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Mixed valency in polynuclear Mn^{II}/Mn^{III}, Mn^{III}/Mn^{IV} and $Mn^{II}/Mn^{III}/Mn^{IV}$ clusters: a foundation for high-spin molecules and single-molecule magnets

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Mixed-valent Mn/O dinuclear and polynuclear molecular compounds containing Mn^{III} are almost without exception trapped valence. Large differences between the strengths of the exchange interactions within $Mn^{II}Mn^{III}$, $Mn^{III}Mn^{III}$ and $Mn^{III}Mn^{IV}$ pairs lead to situations where $Mn^{III}Mn^{IV}$ interactions, the strongest of the three mentioned and antiferromagnetic in nature, dominate the intramolecular spin alignments in trinuclear and higher nuclearity mixed-valent complexes and often result in molecules that have large, and sometimes abnormally large, values of molecular spin (S). When coupled to a large molecular magnetoanisotropy of the easy-axis-type (negative zero-field splitting parameter, D), also primarily resulting from individual Jahn–Teller distorted Mn^{III} centres, such molecules will function as single-molecule magnets (molecular nanomagnets). Dissection of the structures and exchange interactions within a variety of mixed-valent Mn_x cluster molecules with metal nuclearities of Mn_4, Mn_{12} and Mn_{25} allows a ready rationalization of the observed S, D and overall magnetic properties in terms of competing antiferromagnetic exchange interactions within triangular subunits, resulting spin alignments and relative orientation of Mn^{III} JT axes. Such an understanding has provided a stepping stone to the identification of a 'magnetically soft' Mn_{25} cluster whose groundstate spin S value can be significantly altered by relatively minor structural perturbations. Such 'spin tweaking' has allowed this cluster to be obtained in three different forms with three different groundstate S values.

Keywords: mixed valency; polynuclear Mn complexes; exchange interactions; high-spin molecules; single-molecule magnets

1. Introduction

The search for large clusters of paramagnetic transition metal ions has been greatly stimulated by the discovery of single-molecule magnetism (Sessoli *et al.* 1993*a*,*b*; Christou *et al.* 2000). This is the superparamagnetic-like behaviour of molecular species that combine a large spin groundstate, S, with a relatively large and negative easy-axis-type magnetoanisotropy (as reflected in a large and

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negative zero-field splitting parameter, D; Christou *et al.* 2000). This results in the experimental observation of both hysteresis in magnetization versus DC magnetic field sweeps, and frequency-dependent out-of-phase AC magnetic susceptibility signals. Such a combination of large S and D values leads to a significant barrier (U) to magnetization reversal, whose maximum value is given by $S^2|D|$ or $(S^2-1/4)|D|$ for integer and half-integer spins, respectively. SMMs thus represent a molecular or 'bottom-up' approach to nanoscale magnetism, and they are consequently also called molecular nanomagnets. In addition, they clearly straddle the classical/quantum interface, displaying not just the classical property of a magnet, named magnetization hysteresis, but also the quantum property of quantum tunnelling of magnetization (QTM) through the anisotropy barrier to magnetization relaxation (Christou *et al.* 2000; Christou 2005).

There are now many structural types of molecular complexes that display such SMM behaviour, and the majority of these are Mn species, since coordination clusters of this metal often display large groundstate spin (S) values, and large and negative magnetoanisotropies associated with the presence of Jahn–Teller (JT) distorted Mn^{III} atoms (Christou 2005; Aromi & Brechin 2006). Thus, it becomes apparent why most successful searches for new high-spin molecules and SMMs have involved Mn^{III} chemistry, partially or exclusively. In fact, only a relatively few SMMs have contained Mn^{III} exclusively, those being Mn_2 (Miyasaka *et al.* 2004), Mn_3 (Stamatatos *et al.* 2005, 2007*a*) Mn_4 (Milios *et al.* 2007), Mn_6 (Milios *et al.* 2004), Mn_{26} (Jones 2004) and Mn_{84} (Tasiopoulos *et al.* 2004) complexes. Most Mn SMMs have instead been mixed valent, and such mixed-valence clusters containing Mn^{III} are almost without exception valence localized (class II), involving Mn^{II}/Mn^{III}, Mn^{III}/Mn^{IV} and/or $Mn^{II}/Mn^{III}/Mn^{IV}$ oxidation state mixtures (Christou 2005; Aromi & Brechin 2006).

Understanding why a particular molecule has a large groundstate spin S is obviously of importance. In a general sense, it obviously results from the various exchange couplings between the constituent Mn atoms within a molecule, specifically from (i) dominant ferromagnetic (or ferrimagnetic) exchange interactions between the metal centres and/or (ii) spin frustration effects from the presence in certain M_x topologies of competing antiferromagnetic exchange interactions that prevent (frustrate) the preferred spin alignments that would normally yield low-spin species. In case (i), the ferromagnetic interactions would result from ligands or structural characteristics known to mediate ferromagnetic coupling between metal centres (Aromi *et al.* 1999); these ferromagnetic interactions must also be able to overcome any antiferromagnetic interaction within the molecule mediated by OH^-, OR^-, O^{2-} and/or RCO_2^- groups, which favour antiferromagnetic coupling. One of the best ferromagnetic couplers is the azide (N_3^-) group when it bridges metal ions in the 1,1-fashion (end-on) in which case the exchange coupling is ferromagnetic for a wide range of M–N–M angles (Stamatatos *et al.* 2006). Others include pyridine-based alkoxide ligands (Stamatatos *et al.* 2006, 2007*b*), or diolate- (Moushi *et al.* 2006) and triolate-based (Brechin 2005) groups that are versatile chelating/bridging ligands whose alkoxide arms often support ferromagnetic coupling between the metal atoms they bridge. Thus, rationalization of a spin groundstate in such situations is clearly trivial, resulting from the sum of all the local ferromagnetic interactions between the metal centres. Similarly, purely ferrimagnetic complexes can be readily understood, arising from the presence of arrays of antiferromagnetically coupled metals with unequal single-ion spin values, leading to a significant net molecular spin S.

In case (ii), which includes the majority of polynuclear valence-trapped Mn clusters exhibiting a paramagnetic (non-zero) groundstate, the resultant S value of the molecule is a consequence of competing (predominantly) antiferromagnetic interactions that prevent (frustrate) perfectly antiparallel spin alignments. This is particularly true when triangular M_3 subunits are present, since an antiferromagnetically coupled triangle cannot contain spins that are all aligned antiparallel to their two neighbours. The groundstate then becomes extremely difficult to predict from a simple structural examination. In fact, the net molecular S is highly dependent on the precise topology of the Mn_x framework and the relative strengths of the competing interactions. Crucial to the latter in mixed-valence Mn chemistry is the fact that Mn^{III}–O–Mn^{IV} (and Mn^{IV}–O–Mn^{IV}) interactions are strongly antiferromagnetic when compared with Mn^{II}–O–Mn^{III} and Mn^{III}–O–Mn^{III} interactions, which are either weakly antiferromagnetic or, occasionally, weakly ferromagnetic (Kahn 1993). Note that in this discussion we use the more recent, more general definition of spin frustration, as stated above, i.e. the presence of competing (usually) antiferromagnetic exchange interactions that prevent (frustrate) the preferred spin alignments that would give a low or zero molecular S. This is different from the original definition of spin frustration introduced by solid-state physicists, in which competing interactions lead to a degenerate groundstate (Kahn 1993); in this definition, the mere presence of competing interactions does not mean that the system is frustrated.

In this paper, we shall describe three representative, mixed-valent polynuclear Mn clusters that have been found to be SMMs, and show how we can rationalize their observed high groundstate S values on the basis of considerations of the relative magnitudes of the various pairwise exchange interactions between the constituent Mn_2 pairs. In addition, we shall show how this also rationalizes the observed molecular anisotropy (D value). Finally, we shall briefly describe how, armed with this knowledge, we have been able to develop a 'spin tweaking' process by which targeted changes to the peripheral ligands about a 'magnetically soft' Mn_{25} core allow the groundstate S value to be altered to significantly higher values.

2. The archetypal $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ family

To date, the most studied SMMs are the mixed-valent $[Mn^{III}_8Mn^{IV}_4O_{12}(O_2CR)_{16}(H_2O)_4]$ (Mn_{12}; R=various) family with an $S=10$ groundstate (Lis 1980; Sessoli *et al.* 1993*a*; Chakov *et al.* 2006). These have attracted most study by many groups around the world. The first example was the R=Me derivative $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]\cdot 2MeCO_2H\cdot 4H_2O$ (Mn_{12}-Ac) (Lis 1980). Since then, more than 50 Mn_{12} derivatives have been synthesized, several having a higher magnetization barrier than Mn_{12}-Ac; for example, the $R=BrCH_2CO_2^-$ derivative $[Mn_{12}O_{12}(O_2CCH_2Br)_{16}(H_2O)_4]$ has a barrier of approximately 74 K (Chakov *et al.* 2006). This and other derivatives can be readily prepared by carboxylate substitution on Mn_{12}-Ac (equation (2.1); Chakov *et al.* 2006).

$$\begin{aligned}&[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4] + 16BrCH_2CO_2H\\ &\quad\rightarrow [Mn_{12}O_{12}(O_2CCH_2Br)_{16}(H_2O)_4] + 16MeCO_2H.\end{aligned}\tag{2.1}$$

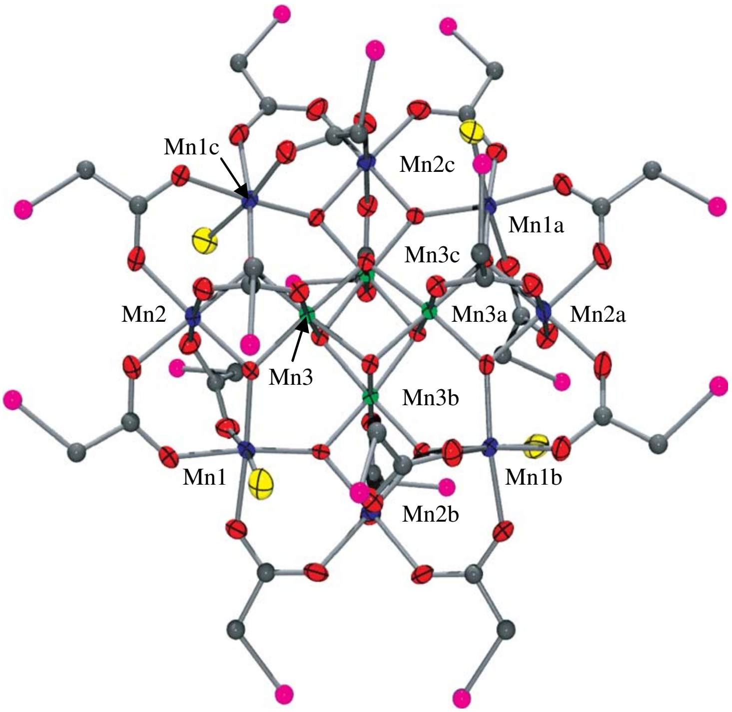

Figure 1. Partially labelled PovRay representation of $[Mn_{12}O_{12}(O_2CCH_2Br)_{16}(H_2O)_4]$, with H atoms omitted for clarity. Green, Mn^{IV}; blue, Mn^{III}; yellow, H_2O; red, other O; purple, Br; dark grey, C.

The structure of $[Mn_{12}O_{12}(O_2CCH_2Br)_{16}(H_2O)_4]$ is depicted in figure 1; it has crystallographic S_4 symmetry. It is valence-localized (Robin and Day class II), with a central $[Mn_4^{IV}O_4]^{8+}$ cubane unit held within a non-planar ring of eight Mn^{III} atoms by eight μ_3-O^{2-} ions. Peripheral ligation is provided by 16 bridging $BrCH_2CO_2^-$ and four terminal H_2O groups. All of the Mn atoms are six-coordinate with near-octahedral geometry. The eight Mn^{III} atoms exhibit a JT distortion, as expected for a high-spin d^4 ion in the near-octahedral geometry.

Various variable-temperature DC and AC magnetization studies have established that the Mn_{12} complexes have $S=10$ groundstates and $D\approx-0.5\ cm^{-1}$. These significant values of S and D have long been recognized as due to the relative spin alignments shown in figure 2*a*,*b*, respectively. The four central Mn^{IV} atoms are ferromagnetically coupled, as is often the case for cubane systems as a result of the acute M–(μ_3-O)–M angles just over 90° (Halcrow *et al.* 1995). The remaining interactions are all expected to be antiferromagnetic, i.e. the $[Mn^{III}Mn^{IV}O_2(O_2CR)]^{2+}$ and $[Mn_2^{III}O(O_2CR)_2]^{2+}$ subunit interactions, with the former being much stronger than the latter; this conclusion is based on the interactions determined for dinuclear Mn complexes at various oxidation levels (tables 1 and 2). As a result, the stronger Mn^{III}–Mn^{IV} interactions overwhelm the weaker Mn^{III}–Mn^{III} ones, aligning the spins of the outer Mn^{III} atoms all parallel, and thus antiparallel to the central Mn^{IV} atoms, predicting an $S=16-6=10$ groundstate, as seen

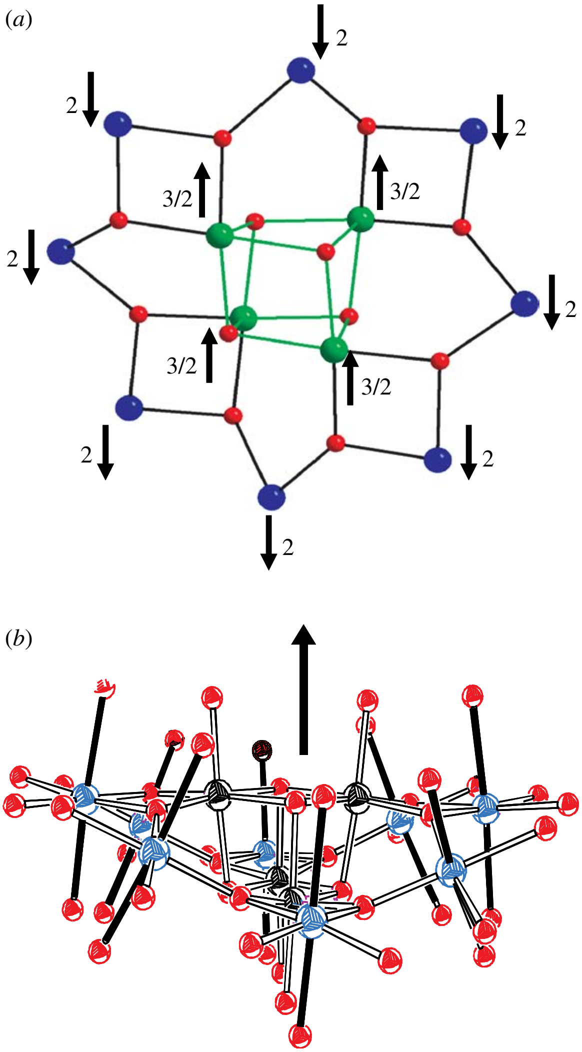

Figure 2. (*a*) Spin alignments in Mn_{12} rationalizing the observed $S=10$ groundstate. (*b*) Side view showing the orientations of the Mn^{III} JT axes as solid black bonds, and rationalizing the easy-axis location (black arrow). Green, Mn^{IV}; blue, Mn^{III}; red, O.

experimentally from bulk magnetization data. These spin alignments have been directly confirmed by polarized neutron scattering studies on a single crystal of Mn_{12}-Ac (Robinson *et al.* 2000).

Similarly, anisotropy (D value) can be rationalized as resulting primarily from the Mn^{III} atoms. Each Mn^{III} undergoes a JT distortion (elongation), as expected for high-spin d^4 ions in the near-octahedral geometry, and the JT axis represents the single-ion anisotropy (z) axis. Since the JT elongation axes avoid the bridging oxide ions (which form the shortest, strongest bonds in the molecule), they align approximately parallel. The latter leads to a significant molecular anisotropy because the molecular anisotropy is the tensor projection of single-ion anisotropies onto the molecular anisotropy axis.

Table 1. Exchange interactions and selected structural parameters for representative $[Mn_2^{III}(\mu\text{-}O)(O_2CR)_2]^{2+}$ complexes. (n.a., not available.)

complex	Mn–O (Å)	Mn–O–Mn (°)	J (cm^{-1})[a]	references
$[Mn_2O(O_2CMe)_2(Me_3TACN)_2](ClO_4)_2$	1.810	120.9	+9	Wieghardt *et al.* (1985)
$[Mn_2O(O_2CMe)_2(TACN)_2](ClO_4)_2$	1.80	117.9	+10	Wieghardt *et al.* (1985)
$[Mn_2O(O_2CMe)_2(HB(pz)_3)_2]$	1.780	125.1	−0.5	Sheats *et al.* (1987)
$[Mn_2O(O_2CMe)_2(bipy)_2(H_2O)_2](PF_6)_2$	1.78	122.9	−3.4	Menage *et al.* (1988)
$[Mn_2O(O_2CMe)_2Cl_2(bipy)_2]$	1.78[b]	124.3	−4.1	Vincent *et al.* (1988)
$[Mn_2O(O_2CMe)_2(TMIP)_2](ClO_4)_2$	1.79[b]	124.4	−0.5	Vincent *et al.* (1993)
$[Mn_2O(O_2CPh)_2(N_3)_2(bipy)_2]$	1.80	122.0	+8.8	Vincent *et al.* (1988)
$\{[Mn_2O(O_2CMe)_2(H_2O)]^{2+}\}$[c]	1.90[b]	122.4[b]	n.a.	Sessoli *et al.* (1993*c*)
$\{[Mn_2O(O_2CCH_2Br)_2(H_2O)]^{2+}\}$[c]	1.88[b]	128.0[b]	n.a.	Chakov *et al.* (2006)

[a] $-2J\hat{S}_1\cdot\hat{S}_2$ convention. [b] Average values. [c] Sub-fragment within the Mn_{12}-complexes.

Table 2. Exchange interactions and selected structural parameters for representative $[Mn_2^{III/IV}(\mu\text{-}O)]^{5+}$ and $[Mn_2^{III/IV}(\mu\text{-}O)_2]^{3+}$ complexes. (n.a., not available.)

complex	Mn–O (Å)	Mn–O–Mn (°)	J (cm^{-1})[a]	references
$[Mn_2O(O_2CMe)_2(Me_3TACN)_2](ClO_4)_3$	1.89[b]	125.1	−40	Wieghardt *et al.* (1986)
$[Mn_2O_2(phen)_4](PF_6)_3$	1.81	96.0	−148	Stebler *et al.* (1986)
$[Mn_2O_2(bipy)_4](ClO_4)_3$	1.81	96.0	−150	Plaksin *et al.* (1972)
$[Mn_2O_2(TPA)_2](S_2O_3)_{3/2}$	1.81[b]	94.0	−159	Towle *et al.* (1988)
$[Mn_2O_2(O_2CMe)(TACN)_2](BPh_4)_2$	1.81	91.1	−220	Wieghardt *et al.* (1987)
$[Mn_2O_2(O_2CMe)(bipy)_2Cl_2]$	1.82	94.0	−114	Bashkin *et al.* (1988)
$\{[Mn_2O_2(O_2CMe)]^{2+}\}$[c]	1.89[b]	94.6[b]	n.a.	Sessoli *et al.* (1993*c*)
$\{[Mn_2O_2(O_2CCH_2Br)]^{2+}\}$[c]	1.87[b]	96.1[b]	n.a.	Chakov *et al.* (2006)

[a] $-2J\hat{S}_1\cdot\hat{S}_2$ convention. [b] Average values. [c] Sub-fragment within the Mn_{12}-complexes.

The significant S and D values lead to hysteresis loops in magnetization versus applied field scans, the diagnostic behaviour of a magnet. These loops are shown for $[Mn_{12}O_{12}(O_2CCH_2Br)_{16}(H_2O)_4]$ in figure 3, and they can be seen to also exhibit the steps at periodic values of applied field that are characteristic of QTM through the reorientation anisotropy barrier (Chakov *et al.* 2006).

The Mn_{12} complexes can be reversibly reduced by one and two electrons to yield the corresponding $[Mn_{12}]^-$ and $[Mn_{12}]^{2-}$ complexes, as summarized in equation (2.2) (Chakov *et al.* 2005). With electron-withdrawing carboxylate substituents, e.g. $R = CHCl_2$, both reductions are within the reducing strength of I^-, our preferred stoichiometric reductant.

$$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4] + nI^- \rightarrow [Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]^{n-} + n/2I_2. \quad (2.2)$$

The reduced materials may be isolated and crystallized, and crystallography has determined that the reduced products are also valence-localized (class II) species, with the added electrons localized on outer, formerly Mn^{III} atoms, thus converting them to Mn^{II}. The $[Mn_{12}]^-$ and $[Mn_{12}]^{2-}$ complexes are consequently

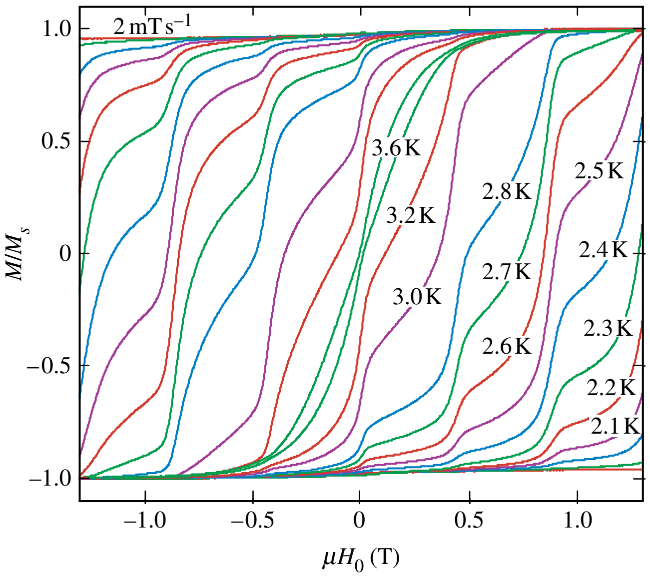

Figure 3. Magnetization hysteresis loops for a single crystal of $[Mn_{12}O_{12}(O_2CCH_2Br)_{16}(H_2O)_4]\cdot 4CH_2Cl_2$ at a field scan rate of 2 mT s^{-1} and at the indicated temperatures. The magnetization M is normalized to its saturation value, M_S.

Mn^{II}, $7Mn^{III}$, $4Mn^{IV}$ and $2Mn^{II}$, $6Mn^{III}$, $4Mn^{III}$, with groundstate spin values of $S=9.5$ and 10, respectively. These result in the $[Mn_{12}]^{-}$ and $[Mn_{12}]^{2-}$ complexes also being SMMs (Chakov *et al.* 2005).

3. The $[Mn_4O_3X(O_2CR)_3(dbm)_3]$ family of distorted cubane complexes

A second representative example of Mn^{III}–Mn^{IV} mixed valency within the Mn SMM field is provided by the tetranuclear $[Mn_3^{III}Mn^{IV}O_3X(O_2CR)_3(dbm)_3]$ complexes (dbm^{-} = the anion of dibenzoylmethane; R = various; X = Cl^{-}, Br^{-}, F^{-}, $MeCO_2^{-}$, NCO^{-}, OH^{-}, N_3^{-}, etc.; Wernsdorfer *et al.* 2002; Aliaga-Alcalde *et al.* 2004). These complexes contain a $[Mn^{IV}Mn_3^{III}(\mu_3\text{-}O)_3(\mu_3\text{-}X)]^{6+}$ very-distorted cubane core, and represent the second most studied family of SMMs after the $[Mn_{12}]$ family. The core comprises a $Mn_3^{III}Mn^{IV}$ trigonal pyramid of virtual or exact C_{3V} symmetry; when X = Ph, C_6H_4–*p*–R′ (R′ = Me, OMe) or C_6H_4–*o*–Cl, the core symmetry is C_S (figure 4). The average $Mn^{III}\ldots Mn^{IV}$ and $Mn^{III}\ldots Mn^{III}$ distances of approximately 2.8 and 3.3 Å, respectively, reflect the severe distortion from a true cubane core.

All these Mn_4 complexes possess $S=9/2$ groundstates, which can easily be rationalized as a result of strong antiferromagnetic coupling between the Mn^{IV} and each of the Mn^{III} atoms. This aligns the three Mn^{III} spins parallel and antiparallel to the Mn^{IV} spin, giving the $S=6-3/2=9/2$ groundstate observed experimentally; these groundstate spin alignments are shown in figure 4*b*. In fact, fitting the variable-temperature susceptibility data to the appropriate Van Vleck equation derived with a two-J model appropriate for a C_{3V} $Mn_3^{III}Mn^{IV}$ trigonal pyramid shows that the Mn^{III}–Mn^{III} interactions are ferromagnetic and typically

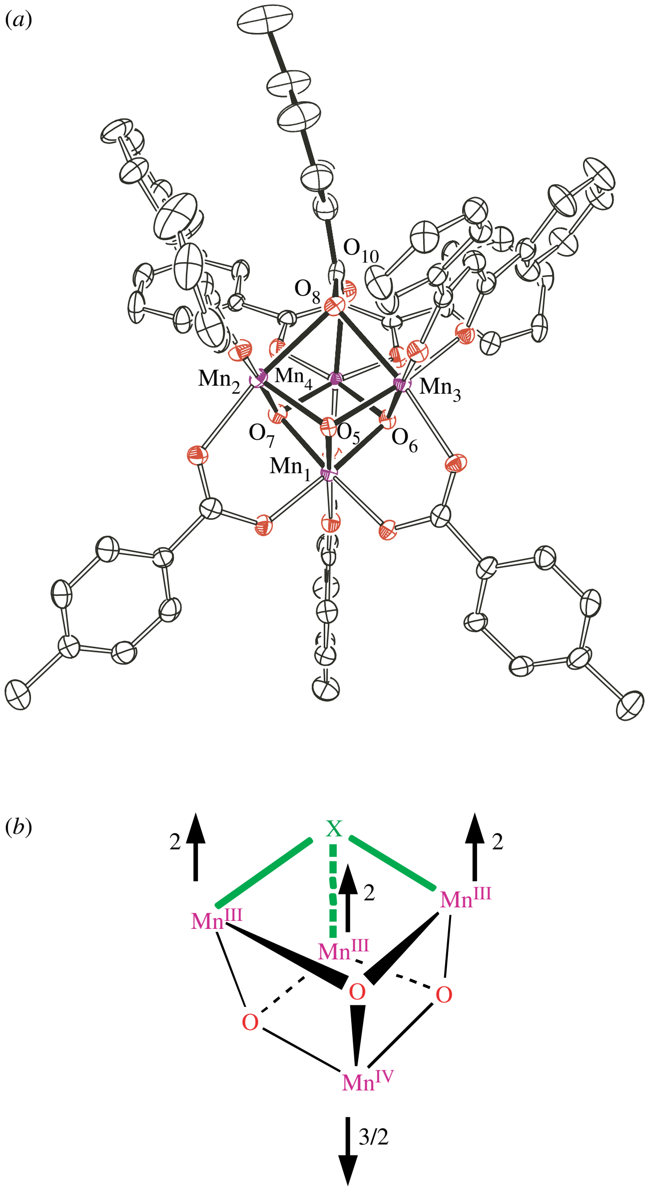

Figure 4. (*a*) ORTEP plot at the 50% probability level of $[Mn_4O_3(O_2CPh\text{-}p\text{-}Me)_4(dbm)_3]$. Purple, Mn; red, O; grey, C. (*b*) The central distorted cubane core of the Mn_4 complexes showing the spin alignments in the groundstate. The Mn^{III} JT axes intersect at the X group and are shown in green.

in the $J_{33}=+5$ to $+10\ cm^{-1}$ range. Thus, these interactions do not compete with the Mn^{III}–Mn^{IV} interactions, which are typically in the $J_{34}=-20$ to $-30\ cm^{-1}$ range. As a consequence, the groundstate is very well isolated from the $S=7/2$ first excited state, which is typically exceeding $100\ cm^{-1}$ above the groundstate, the exact energy gap depending on the X group.

As for the Mn_{12} complexes in §2, the anisotropy of $D\sim-0.3$ to $-0.5\ cm^{-1}$ for the Mn_4 complexes can be rationalized by considering the orientation of the Mn^{III}

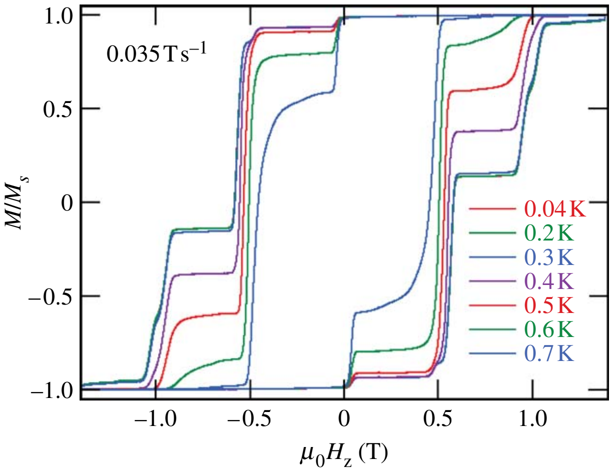

Figure 5. Hysteresis loops for the $[Mn_4O_3X(O_2CR)_3(dbm)_3]$ ($X=OSiMe_3$) complex at a field sweep rate of 0.035 T s^{-1} and at the indicated temperatures. The magnetization (M) is normalized to its saturation value, M_S.

JT elongation axes. The three JT axes intersect at the bridging X group (figure 4*b*) with a net component in the z-direction, thus resulting in a significant molecular anisotropy. The combination of significant S and D values results in the Mn_4 complexes being among the smallest SMMs known, and the obtained hysteresis loops for a representative complex are shown in figure 5.

4. Understanding larger nuclearity molecules: a Mn_{25} SMM

The type of discussion presented above as a means of helping to understand the observed spin and anisotropy of polynuclear mixed-valence clusters would be of much greater use if it also stimulated further studies and/or reactivity chemistry that might allow an extension of the field in a useful direction. We shall now present an area in which such an extension has been accomplished.

The mixed-valent $[Mn_{25}O_{18}(OH)_2(N_3)_{12}(pdm)_6(pdmH)_6]^{2+}$ (Mn^{II}_6, Mn^{III}_{18} and Mn^{IV}) cluster (figure 6) is one of the biggest yet synthesized in Mn chemistry, and it has a large spin of $S=51/2$ but a small anisotropy of $D=-0.020\ cm^{-1}$. Despite this small D value, the compound has a barrier big enough (related to $(S^2-1/4)|D|$) to be an SMM (Murugesu *et al.* 2004). The compound has an unusual five-layer structure with an A : B : C : B : A pattern. Unlike the Mn_{12} and Mn_4 complexes, it is not possible to rationalize the large $S=51/2$ groundstate on the basis of predicted spin alignments, because there are simply too many triangular subunits within the structure, both within the five layers and between layers. Many of these will involve competing antiferromagnetic $Mn^{II}Mn^{III}$ and $Mn^{III}Mn^{III}$ interactions, and the resulting spin alignments will thus be very sensitive to the relative magnitude of these competing interactions. Probably, the only safe prediction that can be made is that the central layer of the six Mn^{III} atoms surrounding a central Mn^{IV} atom will have an $S=21/2$ subunit spin, resulting from strong $Mn^{III}Mn^{IV}$ interactions dominating the weaker $Mn^{III}Mn^{III}$ interactions and (as in

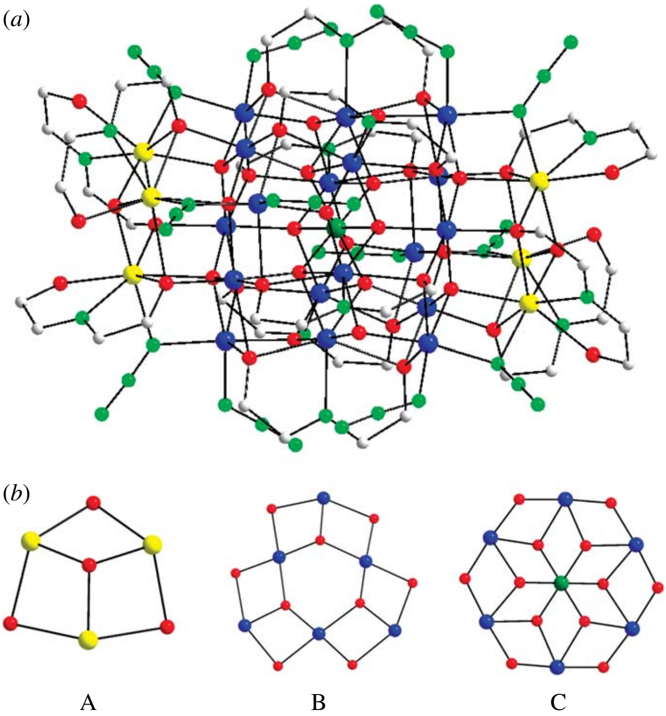

Figure 6. (*a*) Structure of the Mn_{25} complex, and (*b*) the three types of constituent Mn_x layers in the A : B : C : B : A structure. Colour code: yellow, Mn^{II}; blue, Mn^{III}; deep green, Mn^{IV}; red, O; light green, N; grey, C.

Mn_{12} complexes) aligning all the Mn^{III} spins parallel to each other and antiparallel to the central Mn^{IV} spin, giving $S=12-3/2=21/2$. This putative large spin of the central layer then represents a foundation for the overall large spin of the molecule, which is determined by the exact nature and relative magnitude of all the other ferro- and antiferromagnetic interactions in the molecule.

The low anisotropy of the molecule ($D=-0.020\,\mathrm{cm}^{-1}$) can, however, be rationalized from a consideration of the relative orientations of the 18 Mn^{III} JT elongation axes. These are found to be essentially equally oriented among the x, y and z directions, i.e. there is no preferential orientation and thus little net molecular anisotropy. Nevertheless, there is enough to make the compound an SMM, given the abnormally large S value.

Recognizing that the net $S=51/2$ spin of Mn_{25} is the net resultant of competing interactions within and among the many triangular Mn_3 subunits within the structure suggested to us that the complex might be magnetically soft in the sense that small structural perturbations could cause significant changes in the ratios of the competing interactions and thus alter the groundstate spin alignments. This was explored by an investigation into whether we could alter the peripheral ligation in a significant way, without of course major changes to the structure of the core. This was successfully accomplished by replacing the six pairs of adjacent bridging and terminal N_3^- groups with six chelating/bridging hmp^- groups, where hmp^- is the anion of 2-(hydroxymethyl)pyridine. This was successfully accomplished, as summarized in equation (4.1), and the product was confirmed by crystallography to have retained the five-layer structure of the starting material (Stamatatos *et al.* 2007*b*).

$$[\mathrm{Mn_{25}O_{18}(OH)_2(N_3)_{12}(pdm)_6(pdmH)_6}]^{2+} + 6\mathrm{Na(hmp)} \rightarrow [\mathrm{Mn_{25}O_{18}(OH)(OMe)(hmp)_6(pdm)_6(pdmH)_6}]^{8+} + 12\mathrm{NaN_3}. \tag{4.1}$$

However, small changes to many bond distances and angles result from this modification of the peripheral ligation, and the product was found to now have an $S=61/2$ groundstate. In effect, the ligation change represents the application of 'chemical pressure' on the magnetic core, leading to an increase in the groundstate by approximately 20%. This alteration, which we named spin tweaking, was recently extended to a third member of this family containing a further alteration of the peripheral ligation, and this was found to have an even higher groundstate spin value of $S=65/2$. As implied above, we rationalize these changes as a direct consequence of the presence of many competing exchange interactions within the core, making the spin alignments sensitive to their precise relative magnitude. Thus, a change in the latter caused by introduction of chelating ligands onto the periphery of the molecule alters the spin alignments and causes a corresponding change in the overall molecular spin. The suspicion that the $\mathrm{Mn_{25}}$ core might well be magnetically soft has therefore been confirmed. We see no reason why many other high nuclearity metal complexes that also contain such competing exchange interactions should not also be capable of undergoing spin tweaking with suitably chosen ligand alteration.

In conclusion, we have described three representative examples of polynuclear, mixed-valence Mn complexes with nuclearities of $\mathrm{Mn_{12}}$, $\mathrm{Mn_4}$ and $\mathrm{Mn_{25}}$ whose spin and anisotropies can be understood completely, or in one case partially, by the application of simple ideas of competing exchange interactions, the expected magnitude of $\mathrm{Mn^{II}Mn^{III}}$, $\mathrm{Mn^{III}Mn^{III}}$ and $\mathrm{Mn^{III}Mn^{IV}}$ pairwise interactions, and the relative orientations of the multiple $\mathrm{Mn^{III}}$ JT single-ion elongation axes. The importance of this basic understanding has been demonstrated in the development of spin tweaking methods that have allowed the $\mathrm{Mn_{25}}$ cluster to be obtained with three different values of groundstate spin S.

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