

Enhancing U_{eff} in Oxime-Bridged $[\text{Mn}^{\text{III}}_6\text{Ln}^{\text{III}}_2]$ Hexagonal Prisms

Guillaume Rigaux,^{a,b} Ross Inglis,^b Susan Morrison,^b Alessandro Prescimone,^b Cyril Cadiou,^b Marco Evangelisti^{*c} and Euan K. Brechin^{*b}

Received (in XXX, XXX) Xth XXXXXXXXXX 200X, Accepted Xth XXXXXXXXXX 200X

5 First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

The first 3d-4f clusters built using derivatised salicylaldoximes (R-saoH₂) describe unusual hexagonal prisms. Replacement of the paramagnetic Gd(III) ions with diamagnetic Ln(III) ions allows for a more thorough understanding of the magnetic properties, whilst replacement with Tb(III) doubles U_{eff} .

The re-ignition of interest in the synthesis of polymetallic 3d-4f clusters¹ originates from two major sources: single-molecule magnetism² and molecular cooling.³ One way to increase the effective energy barrier to magnetisation reversal in the former class of compounds is through the introduction of highly anisotropic f-block ions such as Dy(III), Tb(III), Ho(III) or Er(III)⁴ since it has been shown that even single-ion complexes containing these metals can display hysteresis loops in magnetisation versus field studies.⁵ High spin isotropic molecules with weak exchange interactions, on the other hand, are ideal candidates for enhanced magnetic cooling⁶ since the negligible anisotropy permits easy polarisation of the net molecular spin leading to large changes in magnetic entropy, and the presence of degenerate or low-lying excited spin states results in extra magnetic entropy from the so-added degrees of freedom. The Gd(III) ion is thus an ideal choice for building molecular refrigerants.⁷

Since derivatised salicylaldoxime ligands (R-saoH₂; Figure 1) have been remarkably successful in the mediation of ferromagnetic exchange interactions between Mn(III) ions and thus in the synthesis of high spin Mn(III) molecules,⁸ a sensible extension to this synthetic strategy is the incorporation of lanthanide ions into the clusters.⁹ While the coordinative flexibility of Ln(III) ions makes the prediction of molecular structure even more difficult, it is likely that any high-spin Mn(III)-Ln(III) cluster built with these ligands will be an SMM or magnetic cooler. Herein we report the first examples of 3d-4f complexes employing R-sao²⁻ (R = Me, Et) - unusual $[\text{Ln}^{\text{III}}_2\text{Mn}^{\text{III}}_6]$ (Ln = Gd, La, Tb) hexagonal prisms.

Reaction of Gd(acac)₃·2H₂O, Mn(NO₃)₂·6H₂O, Et-saoH₂ and NaOH in a 1:1 mixture of MeCN/MeOH for 2 hours, followed by filtration and slow evaporation of the mother liquor affords black crystals of $[\text{Gd}_2\text{Mn}_6\text{O}_3(\text{OMe})_4(\text{Et-sao})_6(\text{acac})_2(\text{MeOH})_4] \cdot 0.7\text{MeCN}$ (**1**·0.7MeCN; Figure 1) in the monoclinic space group P2₁/c.^{†‡} The metallic core contains a non-planar (chair-like) wheel of six Mn(III) ions capped top and bottom by a Gd(III) ion, such that the skeleton describes a distorted hexagonal prism (Figure 1). The Gd(III) ions are connected to the Mn(III) ions via three $\mu_4\text{-O}^{2-}$ ions (O13, O24, O56), which also bridge pairs of Mn(III) ions (Mn1-Mn3; Mn2-Mn4; Mn5-Mn6) to give a

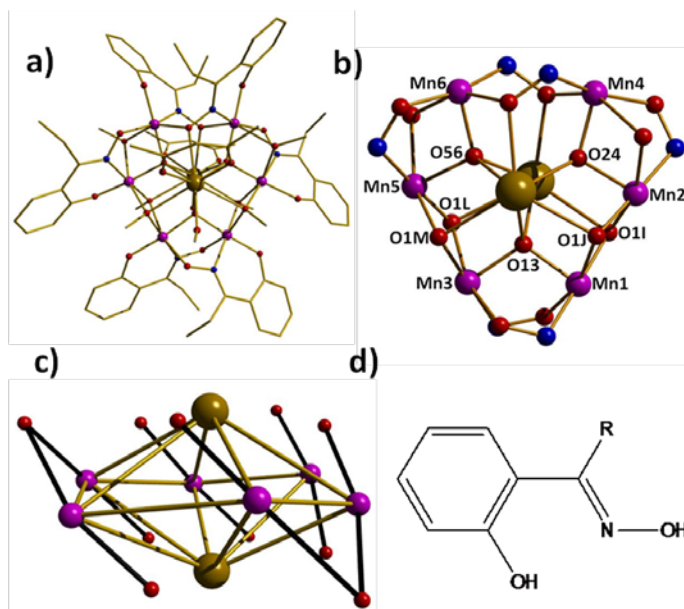


Figure 1. a) The molecular structure of **1** viewed down the Gd...Gd vector; H-atoms omitted for clarity. b) Magnetic core of **1**. c) The metallic skeleton of **1** viewed perpendicular to the Mn^{III}₆ wheel with the Jahn-Teller axes of the Mn(III) ions highlighted in black. d) Generic structure of the phenolic oxime, R-saoH₂; R = H, saoH₂; R = Me, Me-saoH₂; R = Et, Et-saoH₂.

$[\text{Gd}^{\text{III}}_2\text{Mn}^{\text{III}}_6\text{O}_3]^{18+}$ central core. The Gd and Mn ions are further linked by four $\mu_3\text{-MeO}$ ligands (O1I, O1J, O1L, O1M; Mn-O-Mn, 92.5-95.9°; Mn-O-Gd, 97.3-101.6°) all of which cap triangular faces on the “same side” of the trigonal prism (with respect to a plane through Mn2, Mn5, Gd1, Gd2) affording the asymmetrically bridged $[\text{Gd}^{\text{III}}_2\text{Mn}^{\text{III}}_6\text{O}_3(\text{MeO})_4]^{14+}$ moiety. The Et-sao²⁻ ligands are of two types: four bond in the common $\eta^1:\eta^1:\eta^1:\mu$ -fashion between neighbouring Mn(III) ions in the $[\text{Mn}_6]$ wheel while the remaining two bond in a $\eta^1:\eta^1:\eta^2:\mu_3$ -fashion between Mn4, Mn6 and Gd1; and Mn4, Mn6 and Gd2. The Mn-N-O-Mn torsion angles fall into three distinct categories: those that bridge between Mn4 and Mn6 are very large/puckered (72.5-73.3°), those that bridge between Mn2-Mn4 and Mn5-Mn6 are very small/flat (4.73-7.42°), and those between Mn1-Mn3 are intermediate, but still rather large (29.5-34.5°).

The Gd(III) ions are 9-coordinate and in distorted monocapped square-antiprismatic geometries with their coordination spheres each completed by the presence of one chelating acac¹⁻ ligand and one terminally bonded MeOH molecule. The Mn ions are all six-coordinate and in distorted

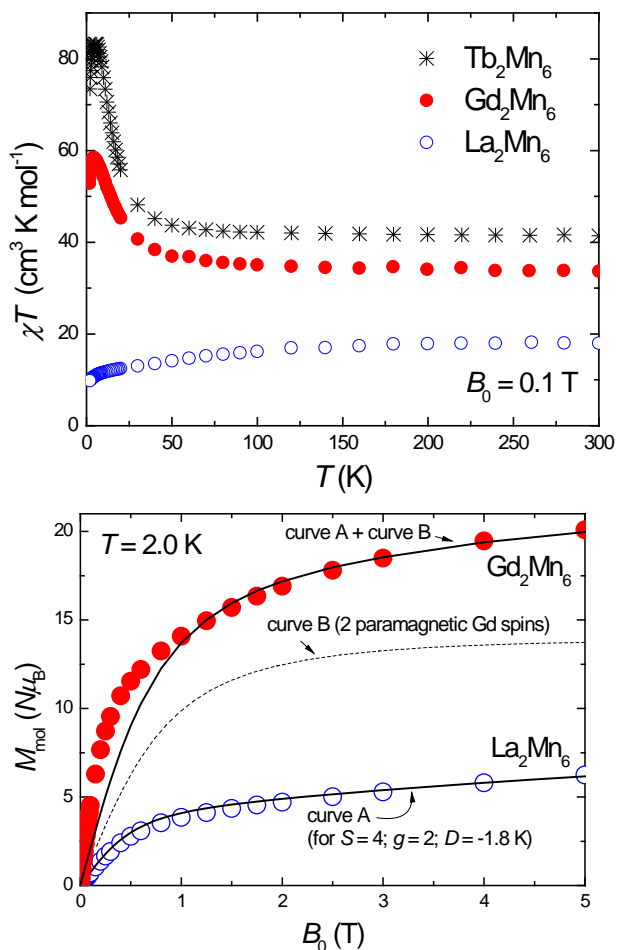


Figure 2. Plot of $\chi_M T$ versus T for complexes **1-3** in an applied field of 0.1 T (top). Plot of $M_{\text{mol}}/N\mu_B$ versus B_0 for **1** (blue) and **2** (red) at $T = 2$ K (bottom). The data for **2** can be fitted to an axial zero-field splitting Hamiltonian to afford $S = 4$, $g = 2.00$ and $D = -1.8$ K (curve A). The magnetisation of **1** above 1 T can be reproduced well by adding the calculated magnetisation of two paramagnetic Gd(III) ions (curve B) to the magnetisation data for **2**.

octahedral geometries, with the exception of Mn4 and Mn6 which are both 5-coordinate and square-pyramidal with a longer sixth axial contact to the O-atom of a terminally bonded MeOH molecule (Mn4...O1K, 2.525 Å; Mn6...O1N, 2.735 Å). The O-atoms of the MeOH molecules are also H-bonded to the O-atoms of the acac⁻ ligands (O1N...O4H, 2.697 Å) and terminally bonded oximic O-atoms (O1P...O23C, 2.568 Å). All six Mn ions are in the III+ oxidation state, as confirmed by charge balance and bond length considerations, and BVS calculations. The Jahn-Teller axes of the six Mn(III) ions occupy the plane perpendicular to the $[\text{Mn}_6]$ wheel, but are not co-parallel (Figure 1). In the crystal there are no significant inter-molecular H-bonds, with the closest inter-cluster contacts being of the order of 3.6 Å between methoxide carbon atoms and phenolic oxygen atoms. $[\text{Mn(III)Gd(III)}]$ clusters are surprisingly uncommon – a CCDC search returning only sixteen hits. There are none with the $[\text{Mn(III)}_6\text{Gd(III)}_2]$ stoichiometry and none whose metallic skeleton describes a hexagonal prism. Indeed the majority possess very irregular topologies.

The magnetic properties of **1** were investigated by dc-susceptibility measurements in the 300 – 2 K temperature range in an applied field of 0.1 T (Figure 2). The experimental room temperature $\chi_M T$ value of ~ 33.6 $\text{cm}^3 \text{K mol}^{-1}$ is close to the spin-only ($g = 2.0$) value expected for an uncoupled $[\text{Mn}^{\text{III}}_6\text{Gd}^{\text{III}}_2]$ unit of ~ 33.75 $\text{cm}^3 \text{K mol}^{-1}$. The value stays essentially constant as the temperature is decreased until approximately 100 K, below which it increases reaching a maximum value of ~ 58.4 $\text{cm}^3 \text{K mol}^{-1}$ at 4.0 K. Below this temperature $\chi_M T$ decreases reaching a value of ~ 52.8 $\text{cm}^3 \text{K mol}^{-1}$ at 1.8 K, likely a result of magnetic anisotropy and/or inter-molecular anti-ferromagnetic exchange interactions. Figure 2 shows the measured molar magnetisation M_{mol} in fields up to 5 T for $T = 2$ K. The data show a rapid initial rise in magnetisation, with the high field data tending towards saturation at $\sim 20 N\mu_B$. Assuming that the larger Mn-O-N-Mn angles favour ferromagnetic exchange,⁸ the dc data are thus suggestive of the two Gd(III) ions being very weakly coupled to an antiferromagnetic ($S = 4$) $[\text{Mn(III)}_6]$ wheel (Mn1, Mn3, Mn4, Mn6 “spin-up”, Mn2, Mn5 “spin-down”).

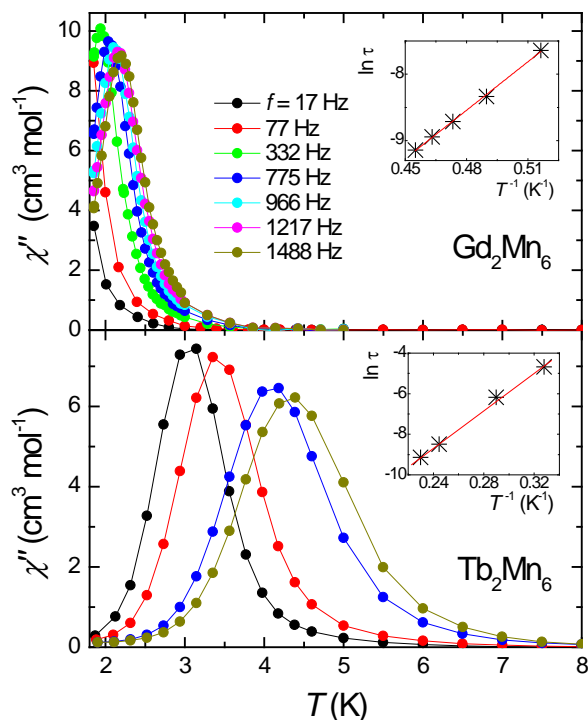


Figure 3. Plot of the out-of-phase (χ'') ac susceptibility for **1** (top) and **3** (bottom) measured at the indicated temperatures and frequencies with an applied field of 3.5 G. The insets are a fit of the χ'' data to the Arrhenius Law to afford $U_{\text{eff}} = 24$ K for **1** and $U_{\text{eff}} = 46$ K for **3**.

In order to address this speculation the La(III) (f^0) analogue of complex **1**, $[\text{La}_2\text{Mn}_6\text{O}_3(\text{OME})_4(\text{Et-sao})_6(\text{acac})_2(\text{MeOH})_4] \cdot \text{C}_6\text{H}_{14}$ (2-hex) was synthesised. The structure^{††} of complex **2** is analogous to **1**, with small changes to the Mn-N-O-Mn torsion angles. The experimental room temperature $\chi_M T$ value of ~ 18 $\text{cm}^3 \text{K mol}^{-1}$ for **2** is as expected for an uncoupled $[\text{Mn}^{\text{III}}_6]$ unit with $g = 2.00$. The value drops steadily with temperature to a value of approximately 10 $\text{cm}^3 \text{K mol}^{-1}$ at 2 K. The low temperature value is suggestive of $S = 4$. The magnetisation data for **2** at 2 K is

shown in the lower panel of Figure 2 and can be fitted to an axial zero-field splitting plus Zeeman Hamiltonian ($H = DS_z^2 + g\mu_B B_0 S$) to yield $S = 4$, $g = 2.00$ and $D = -1.8$ K. The magnetisation data for **1** can be well reproduced above $B_0 \sim 1$ T by adding two Brillouin functions (“curve B” in Figure 2) for two paramagnetic Gd(III) ions to the magnetisation data for **2**. Figure 2 shows that fields lower than 1 T do not decouple the Gd(III) ions from the inner $[\text{Mn(III)}_6]$ wheel, and that this coupling is ferromagnetic since the experimental M_{mol} for **1** lies above the calculated curve in this field region.

The relatively large and anisotropic spin associated with complexes **1** and **2** suggest that they are likely to be SMMs, and this is confirmed through the appearance of frequency-dependent out-of-phase (χ_M'') signals for both. For **2** only the tails of the peaks are observed, but fully visible peaks are seen for **1** in the 332–1488 Hz range between 2 and 4 K (Figure 3). The difference between the two complexes is simply attributed to the differences in the Mn–N–O–Mn torsion angles which are smaller in magnitude for **2** than for **1**.⁸ The χ_M'' data obtained for **1** were fit to the Arrhenius equation to give an effective energy barrier, $U_{\text{eff}} = 24$ K with $\tau_0 = 1.7 \times 10^{-9}$ s. In order to enhance the energy barrier to magnetisation relaxation the Tb(III) analogue of complex **1**, $[\text{Tb}_2\text{Mn}_6\text{O}_3(\text{OMe})_4(\text{Me-sao})_6(\text{acac})_2(\text{MeOH})_4] \cdot \text{C}_6\text{H}_{14}$ (**3-hex**) was synthesised. The structure^{††} of complex **3** is again analogous to **1**, but with Me-sao²⁻ replacing Et-sao²⁻ and with minor changes to bond lengths and angles.^{††} As illustrated in Figure 3, the effect on the relaxation behaviour is rather dramatic. Fully visible out-of-phase χ_M'' signals are now seen for all the frequencies employed (including 17 Hz) and each signal is shifted to higher temperatures; indeed the 1488 Hz signal is shifted by approximately 2.5 K. The result is that the energy barrier to magnetisation reversal in complex **3** ($U_{\text{eff}} = 46.3$ K) is effectively double that of complex **1**.

In conclusion, we have reported the first examples of $3d-4f$ clusters built with derivatised salicylaldoximes – unusual $[\text{Ln}^{\text{III}}_2\text{Mn}^{\text{III}}_6]$ hexagonal prisms. Replacement of the paramagnetic Gd(III) ions with the diamagnetic La(III) ions confirms the presence of an antiferromagnetic $[\text{Mn}^{\text{III}}_6]$ wheel coupled very weakly to two apical Gd(III) ion caps. The anisotropic spin renders **1** and **2** SMMs and replacement of Gd(III) with Tb(III) in **3** effectively doubles the observed U_{eff} . Attempts to synthesise and characterise all the post-Gd versions of **1** are in progress.

Notes and references

^aUniversité de Reims Champagne-Ardenne, Institut de Chimie Moléculaire de Reims (ICMR), Groupe Chimie de Coordination, CNRS UMR 6229, Bât. Europol'Agro - Moulin de la Housse, BP 1039 - 51687 Reims cedex 2, France

^bEaStCHEM School of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ (UK). Fax: (+44)131-650-6453; E-mail: ebrechin@staffmail.ed.ac.uk

^cInstituto de Ciencia de Materiales de Aragón, CSIC-Universidad de Zaragoza, Departamento de Física de la Materia Condensada, 50009 Zaragoza, Spain, E-mail: evange@unizar.es

^{††} The complex analysed as 10.7MeCN . Elemental analysis, expected (found): C, 40.82 (41.11); H, 4.41 (4.60); N, 4.57 (4.76)%. Diffraction data were collected with Cu radiation ($\lambda = 1.5418$ Å) on an Oxford

Diffraction SuperNova Dual wavelength diffractometer with an Atlas CCD detector. Crystal data: $\text{C}_{73.4}\text{H}_{94.1}\text{Gd}_2\text{Mn}_6\text{N}_{6.7}\text{O}_{27}$, $M = 2146.39$, red block, monoclinic, P 21/c, $a = 26.3789(3)$, $b = 14.04527(13)$, $c = 25.8211(3)$ Å, $\alpha = 90.0$, $\beta = 117.7884(14)$, $\gamma = 90.0^\circ$, $V = 8463.41(15)$ Å³, $Z = 4$, $T = 100$ K, 83524 reflections collected of which 16710 were independent ($R_{\text{int}} = 0.0937$), 1049 parameters and 4 restraints, $R1 = 0.0445$ [based on $F > 4\sigma(F)$], $wR2 = 0.1151$ (based on F^2 and all data). CCDC XXXXXXX.

The complex analysed as $2\text{C}_6\text{H}_{14}$. Elemental analysis, expected (found): C, 43.25 (43.40); H, 4.89 (4.85); N, 3.88 (3.84)%. Diffraction data were collected with Mo-K α radiation ($\lambda = 0.71073$ Å) on a Bruker Smart Apex CCD diffractometer. Crystal data: $\text{C}_{78}\text{H}_{105}\text{La}_2\text{Mn}_6\text{N}_6\text{O}_{27}$, $M = 2166.15$, black cuboid, orthorhombic, $C 2 2 2_1$, $a = 15.3154(6)$, $b = 22.8884(6)$, $c = 25.7786(8)$ Å, $\alpha = \beta = \gamma = 90.0^\circ$, $V = 9036.6(5)$ Å³, $Z = 4$, $T = 100$ K, 66786 reflections collected of which 9309 were independent ($R_{\text{int}} = 0.0391$), 766 parameters and 505 restraints, $R1 = 0.0223$ [based on $F > 4\sigma(F)$], $wR2 = 0.0578$ (based on F^2 and all data). CCDC XXXXXXX.

- (a) A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc.*, 1985, **107**, 8128; (b) Y. Pei, Y. Journaux, O. Kahn, A. Dei and D. Gatteschi, *J. Chem. Soc., Chem. Commun.*, 1986, 1300; (c) C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou and L. Pardi, *Inorg. Chem.*, 1990, **29**, 1750; (d) R. E. P. Winpenny, *Chem. Soc. Rev.*, 1998, **27**, 447.
- (a) R. Sessoli, D. Gatteschi and J. Villain, *Molecular Nanomagnets*, Oxford University Press, 2006; (b) G. Aromí and E. K. Brechin, *Struct. Bonding*, 2006, **122**, 1; (c) M. Murrie and D. J. Price, *Annu. Rep. Prog. Chem., Sect. A*, 2007, **103**, 20; (d) A. K. Boudalis, Y. Sanakis, C. P. Raptopoulou, V. Psycharis, *Magnetism and Superconductivity in Low-Dimensional Systems: Utilization in Future Applications*, D. Stamopoulos (Ed.) Nova Science Publishers Inc., New York, 2008, pp. 1-77; (e) G. Christou, *Polyhedron*, 2005, **24**, 2065.
- M. Evangelisti, F. Luis, L. J. de Jongh and M. Affronte, *J. Mater. Chem.*, 2006, 2534.
- R. Sessoli and A. K. Powell, *Coord. Chem. Rev.*, 2009, **253**, 2328 and references therein.
- (a) N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara and Y. Kaizu, *J. Am. Chem. Soc.*, 2003, **125**, 8694; (b) M. A. AlDamen, J. M. Clemente-Juan, E. Coronado, C. Martí-Gastaldo and A. Gaita-Ariño *J. Am. Chem. Soc.*, 2008, **130**, 8874.
- M. Evangelisti and E. K. Brechin, *Dalton Trans.*, 2010, **20**, 4672 and references therein.
- (a) G. Karotsis, S. Kennedy, S. J. Teat, C. M. Beavers, D. A. Fowler, J. J. Morales, M. Evangelisti, S. J. Dalgarno and E. K. Brechin, *J. Am. Chem. Soc.*, 2010, **132**, 12983; (b) Y.-Z. Zheng, M. Evangelisti and R. E. P. Winpenny, *Chem. Sci.*, 2011, 99.
- (a) R. Inglis, S. M. Taylor, L. F. Jones, G. S. Papaefstathiou, S. P. Perlepes, S. Datta, S. Hill, W. Wernsdorfer and E. K. Brechin, *Dalton Trans.*, 2009, 9157; (b) R. Inglis, L. F. Jones, C. J. Milios, S. Datta, A. Collins, S. Parsons, W. Wernsdorfer, S. Hill, S. P. Perlepes, S. Piligkos and E. K. Brechin, *Dalton Trans.*, 2009, 3403; (c) C. J. Milios, S. Piligkos and E. K. Brechin, *Dalton Trans.*, 2008, 1809; (d) C. J. Milios, R. Inglis, A. Vinslava, R. Bagai, W. Wernsdorfer, S. Parsons, S. P. Perlepes, G. Christou and E. K. Brechin, *J. Am. Chem. Soc.*, 2007, **129**, 12505; (e) C. J. Milios, A. Vinslava, W. Wernsdorfer, A. Prescimone, P. A. Wood, S. Parsons, S. P. Perlepes, G. Christou and E. K. Brechin, *J. Am. Chem. Soc.*, 2007, **129**, 6547.
- M. Andruh, J. P. Costes, C. Diaz and S. Gao, *Inorg. Chem.*, 2009, **48**, 3342 and references therein.