cm}^{-1} \) and \( g = 1.99 \). These parameters lead to a band of near degenerate \( S \) states of value \( S = 4, S = 3, S = 2 \) and \( S = 1 \), all within ~5 cm\(^{-1} \). Again, the ferromagnetic nature of \( J_2 \) corresponds to Mn pairs bridged by –N-O- oximate species with large torsion angles.

Finally, for complex 2 we adopted an analogous 3-\( J \) model (Figure 7) assuming one \( J_1 \) interaction between a) Mn1-Mn3 and Mn2-Mn3 mediated by an \( \mu_3 \)-oxo bridge and an oximate ligand with torsion angles of 24.78° and -16.42° respectively, b) Mn4-Mn5, Mn4-Mn6 and Mn5-Mn6 mediated by an \( \mu_4 \)-oxo bridge and an oximate ligand with torsion angles of -3.87°, -29.82° and 20.38° respectively, and c) Mn5-Mn2 mediated by a monoatomic \( \text{O}_{\text{oxim}} \) bridge (Mn-\( \text{O}_{\text{oxim}} \)-Mn: 100.9°), one \( J_2 \) interaction between a) Mn1-Mn2 mediated by an \( \mu_3 \)-oxo bridge and an oximate ligand with torsion angle of 49.98°, and b) Mn3-Mn4 mediated by an oximate ligand with torsion angle of -85.93° (inter-triangular linkage), and one \( J_3 \) between a) Mn1-Mn4 mediated by an \( \mu_4 \)-oxo bridge and an \( \text{O}_{\text{oxim}} \) bridge, b) Mn1-Mn5 mediated by an \( \mu_4 \)-oxo bridge and an oximate ligand, and c) Mn1-Mn6 mediated by an \( \mu_4 \)-oxo bridge and an alkoxo group of the oximate ligand. Using the program MAGPACK and spin-Hamiltonian (4),

\[
\hat{H} = -2J_1(\hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_3 + \hat{S}_4\hat{S}_5 + \hat{S}_4\hat{S}_6 + \hat{S}_5\hat{S}_6 + \hat{S}_3\hat{S}_5) -2J_2(\hat{S}_1\hat{S}_2 + \hat{S}_4\hat{S}_5) -2J_3(\hat{S}_1\hat{S}_4 + \hat{S}_1\hat{S}_5 + \hat{S}_1\hat{S}_6) (4)
\]
afforded the parameters $J_1 = -0.65$ cm$^{-1}$, $J_2 = +3.20$ cm$^{-1}$, $J_3 = -0.8$ cm$^{-1}$ and $g = 2.01$. Again, as in the previous case, these parameters lead to a non-isolated spin ground-state for the cluster, since the $S = 3$, $S = 2$, $S = 1$ and $S = 0$ spin states are located within ~4 cm$^{-1}$. All parameters obtained from the magnetic analyses are summarized in Table 3.

Figure 6. Exchange interaction schemes for complexes 5 (left) and 3, 4 (right).

Figure 7. Exchange interaction scheme for complexes 1 and 2.
<table>
<thead>
<tr>
<th>Complexes</th>
<th>Torsion Angles (°)</th>
<th>$J$ coupling (cm⁻¹) $J_1/J_2/J_3$</th>
<th>$g$ factor</th>
<th>Hamiltonian Equation</th>
<th>$S$, ground state</th>
<th>$S$, 1ˢᵗ excited state</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 4MeCN</td>
<td>15.95 17.75 33.96 21.25 19.69 39.56</td>
<td>-1.25/+3.7/-1.0</td>
<td>1.99</td>
<td>(3) n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>2 3MeCN 0.1H₂O</td>
<td>49.98 16.42 24.78 3.87 20.38 29.82</td>
<td>-0.75/+3.2/-0.8</td>
<td>2.01</td>
<td>(4) n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>3</td>
<td>41.45 40.56 33.74</td>
<td>+1.35</td>
<td>2.00</td>
<td>(2) 12</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>42.77 33.29 38.48</td>
<td>+0.82</td>
<td>2.00</td>
<td>(2) 12</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>5 6EtOH</td>
<td>28.24 15.94 20.76</td>
<td>-7.95/+13.80</td>
<td>2.00</td>
<td>(1) 4</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Magnetostructural parameters for complexes 1-5.
In order to investigate possible SMM behaviour, ac magnetic susceptibility measurements were carried out under zero static field in the temperature range 1.8 – 10 K with a 3.5 G ac field oscillating in the 500-1500 Hz frequency range. We chose to measure only complexes 5 and 6 due to their high spin ground-state of $S = 12$. The in-phase and out-of-phase signals are plotted as $\chi_M' T$ vs. $T$ and $\chi_M'' vs. T$, respectively, in Figure 9. The ac susceptibility measurements reveal features typical of SMM behaviour for both complexes. For complex 5 the $\chi_M' T$ value increases slightly upon cooling until ~5 K, indicating the presence of exited states with $S$ values smaller than the ground state, before it drops rapidly to a minimum at ~4 K. Below 5 K, frequency-dependent fully formed out-of-phase ($\chi_M''$) signals are observed. Complex 6 display similar behaviour with fully formed out-of-phase signals at ~3.5 K. The ac data of complexes 5 and 6 were fitted to the Arrhenius relationship (eq. 6),

$$\tau = \tau_0 \exp(U_{eff}/kT)$$ (6)

where $U_{eff}$ is the effective relaxation barrier, $\tau$ is the relaxation time, $\tau_0$ is the pre-exponential factor and $k$ is the Boltzmann constant, yielding $U_{eff} = 63$ K and $\tau_0 = 1.52 \times 10^{-10}$ s for complex 5 and $U_{eff} = 36$ K and $\tau_0 = 1.42 \times 10^{-8}$ s for complex 6 (Figure 10).
4. Conclusions

In this work we have reported the synthesis and magnetic studies of seven new members of the [Mn₆/oxime] family. The use of substituted salicylaldoxime ligands, R-saoH₂ (R = H-, Me- and Et-) and carboxylate ligands, R’-CO₂H (R’ = 1-naphthalene, 2-naphthalene, 9-fluorene and 1-pyrene) in manganese chemistry yielded seven complexes with formulae [Mn₆O₂(sao)₆(1-naphth-CO₂)₂(H₂O)₂]3EtOH (1·3EtOH); [Mn₆O₂(sao)₆(2-naphth-CO₂)₂(H₂O)]₂ (2); [Mn₆O₂(Me-sao)₆(1-naphth-CO₂)₂(H₂O)(MeCN)]4MeCN (3·4MeCN); [Mn₆O₂(Me-sao)₆(2-naphth-CO₂)₂(H₂O)(MeCN)]3MeCN·0.1H₂O (4·3MeCN·0.1H₂O); [Mn₆O₂(Et-sao)₆(2-naphth-
CO\(_2\)(EtOH)\(_4\)(H\(_2\)O)\(_2\) \(\text{(5)}\); [Mn\(_6\)O\(_2\)(Et-sao)\(_6\)(2-naphth-CO\(_2\))\(_2\)(MeOH)\(_6\)] \(\text{(6)}\) and [Mn\(_6\)O\(_2\)(sao)\(_6\)(1-pyrene-CO\(_2\))\(_2\)(H\(_2\)O)\(_2\)(EtOH)\(_2\)]\(_6\)EtOH \(\text{(7 6EtOH)}\). All clusters, besides complexes 3 and 4, display the typical [Mn\(_6\)/oxime] core, which describes two parallel [Mn\(_3\)] planes bridged by oximate ligands. On the contrary, in complexes 3 and 4 the [Mn\(_3\)] sub-units are bridged with an extra \(\mu_4\)-oxo bridge and, as such, the triangular [Mn\(_3\)] planes are converging with a deviation from the parallel arrangement of 21.58° for complex 3, and 27.55° for complex 4. Dc magnetic susceptibility studies for all complexes revealed dominant antiferromagnetic behaviour for complexes 1, 2, 3, 4 and 7 with spin ground states of \(S = 4\) for complexes 1, 2 and 7. For complexes 3 and 4 susceptibility data suggests the presence of a band of \(S\) states (\(S \leq 4\)) that are likely to be populated even at the very lowest temperatures. Complexes 5 and 6 display dominant ferromagnetic interactions between the metallic centres with spin ground states of \(S = 12\). Finally, these two clusters display Single-Molecule Magnet behaviour with \(U_{\text{eff}}\) values of 62.67 K for complex 5, and 35.74 K for complex 6.

From these results three significant conclusions may be extracted: i) the [Mn\(_6\)/oxime] family is further extended with seven new complexes; ii) the “torsion angle” rule is valid for the five new classical (Type I, Type II) [Mn\(_6\)/oxime] complexes. The Type III structures characterized also appear to follow this general trend, although several new analogues will need to be made to confirm this very tentative conclusions; iii) despite more than 10 years of research into manganese-oxime cluster chemistry, new species with novel structural topologies and magnetic behavior are still uncovered, highlighting the enormously rich coordination chemistry and magnetochemistry that can be discovered via thorough investigation of synthetic space.

**Supplementary material**

CIF files of complexes 1-5.

**Acknowledgements**

This work was supported by the project "IRAKLITOS II - University of Crete" of the Operational Programme for Education and Lifelong Learning 2007 - 2013 (E.P.E.D.V.M.) of the NSRF (2007 - 2013), which is co-funded by the European Union (European Social Fund) and National Resources.
References


