



# THE UNIVERSITY *of* EDINBURGH

## Edinburgh Research Explorer

### **A cationic and ferromagnetic hexametallic Mn(III) single-molecule magnet based on the salicylamidoxime ligand**

**Citation for published version:**

Martinez-Lillo, J, Dolan, N & Brechin, EK 2013, 'A cationic and ferromagnetic hexametallic Mn(III) single-molecule magnet based on the salicylamidoxime ligand' Dalton Transactions, vol 42, no. 36, pp. 12824-12827., 10.1039/c3dt51512e

**Digital Object Identifier (DOI):**

[10.1039/c3dt51512e](https://doi.org/10.1039/c3dt51512e)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Author final version (often known as postprint)

**Published In:**

Dalton Transactions

**Publisher Rights Statement:**

Copyright © 2013 by the Royal Society of Chemistry. All rights reserved.

**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](mailto:openaccess@ed.ac.uk) providing details, and we will remove access to the work immediately and investigate your claim.



Post-print of peer-reviewed article published by the Royal Society of Chemistry.

Published article available at: <http://dx.doi.org/10.1039/C3DT51512E>

Cite as:

Martínez-Lillo, J., Dolan, N., & Brechin, E. K. (2013). A cationic and ferromagnetic hexametallic Mn(III) single-molecule magnet based on the salicylamidoxime ligand. *Dalton Transactions*, 42(36), 12824-7.

Manuscript received: 10/06/2013; Accepted: 09/07/2013; Article published: 11/07/2013

## A cationic and ferromagnetic hexametallic Mn(III) single-molecule magnet based on the salicylamidoxime ligand\*\*†

José Martínez-Lillo,\* Neil Dolan and Euan K. Brechin\*

<sup>[1]</sup>EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

<sup>[\*]</sup>Corresponding authors; J.M.L. e-mail: [fmartine@staffmail.ed.ac.uk](mailto:fmartine@staffmail.ed.ac.uk); E.K.B. e-mail: [ebrechin@staffmail.ed.ac.uk](mailto:ebrechin@staffmail.ed.ac.uk), fax: +44 (0)131 650 6453, tel: +44 (0)131 650 7545

<sup>[\*\*]</sup>Financial support from the European Union (Marie-Curie Project No. 272659) and the University of Edinburgh is gratefully acknowledged. The authors thank Dr. Gary Nichol for single-crystal X-ray diffraction measurements. JML is indebted to the European Union for a postdoctoral Marie Curie Intra-European Fellowship.

<sup>[†]</sup>Celebrating 300 years of Chemistry at The University of Edinburgh.

### Supporting information:

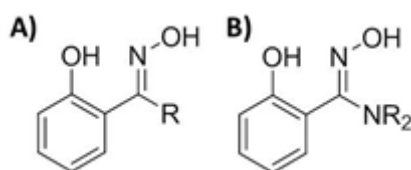
‡ Electronic supplementary information (ESI) available: Preparation of 1, Fig. S1–S3. CCDC 943039. For ESI and crystallographic data in CIF or other electronic format see <http://dx.doi.org/10.1039/C3DT51512E>

## Abstract

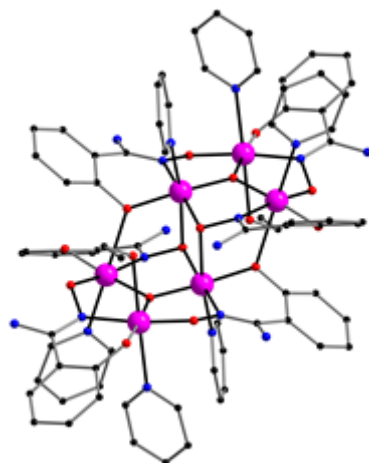
The salicylamidoxime-based complex  $[\text{Mn}_6(\mu_3\text{-O})_2(\text{H}_2\text{N-sao})_6(\text{py})_6(\text{EtOH})_2](\text{ClO}_4)_2 \cdot 4\text{EtOH}$  ( $1 \cdot 4\text{EtOH}$ ) constitutes the first example of a cationic and ferromagnetic member of the oxime-based family of  $[\text{Mn}^{\text{III}}_6]$  Single-Molecule Magnets.

## Introduction

In the multidisciplinary field of molecule-based magnetism, the structural and magnetic properties of molecular nanomagnets have been thoroughly investigated for their fundamentally interesting chemistry and physics that can potentially provide a gateway for the discovery of new physical phenomena and application in a diverse array of technological applications.<sup>1</sup> The latter can include quantum information processing,<sup>2</sup> low temperature cooling<sup>3</sup> and molecular spintronics.<sup>4</sup> The development of novel synthetic methodologies which afford new magnetic materials is therefore a fundamentally important issue. In this respect, the use of phenolic oximes has proven to be particularly successful, especially for the preparation of Mn(III)-based Single-Molecule Magnets (SMMs).<sup>1</sup> Derivatised salicylaldoximes (Scheme 1) have been employed to generate a large family of hexametallc ( $[\text{Mn}^{\text{III}}_6]$ ), and trimetallic ( $[\text{Mn}^{\text{III}}_3]$ ), complexes with SMM behaviour, in which chemically-induced structural distortion of the Mn-N-O-Mn torsion angles allowed the preparation and isolation of family members displaying remarkably different magnetic properties.<sup>5</sup> This in turn resulted in the formulation of a semi-quantitative magnetostructural correlation which enables prediction of the magnetic properties of new family members.<sup>6</sup> The coordination chemistry of the related salicylamidoxime ligand<sup>7</sup> and its dialkyl derivatives<sup>8</sup> (Scheme 1) towards the  $\text{Mn}^{\text{III}}$  ion has also been explored extensively. Indeed in a recent experimental and theoretical study these salicylamidoxime-based  $[\text{Mn}^{\text{III}}_6]$  SMMs were shown to possess spin ground states varying from 4 to 12 and anisotropy energy barriers from 24 to 86 K.<sup>7,8</sup> Interestingly in these latter complexes it was established that the critical angle where the exchange coupling between neighbouring Mn(III) ions switches from antiferromagnetic to ferromagnetic is *ca.*  $27^\circ$ , somewhat lower than that of the related salicylaldoxime-based complexes (*ca.*  $31^\circ$ ).



**Scheme 1.** The structures of: (A) salicylaldoxime ( $\text{R-saoH}_2$ ) and (B) salicylamidoxime ( $\text{R}_2\text{N-saoH}_2$ ).  
 $\text{R} = \text{H, Me, Et, Ph etc.}$



**Figure 1.** Perspective view of the molecular structure of the  $[\text{Mn}_6(\mu_3\text{-O})_2(\text{H}_2\text{N-sao})_6(\text{py})_6(\text{EtOH})_2]^{2+}$  cation of **1**. H atoms,  $\text{ClO}_4^-$  anions and EtOH solvent molecules have been omitted for clarity. [Colour code: pink, Mn; red, O; blue, N; black, C].

Herein we report the synthesis and magnetostructural characterization of the first cationic, ferromagnetically coupled salicylamidoxime-based family member; namely the complex  $[\text{Mn}_6(\mu_3\text{-O})_2(\text{H}_2\text{N-sao})_6(\text{py})_6(\text{EtOH})_2](\text{ClO}_4)_2 \cdot 4\text{EtOH}$  (**1**·4EtOH). The only previously reported cationic complex,  $[\text{Mn}_6(\mu_3\text{-O})_2(\text{H}_2\text{N-sao})_6(\text{MeOH})_8]\text{Cl}_2 \cdot 9\text{MeOH}$  (**2**·9MeOH), possesses a small spin ground state on account of the presence of one dominant antiferromagnetic nearest-neighbour exchange interaction.<sup>7c</sup> Control of the overall charge (and magnetic exchange) of the  $[\text{Mn}_6]$  cluster is an important step towards making more ‘advanced materials’, not simply because it can be used to tune, for example, solubility, reactivity, purification, stability and substrate specificity, but also because the cluster cation/anion produced can be charged balanced through the incorporation of anions/cations that bring another physical property or functionality to the material. For example, paramagnetism, conductivity, luminescence etc.

The reaction of  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  with  $\text{H}_2\text{N-saoH}_2$  and pyridine (py) in a basic, alcoholic solution, (see the ESI for full details) results in the formation of dark green crystals after slow evaporation of the filtered mother liquor, after 1 day. The crystals were in a monoclinic crystal system and structure solution was performed in the  $P2_1/n$  space group. The structure of **1** is made up of the hexametallc cluster cation  $[\text{Mn}_6(\mu_3\text{-O})_2(\text{H}_2\text{N-sao})_6(\text{py})_6(\text{EtOH})_2]^{2+}$ , two  $\text{ClO}_4^-$  anions and EtOH solvent molecules of crystallisation. A perspective drawing of the  $[\text{Mn}_6]^{2+}$  cation is shown in Figure 1. Each  $[\text{Mn}_6(\mu_3\text{-O})_2(\text{H}_2\text{N-sao})_6(\text{py})_6(\text{EtOH})_2]^{2+}$  unit contains two symmetry equivalent  $\{\text{Mn}_3(\mu_3\text{-O})\}$  triangular moieties, which are linked by two phenolate and two oximate O-atoms and related by an inversion centre. Each edge of the triangle is spanned by the -N-O- moiety of the oxime ligand, with the central

O<sup>2-</sup> ion displaced 0.162 Å above the plane of the [Mn<sub>3</sub>] triangle, towards the terminally ligated py molecules. The hexametalllic core of **1** is thus rather similar to both its salicylamidoxime-based [Mn<sub>6</sub>] predecessors and to that of complex **2**, the main difference being the replacement of the terminally bonded carboxylates, halides or ROH molecules on the outwardly facing triangular faces by six terminal pyridine molecules. This is actually a very surprising result, since addition of pyridine to all previously reported salicylaldehyde-based [Mn<sub>6</sub>] clusters results in the cleaving of the molecule into its constituent [Mn<sub>3</sub>] triangles, *i.e.* the formation of a triangle capped on one face by three py molecules and on the other by the charge-balancing anion (here ClO<sub>4</sub><sup>-</sup>).<sup>6</sup> This observation highlights the relevant importance of the -NH<sub>2</sub> group of the salicylamidoxime ligand, and suggests its role may not simply be steric. The six Mn(III) ions exhibit distorted octahedral geometries with their Jahn-Teller axes approximately perpendicular to the [Mn<sup>III</sup><sub>3</sub>] planes. The remaining coordination site on Mn2 (and symmetry equivalent) is occupied by an EtOH molecule. As observed previously, the salicylamidoxime ligands can promote significant twisting of the [Mn<sup>III</sup><sub>3</sub>(μ<sub>3</sub>-O)(H<sub>2</sub>N-sao)<sub>3</sub>] triangular units, producing Mn-N-O-Mn torsion angles with magnitudes as large as those obtained with the bulkiest salicylaldehyde ligands.<sup>7ac</sup> Indeed the Mn-N-O-Mn torsion angles in **1** are 42.0(4), 39.4(5) and 30.8(5)°.

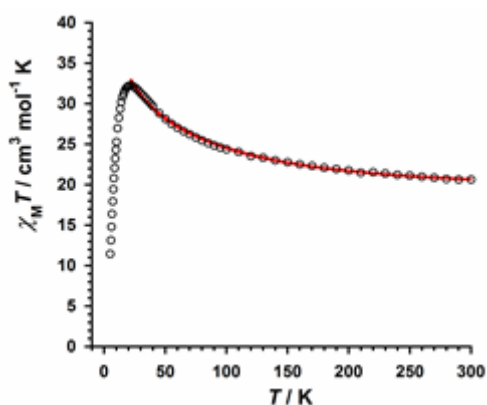
In the crystal lattice the ClO<sub>4</sub><sup>-</sup> anions sit between neighbouring [Mn<sub>6</sub>]<sup>2+</sup> cations and are H-bonded to the -NH<sub>2</sub> groups on the salicylamidoxime ligands of each (O···N, ~2.9 Å), linking them into square sheets (Figure S1). They are also H-bonded to one EtOH molecule of crystallisation (O···O, ~2.8 Å), with the latter H-bonded to a different salicylamidoxime -NH<sub>2</sub> moiety (O···N, ~3 Å). The second EtOH molecule of crystallization (and symmetry equivalent) H-bonds to the terminally bonded phenolic O-atom (O···O, 2.9 Å). The result is a 2D H-bonded sheet (Figure S1) with the terminally bonded py molecules interdigitated in the third dimension, with the closest C···C interactions being of the order of 3.5 Å.

Dc magnetic susceptibility measurements were carried out on a microcrystalline sample of **1** in the 300–5 K temperature range and an external magnetic field of 0.1 T. The  $\chi_M T$  versus  $T$  plot is given in Fig. 2. At room temperature the  $\chi_M T$  value is 20.7 cm<sup>3</sup> mol<sup>-1</sup> K, somewhat higher than that expected for six uncoupled Mn(III) ( $S = 2$ ) centres (18.0 cm<sup>3</sup> mol<sup>-1</sup> K), indicating the presence of dominant ferromagnetic exchange interactions between the metal ions. The value of  $\chi_M T$  rises gradually with decreasing temperature, increasing more abruptly at approximately 100 K and reaching a maximum value of 32.3 cm<sup>3</sup> mol<sup>-1</sup> K at 22 K. Below this temperature the value of  $\chi_M T$  drops to a final value of 11.5 cm<sup>3</sup> mol<sup>-1</sup> K at 5 K (Fig. 2), likely due to the presence of intermolecular interactions and (at lower temperature) zero-field splitting (zfs) effects. Simulation of these data to the maximum in  $\chi_M T$ , having in mind the torsion angles set in **1** and using the  $2J$  model described by the Hamiltonian of eqn

(1) and Fig. S2, afforded the parameters  $g = 1.99 \pm 0.01$ ,  $J_1 = +1.90 \pm 0.05 \text{ cm}^{-1}$  and  $J_2 = +0.85 \pm 0.05 \text{ cm}^{-1}$ .



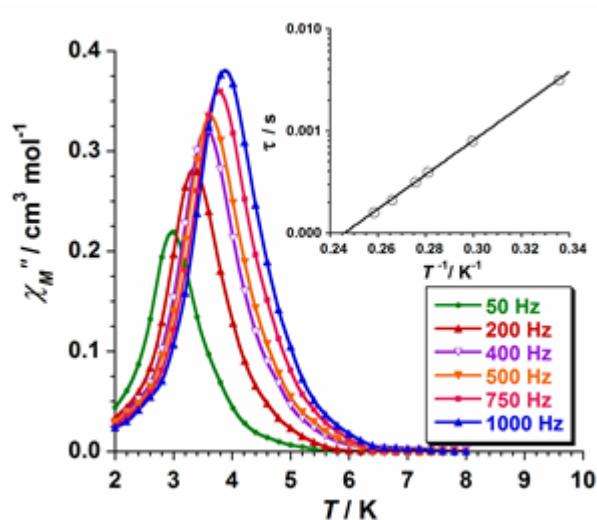
A  $2J$  model was used because in **1** there is one Mn–N–O–Mn torsion angle ( $30.8^\circ$  associated to  $J_2$ ) which is somewhat smaller than the other two ( $42.0$  and  $39.4^\circ$  associated to  $J_1$ ), thus the exchange pathways are divided in two groups in the core of the cationic  $\text{Mn}_6$  complex (Fig. S2). This is nicely reflected in the subsequent simulation values, which reflect a more positive  $J$  with increasing torsion angle ( $J_1 = +1.90 \text{ cm}^{-1}$  and  $J_2 = +0.85 \text{ cm}^{-1}$ ). This data treatment has satisfactorily been performed in previous works.<sup>5</sup> Attempts to fit the experimental data in the whole temperature region led to numerous solutions of similar quality, since the low temperature drop in  $\chi_{\text{M}}T$  can be modelled through inclusion of both intermolecular interactions and zfs, and both are correlated.



**Figure 2.** Plot of  $\chi_{\text{M}}T$  vs.  $T$  obtained for compound **1** (o). The solid red line represents the simulation of the data obtained for **1**.

Variable temperature–variable field dc magnetisation data were collected in the ranges 2–7 K and 0.5–7 T and fitted to a Zeeman plus axial zero-field splitting Hamiltonian [ $\hat{H} = D(\hat{S}_z^2 - S(S + 1)/3) + \mu_B g H \hat{S}$ ] assuming only the ground state is populated.<sup>5–8</sup> The experimental data for **1** are plotted as reduced magnetisation ( $M/N\mu_B$  vs.  $H/T$ ) in Fig. S3. The best fit afforded the parameters  $S = 12$ ,  $g = 1.98 \pm 0.02$  and  $D_{\text{cluster}} = -0.34 \pm 0.02 \text{ cm}^{-1}$ . These are consistent with other congeners of the  $[\text{Mn}^{\text{III}}_6]$  family. Ac susceptibility measurements were performed on a sample of **1** in the temperature range 2–10 K in zero applied dc field and a 3.5 G ac field oscillating at 50–1000 Hz. Out-of-phase ac signals for **1** are shown as  $\chi_{\text{ac}}''$  vs.  $T$  plot in Fig. 3 and are consistent with SMM behaviour. Indeed, a clear

frequency-dependent decrease of the  $\chi_{ac}''$  maxima is observed. These also decrease with decreasing frequency, a feature typical of strong intermolecular interactions in single-molecule and chain magnets (SMMs and SCMs), and consistent with the packing of the clusters in the crystal of **1**.<sup>9</sup> These data were fitted to the Arrhenius equation [ $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$ , where  $\tau_0$  is the pre-exponential factor,  $\tau$  is the relaxation time,  $U_{\text{eff}}$  is the barrier to the relaxation of the magnetisation and  $k_B$  is the Boltzmann constant] and plotted in the inset of Fig. 3. The obtained values for  $\tau_0$  and  $U_{\text{eff}}$  are  $5.3 \times 10^{-9}$  s and 40 K, respectively. The  $U_{\text{eff}}$  value for **1** falls into the range ( $24 \text{ K} < U_{\text{eff}} < 86 \text{ K}$ ) for previously reported salicylamidoxime-based  $\text{Mn}_6$  complexes.<sup>7</sup>



**Figure 3.** Out-of-phase ac susceptibility ( $\chi_{ac}''$ ) versus  $T$  plot for **1**. The inset shows the Arrhenius best-fit plot (see text).

In summary, the crystal structure and initial magnetic studies of a new salicylamidoxime-based  $[\text{Mn}^{\text{III}}_6]$  compound of formula  $[\text{Mn}_6(\mu_3\text{-O})_2(\text{H}_2\text{N-sao})_6(\text{py})_6(\text{EtOH})_2](\text{ClO}_4)_2 \cdot 4\text{EtOH}$  (**1**·4EtOH) are reported. **1** constitutes a highly unusual example of a cationic and ferromagnetic  $[\text{Mn}^{\text{III}}_6]$  single-molecule magnet. The preparation of **1** opens a new and appealing synthetic route to obtaining new magnetic materials: the ability to face-cap  $\text{Mn}_6$  with pyridine ligands suggests the use of polypyridine-type ligands should afford a plethora of supramolecular  $\text{Mn}_6$  cages in which additional paramagnetic moieties can be attached to the Mn(III) ions in order to modify the relaxation dynamics. In addition the [diamagnetic]  $\text{ClO}_4^-$  counter anion can be replaced with alternative ions that bring another physical property or functionality to the material to produce a family of multifunctional  $\text{Mn}_6$  salts.

## Notes and references

§ *Crystal data for 1*: C<sub>84</sub>H<sub>102</sub>Cl<sub>2</sub>O<sub>28</sub>N<sub>18</sub>Mn<sub>6</sub>,  $M = 2212.38$ , monoclinic, space group  $P2(1)/n$ ,  $a = 13.039(1)$ ,  $b = 22.772(1)$ ,  $c = 16.487(1)$  Å,  $\beta = 102.87(1)^\circ$ ,  $V = 4772.2(5)$  Å<sup>3</sup>,  $T = 120(2)$  K,  $Z = 2$ ,  $\mu = 0.912$  mm<sup>-1</sup>,  $D_c = 1.540$  gcm<sup>-3</sup>, 36867 reflections collected, 9828 unique ( $R_{\text{int}} = 0.0524$ ), final  $R_1 = 0.0812$ ,  $wR_2 = 0.2070$ ,  $GoF = 1.043$ , data/restraints/parameters = 9828/2/618. Single crystal X-ray diffraction data of **1** were collected on a Bruker ApexII CCD area detector diffractometer using monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by standard direct methods and subsequently completed by Fourier recycling using the SHELXTL<sup>10</sup> software packages and refined by the full-matrix least-squares refinements based on  $F^2$  with all observed reflections. The final geometrical calculations were carried out with the PARST97 program<sup>10</sup> whereas the graphical manipulations were performed with the DIAMOND program.<sup>11</sup> CCDC 943039.

- [1] See for example: (a) R. Sessoli and D. Gatteschi, *Angew. Chem., Int. Ed.*, 2003, **42**, 268; (b) D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, Oxford University Press, Oxford, 2006; (c) G. Aromí and E. K. Brechin, *Struct. Bonding*, 2006, **122**, 1; (d) E. J. L. McInnes, *Struct. Bonding*, 2006, **122**, 69; (e) R. Bagai and G. Christou, *Chem. Soc. Rev.*, 2009, **38**, 1011; (f) M. Andruh, *Chem. Commun.* 2011, **47**, 3015; (g) K. S. Murray, *Aust. J. Chem.*, 2009, **62**, 1081; (h) G. E. Kostakis, I. J. Hewitt, A. M. Ako, V. Mereacre and A. K. Powell, *Phil. Trans. R. Soc. A*, 2010, **368**, 1509.
- [2] (a) R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2008, **47**, 7992; (b) G. A. Timco, E. J. L. McInnes and R. E. P. Winpenny, *Chem. Soc., Rev.*, 2013, **42**, 1796; (c) G. A. Timco, T. B. Faust, F. Tuna and R. E. P. Winpenny, *Chem. Soc. Rev.*, 2011, **40**, 3067. (d) F. Luis, A. Repollés, M. J. Martínez-Pérez, D. Aguilá, O. Roubeau, D. Zueco, P. J. Alonso, M. Evangelisti, A. Camón, J. Sesé, L. A. Barrios and G. Aromí, *Phys. Rev. Lett.*, 2011, **107**, 117203.
- [3] (a) M. Evangelisti, F. Luis, L. J. De Jongh and M. Affronte, *J. Mater. Chem.*, 2006, **16**, 2534; (b) M. Evangelisti and E. K. Brechin, *Dalton Trans.*, 2010, **39**, 4672.
- [4] L. Bogani and W. Wernsdorfer, *Nat. Mater.*, 2008, **7**, 179.
- [5] (a) C. J. Milios, C. P. Raptopoulou, A. Terzis, F. Lloret, R. Vicente, S. P. Perlepes and A. Escuer, *Angew. Chem., Int. Ed.*, 2004, **43**, 210. (b) C. J. Milios, A. Vinslava, P. A. Wood, S. Parsons, W. Wernsdorfer, G. Christou, S. P. Perlepes and E. K. Brechin, *J. Am. Chem. Soc.*, 2007, **129**, 8. (c) C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou and E. K. Brechin, *J. Am. Chem. Soc.*, 2007, **129**, 2754. (d) 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. (e) C. J. Milios, R. Inglis, R. Bagai, W. Wernsdorfer, A. Collins, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou and E. K. Brechin, *Chem. Commun.*, 2007, 3476. (f) 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. (g) C. J. Milios, S. Piligkos and E. K. Brechin, *Dalton Trans.*, 2008, 1809.
- [6] (a) R. Inglis, C. J. Milios, L. F. Jones, S. Piligkos and E. K. Brechin *Chem. Commun.*, 2012, **48**, 181; (b) C. J. Milios, S. Piligkos and E. K. Brechin, *Dalton Trans.*, 2008, **0**, 1809.
- [7] (a) A.-R. Tomsa, J. Martínez-Lillo, Y. Li, L.-M. Chamoreau, K. Boubekur, F. Farias, M. A. Novak, E. Cremades, E. Ruiz, A. Proust, M. Verdaguer and P. Gouzerh, *Chem. Commun.*, 2010, **46**, 5106. (b) G.-Y. An, A.-L. Cui and H.-Z. Kou, *Inorg. Chem. Commun.* 2011, **14**, 1475. (c) J. Martínez-Lillo, A.-R. Tomsa, Y. Li, L.-M. Chamoreau, E. Cremades, E. Ruiz, A.-L. Barra, A. Proust, M. Verdaguer and P. Gouzerh, *Dalton Trans.* 2012, **41**, 13668.
- [8] J. Martínez-Lillo, L.-M. Chamoreau, A. Proust, M. Verdaguer, P. Gouzerh, *C. R. Chimie*, 2012, **15**, 889.
- [9] (a) L. M. Toma, R. Lescouëzec, J. Pasán, C. Ruiz-Pérez, J. Vaissermann, J. Cano, R. Carrasco, W. Wernsdorfer, F. Lloret, and M. Julve, *J. Am. Chem. Soc.* 2006, **128**, 4842. (b) L. M. Toma, C. Ruiz-Pérez, J. Pasán, W. Wernsdorfer, F. Lloret, and M. Julve, *J. Am. Chem. Soc.* 2012, **134**, 15265.
- [10] M. Nardelli, *J. Appl. Crystallogr.*, 1995, **28**, 659.
- [11] DIAMOND 3.2d, Crystal Impact GbR, CRYSTAL IMPACT; K. Brandeburg & H. Putz GBR, Bonn, Germany, 2000.