A rare ligand bridged ferromagnetically coupled Mn^{IV}_3 complex with a ground spin state of $S = 9/2$†

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An exclusively chelating ligand bridged high-valent $[Mn^{IV}_3]$ complex has been synthesized, in which all Mn^{IV} ions are ferromagnetically-coupled to exhibit an $S_T = 9/2$ spin ground state.

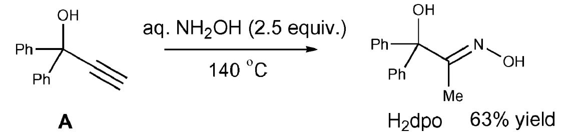
In recent years, high-valent manganese cluster compounds have been the focus of considerable research efforts due to their potential for use in catalysis,[1] in modelling photosystem II[2] and in magnetochemistry.[3] In most cases, the coordination chemistry of manganese is dominated by low-valent Mn^{II}, Mn^{III}, or mixed-valent Mn complexes. To date, only a handful of Mn^{IV} clusters have been obtained, all of which contain O^{2-}/OH^- bridging ligands. To our knowledge, no examples of exclusively chelating ligand bridged Mn^{IV} polynuclear ($n > 2$) complexes have been reported.[2c] This is presumably due to the difficulty in stabilizing Mn^{IV} ions in the absence of metal oxide cores.

In order to obtain such a unique complex, we have developed an alternative approach that is contrary to the common practice of utilizing strong oxidizing agents, such as MnO_4^- in acidic conditions which, in general leads to O^{2-}/OH^- bridged complexes.[4] By employing aerial oxidation of Mn ions in mildly basic conditions and aprotic solvents, we avoid the formation of undesirable metal–oxide side products and ligand protonation, and promote high-valent Mn ions and the deprotonation of ligand molecules, as required for chelation.

Currently, with this synthetic strategy, we are investigating the use of tunable, tridentate, oximate-based chelating ligands. To date, the majority of previously reported oximate-based metal complexes have been synthesized using either commercially available or Schiff base reaction generated oximates. In order to gain the controllability and tunability of the oximate ligands and in turn of the resulting metal compounds, we have developed a new synthetic approach to bulky oximate ligands involving direct hydroamination of alkynes.[5] The chosen oximate chelate has been carefully designed to incorporate bulky steric groups that induce large torsion angles between spin carriers *via* bridging oximate groups, which should influence the nature and strength of the magnetic interactions between the metal ions.

Herein, we report the synthesis, structure, DFT calculations and magnetic properties of the first ferromagnetic $\{Mn^{IV}_3\}$ linear complex obtained using the chelating ligand, 1-hydroxy-1,1-diphenylpropan-2-one oxime (H_2dpo).

The H_2dpo chelating ligand was obtained upon heating alkynol **A** with aqueous NH_2OH overnight (eqn (1)).



(1)

The reaction proceeds with high "Markovnikov" regioselectivity and can routinely be performed on the gram-scale to afford the desired oxime.

Reaction of $Mn(ClO_4)_2{\cdot}4H_2O$ (1 equiv.) with H_2dpo (2 equiv.) and triethylamine (1 equiv.) in MeCN (20 ml) gave a dark-brown opaque solution. After 4 days, black rectangular crystals of $[Mn_3(dpo)_6]{\cdot}2CH_3CN$ (**1**·$2CH_3CN$) were isolated in 45% yield. The structure of the centrosymmetric complex **1** consists of a trinuclear Mn^{IV}_3 core capped by six dpo^{2-} ligands (Fig. 1).‡ The three Mn centers are linked solely *via* the oximate groups in a linear fashion with a 180° [Mn1–Mn2–Mn1] angle. The octahedral coordination environments of the metal centers are completed by O and N atoms from the ligands.

In contrast to previously reported trinuclear Mn complexes, **1** is the first example of a high-valent linear trinuclear complex. In addition, **1** exhibits higher torsion angles than other trinuclear oximate bridged complexes (0–20°).[6] For **1**, the average torsion angle between the terminal and the central manganese ions [Mn1–N–O–Mn2] was determined to be 51.3°. This increase in torsion angles is due to the presence of bulky substituents on the oximate ligand (see below) and is also likely to be the origin of the ferromagnetic superexchange interactions observed. Furthermore, in comparable N–N diazine bridged systems, similar torsion angles generally lead to ferromagnetic interactions between the metal centers.[7]

To establish the electronic structure of **1** and the influence of the ligand's bulky groups on the torsion angles, DFT calculations at the BPE/TZVP level were performed.[8] The calculated optimized structure of **1** has S_6 symmetry and is in good agreement with the X-ray structure [calculated (X-ray) Mn1–N: 2.02 (1.99), Mn1–O: 1.86 (1.82) and Mn2–O: 1.95 (1.91) Å]. The ground spin state was calculated to be $S_T = 9/2$

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† Electronic supplementary information (ESI) available: LUMO of **1**, computational details and crystallographic details. CCDC 676451. See DOI: 10.1039/b802279h

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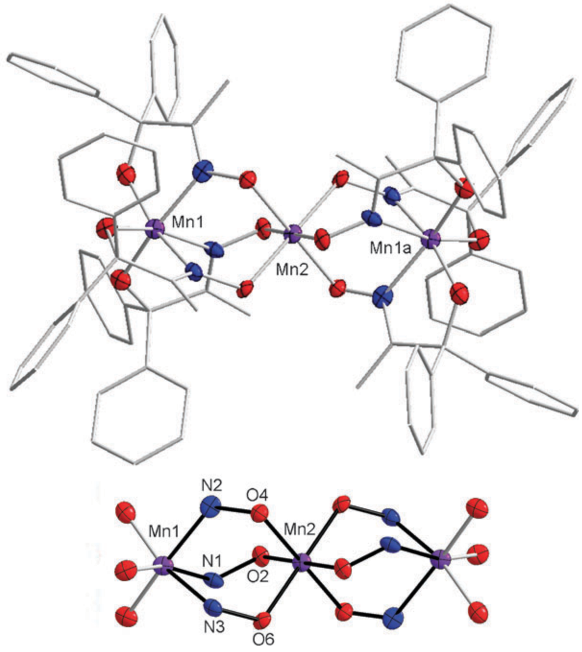

Fig. 1 **Top**: the molecular structure of [Mn$_3$(dpo)$_6$], **1**. The central Mn atom (Mn2) lies on an inversion centre. Symmetry equivalent position ($1 - x, 2 - y, 1 - z$) denoted by an additional "a" in the label (Mn1a). Color code: purple (Mn), red (O), blue (N). **Bottom**: the linear central core of **1**, revealing the (Mn–N–O–Mn) superexchange pathway between the metal centres.

with three unpaired electrons on each Mn ion. The calculated Mn oxidation states are consistent with those determined by charge considerations, short bond Mn^{IV}–L bond lengths (avg. of 1.90 Å) and bond valence sum (BVS) calculations.[9] The NPA-derived atomic charges of the Mn ions are +1.03 and +1.24 au for Mn1 and Mn2, respectively. Such low charges for the Mn^{IV} atoms indicate significant covalency in the Mn–N and Mn–O bonds in the complex. Indeed, the Mayer bond orders for Mn1–N, Mn1–O, and Mn2–O are 0.58, 1.03, and 0.78, respectively. This covalency helps to stabilize the high oxidation state of the Mn ions *via* ligand-to-metal charge donation (2.65 e$^-$ to the 3d orbitals, 0.26 e$^-$ to the 4s orbital of Mn1, 2.46 e$^-$ to the 3d orbitals and 0.26 e$^-$ to the 4s orbital of Mn2) of the complex **1**.

The cyclic voltammogram of **1** in CH$_3$CN contains one irreversible one-electron reduction wave at −0.60 V (*vs.* Fc/Fc$^+$) indicating that only one Mn ion is reduced. The higher positive charge of Mn2 (+1.24), relative to Mn1 (+1.03), makes this ion a better electron acceptor. In agreement with this, the α-spin LUMO of the complex (Fig. S1, ESI†) has a 45% Mn2 3d orbital contribution while the two Mn1 ions contribute only 6%. As a result, the DFT calculation on the reduced complex produces a Mn^{IV}Mn^{III}Mn^{IV} species ($S_T = 5$) with the central Mn ion in a high-spin d^4 electron configuration. Such an electron configuration undergoes Jahn–Teller distortion at Mn2 and the MnO$_6$ octahedral environment becomes axially elongated with 1.98 Å (eq.) and 2.19 Å (axial) Mn2–O bond distances.

In order to probe the effects of ligand substituents on the geometry and electronic structure of **1**, a series of DFT calculations were performed for simplified ligands. In these calculations, the 12 Ph groups and 6 Me groups were replaced by H atoms (Fig. 2). It was found that removal of the Me groups does not affect the Mn2–O–N–Mn1 torsion angles significantly. On the other hand, removal of the Ph groups causes the torsion angles to decrease from an average of 51° to 43°. Thus, the steric hindrance caused by the Ph groups on the oximate ligand plays a key role in imposing the higher torsion angles in **1** which, in turn, help to stabilize the structure.

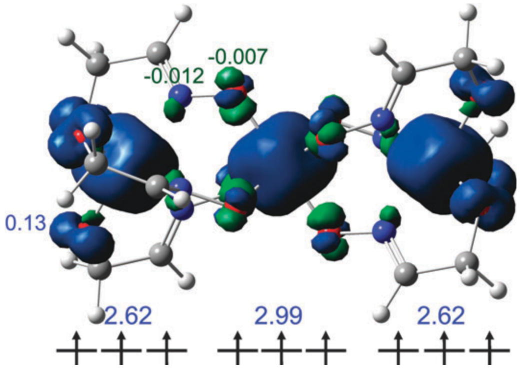

Fig. 2 Spin density distribution for the simplified complex **1** (R = H, not Ph) for clarity. NPA-derived atomic spin densities are shown for Mn, N, and O atoms.

The dc magnetic susceptibility of **1** was measured in an applied magnetic field of 1000 Oe and can be seen plotted as χT *vs.* T in Fig. 3. As the temperature decreases from 300 to 7 K, the χT product gradually increases from 6.7 cm^3 K mol^{-1} to reach a maximum of 13.1 cm^3 K mol^{-1} then slightly decreases to 12.4 cm^3 K mol^{-1} at 1.8 K. The increase in the χT product above 7 K is consistent with dominant ferromagnetic interactions present within the trinuclear Mn^{IV} complex and the observed maximum value of χT is in agreement with an $S_T = 9/2$ ground state (expected value: 12.375 cm^3 K mol^{-1} with $g = 2$). The final decrease at low temperature is presumably due to very weak magnetic anisotropy and/or intermolecular antiferromagnetic interactions. As seen in Fig. 1, the molecular structure of **1** reveals that the main magnetic interactions between the metal centers are mediated by the

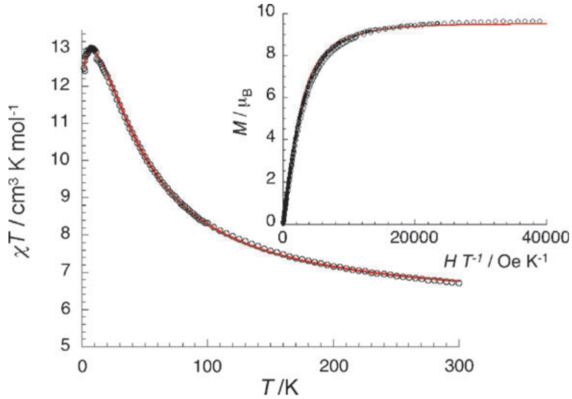

Fig. 3 Plot of χT *vs.* T for **1** at 1000 Oe. The solid line is the best fit obtained with the Heisenberg trinuclear model described in the text. **Inset**: M *vs.* H data at various temperatures (1.8, 3, 5 and 8 K) are shown on a single M *vs.* H/T plot. The solid line is the best fit obtained with an $S = 9/2$ Brillouin function considering all the data between 1.8 and 8 K.

–NO groups from the dpo^{2-} ligands. In order to quantify the magnitude of the magnetic interactions, an isotropic Heisenberg trinuclear model of $S = 3/2$ spins was employed using the following spin Hamiltonian: $H = -2J(S_1S_2 + S_2S_3)$ where J is the exchange interactions between Mn^{IV} ions in **1** and S_i the spin vector for each metal ion ($S_i = 3/2$ for Mn^{IV} with $i = 1$–3). Application of the van Vleck equation[10] to Kambe's vector coupling scheme[11] gives an excellent fit of the experimental data from 300 K to 10 K. In order to fit the low temperature χT product below 10 K, intermolecular interactions (J') were introduced in the frame of the mean field theory.[12] This approach leads to an excellent least-squares fit of the experimental data down to 1.8 K and affords the following parameters: $J/k_B = +11.5(1)$ K, $g = 2.06(1)$ and $J'/k_B = -0.06(1)$ K. This magnetic behavior is consistent with a ground state of $S_T = 9/2$ with the first ($S = 7/2$) and second ($S = 5/2$) excited states being 34.2 and 69.7 K higher in energy, respectively.

The field dependence (up to 7 T) of the magnetization at different temperatures (1.8 to 8 K) has also been measured for **1** (inset Fig. 3). The magnetization at 1.8 K saturates above 4 T at 9.6 μ_B in good agreement with the $S_T = 9/2$ ground state. The clear saturation of the magnetization suggests the absence of a significant magnetic anisotropy and also the presence of a well defined $S_T = 9/2$ ground state with well-separated excited states as shown by the analysis of the χT *vs.* T data. To further confirm the $S_T = 9/2$ ground state, the M *vs.* H/T data have been fitted to an $S_T = 9/2$ Brillouin function that leads to an excellent theory–experiment agreement with a g factor of 2.11(4). Furthermore, ac susceptibility measurements have also been performed on **1**; however, no out-of-phase signal has been detected and thus, **1** does not exhibit single molecule magnet (SMM) behavior. To our knowledge there is only one linear trinuclear manganese SMM reported to date,[13] which comprises a central Mn^{III} ion and two peripheral Mn^{II} ions coupled ferromagnetically with an $S = 7$ spin ground state. The magnetic anisotropy of the latter SMM originates mainly from the central Mn^{III} ion. With this in mind, the DFT calculations and electrochemical studies on **1** clearly show that the central Mn^{IV} ion is likely to be reduced to a Mn^{III} ion. We therefore believe a reduction of the central Mn2 ion to Mn^{III} would introduce magnetic anisotropy to **1**, which could then lead to SMM properties. Synthetic efforts to isolate the one electron reduced Mn^{IV}Mn^{III}Mn^{IV} complex are currently underway.

In conclusion, we have synthesized the first example of a ferromagnetically coupled exclusively chelating ligand bridged high-valent trinuclear Mn^{IV} complex. The presence of bulky Ph groups on the specifically designed and synthesized oximate ligand have a direct influence on the bridging torsion angles; confirmed by DFT calculations. We believe this could, in turn, induce the ferromagnetic interactions observed between the metal centers. Further calculations investigating the influence of the Mn–N–O–Mn torsion angle on the strength and nature of the magnetic interactions are currently underway.

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Notes and references

‡ Crystal data for **1**: $C_{98}H_{90}Mn_3N_{10}O_{12}$, $M = 1764.6$, dark brown rectangle, triclinic, $P\bar{1}$, $a = 11.583(5)$, $b = 12.119(6)$, $c = 17.112(8)$ Å, $\alpha = 84.547(10)$, $\beta = 85.258(9)$, $\gamma = 67.058(10)°$, $V = 2199.3(18)$ Å^3, $Z = 1$, $T = 201(2)$ K, 13 737 reflections collected of which 6248 were independent ($R_{int} = 0.1183$), 587 parameters and 54 restraints, $R1 = 0.0868$ [based on $I > 2\sigma(I)$], w$R2 = 0.2347$ (based on F and all data). CCDC 676451.

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$$\chi = \frac{\chi_{\mathrm{trimer}}}{1 - \frac{2zJ'}{Ng^2\mu_B^2}\chi_{\mathrm{trimer}}}$$

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