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Twisted molecular magnets

Twisted Molecular Magnets**

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Abstract

The use of derivatised salicylaldoximes in manganese chemistry has led to the synthesis of a family of approximately fifty hexanuclear ($[Mn^{III}_6]$) and thirty trinuclear ($[Mn^{III}_3]$) Single-Molecule Magnets (SMMs). Deliberate, targeted structural distortion of the metallic core afforded family members with increasingly puckered configurations, leading to a switch in the pairwise magnetic exchange from antiferromagnetic to ferromagnetic. Examination of both the structural and magnetic data revealed a semi-quantitative magneto-structural correlation, from which the factors governing the magnetic properties could be extracted and used for predicting the properties of new family members and even more complicated structures containing analogous building blocks. Herein we describe an overview of this extensive body of work and discuss its potential impact on similar systems.

Introduction

The discovery that molecules, containing only a handful of paramagnetic metal centres, could display magnetic properties reminiscent of bulk magnets was a seminal moment in the field of molecular magnetism. Such zero-dimensional nanomagnets, now known as Single Molecule Magnets (SMMs), can, once magnetised, retain their magnetisation in the absence of an external magnetic field, at very low temperatures.[1] Their intrinsic *molecular* behaviour, established by magnetometry[2-4] and magneto-optical measurements[5-7] *in solution*, is due to the existence of an energy barrier to magnetisation reversal[8] associated to the double-well potential energy pattern of the Zeeman sublevels of the ground spin-state, S, resulting from a negative zero-field splitting, D, of this ground spin-state. Thus, these bi-stable molecules present potential for information storage at the molecular level.[9] For about two decades now, the prototype SMM has been represented by the dodecanuclear mixed-valence manganese complex $[Mn_{12}O_{16}(O_2CMe)_{16}(H_2O)_4]\cdot 4H_2O\cdot 2CH_3CO_2H$, "Mn$_{12}$OAc", which comprises eight Mn^{III} and four Mn^{IV} ions and can be easily obtained from the reaction of manganese acetate and potassium permanganate in acetic acid. The complex was first reported[10] by Lis in 1980 almost thirteen years before its exciting magnetic properties were revealed,[8] and almost sixty years after Weinland and Fischer had first "predicted" its existence.[11] Lis prophetically wrote in his initial report that "*...such a complicated dodecameric unit should have interesting magnetic properties*". Indeed, this molecule has been studied extensively for the past 18 years and was the gateway and inspiration to not only the field of Single-Molecule Magnetism, but in a more general sense to the emerging field of "Molecular Nanomagnetism" in which magnetically interesting molecules have potential applications in, for example, quantum information processing,[12] low temperature cooling[13] and molecular spintronics.[14]

For SMMs, the energy barrier for the classical, thermally activated, reversal of the magnetisation is given by $U = S^2 \cdot |D|$ (for integer S values) or $U = (S^2 - 1/4) \cdot |D|$ (for half-integer S values).[15] For $[Mn_{12}OAc]$ this is equal to 50 cm^{-1} ($\approx$ 70 K) since $S = 10$ and $D = -0.5$ cm^{-1}. However, there exists another mechanism allowing the relaxation of the molecular magnetisation in SMMs: quantum tunneling of the magnetisation (QTM). QTM has been observed on both oriented polycrystalline powders[16] and single-crystals of $[Mn_{12}OAc]$.[17] The experimental manifestation of these two mechanisms for relaxation of the magnetisation in $[Mn_{12}OAc]$ was the observation of hysteresis loops in magnetisation versus field measurements with a blocking temperature, T_b, of approximately 3 K[9] and the subsequent observation, on these same hysteresis loops, of steps, providing for the first time clear evidence for the existence of macroscopic QTM.[16,17] These initial reports on $[Mn_{12}OAc]$ precipitated an explosion of interest in the area of molecular nanomagnetism and a glut of Mn-based SMMs followed. Manganese was the metal of choice for several important reasons: a) the preponderance for Mn to exist in a variety of oxidation states (II, III and IV) in molecular clusters is a huge advantage since even antiferromagnetic exchange can lead to non-zero ground spin-states; b) the presence of the Jahn-Teller distorted Mn^{III} ion is likely to afford anisotropy since, to a first approximation, cluster anisotropy is dictated by single ion anisotropy;[18] c) a number of very high-spin Mn molecules were already being reported in the literature throughout the 1980's and 1990's in the pursuit of model complexes for biologically important systems such as PSII and these essentially then acted as a "pre-made library" from which molecules could be examined for SMM properties.[19]

Mn-based SMMs are almost entirely made through serendipitous self-assembly (indeed this has proven by far the most successful way of making SMMs of any metal), albeit *via* judicious choice of bridging ligand. The cores of polymetallic molecules containing high oxidation state (III, IV) Mn ions are almost always stabilised by the presence of bridging (μ_2-μ_4) O^{2-} ions. Although knowledge of the chemistry of the metal ions and literature precedents informs us that the cluster building blocks are likely to be based on $[Mn_3O]^{n+}$ triangles, $[Mn_4O]^{n+}$ tetrahedra and $[Mn_4O_2]^{n+}$ butterflies, their self-assembly in the presence of coordinatively flexible ligands and in reaction conditions which include variables such as solvent and counter ions, which can all influence the outcome of the reaction, renders prediction of their structures, at least initially, impossible. This is in fact also an enormous advantage[20] because of the sheer variety of clusters that results. Even a quick scan of the SMM/cluster literature will reveal compounds with [beautiful] structures beyond the imagination of the humble scientist. Such a plethora of information is vital for the chemists and physicists to be able to understand the relationship between molecular structure and magnetism, and this in turn engenders the design principles required for building new molecules with enhanced properties.

Until recently, the most common methodology employed to obtain SMMs with improved properties, was to synthesise molecules of the highest possible ground spin-state built from components

incorporating anisotropic metal centres. This strategy is based on the assumption that the energy barrier for the classical, thermally activated, reversal of the magnetisation follows a quadratic dependence on S and a linear dependence on D. Thus, *simultaneously* maximising S and D should lead to molecular systems displaying optimal SMM properties. One of the main problems in making molecules with large ground spin-states is that the vast majority of nearest-neighbour exchange interactions are antiferromagnetic, and the likelihood of antiferromagnetic exchange is further increased as the nuclearity of the cluster increases, since more exchange pathways are present. Thus, only a limited number of really high ground spin-state molecules have so far been reported in the literature.[21] However, these high ground spin-state magnetic molecules failed to deliver the expected improvement in SMM behaviour. The underlying cause of this failure[22-26] is the fact that the anisotropy, D, of a given spin-state of a polymetallic system itself depends on the magnitude of S and will decrease with increasing S as a consequence of the decreasing magnitude of the single-ion anisotropy projection coefficients on the anisotropy of the ground spin-state. It has been suggested that, for large S, the barrier for the thermally activated reversal of the molecular magnetisation of a polynuclear metal cluster increases as S^0 or follows a more complex dependence approaching S^1 for moderate values of S.[22] This has been experimentally verified for $[Mn^{III}_6]$, where a dependence of the energy barrier to magnetisation reversal close to linear to S has been estimated by INS and FDMRS,[26-28] and EPR[29] measurements on $[Mn^{III}_6]$ systems of $S = 4$ and $S = 12$ ground spin-states. Thus, a very large value of the total spin, S, does not guarantee an accordingly large energy barrier to the relaxation of the magnetisation. Indeed, if one is aiming to maximise SMM properties, it is probably a more sensible approach to aim for small or moderately sized ferro- or ferrimagnets, in which $|D|$ is maximised, rather than to attempt to build large or very large nuclearity compounds in an attempt to maximise S.

In 2005 we instigated an alternative approach to SMM synthesis. Instead of relying wholly on serendipitous self-assembly we decided to deliberately modify the structure, and hence magnetic properties, of a known SMM, $[Mn^{III}_6O_2(O_2CMe)_2(sao)_6(EtOH)_4]$ (**1**; $saoH_2$ = salicylaldoxime, Scheme 1).[30] Herein, we present an overview of what turned out to be one of the most fruitful synthetic programs in our laboratory, resulting in an extensive magneto-structural correlation and the construction of a SMM whose blocking temperature has only recently been surpassed.[31] We describe the story behind how the $[Mn^{III}_6]$ family came to pass, our inspirations, and our thoughts on future directions.
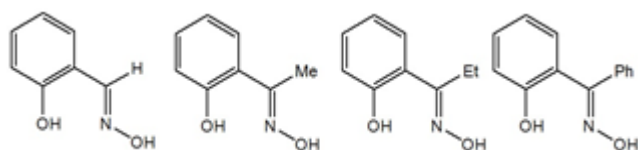
← **Scheme 1**. The structures of (left to right) $saoH_2$, Me-$saoH_2$, Et-$saoH_2$ and Ph-$saoH_2$.

Results and Discussion

Table 1 presents all the salicylaldoxime-based [Mn$^{III}_6$] complexes made in Edinburgh from 2005 to the present day. The story however begins in Patras, Greece, in 2003 with the synthesis of the clusters of general formula [Mn$^{III}_6$O$_2$(O$_2$CR)$_2$(sao)$_6$(EtOH)$_4$] (structure type **A**; saoH$_2$ = salicylaldoxime; Figure 1), from the simple reaction of Mn(O$_2$CR)$_2$·2H$_2$O and salicylaldoxime (saoH$_2$) in EtOH.[30] The metallic core common to all complexes of this structural type (**A**) consists of two off-set, stacked [Mn$^{III}_3$(μ$_3$-O)(sao)$_3$]$^+$ triangles in which each edge of the triangle is bridged by one oximate -N-O- group; thus, creating an oxo-centred {Mn-N-O-}$_3$ ring. The two triangles (related by an inversion centre) are linked together *via* two central oxime groups to form the [Mn$^{III}_6$(μ$_3$-O^{2-})$_2$(NO$_{oxime}$)$_6$] magnetic core, with the triangular faces of the cluster occupied by two μ-bridging carboxylates and terminally bonded solvent molecules. The Mn ions are all in the 3+ oxidation state and in distorted octahedral geometries with their Jahn-Teller axes all approximately perpendicular to the [Mn$_3$] planes. The only exceptions to this are the "outermost" Mn ions which are 5-coordinate and square-based pyramidal in geometry with a long (axial) contact to the proximal phenolate O-atom (~3.5 Å). Magnetic studies revealed $S = 4$ ground states with axial anisotropies of the order $D \approx$ -1.2 cm^{-1} and "moderate" energy barriers to magnetisation reversal of $U_{eff} \approx$ 28 K.[30]
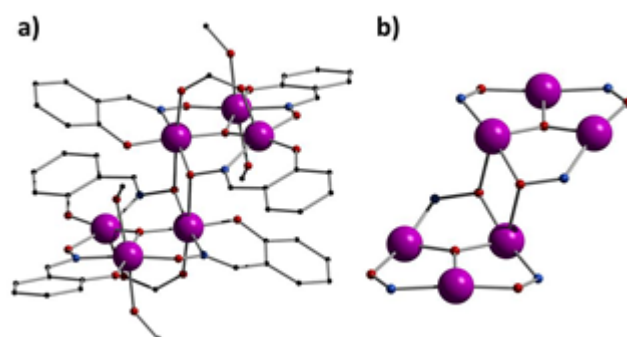
Figure 1. **a)** The molecular structure of [Mn$^{III}_6$O$_2$(O$_2$CH)$_2$(sao)$_6$(MeOH)$_4$] (**1**) of structure type **A** and **b)** its magnetic core. Colour code: Mn^{III} = purple; O = red; N = blue; C = black. H-atoms are omitted for clarity. Atoms are not to scale.

The ground state is easily rationalised by considering two antiferromagnetically coupled ($S = 2$) triangles, coupled ferromagnetically to each other. This can be experimentally corroborated *via* the synthesis of the analogous "half-molecules" [Mn$_3$O(sao)$_3$(O$_2$CR)(py)$_3$] (structure type **B**; Figure 2) which are easily prepared by, for example, dissolving the appropriate [Mn$^{III}_6$] precursor in pyridine;[32] the latter capping the triangular faces and preventing dimerisation. The nature and magnitude of the

exchange in **A** and **B** were, as expected, relatively weak and antiferromagnetic, considering those already observed for the structurally similar Mn^{III} basic carboxylates, $[Mn^{III}_3O(O_2CR)_6(H_2O)_3]^{+}$.[33] Despite the relatively small energy barrier in $[Mn^{III}_6O_2(O_2CR)_2(sao)_6(EtOH)_4]$, the magnitude of the axial anisotropy, *D*, was however rather large; indeed at the time it was the largest observed for any manganese cluster and can be attributed to the parallel orientation of the Jahn-Teller axes.[30]

Two years after the publication of the original $[Mn^{III}_6]$, a paper appeared (also originating from the Perlepes lab) which described the serendipitous self-assembly and magnetic properties of the trinuclear Mn^{III} complexes $[Mn_3O(mpko)_3(O_2CR)_3]^{+}$ (mpkoH = methyl 2-pyridyl ketone oxime; structure type **C**; Figure 2).[34] This was both a fascinating and confusing paper for us, and indeed it was this result that inspired further experimentation on the $[Mn^{III}_6]$ family. Structure type **C** has many similarities to **A** and **B**, as the comparison in Figure 2 shows, and is probably best thought of as a basic Mn^{III} carboxylate structure in which three of the six carboxylates (one on each edge) have been replaced with pyridyl oxime ligands.
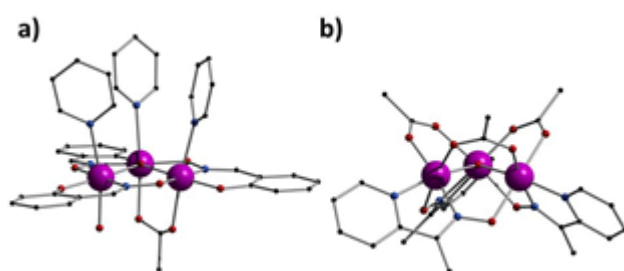
***Figure 2.* a)** The molecular structure of $[Mn_3O(sao)_3(O_2CCH_3)(py)_3(H_2O)]$ of structure type **B** and **b)** $[Mn_3O(mpko)_3(O_2CR)_3]^{+}$ of structure type **C**. Colour code as Figure 1.

Surprisingly, magnetic studies of **C** showed them to be ferromagnetic with *S* = 6 ground-states. The explanation given was that the non-planarity of the central μ_3-oxide, which resides ~0.27 Å above the plane defined by the three manganese ions, results in the ferromagnetic component of this exchange pathway becoming dominant.[34] While that is a perfectly sensible explanation and may well be true for **C**, we knew it could not be the case (or at least not the whole explanation) for **A** and **B**, since in both, the central O^{2-} ion is located more than 0.3 Å above the Mn_3 plane and yet the exchange within the $[Mn^{III}_3O]$ triangles is antiferromagnetic. Nor could it be the explanation for the oxime-based complex $[Mn^{III}_3O(bamen)]^{+}$ (H_2bamen = 1,2-bis(biacetylmonoximeimino)ethane) published in 2003, in which the Mn^{III} ions are ferromagnetically coupled despite the O^{2-} being placed within the Mn_3 plane (displacement of 0 Å).[35] The confusion prompted us to ask the question: *what is the structural*

*difference between **C** and **A/B**?* On looking at Figure 2 our immediate answer was that in **A** and **B** the Mn-O-N-Mn unit is in the same plane as the Mn$^{III}_3$ triangle, whereas in **C**, it is clearly not. The key to unlocking the answer was therefore to try to make **A** and **B** look "more like" **C** and our approach was simple: derivatise the oximic carbon atom in such a way that, by simple steric considerations, the appended group would make it impossible for the Mn-O-N-Mn unit to be flat, *i.e.* let's "twist" the Mn-O-N-Mn moiety (increase its torsion angle) and see what happens to the magnetic exchange between the two Mn ions.

"Twisted" [Mn$^{III}_6$] clusters of general formula [Mn$_6$O$_2$(R-sao)$_6$(O$_2$CR')$_2$(L)$_{4-6}$] (R, R' = Me, Et, Ph *etc*; L = solvent; structure type **D,** Figure 3) can be made by replacing saoH$_2$ with R-saoH$_2$ (Scheme 1; R = Me, Et, Ph *etc*).[36] There are three important structural differences between **D** and **A**: i) the distance between the square-pyramidal Mn ion and the proximal phenolate O-atom decreases by approximately 1 Å; ii) the carboxylates become monodentate, with the vacated coordination site on the neighbouring Mn ion now occupied by an additional solvent molecule; iii) the Mn-O-N-Mn torsion angles increase significantly.[37] As an example of the latter we compare the complexes [Mn$_6$O$_2$(sao)$_6$(O$_2$CH)$_2$(EtOH)$_4$] (**1**; Mn-O-N-Mn = 25.6, 18.0, 10.4º), [Mn$_6$O$_2$(Et-sao)$_6$(O$_2$CCMe$_3$)$_2$(EtOH)$_5$] (**9**; Mn-O-N-Mn = 42.1, 36.9, 23.3º and 42.2, 32.4, 16.7º (**9** has no inversion centre)) and [Mn$_6$O$_2$(Et-sao)$_6$(O$_2$CPh)$_2$(EtOH)$_4$(H$_2$O)$_2$] (**14**; Mn-O-N-Mn = 39.9, 38.2, 31.1º).
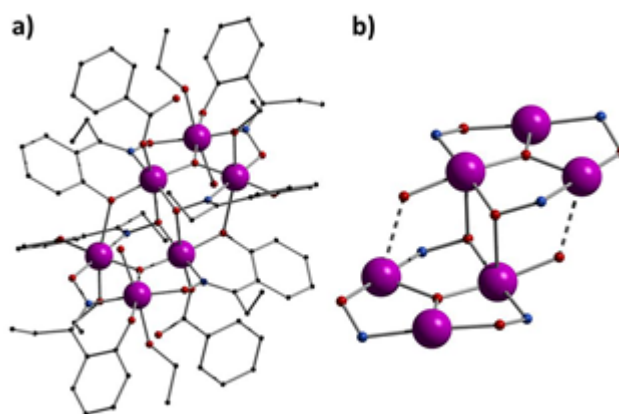
***Figure 3.* a)** The molecular structure of [Mn$_6$O$_2$(Et-sao)$_6$(O$_2$CPh)$_2$(EtOH)$_4$(H$_2$O)$_2$] (**14**) and **b)** its magnetic core. Colour code as Figure 1.

Complex **14** was an important discovery because it was the first [Mn^{III}_6] complex in which all the Mn-O-N-Mn torsion angles within the Mn_3 triangles were above 30º, and as the plot of $\chi_M T$ *vs* T for **1**, **9** & **14** in Figure 4 clearly shows, it was the first [Mn^{III}_6] complex to display ferromagnetic exchange.[36] Dc magnetisation measurements afforded the parameters $S = 12$ and $D = -0.43$ cm^{-1} and were therefore suggestive of $U \approx 89$ K, but dynamic susceptibility studies revealed U_{eff} to be only ~53 K, some 36 K lower than expected. Single crystal (dc) hysteresis loop measurements showed hysteresis only at temperatures up to 3 K at a field sweep rate of 0.14 Ts^{-1}.[37] The origin of this dramatic reduction in barrier height, as confirmed by INS, FDMRS[26-28] and EPR[29,38] is of course the very reason the pairwise exchange could be "switched" from antiferromagnetic to ferromagnetic in the first place: the weak magnetic exchange interactions. Indeed in **14**, the isotropic exchange, *J*, (in the $\hat{H} = -2J\hat{S}_i\hat{S}_j$ convention) was estimated to be only $J = +0.93$ cm^{-1}.[36] The small magnitude of the isotropic exchange parameter, *J*, in combination with the existence in [Mn^{III}_6] of anisotropy terms of the same order of magnitude (actually even bigger) than *J*, result in the presence of many low-lying excited spin-states in these systems. In fact, it has been shown that sublevels of several of the lowest lying excited spin-states are located within the manifold of the anisotropy split ground spin-state (Figure 5) and that these excited-state sublevels admix, to varying extent in the different [Mn^{III}_6] systems, with the components of the ground spin-state.[24,26-28] This situation is referred to as the breakdown of the *Giant Spin* model.[39] The nesting of the excited state sublevels within the ground state manifold and the mixing between these (*S*-mixing), strongly influences the relaxation characteristics of [Mn^{III}_6] by offering alternative inter-well relaxation pathways.[26-28,39] Thus, the breakdown of the *Giant Spin* model plays a crucial role in lowering the energy barrier for relaxation of the molecular magnetisation *via* creation of a finite probability for inter-well relaxation processes. Such inter-well relaxation processes are absent in the strong exchange limit where only thermal activation and QTM related relaxation processes occur *within* the thermally isolated ground spin state.
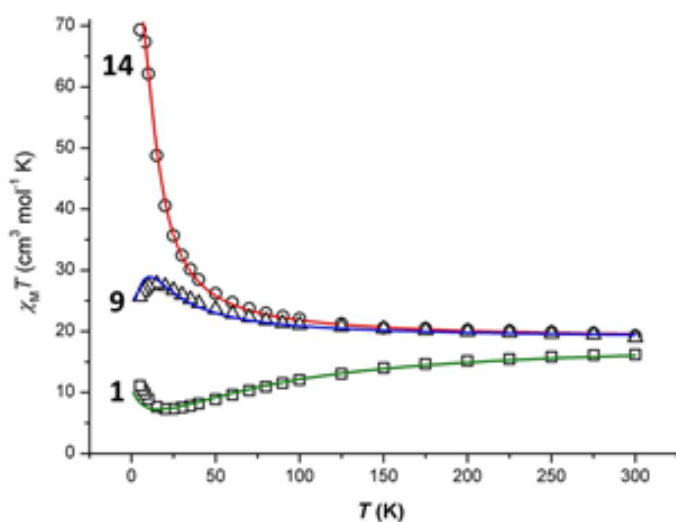
← *Figure4.* A plot of $\chi_M T$ versus *T* for complexes **1**, **9** and **14** showing the transition from antiferromagnetic to ferromagnetic exchange within the triangular sub-units. The solid lines are a fit of the data – see text for details.
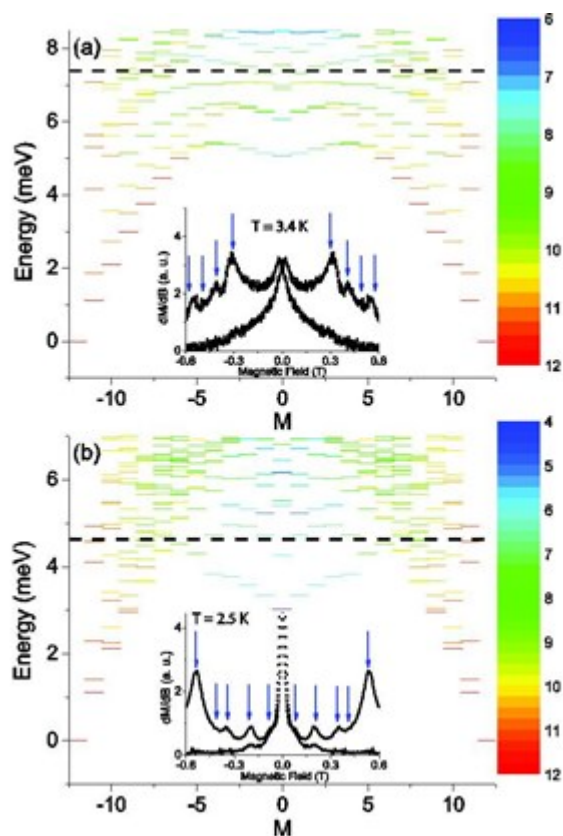
Figure 5. Energy levels as a function of the z-component of the total spin for **(a) 15** and **(b) 14**. The colour maps S_{eff}, where $<S^2> := S_{eff}(S_{eff} + 1)$. The black dashed lines correspond to the observed value of U. Insets: examples of derivative of the hysteresis curves measured showing the presence of tunneling peaks absent in a giant-spin model. For each value of field, there are two points corresponding to increasing or decreasing field in the hysteresis cycle. Arrows indicate the calculated (anti-)crossing positions. See reference 27.

Thus, in order to increase the energy barrier for relaxation of the molecular magnetisation, the energy gap between ground and excited spin-states had to be increased. In order to increase this energy gap, J has to be increased. For the $[Mn^{III}_6]$ family this equates to an increased twisting of the Mn-O-N-Mn moieties. This was achieved[31] by replacing benzoate with 3,5-dimethylbenzoate and the formation of the complex $[Mn_6O_2(Et-sao)_6(O_2CPhMe_2)_2(EtOH)_6]$ (**15**; Mn-O-N-Mn = 43.1, 39.1, 34.9º). Magnetometry showed that the low temperature, high field magnetisation data could be fitted with exactly the same S and D as complex **14**, but the susceptibility data revealed that J had nearly doubled ($J = +1.63$ cm^{-1}; Figure 6). Consequently, the *observed characteristic relaxation times at various frequencies of the ac field were shifted to higher temperatures as compared to **14**, and the experimentally observed magnetisation reversal barrier, U_{eff}, increased to ~86 K.[37] Single crystal*

(dc) hysteresis loop measurements now revealed hysteresis at temperatures up to 5 K at a field sweep rate of 0.14 Ts^{-1}.[31]
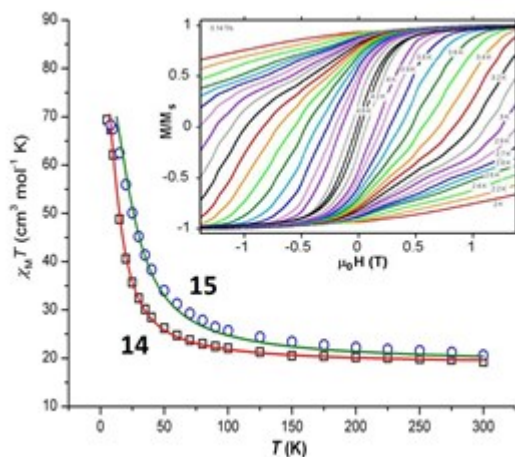

***Figure 6.* a)** A plot of $\chi_M T$ versus T for complexes **14** and **15,** reflecting the increase in |*J*| as a result of the increased twisting of the Mn-O-N-Mn torsion angles. The inset shows single crystal hysteresis loop measurements for **15** at temperatures up to 4.6 K at a field sweep rate of 0.14 T/s.

*An examination of the structural parameters of the fif*ty or so [Mn$^{III}_6$] clusters in Table 1[30-32,36-40,43-49] allowed us to establish a semi-quantitative magneto-structural correlation[40] whose main conclusion stated that at Mn-O-N-Mn torsion angles above approximately 31° the exchange between neighbouring Mn^{III} ions within the triangular subunits of the [Mn$^{III}_6$] clusters will be ferromagnetic, a statement now corroborated by recent theoretical analyses.[41,42]

Frozen solution studies of the dynamic susceptibility of [Mn$^{III}_6$] species confirmed the previously described solid state magneto-structural correlations as well as the influence of the structural parameters on their spin-relaxation characteristics.[43,44] Studies on [Mn$_6$O$_2$(Et-sao)$_6$(benz)$_2$(EtOH)$_4$(H$_2$O)$_2$] (**14**) and [Mn$_6$O$_2$(Et-sao)$_6$(Me$_2$benz)$_2$(EtOH)$_6$] (**15**) showed that the solid state magnetic properties of (**14**) and (**15**) emanate from strained solid-state molecular structures, the strains being induced by crystal packing effects.[44] The small differences in the outer coordination sphere of the Mn^{III} ions, *i.e.* the differences in the bulkiness of the carboxylate or the substitution of the terminally bound EtOH molecules by H$_2$O, did not result in statistically significant differences in the dynamic magnetic properties of these complexes in solution, where the solid state strain effects are relaxed.[43] This is in complete contrast to the enormous difference in the spin-relaxation properties

observed in the solid state. Indeed an *increase* in U_{eff} upon dissolution was observed for $[Mn_6O_2(Et\text{-}sao)_6(benz)_2(EtOH)_4(H_2O)_2]$ (**14**).[43]

$[Mn^{III}_6]$ clusters have also proven to be excellent starting materials and their ease of synthesis and structural and magnetic integrity in solution[43,44] suggest them as useful building blocks for the construction of [multifunctional] supra-molecules and coordination polymers. In essence they can (and should) be regarded as simple coordination compounds of the type $\{MX_6\}$ since the monodentate "X" ligands on the triangular faces (the carboxylates and alcohols) are easily replaced. This suggests much exciting scope for future design, and indeed it has already been shown that these can be replaced with halides,[45] phosphinates,[46] monometallic M^{II} "cluster ligands"[47] and di-, tri- and tetra-carboxylates.[48] The latter (polycarboxylates) can be used to construct 1-3D assemblies of SMMs, and by analogy to MOF chemistry,[50] and by recognising the sheer number and variety of polycarboxylate ligands available, one can envisage constructing an enormous breadth of framework materials from these magnetically interesting building blocks.

When attempting to understand the magnetic behaviour of large and complicated molecules (as the $[Mn^{III}_6]$ clusters are) it is always useful to try to isolate and characterise the smaller building blocks from which they are constructed. In the case of $[Mn^{III}_6]$ this is obviously the $[Mn^{III}_3]$ triangles (Table 2). Fortunately the synthesis of the molecules $[Mn^{III}_3O(R\text{-}sao)_3(X)(solvent)_{3-5}]$ (X = ^-O_2CR, ClO_4^-, ReO_4^-; solvent = alcohol, pyridine) is straightforward and high yielding (Figure 7).[51-57] There are a number of ways of doing this but the simplest is to repeat the $[Mn^{III}_6]$ reactions, replacing the alcohol solvent with pyridine. The pyridine molecules bond terminally to each of the three Mn^{III} ions, capping one face of the triangle and preventing dimerisation into the hexametallic structure. Triangles are only formed in alcohol when both the R-substituent on the oxime ligand and the carboxylate group are very bulky.[51]
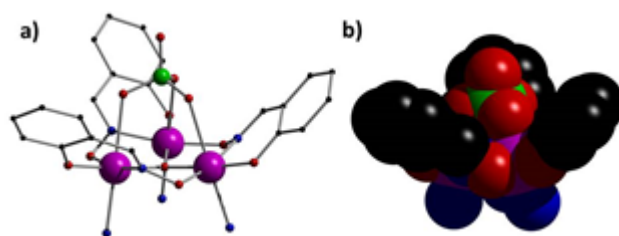

Figure 7. **a)** The molecular structure of complex **68**, highlighting the bowl-shaped nature of the core, **b)**. Only the N-atoms of the β–picoline ligands are shown. Colour code as Figure 1; Cl = green.

The [Mn$^{III}_3$] molecules offer more opportunities for structural distortion than their [Mn$^{III}_6$] parents, however, because now *both* the triangular faces (upper and lower) and their triangular edges can be targeted. In a manner entirely analogous to that seen for the [Mn$^{III}_6$] complexes the change from, for example, sao^{2-} to Me-sao^{2-} to Et-sao^{2-} sees a smooth transition from very flat molecules in which the Mn-O-N-Mn torsion angles typically fall in to the 4-26° range (sao^{2-}) to very puckered molecules in which the Mn-O-N-Mn torsion angles have increased to values in the 32-47° range (Et-sao^{2-}). As before the result is a switch in the intra-molecular pairwise exchange from antiferromagnetic to ferromagnetic (Figure 8) and an enormous enhancement of the SMM properties. If one wants to convert a flat triangle into something more bowl-shaped, an alternative method of distortion is to employ small, facially-capping tripodal ligands such as ClO$_4^-$ or ReO$_4^-$. The Jahn-Teller axes of the three Mn^{III} ions are perpendicular to the [Mn$_3$] plane and so the latter are in fact ideal ligands. They can be thought of as pincers that force the triangle to pucker because of their size; the distance between the O-arms of the tripodal ligand (O…O, ~2.4 Å) being smaller than the Mn…Mn distances in the [Mn$^{III}_3$] triangles (Mn...Mn, ~3.2 Å). For example the molecule [Mn$^{III}_3$O(Et-sao)$_3$(MeOH)$_3$(ClO$_4$)] (**65**), synthesised in a simple one pot reaction between Mn(ClO$_4$)$_2$·2H$_2$O, Et-saoH$_2$ and NEt$_3$ in MeOH,[52] contains Mn-O-N-Mn torsion angles of ~42° between the symmetry equivalent Mn^{III} ions.
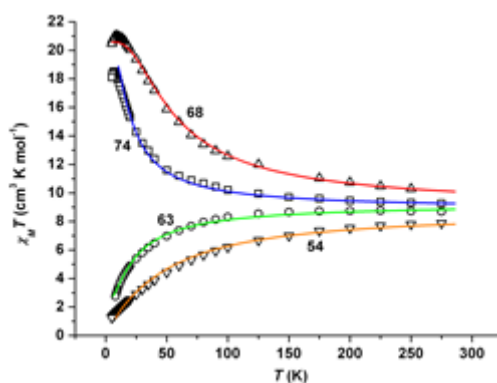
Figure 8. A plot of $\chi_M T$ versus T for complexes **54**, **63**, **68** and **74** showing the transition from antiferromagnetic to ferromagnetic exchange. The solid lines are a fit of the data – see text for details.

The magnetisation relaxation dynamics[51] of the [Mn$^{III}_3$] triangles containing terminally bonded alcohol molecules are however complicated by the packing of the molecules in the crystal, because the pendant O-atoms create extended H-bonding networks of triangles throughout the crystal. The hysteresis loops show that the collective spins of each [Mn$^{III}_3$] molecule are coupled antiferromagnetically to neighbouring molecules, acting as a bias[58] that shifts the quantum tunnelling

resonances with respect to the isolated SMM. The inter-molecular interactions are strong enough to cause a clear field bias, but too weak to transform the spin network into a classical antiferromagnet. Replacement of these terminally bonded alcohols with molecules that do not propagate inter-molecular H-bonds or short contacts, such as py, Et-py, ^{t}Bu-py or β-picoline (Figure 7), removes this effect, resulting in the observation of rather beautiful hysteresis loops – particularly at the lowest temperatures measured where the data are remarkably simple, showing only steps originating from the ground state. For example, those for complex [Mn^{III}$_3$O(Et-sao)$_3$(β-pic)$_3$(ClO$_4$)] (**68**) are shown in Figure 9.[56]
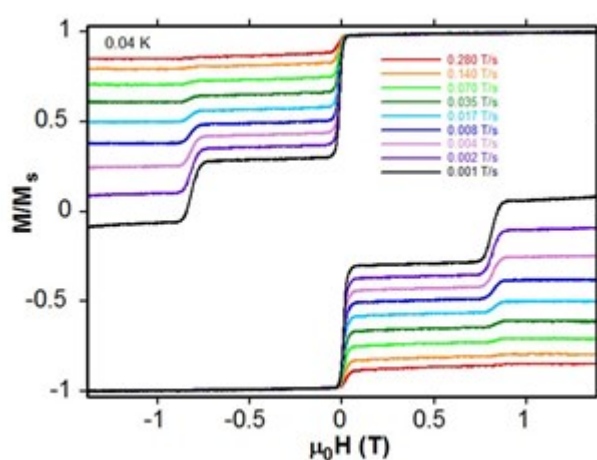

Figure 9. Single crystal hysteresis loops for complex **68** at 40 mK and the indicated field-sweep rates. M is normalised to its saturation value.

The ease with which one pyridine-like molecule can be replaced with another also suggests that the formation of supra-molecules and coordination polymers of triangles can be achieved by employing poly-pyridines and their many analogues, as has been so elegantly exploited in Pd(II) and Pt(II) chemistry.[59] Indeed this seems to be the case.[53,57] The terminally bonded solvent molecules of flat triangles, *i.e.* those built from sao^{2-} - are essentially perpendicular to the [Mn^{III}$_3$] plane and hence parallel to one another. If these are replaced by 4,4'-bipyridine (4,4'-bpy) or *trans*-1,2-bis(4-pyridyl)ethylene (4,4'-bpe), for example, then the expected 1D chain of [Mn^{III}$_3$] triangles is formed.[57] If a carboxylate is introduced into the reaction mixture then a molecular dimer of triangles is formed, because the bridging RCO$_2$$^-$ ligands prevent polymerisation.[57] If the analogous reactions are repeated with the puckered triangles, *e.g.* the perchlorate capped triangles, the resulting materials are quite different because the three bridging "legs" are no longer parallel to one another, nor perpendicular to the [Mn^{III}$_3$] plane. Indeed the triangles can be thought of as resembling a three-legged milking stool in

which the [Mn$^{III}_3$] triangle is the seat and the three bipyridine (or solvent) molecules are the legs. The result is that the three bridging ligands all point in different directions and thus must each bridge to different triangles.

For example, the reaction of 4,4'-bpe, Mn(ClO$_4$)$_2$·6H$_2$O and saoH$_2$ affords the 2D coordination polymer {[Mn$^{III}_3$O(sao)$_3$(4,4'-bpe)$_{1.5}$]ClO$_4$ (**78**, Figure 10).[53,57] The 2D network adopted conforms to a (6,3) regular net with the [Mn$^{III}_3$] units acting as three-connected nodes. This arrangement gives rise to the formation of conical (ice-cream cone like) cavities within the body of the 2D framework which are large enough to host a [Mn$^{III}_3$] unit of an adjacent net (Figure 10). Each layer is interlocked with two other layers, one above and one below the middle layer's plane, resulting in an entangled array with an increased dimensionality (*i.e.* from 2D to 3D). This interlocking is purely supramolecular in nature since it is based on host–guest and hydrogen bonding interactions. Given this structure type, we then reasoned that the use of mononucleating stilbazoles (sbz) in place of the binucleating 4,4'-bpy or 4,4'-bpe molecules would create a cavity at the base of the [Mn$^{III}_3$] triangles. Indeed, this turns out to be the case: neighbouring molecules pack in a head-to-head fashion in which the stilbazole ligands on adjacent clusters inter-digitate, forming supramolecular dimers with a central closed cavity in which the anions (ClO$_4^-$ or NO$_3^-$) are encapsulated (Figure 11).[57]
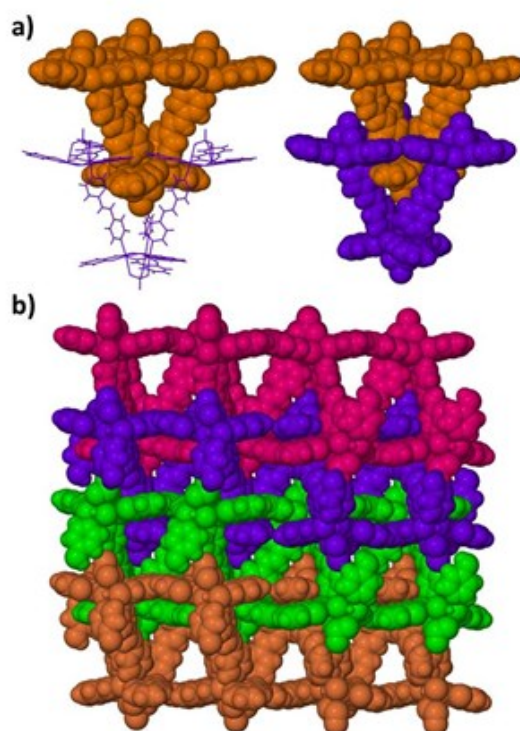

Figure 10. **a)** Views of the conical "ice-cream cone" within "an ice-cream cone" units in **78**. **b)** View of four entangled layers in the crystal of **78**.
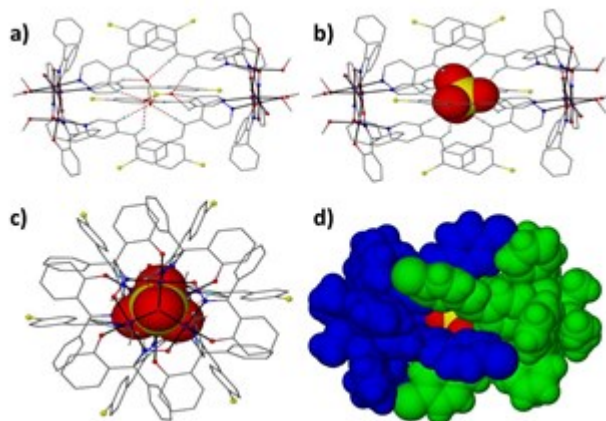
Figure 11. **a)-c)** Perspective views of the $\{[\text{Mn}_3]\text{-}(\text{ClO}_4^-)\text{-}[\text{Mn}_3]\}^+$ assembly found in the crystals of **75**, highlighting the encapsulated anion. **d)** Space filling model of the assembly with the $[\text{Mn}_3]^+$ triangles in blue and green.

Conclusions

By building a family of approximately fifty $[\text{Mn}^{\text{III}}_6]$ and approximately thirty $[\text{Mn}^{\text{III}}_3]$ complexes a semi-quantitative magneto-structural correlation could be established whose main conclusion is that the *dominant* structural factor dictating the pairwise magnetic exchange within the triangular units is the twisting of the Mn-O-N-Mn unit. Controlling the degree of twisting is relatively trivial, requiring the simple substitution of the H-atom on the oximic C-atom with more sterically demanding R-groups (Me, Et, Ph *etc*). To a certain extent the reaction system is also well understood and thus can be controlled. In basic alcoholic solutions a $\text{Mn}^{\text{III}}/\text{R-sao}^{2-}$ reaction mixture is almost always going to produce cluster compounds whose basic building block is the $[\text{Mn}^{\text{III}}_3\text{O}(\text{R-sao})_3]^+$ triangular unit, and how this self-assembles is then dependent on the choice of co-ligand. This basic unit is magnetically tuneable and possesses two reactive triangular faces on which ligand substitution is relatively trivial, allowing enormous scope for design. This is a huge advantage for the construction of molecules, supramolecules and coordination polymers based on this moiety. The serendipitous self-assembly of all cluster compounds is of course dependent upon subtle changes in reaction conditions. In a standard reaction a metal salt (or combination of metal salts) is dissolved in a solvent and reacted with a ligand, co-ligand(s) and base in the presence of anions/cations. Variations in each of these factors can alter the identity of the crystalline product obtained and so the synthetic chemist must work his/her way through each of these combinations in order to gain an understanding of the system. Our most recent research attempts have focussed on deliberately targeting Mn^{III} clusters whose building blocks are *not* $[\text{Mn}^{\text{III}}_3\text{O}(\text{R-sao})_3]^+$ triangular units by varying these very reaction conditions. This might be perceived as a little odd given the degree of control and understanding we now have, but of course it may lead

us to fascinating new compounds. Our initial approach is simple and threefold: a) use solvents other than ROH, b) employ co-ligands that are able to compete with the oximes for the metal coordination sites, and c) make heterometallic clusters in which the second [dia- or paramagnetic] metal ion does not favour the formation of the oxo-centred triangles. This has already borne some success with the synthesis of a [Mn$_{32}$] double-decker wheel,[60] a chiral [Mn$_9$] partial super-tetrahedron,[61] and a family of [Mn$^{III}_6$Ln$^{III}_2$] hexagonal prisms.[62]

Given that there are now literally hundreds, or even thousands, of beautiful cluster compounds in the literature whose initial magnetic properties have been deemed (relatively) "uninteresting", perhaps the most pertinent question we can now ask is: *what would happen if they were given a little twist*?

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