Magnetic and theoretical characterization of a ferromagnetic Mn(III) dimer

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Abstract

Reaction of 1,1,1-tris(hydroxymethyl)ethane (H_3thme) with the complex $[Mn_2O_2(bpy)_4](ClO_4)_3$ produces the dimeric species $[Mn_2(Hthme)_2(bpy)_2](ClO_4)_2$ in high yield. Magnetic measurements in the temperature range 1.8–300 K and in fields up to 7 T reveal weak ferromagnetic exchange between the metal centres with $J = +2.13$ cm^{-1}. A fit of the magnetization data, assuming only the ground state is populated, gives $S = 4$, $g = 1.71$ and $D = -0.65$ cm^{-1}. Low temperature single crystal measurements suggest the co-existence of SMM behaviour and strong intermolecular interactions. Density functional calculations also support a weak exchange interaction between the Mn ions.
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1. Introduction

Manganese complexes have been the subject of intense study for many years mainly as a result of their role in a number of biologically important molecules such as the oxygen-evolving complex of photosystem II [1]. More recently some manganese complexes have been shown to exhibit single-molecule magnetism behaviour. Single-molecule magnets (SMMs) are of current interest because they represent the ultimate in small size magnetic memories and allow for the study of quantum effects in mesoscopic systems [2]. The number of SMMs has increased in recent years and complexes involving manganese in nuclearities up to eighty four

have been characterised [3]. The smallest classes of SMMs containing only Mn are the tetranuclear species $[Mn_4(pdmH)_6(OAc)_2](ClO_4)_2$ [4], $[Mn_4(hmp)_6Br_2(H_2O)_2]$-$Br_2$ [5], and $[Mn_4O_3X(dbm)_3]$ [6]. We have been using the pro-ligand 1,1,1-tris(hydroxymethyl)ethane (H_3thme) and its analogues in the synthesis of manganese and iron clusters and herein report the synthesis, structure, magnetic properties, and theoretical study of the dinuclear species $[Mn_2(Hthme)_2(bpy)_2](ClO_4)_2$.

2. Experimental

2.1. Synthesis

The complex $[Mn_2O_2(bpy)_4](ClO_4)_3$ was made as previously described [7]. Treatment of $[Mn_2O_2(bpy)_4]$-$(ClO_4)_3$ with one equivalent of H_3thme in acetonitrile

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immediately affords a red-brown solution which was then stirred for a further hour. The complex $[Mn_2(Hthme)_2(bpy)_2](ClO_4)_2$ (**1**) was obtained in high yield ($\sim$50 %) via diethylether diffusion after 3 days. Elemental *Anal*. Calc. for $Mn_2C_{30}H_{36}O_{14}Cl_2$: C, 42.02; H, 4.23; N, 6.53. Found: C, 42.00; H, 4.11; N, 6.50%.

2.2. X-ray crystallography and structure solution

A crystal was mounted using a drop of fomblin (perfluoropolymethylisopropyl ether) oil in a Hamilton Cryoloop and data were collected on a Bruker Smart Apex CCD diffractometer at 100 K using Mo radiation. The structure was solved by direct methods.

The asymmetric unit contains half the dimer, together with a ClO_4^- ion. The non-H atoms were refined anisotropically. H atoms bonded were included in calculated positions. It was clear from the diffraction pattern that the crystal was a non-merohedral twin, and the *R* value initially was about 9.9%. However, accounting for the twinning using the matrix $-1\,0\,0\,0\,-1\,0\,-0.489\,-0.305\,1$ (a 180° rotation about the $0\,0\,1$ reciprocal lattice direction) and including the BASF and HKLF 5 commands, led to a refined scale factor of 0.275 for the twinned component, and a much improved R value of 5.86%. CCDC 255232. Crystallographic parameters are collected in Table 1.

2.3. Crystal structure

The centrosymmetric cation of **1** (Fig. 1) contains two Mn^{III} ions ($Mn\cdots Mn$ separation, 3.0964(14) Å) bridged by two μ_2-oxygens from the two Hthme^{2-} ligands. The

Table 1
Crystal data and structure refinement for complex **1**

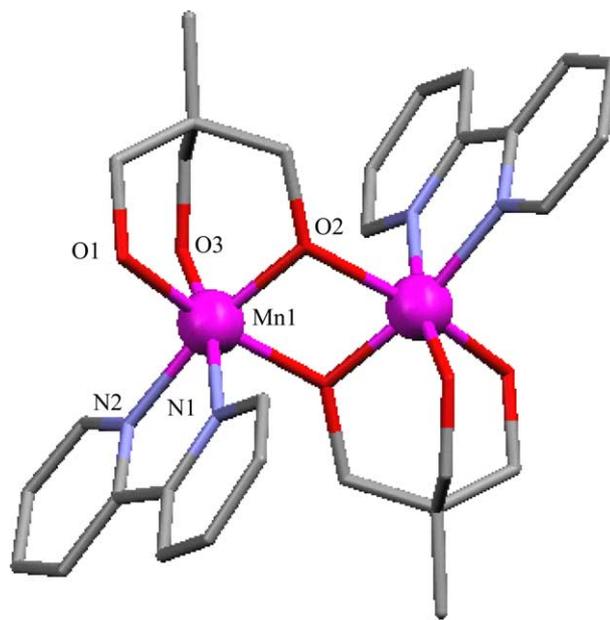|	**1**[Mn$_2$]
Formula	$C_{30}H_{34}Cl_2Mn_2N_4O_{14}$
M (g mol^{-1})	855.39
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	8.254(3)
b (Å)	10.002(3)
c (Å)	10.374(3)
α (°)	81.248(5)
β (°)	78.557(5)
γ (°)	88.519(5)
V (Å^3)	829.6(5)
T (K)	100(2)
Z	1
ρ_{calc} (g cm^{-3})	1.712
Crystal shape/colour	brown-green block
Crystal size [mm]	$0.25 \times 0.10 \times 0.03$
μ (mm^{-1})	1.000
Unique data	5951
Unique data, ($I > 2\sigma(F)$)	4988
R_1, wR_2	0.0586, 0.1445
Goodness-of-fit	1.101

Fig. 1. The structure of the cation of **1**. Selected interatomic distances [Å] and angles [°], Mn–O1,1.990(3); Mn–O2, 1.878(3); Mn–O3,1.798(3); Mn–O2A, 2.114(3); Mn–N1, 2.081(3); Mn–N2, 2.034(3) and Mn1–O2–Mn1A, 101.6(1).

other two arms are both terminal but differ in that one is deprotonated ($O3\cdots Mn$, 1.798(3) Å) and one is protonated ($O1\cdots Mn$, 1.990(4) Å), with the protonated arm H-bonded to the ClO_4^- counter ion ($O1\cdots O4$, 3.022(4) Å). The coordination sphere of each manganese centre is completed by a chelating bpy ligand. The Mn^{III} ions are in distorted octahedral geometries (*cis*, 78.0–98.7°; *trans*, 167.4–168.7°) but do not display an obvious Jahn-Teller elongation, with each of the six bonds distinctly different (Table 2). It appears that the trigonal field of the Hthme^{2-} ligand causes a rhombic distortion of the Mn^{III} ion preventing the expected Jahn-Teller elongation along O1–Mn1–O2A: although the Mn–O2A bond is much longer (2.114 Å) than the other bonds, the Mn–O1 bond (1.990 Å) is not.

The oxidation state of the Mn ions was confirmed by BVS analysis. The cations of **1** pack in columns with each molecule stacked directly upon the next (Fig. 2), such that the π-rings of adjacent bpy ligands interact though are not fully eclipsed ($C\cdots C$, $\sim$3.5 Å), with the ClO_4^- anions filling the channels between these columns.

3. Magnetic measurements

3.1. Bulk measurements

Solid state dc magnetization measurements were performed on **1** in the range 1.8–300 K in a field of 5.0 kG (Fig. 3). The $\chi_M T$ value of approximately 6.3 cm^3 K mol^{-1} at 300 K remains constant as the

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**

Mn(1)–O(3)	1.798(3)
Mn(1)–O(2)	1.878(3)
Mn(1)–O(1)	1.990(4)
Mn(1)–N(2)	2.034(3)
Mn(1)–N(1)	2.081(3)
Mn(1)–O(2)A	2.114(3)
Mn(1)–Mn(1)A	3.0964(14)
O(3)–Mn(1)–O(2)	93.72(13)
O(3)–Mn(1)–O(1)	91.16(14)
O(2)–Mn(1)–O(1)	90.70(14)
O(3)–Mn(1)–N(2)	92.45(13)
O(2)–Mn(1)–N(2)	168.67(11)
O(1)–Mn(1)–N(2)	98.67(14)
O(3)–Mn(1)–N(1)	168.73(14)
O(2)–Mn(1)–N(1)	96.73(12)
O(1)–Mn(1)–N(1)	84.53(12)
N(2)–Mn(1)–N(1)	77.97(12)
O(3)–Mn(1)–O(2)A	95.79(13)
O(2)–Mn(1)–O(2)A	78.43(11)
O(1)–Mn(1)–O(2)A	167.43(14)
N(2)–Mn(1)–O(2)A	91.51(11)
N(1)–Mn(1)–O(2)A	90.43(11)

Fig. 2. The packing of **1** in the crystal.

temperature is decreased until ca. 150 K when it begins to increase to a maximum value of 7.6 cm³ K mol⁻¹ at 25 K before decreasing rapidly to 6.5 cm³ Kmol⁻¹ at 5 K. This suggests that the exchange between the metal centres is ferromagnetic with the low temperature decrease assigned to zero-field splitting and/or intermolecular interactions. In order to fit the data, the Hamiltonian given in Eq. (1) was employed.

$$\hat{H} = -2J\hat{S}_{1a}\hat{S}_{1b}. \tag{1}$$

The fit at high temperatures (>50 K) to the experimental $\chi_M T$ data suggests a ground state spin of $S = 4$ with the following parameters: $g = 1.99$ and $J = +2.13$ cm⁻¹.

In order to confirm the ground state spin, magnetization data were collected in the ranges 1.8–10 K and 10–70 kG (Fig. 3). The data were fit, assuming only the ground state is populated, to give $S = 4$, $g = 1.71$ and
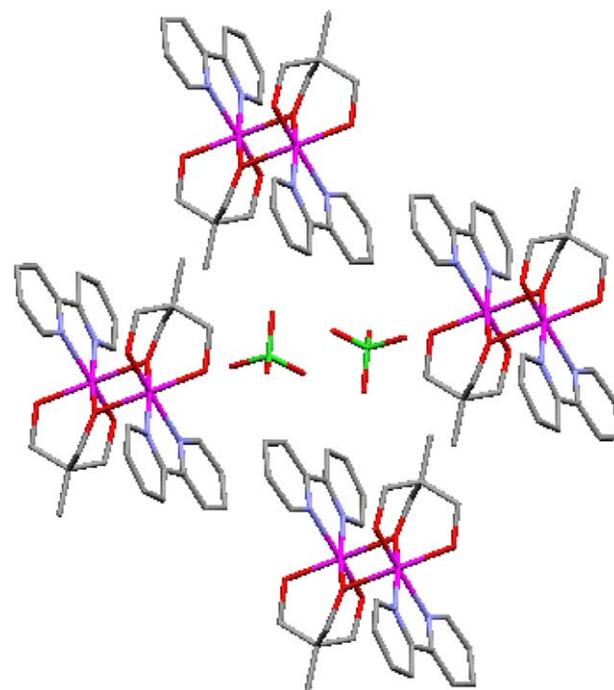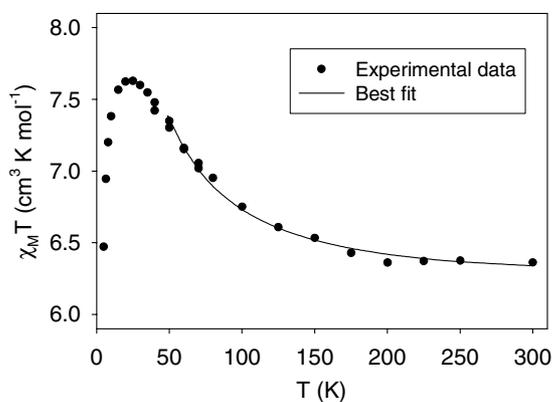
$D = -0.65$ cm⁻¹. Given the value and sign of S and D, ac magnetization measurements were performed to see if **1** acts as an SMM. However measurements taken in the 1.8–10 K range in a 3.5 G ac field oscillating at 50–1000 Hz gave no out-of-phase signal. The obtained g-value is rather low for Mn^{III} and multi-frequency EPR and INS experiments are currently underway to probe the magnetic behaviour of **1** more thoroughly.

3.2. Single crystal measurements

Single crystal magnetic measurements were performed on **1** using an array of micro-squids. Fig. 4 shows hysteresis loops for **1** at temperatures below 1.2 K and at various sweep rates, with the field applied in
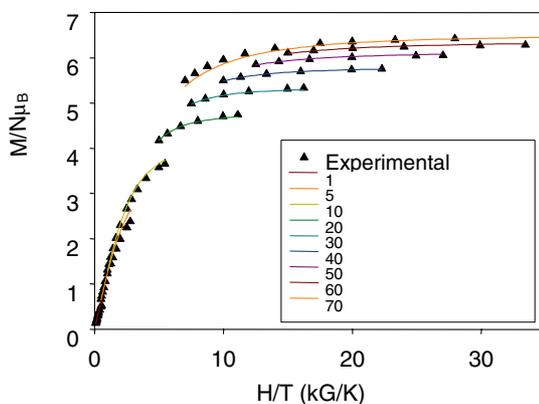

Fig. 3. Plot of $\chi_M T$ vs. T for complex **1**. The solid line is a fit to the data with $J = +2.13$ cm⁻¹ and $g = 1.99$ (left). Plot of reduced magnetization vs. H/T for **1**, in the temperature range 1.8–10 K and 10–70 kG. The solid lines are fits of the data to an $S = 4$ state with $g = 1.71$ and $D = -0.65$ cm⁻¹ (right).
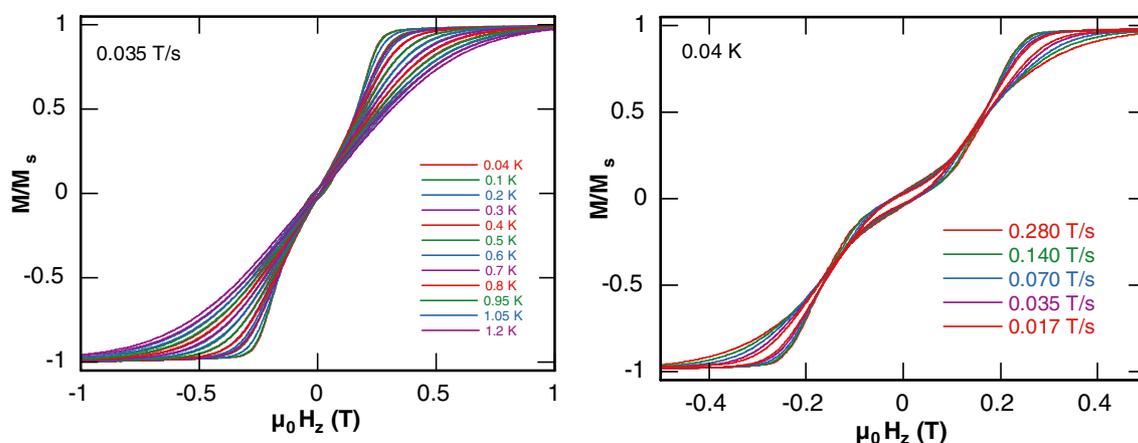
Fig. 4. Magnetization (M) of **1** (plotted as fraction of maximum value M_s vs. applied field $\mu_0 H$). The resulting loops are shown at different temperatures (left) and different field sweep rates (right).

the direction of the easy axis of the molecule. The hysteresis loops have a small coercive field and two step-like features. These step-like features however, do not originate at zero-field, the first step being shifted by approximately −0.2 T. The measurements taken at 0.04 K in particular show small openings in the loops at different sweep rates indicative of slow relaxation of the magnetization. The small coercive field and the overall shape of the loops suggest the presence of strong intermolecular interactions consistent with the extensive intermolecular interactions throughout the crystal lattice as mediated via the π–π stacking of the bpy rings and the H-bonding interactions of the ClO_4^- ions. In principle therefore, complex **1** can be regarded as an exchange-biased SMM [8] although it is clearly difficult to separate the intermolecular interactions and the SMM behaviour. Studies of analogues of complex **1** that contain different peripheral ligands and which pack differently are currently in progress and will be reported in full elsewhere.

4. Theoretical calculations

The broken symmetry model developed by Noodleman [9] has been widely used to compute J-values using HF or DFT calculations. For binuclear transition metal complexes the following equation has been advocated by Ruiz et al. [10]:

$$J = \frac{2(E_{BS} - E_{HS})}{S_{HS}(S_{HS} + 1)}. \tag{2}$$

The combination of a hybrid B3LYP [11] functional with Ahlrichs' TZV [12] basis set as implemented on GAUSSIAN 98 [13] has been shown previously to give good numerical estimates of J-values, and therefore all the calculations on complex **1** were performed using this methodology. To avoid convergence problems, the initial guess for the calculations was generated using JAGUAR [14] and this guess was then transferred to GAUSSIAN to proceed fur-

ther. Calculations performed on the full structure of **1**, ($[Mn_2(Hthme)_2(bpy)_2](ClO_4)_2$), gives the estimate of $J = -0.55$ cm^{-1}. The calculations thus support a weak exchange between the metal centres, but give the wrong sign in comparison to the experimental data – although the overall numerical difference between the two is small, making the change in sign unsurprising. Over-estimation of J-values using the DFT-BS approach has been encountered previously [10,15]. Calculations were also performed on a model complex of **1**, in which the terminal bpy ligands were replaced with NH_3 molecules and including only the cation: $[Mn_2(Hthme)_2(NH_3)_4]^{2+}$. This gives $J = -1.1$ cm^{-1}, suggesting that the terminal ligands have significant influence on the coupling.

Spin density distributions provide information about the mechanism of the exchange interaction. The high spin state spin density plot of **1** is shown in Fig. 5. The white
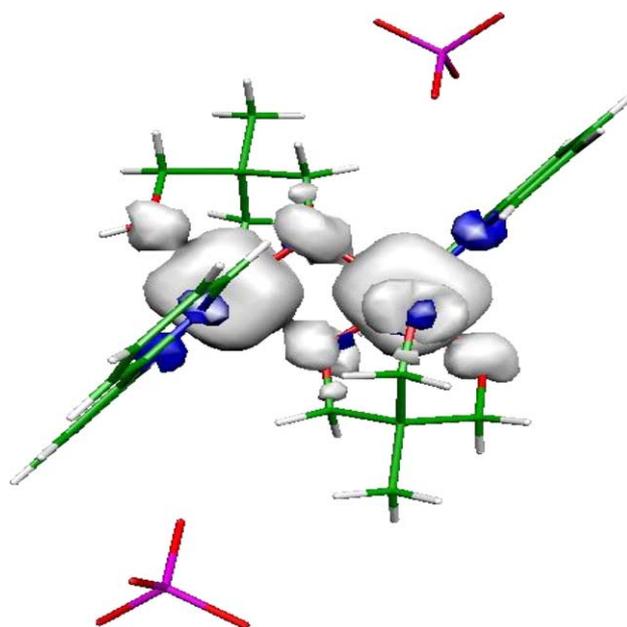

Fig. 5. The high spin state spin density plot of complex **1**.

colour represents a positive spin density and the blue colour represents a negative spin density. It is clear from the figure that in this case both spin delocalisation and spin polarisation mechanisms operate. Previously we have shown that for Mn(III) ions, the Jahn-Teller axis favours a spin delocalisation mechanism with the other axes favouring spin polarisation [16]. Here the O1–Mn1–O2A axis favours spin delocalisation, and the others show a predominantly spin polarisation mechanism. Therefore we can conclude that the O1–Mn1–O2A axis is indeed the Jahn-Teller axis of the molecule.

5. Conclusions

Reaction of H_3thme with $[Mn_2O_2(bpy)_4](ClO_4)_3$ produces the dimetallic complex $[Mn_2(Hthme)_2(bpy)_2](ClO_4)_2$. Magnetic measurements suggest the presence of a weak ferromagnetic interaction between the Mn^{III} ions. Low temperature single crystal measurements show the co-existence of SMM behaviour and strong intermolecular interactions. DFT calculations support a weak exchange between the metal centres, and also provide an insight into the mechanism of the exchange. Spin density distributions help to identify the Jahn-Teller axis of the Mn ions.

Acknowledgements

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