Thioester-functionalised and oxime-based hexametallic manganese(III) single-molecule magnets†

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Two novel hexametallic MnIII complexes of formulae \([\text{Mn}_6(\mu_3-O)_2(\text{H}_2\text{N-sao})_6(3\text{-atpa})_2(\text{EtOH})_6\cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}\) (1) and \([\text{Mn}_6(\mu_3-O)_2(\text{H}_2\text{N-sao})_6(6\text{-atha})_2(\text{EtOH})_6\cdot 6\text{EtOH}\) (2) \([\text{H}_2\text{N-saoH}_2 = \text{salicylamidoxime, 3-hatpa} = 3\text{-}(\text{acetylthio})\text{propionic acid, 6-hatha} = 6\text{-}(\text{acetylthio})\text{hexanoic acid}\) have been synthesised by using thioester-carboxylate ligands and magnetostructurally characterised. 1 crystallises in the triclinic system with space group \(P\bar{1}\) and 2 crystallises in the monoclinic system with space group \(P2_1/c\). The study of the dc and ac magnetic susceptibility reveals single-molecule magnet behaviour for both compounds with spin-ground states \(S = 12\) and \(S = 4\) for 1 and 2, respectively. Hence, 1 and 2 are new members of the oxime-based family of \([\text{Mn}_6]\) single-molecule magnets, containing the thioester group functionalisation, which could be used to connect devices in molecular spintronics studies.

Introduction

Single-Molecule Magnets (SMMs) have attracted much interest because of their spin properties and potential applications, and have also been considered a fundamental link between two novel scientific disciplines, molecular spintronics and molecular electronics.\textsuperscript{1–4} In recent years, great research effort has been devoted to the synthesis of single-molecule systems, with large magnetic anisotropies, and their functionalization, which is made with functional groups convenient to connect suitable SMMs to junction devices or to perform their grafting on surfaces of Si or Au substrates;\textsuperscript{5–18} in many cases, looking for the improvement of their magnetic properties,\textsuperscript{7,8} the control of the nanoscale organization\textsuperscript{16} or simply to get a reliable description of the electronic structure of the investigated system.\textsuperscript{11}

Thioesters-based ligands have proven to be particularly useful to get derivatised and suitable SMMs for this research field (Scheme 1). Indeed, \([\text{Fe}_{III}\text{Ni}_{II}]\) cages have been connected to junction devices,\textsuperscript{9} besides that, complexes such as the well-known \([\text{Mn}_{III}\text{Mn}_{II}]\) system and the \([\text{Fe}_{III}\text{II}]\) and \([\text{Fe}_{III}\text{Cr}_{III}]\) complexes with star-like structures have been grafted on Au surfaces after being thioester-functionalised.\textsuperscript{10}

Oxime-based hexanuclear MnIII SMMs have intensively been studied in the field of molecular magnetism.\textsuperscript{12–16} In these systems, the magnetic exchange between MnIII ions depends basically on the Mn–N–O–Mn torsion angles, they possess generally spin ground states varying from 4 to 12, and the anisotropy energy barriers vary from 24 to 86 K.\textsuperscript{12–16} Some of these \([\text{Mn}_{III}]\) SMMs have also been grafted on Au surfaces and studied, as thiophene-carboxylate \([\text{Mn}_{III}]\) derivatives.\textsuperscript{7,8} Nevertheless, no thioester-functionalised \([\text{Mn}_{III}]\) compound has been reported up to date.

Herein we report the synthesis and magnetostructural characterisation of two novel hexanuclear MnIII compounds of formulae \([\text{Mn}_6(\mu_3-O)_2(\text{H}_2\text{N-sao})_6(3\text{-atpa})_2(\text{EtOH})_6\cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}\) (1) and \([\text{Mn}_6(\mu_3-O)_2(\text{H}_2\text{N-sao})_6(6\text{-atha})_2(\text{EtOH})_6\cdot 6\text{EtOH}\) (2) \([\text{H}_2\text{N-saoH}_2 = \text{salicylamidoxime, 3-hatpa} = 3\text{-}(\text{acetylthio})\text{propionic acid, 6-hatha} = 6\text{-}(\text{acetylthio})\text{hexanoic acid}\). 1 and 2 are the first reported structures of thioester-functionalised \([\text{Mn}_{III}]\) SMMs.

Scheme 1 Molecular structures of: (A) 3-(acetylthio)propionic acid and (B) 6-(acetylthio)hexanoic acid.
Results and discussion

Synthetic procedure

By reacting MnCl₂·4H₂O with the salicylamidoxime ligand in the presence of the desired S-acetyl-carboxylic acid and NEt₃ we obtain a dark green microcrystalline solid of hexametallic Mn³⁺ complexes in satisfactory yields. Good-sized crystals were obtained from concentrated solutions of the microcrystalline solid in ethanol by layering them with acetone (1) and ethanol (2) (see Experimental section). Hence, this is a straightforward synthetic procedure to add the S-acetyl function [CH₃–C(O)–S–] to the well-known family of [Mn₆] complexes (Fig. 1, 2, S1 and S2†).

Description of the crystal structures of 1 and 2

Compound 1 crystallises in the triclinic system with space group P̅1, and compound 2 crystallises in the monoclinic system with space group P2₁/c (Table 1). Their structures are made up of neutral hexanuclear [Mn₆] complexes together with water (1) and ethanol (1 and 2) molecules of crystallisation, which are self-assembled through hydrogen-bonding interactions (see Fig. 3 and S3†).

Each hexanuclear [Mn₆(µ₃-O)(H₂N-sao)_6(L)_2(EtOH)_6] [L = 3-acetylthiopropionate (3-atpa) in 1 and 6-acetylhexanoate (6-atha) in 2] complex contains two symmetry equivalent [Mn₆(µ₃-O)] triangular moieties, which are linked by two phenolate and two oximate oxygen atoms that are related by an inversion centre. Their hexanuclear cores are rather similar to previously reported salicylamidoxime-based [Mn₆] complexes.11–16 The six Mn³⁺ ions exhibit distorted octahedral geometries with the Jahn–Teller axes approximately perpendicular to the [Mn₆(µ₃-O)] planes, with the central O²⁻ ion displaced 0.04 Å and 0.03 Å above the plane of the [Mn₆] triangle for 1 and 2, respectively. The monodentate carboxylate ligand is coordinate on the Mn(1) atom in 1, on the Mn(3) atom in 2 and on their symmetry equivalents. The remaining coordination sites are occupied by EtOH molecules. The Mn–N–O–Mn torsion angles of the [Mn₆(µ₃-O)(H₂N-sao)_3] triangular units are 42.6, 30.1 and 27.5 for 1 and 38.9, 36.5 and 26.0 for 2.

In the crystal packing of 1 and 2, the neutral [Mn₆] complexes are mainly connected by hydrogen bonding interactions. In 1, the acetylthio groups are H-bonded through the carbonyl to the –NH₂ groups on the salicylamidoxime ligands of adjacent [Mn₆] units (O···N distance, ~3.01 Å) (see Fig. 3).

Each [Mn₆] is involved in four of these interactions, linking them into chains that grow along the c axis (Fig. 3). In 2, EtOH molecules sit between neighbouring [Mn₆] complexes and are

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Table 1 Summary of the crystal data for compounds 1 and 2

| Compound | 1 | 2 |
|----------|---|---|
| Formula  | C₆₆H₁₄₂O₃₂N₁₂S₂Mn₆ | C₆₆H₁₄₂O₃₂N₁₂S₂Mn₆ |
| Mᵣ      | 1961.34 | 2193.77 |
| Crystal system | Triclinic | Monoclinic |
| Space group | P1 | P2₁/c |
| a/Å     | 12.614(1) | 15.993(1) |
| b/Å     | 13.146(1) | 13.559(1) |
| c/Å     | 14.873(1) | 23.506(1) |
| α°      | 70.67(1) | 90 |
| β°      | 76.15(1) | 97.23(1) |
| γ°      | 66.10(1) | 90 |
| V/Å³    | 2111.8(3) | 5056.6(2) |
| Z       | 1 | 2 |
| D₄/g cm⁻³ | 1.339 | 1.441 |
| μ(Mo-Kα)/mm⁻¹ | 8.283 | 0.850 |
| F(000)  | 1012 | 2296 |
| Goodness-of-fit on F² | 1.008 | 1.009 |
| R₁ [I > 2σ(I)] | 0.0733 | 0.0751 |
| wR₂ [I > 2σ(I)] | 0.1887 | 0.1739 |
simultaneously H-bonded to –NH$_2$ (O···N distance, ~2.85 Å) and carboxylate (O···O distance, ~2.72 Å) groups generating chains that grow along the c axis (Fig. S3†). Intermolecular S···S contacts are observed neither in 1 nor in 2, the shortest S···S distances being ca. 5.31 Å (1) and ca. 7.99 Å (2). Additional weak C···C interactions are also observed, in 1, between aromatic rings of salicylamidoxime ligands of neighbouring [Mn$_6$] complexes (ca. 3.33 Å) and, in 2, between aromatic rings of salicylamidoxime ligands and thioester groups of adjacent [Mn$_6$] units (ca. 3.67 Å), which stabilize the supramolecular arrangement in 1 and 2.

**Magnetic properties of 1 and 2**

DC magnetic susceptibility measurements were performed on microcrystalline samples of 1 and 2 in the 2.0–300 K temperature range, under an external magnetic field of 0.1 T. The magnetic properties of 1 and 2 in the form of $\chi_M T$ vs. $T$ plot ($\chi_M$ being the molar magnetic susceptibility) are shown in Fig. 4. At room temperature the $\chi_M T$ values are 20.0 (1) and 18.0 cm$^3$ mol$^{-1}$ K (2). Upon cooling, these values approximately follows the Curie law to ca. 100 K for both compounds. Then, for complex 1, $\chi_M T$ rises gradually with decreasing temperature, reaching a maximum value of 28.0 cm$^3$ mol$^{-1}$ K at 8.0 K. This feature reveals an intramolecular ferromagnetic coupling between the Mn$^{III}$ ions. $\chi_M T$ is then decreasing at lower temperatures. The value of $\chi_M T$ in 2 decreases with decreasing temperature reaching a final value of ca. 6.5 cm$^3$ mol$^{-1}$ K at 2.0 K, indicating antiferromagnetic interaction as the resulting magnetic exchange (Fig. 4). The decrease of the $\chi_M T$ for both compounds at lower temperatures is likely due to the presence of intermolecular interactions and/or zero-field splitting (zfs) effects.

These experimental data were treated by using the 2J model described by the Hamiltonian of eqn (1) and Fig. S4† affording the parameters: $J_1 = +0.45$ cm$^{-1}$, $J_2 = +0.11$ cm$^{-1}$ and $g = 1.99$ for 1 and $J_1 = +0.86$ cm$^{-1}$, $J_2 = -1.14$ cm$^{-1}$ and $g = 1.99$ for 2. This data treatment has satisfactorily been performed in previous works.$^{12}$

$$
\hat{H} = -2J_1(\hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_3 + \hat{S}_1\hat{S}_4 + \hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_1 + \hat{S}_2\hat{S}_3) - 2J_2(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) + \mu g H \hat{S} \quad (1)
$$

The obtained $J_1$, $J_2$ and $g$ values result to be consistent with the torsion angles found in the crystal structures of 1 and 2, and agree with those previously reported for similar [Mn$_6$] systems.$^{12–16}$

In a previous work dealing with DFT studies on salicylamidoxime-based [Mn$_6$] complexes,$^{13c}$ it was established that the critical angle where the exchange pathway between neighbouring Mn$^{III}$ ions switches from antiferromagnetic ($J < 0$) to ferromagnetic ($J > 0$) is ca. 27.0°, which is somewhat lower than that of the related salicylaldehyde-based [Mn$_6$] complexes.$^{13c}$

Our results nicely reflect that fact, given that compound 1, with the lowest torsion angle being 27.5°, gave positive $J_1$ and $J_2$ values indicating a ferromagnetic exchange, whereas in compound 2, with 26.0° as the lowest torsion angle, the sign and magnitude of the obtained $J_2$ value indicate that the main magnetic exchange is antiferromagnetic. Given that the value of $J_1$ (exchange between Mn$^{III}$ ions of different [Mn$_6$] triangles of the [Mn$_6$] unit) is positive in both compounds, what is making the difference to get a $S = 4$ or $S = 12$ total spin is the value of $J_2$ (exchange constant within each trinuclear [Mn$_3$] subunit).
Variable temperature-variable field dc magnetisation data were measured for 1 and 2 in the 2–7 K temperature and 0.5–7.0 T field ranges. The experimental data are given as reduced magnetisation in Fig. 5 and 6. These data do not reach the saturation values, maybe because excited states with lowest spins are also populated. Anyway, they were well fitted to a Zeeman plus axial zero-field splitting Hamiltonian $\hat{H} = D(\hat{S}_z^2 - S(S + 1)/3) + \mu_B H \hat{S}$, where $D$ is the axial anisotropy of the [Mn$_6$] cluster, $\mu_B$ is the Bohr magneton, $\hat{S}_z$ is the easy-axis spin operator and $H$ is the applied field assuming only the ground state is populated. The best fits afforded the parameters $S = 12, g = 1.98$ and $D = -0.44$ cm$^{-1}$ for 1 and $S = 4, g = 2.00$ and $D = -0.98$ cm$^{-1}$ for 2, which are in line with other members of the [Mn$_6$] family. Besides the results obtained by fitting the experimental data of the reduced magnetisation, ground state spin values of $S = 12$ (1) and $S = 4$ (2) were also obtained from dc susceptibility measurements. Indeed, plots of the energy versus total spin, extracted from the isotropic simulation of the magnetic susceptibility, are shown in Fig. 7 and 8 for 1 and 2, respectively. The first excited state found in 1 is a $S = 11$ located at 1.75 cm$^{-1}$, and the first excited state in 2 is a $S = 3$ located at 0.85 cm$^{-1}$ (Fig. 7 and 8).

Ac susceptibility measurements were performed on samples of 1 and 2 in the temperature range 2–8 K, in zero applied dc field and a 3.9 G ac field oscillating in the 5–1000 Hz range of frequencies. Out-of-phase ac signals ($\chi''$) for 1 and 2 are shown in Fig. 9 (1) and Fig. 10 (2), which exhibit frequency dependence of the $\chi''$ maxima. This feature is consistent with SMM behaviour. In 2, it is observed that the $\chi''$ maxima decrease with decreasing frequency, which is a peculiarity typical of strong intermolecular interactions in single-molecule and chain magnets (SMMs and SCMs).

We fitted these data 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 relaxation of the magnetisation and $k_B$ is the Boltzmann constant. The inset of the Fig. 9...
relative stability, make 1 and 2 suitable SMMs to be studied on devices in the field of molecular spintronics. Indeed, we believe that our compounds could be adequate systems to be connected to junction devices. This investigation is underway.

**Experimental**

**Materials and physical measurements**

All manipulations were performed under aerobic conditions, using chemicals as received from Sigma-Aldrich. Elemental analyses (C, H, and N) were performed by the Central Service for the Support to Experimental Research (SCSIE) at the University of Valencia. Infrared spectra of 1 and 2 were recorded as KBr pellets using a PerkinElmer Spectrum 65 FT-IR spectrometer in the 4000–400 cm\(^{-1}\) region. Dc and ac magnetic susceptibility measurements on microcrystalline samples of 1 and 2 were carried out on a Quantum Design MPMS-XL SQUID magnetometer. The dc studies were performed in the temperature range of 2–300 K in an applied magnetic field of 0.1 T. The ac susceptibility measurements were performed in zero applied dc field and a 3.9 G ac oscillating field with temperature and frequency ranges of 2–8 K and 5–1000 Hz, respectively. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal’s constants.\(^{19,20}\)

**Preparation of the complexes**

1. MnCl\(_2 \cdot 4\)H\(_2\)O (0.594 g, 3.0 mmol) was added dropwise and with constant stirring to a solution formed by H\(_2\)N-saoH\(_2\) (0.456 g, 3.0 mmol) and 3-acyethylthioproionic acid (1.0 g, 6.8 mmol) in EtOH (100 mL), then NEt\(_3\) (2.0 mL, 3.58 mmol) was added. After stirring for 1 h a dark green solution was generated and left to evaporate at room temperature. A dark green microcrystalline solid was formed in 1 day, separated by filtration and washed with EtOH and ether. Yield: 84%. Suitable crystals for X-ray diffraction studies were formed by layering a concentrated acetone solution of the microcrystalline solid with EtOH. Anal. calcd (found) for C\(_{68}\)H\(_{102}\)O\(_{30}\)N\(_{12}\)S\(_{2}\)Mn\(_6\): C, 44.9 (45.1); H, 6.2 (5.9); N, 7.7 (8.1)%. Selected IR peaks (in KBr, cm\(^{-1}\)) for 1: 3326m, 2928m, 1605vs, 1575m, 1530s, 1481m, 1439m, 1440m, 1418m, 1317s, 1254s, 1146m, 1023s, 883s, 750m, 686vs, 579w, 553w, 474w, 416 (41.5); H, 5.2 (4.9); N, 8.6 (9.0)%. Selected IR peaks (in KBr/cm\(^{-1}\)) for 2: 3332m, 2928m, 1605vs, 1575m, 1530s, 1481m, 1439m, 1420m, 1315s, 1253s, 1146m, 1023s, 881s, 757m, 684s, 649m, 579w, 553w, 474w.

2. Complex 2 was prepared as 1 but by using 6-acyethylhexanionic acid (1.0 mL, 6.0 mmol) instead of 3-acyethylthioproionic acid. Yield: 77%. A concentrated acetone solution of the microcrystalline solid with EtOH was evaporated at room temperature to give a dark brown solution. A dark green microcrystalline solid was formed in 1 day, separated by filtration and washed with EtOH and ether. Yield: 84%. Suitable crystals for X-ray diffraction studies were formed by layering a concentrated acetone solution of the microcrystalline solid with EtOH. Anal. calcd (found) for C\(_{68}\)H\(_{102}\)O\(_{30}\)N\(_{12}\)S\(_{2}\)Mn\(_6\): C, 44.9 (45.1); H, 6.2 (5.9); N, 7.7 (8.1)%. Selected IR peaks (in KBr/cm\(^{-1}\)) for 1: 3326m, 2928m, 1605vs, 1575m, 1530s, 1481m, 1439m, 1420m, 1315s, 1253s, 1146m, 1023s, 881s, 757m, 684s, 649m, 579w, 553w, 474w.

**Conclusions**

In summary, the crystal structures and magnetic behaviour of two novel [Mn\(_6\)] single-molecule magnets (SMMs) of formula [Mn\(_6\)(μ\(_3\)-O)\(_2\)(H\(_2\)N-sao)\(_6\)(3-atpa)\(_2\)]\(_2\)EtOH\(_2\)\(_2\)H\(_2\)O (1) and [Mn\(_6\)(μ\(_3\)-O)\(_2\)(H\(_2\)N-sao)\(_6\)(6-atha)\(_2\)]\(_2\)EtOH\(_2\)\(_2\)EtOH (2) [H\(_2\)N-saoH\(_2\) = salicylamidoxime, 3-hatpa = 3-(acyethylthio)propionic acid, 6-atha = 6-(acyethylthio)hexanoic acid] have been reported. 1 and 2 are the first examples of thioester-functionalized complexes in the coordination chemistry of oxime-based [Mn\(_6\)] SMMs, these structures also being the first reported complexes containing the 3-(acyethylthio)propionate (3-atpa) and 6-(acyethylthio)hexanoate (6-atha) ligands. Such features, together with their...
parameters and refinement results are summarized in Table 1. The structures of 1 and 2 were solved by direct methods and subsequently completed by Fourier recycling using the SHELXTL\textsuperscript{21–23} software packages. The final full-matrix least-squares refinements on \( F^2 \), minimising the function
\[ \sum w(|F_{o}| - |F_{c}|)^2 \]
reached convergence with the values of the discrepancy indices given in Table 1. Disorder of free solvent molecules was detected in both compounds (1 and 2). The graphical manipulations were performed with the DIAMOND program.\textsuperscript{24} CCDC 1568972 (1) and 1568973 (2).†

Conflicts of interest

There are no conflicts to declare.

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