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

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^[†]Celebrating 300 years of Chemistry at The University of Edinburgh.

Supporting information:

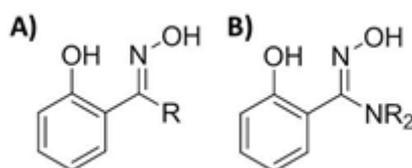
[‡] Electronic supplementary information (ESI) available: Preparation of 1, Fig. S1–S3. CCDC 943039. For ESI and crystallographic data in CIF or other electronic format see <http://dx.doi.org/10.1039/C3DT51512E>

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.¹ The latter can include quantum information processing,² low temperature cooling³ and molecular spintronics.⁴ 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).¹ 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.⁵ This in turn resulted in the formulation of a semi-quantitative magnetostructural correlation which enables prediction of the magnetic properties of new family members.⁶ The coordination chemistry of the related salicylamidoxime ligand⁷ and its dialkyl derivatives⁸ (Scheme 1) towards the Mn^{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.^{7,8} 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° , somewhat lower than that of the related salicylaldoxime-based complexes (*ca.* 31°).



Scheme 1. The structures of: (A) salicylaldoxime (R-saoH_2) and (B) salicylamidoxime ($\text{R}_2\text{N-saoH}_2$).
R =H, Me, Et, Ph *etc.*

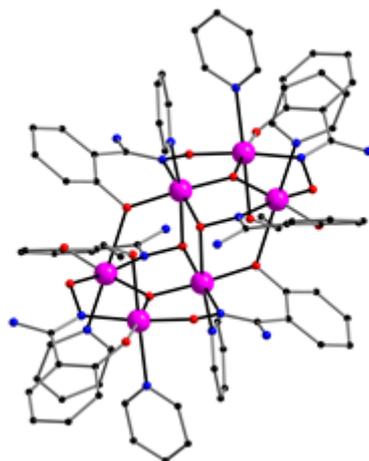


Figure 1. Perspective view of the molecular structure of the $[\text{Mn}_6(\mu_3\text{-O})_2(\text{H}_2\text{N-sao})_6(\text{py})_6(\text{EtOH})_2]^{2+}$ cation of **1**. H atoms, ClO_4^- anions and EtOH solvent molecules have been omitted for clarity. [Colour code: pink, Mn; red, O; blue, N; black, 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.^{7c} 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 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

O²⁻ ion displaced 0.162 Å above the plane of the [Mn₃] triangle, towards the terminally ligated py molecules. The hexametalllic core of **1** is thus rather similar to both its salicylamidoxime-based [Mn₆] 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 [Mn₆] clusters results in the cleaving of the molecule into its constituent [Mn₃] 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 ClO₄⁻).⁶ This observation highlights the relevant importance of the –NH₂ 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^{III}₃] 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^{III}₃(μ₃-O)(H₂N-sao)₃] triangular units, producing Mn–N–O–Mn torsion angles with magnitudes as large as those obtained with the bulkiest salicylaldehyde ligands.^{7ac} 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 ClO₄⁻ anions sit between neighbouring [Mn₆]²⁺ cations and are H-bonded to the –NH₂ 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 –NH₂ 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 cm³ mol⁻¹ K, somewhat higher than that expected for six uncoupled Mn(III) ($S = 2$) centres (18.0 cm³ mol⁻¹ 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 cm³ mol⁻¹ K at 22 K. Below this temperature the value of $\chi_M T$ drops to a final value of 11.5 cm³ mol⁻¹ 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° associated to J_2) which is somewhat smaller than the other two (42.0 and 39.4° associated to J_1), thus the exchange pathways are divided in two groups in the core of the cationic 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.⁵ 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.

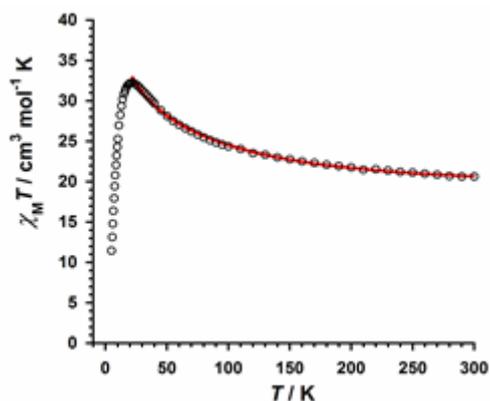


Figure 2. Plot of $\chi_{\text{M}}T$ vs. T obtained for compound **1** (o). The solid red line represents the simulation of the data obtained for **1**.

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.^{5–8} 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 χ_{ac}'' vs. T plot in Fig. 3 and are consistent with SMM behaviour. Indeed, a clear

frequency-dependent decrease of the χ_{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**.⁹ These data were fitted to the Arrhenius equation [$\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$, where τ_0 is the pre-exponential factor, τ is the relaxation time, U_{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 τ_0 and U_{eff} are 5.3×10^{-9} s and 40 K, respectively. The U_{eff} value for **1** falls into the range ($24 \text{ K} < U_{\text{eff}} < 86 \text{ K}$) for previously reported salicylamidoxime-based Mn_6 complexes.⁷

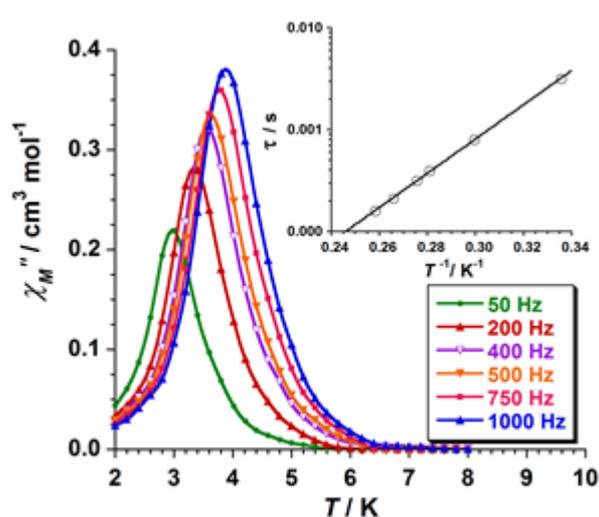


Figure 3. Out-of-phase ac susceptibility (χ_{ac}'') versus T plot for **1**. The inset shows the Arrhenius best-fit plot (see text).

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 Mn_6 with pyridine ligands suggests the use of polypyridine-type ligands should afford a plethora of supramolecular 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] 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 Mn_6 salts.

Notes and references

§ *Crystal data for 1*: C₈₄H₁₀₂Cl₂O₂₈N₁₈Mn₆, $M = 2212.38$, monoclinic, space group $P2(1)/n$, $a = 13.039(1)$, $b = 22.772(1)$, $c = 16.487(1)$ Å, $\beta = 102.87(1)^\circ$, $V = 4772.2(5)$ Å³, $T = 120(2)$ K, $Z = 2$, $\mu = 0.912$ mm⁻¹, $D_c = 1.540$ gcm⁻³, 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 α radiation ($\lambda = 0.71073$ Å). The structure was solved by standard direct methods and subsequently completed by Fourier recycling using the SHELXTL¹⁰ 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 program¹⁰ whereas the graphical manipulations were performed with the DIAMOND program.¹¹ CCDC 943039.

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