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Switching pairwise exchange interactions to enhance SMM properties

Leigh F. Jones [a], Constantinos J. Milios [a], Alessandro Prescimone [a], Marco Evangelisti [b], Euan K. Brechin [a,*]

[a] School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH93JJ, UK
[b] CNR-INFM Nat. Res. Center ''nanoStructures and bioSystems at Surfaces'' (S^3), University of Modena and Reggio Emilia, Via G. Campi 213/A, 41100 Modena, Italy

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Abstract

A simple change in the identity of ''R'' in the family of complexes of general formula $[Mn_6O_2(R\text{-sao})_6(O_2C\text{-th})_2L_{4\text{-}6}]$ (where $saoH_2$ = salicylaldoxime) causes subtle changes in the magnetic core of the compounds that leads to dramatic changes in the magnetic behaviour, switching the pairwise exchange interactions from anti- to ferromagnetic, greatly enhancing the barrier for magnetization relaxation. ***To cite this article: L.F. Jones et al., C. R. Chimie 11 (2008).***

Keywords: Manganese; Single-molecule magnets; Oximes; Structural distortion; Ferromagnets

1. Introduction

For some time, we have been attempting to make polymetallic clusters of transition metal ions with the purpose of synthesizing Single-Molecule Magnets [1]. Our approach, like many others [2], was to employ flexible organic bridging ligands in self-assembly processes and was particularly focused on using manganese [3]. Recently we instigated an alternative approach: a project involving the use of derivatised salicylaldoximes in which we use not only self-assembly, but the deliberate targeted structural distortion of molecules as a means of enhancing SMM properties [4−8]. Phenolic oximes, with the generic structure shown in Scheme 1, have existed for decades with uses not only academically in the formation of polynuclear transition metal complexes, but as industrial metal extractants and anti-corrosive agents in protective coatings [9,10]. In all of the oxime-based Mn clusters we have isolated, the exchange between the metal centres is very weak and typically only a few wavenumbers ($<1-2\ cm^{-1}$) in magnitude. This has allowed us to switch antiferromagnetic pairwise exchange interactions to ferromagnetic pairwise exchange interactions *via* minor structural modifications of the magnetic core. Specifically, changing the R-group (Scheme 1) allows us to distort the planarity of the Mn−N−O−Mn moiety and switch the exchange [4−8]. Here we demonstrate this phenomenon in the family of hexametallic compounds of general formula $[Mn_6O_2(R\text{-sao})_6(O_2C\text{-th})_2L_{4-6}]$ (where R = H (**1**), Et

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* Corresponding author.
E-mail address: ebrechin@staffmail.ed.ac.uk (E.K. Brechin).

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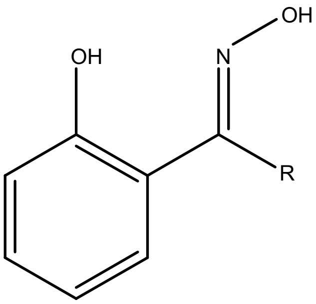

Scheme 1. The structure of the phenolic oxime R−$saoH_2$; R = H ($saoH_2$); R = Me (Me−$saoH_2$); R = Et (Et−$saoH_2$).

(**2**); HO_2C-th = 3-thiophene carboxylic acid; and L = EtOH, H_2O) in which the structures differ only in the identity of the oxime present.

2. Experimental section

2.1. Materials and physical measurements

All manipulations were performed under aerobic conditions using materials as received (reagent grade). *Caution*! Although we encountered no problems care should be taken when using the potentially explosive perchlorate anion. The derivatised oximes (Scheme 1) were synthesized as described elsewhere [11]. Variable temperature, solid-state direct current (dc) and alternating current (ac) magnetic susceptibility data down to 1.8 K were collected on a Quantum Design MPMS-XL SQUID magnetometer. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants.

2.2. General synthetic methodology for complexes *1* and *2*

Method 1. To pale pink solutions of $Mn(ClO_4)_2 \cdot 6H_2O$ in EtOH were added equivalent amounts of the derivatised oximes (R-$saoH_2$), the carboxylic acid (HO_2C-th) and CH_3ONa (or NEt_4OH). The solutions were left stirring for ~30 min, filtered and then left to slowly evaporate.

Method 2. The sodium salt of the carboxylic acid (NaO_2C-th) was treated with equivalent amounts of $Mn(ClO_4)_2 \cdot 6H_2O$, the derivatised oxime and CH_3ONa (or NEt_4OH) in EtOH. Single crystals were grown upon slow evaporation.

Method 3. Method 1 and/or method 2 was repeated using a solvent mixture of 1:1 EtOH/CH_2Cl_2. After stirring for ~30 min, the solution was filtered and layered with diethyl ether (Et_2O).

In each case suitable crystals grew after a period of 3–5 days. For both compounds the yields vary from minimum of 30% to a maximum of 50%. CHN analysis, Found (Calculated). **1** ($Mn_6C_{52}H_{44}N_6S_2O_{22}$): C, 43.02 (42.81); H, 3.17 (3.02); N, 5.81 (5.76) %. **2** ($Mn_6C_{85}H_{107}N_7S_2O_{26}$): C, 50.45 (50.27); H, 5.37 (5.27); N, 4.60 (4.83) %.

2.3. X-ray crystallography and structure solution

Diffraction data were collected at 150 K on a Bruker Smart Apex CCDC diffractometer, equipped with an Oxford Cryosystems LT device, using Mo radiation. See Table 1 and CIF files for full details.

3. Results and discussion

Both complexes, $[Mn_6O_2(sao)_6(O_2C\text{-th})_2(H_2O)_4] \cdot 2CH_2Cl_2 \cdot Et_2O$ ($\mathbf{1} \cdot 2CH_2Cl_2 \cdot Et_2O$), and $[Mn_6O_2(Et\text{-sao})_6(O_2C\text{-th})_2(EtOH)_6] \cdot Et\text{-}saoH_2$ ($\mathbf{2} \cdot Et\text{-}saoH_2$), display very similar molecular structures, crystallizing in the triclinic space group *P*-1, each possessing an inversion centre. They can be described (Fig. 1) as consisting of two parallel off-set, stacked $[Mn_3^{III}(\mu_3\text{-}O)]^{7+}$ triangular subunits linked *via* two 'central' oximate O-atoms and

Table 1
Crystallographic data for complexes **1** and **2**

	1	**2**
Formula	$C_{63}H_{70}C_{16}N_6O_{24}S_2Mn_6$	$C_{85}H_{109}N_7O_{26}S_2Mn_6$
M_w	1901.73	2038.53
Crystal size, mm	0.86 × 0.62 × 0.41	0.49 × 0.45 × 0.23
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a, Å	11.5076(8)	12.8647(5)
b, Å	13.8717(9)	13.1373(5)
c, Å	14.1965(9)	16.1689(6)
α, deg	117.336(3)	92.116(2)
β, deg	90.196(3)	101.617(2)
γ, deg	109.517(3)	114.076(2)
V, $Å^3$	1863.9(2)	2422.07(17)
Z	1	1
D_c, g cm^{-3}	1.694	1.398
μ, (Mo Kα), mm^{-1}	1.337	0.876
T, K	150(2)	150(2)
λ, Å	0.71073	0.71073
Meas/indep (R_{int}) reflns.	41,028, 10,196 (0.0489)	29,271, 11,556 (0.00)
Observed data [$I > 4\sigma(I)$]	8614, 0.0394	6357, 0.0847
R_1 [$I > 2\sigma(I)$], wR_2 [all data]	0.0462, 0.0557	0.0785, 0.000168
GOF on F^2	1.0960	1.0236
$\Delta\rho$ (max/min), e $Å^{-3}$	−1.19, 1.34	1.05, −1.34