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Single-molecule magnets: a molecular approach to nanoscale magnetic materials

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Abstract

A brief survey is provided of single-molecule magnets (SMMs), or molecular nanomagnets. The $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (Mn_{12}; R = various) family of SMMs continues to be the one with the highest blocking temperatures, and the one on which the most detailed studies are being performed within the chemistry and physics communities. For this reason, methods have been developed for their controlled modification in various ways, and these are summarized. In addition, new SMMs continue to be sought to improve knowledge of this phenomenon, and several representative examples of new synthetic procedures and the resulting products are described.

Keywords: Manganese; Single-molecule magnet; Cluster; Hysteresis

1. Introduction

The synthesis of paramagnetic Mn carboxylate clusters has become the focus of much research since the discovery that some molecules can function as single-domain nanoscale magnetic particles [1–9]. In order to do so, a molecule must display slow magnetization relaxation below its blocking temperature, T_B. This behavior results from a large ground spin state (S) combined with a large and negative Ising (or easy-axis) type of magnetoanisotropy, as measured by the axial zero-field splitting parameter, D. This combination 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 spin, respectively. Experimentally, a single-molecule magnet (SMM) shows superparamagnet-like properties, exhibiting both a frequency-dependent out-of-phase AC magnetic susceptibility signal, and hysteresis in a plot of magnetization versus applied DC magnetic field. 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 magnetization hysteresis but also the quantum property of quantum tunneling of the magnetization (QTM) through the anisotropy barrier to magnetization relaxation.

Although complexes displaying SMM behavior are known for several other metals [10–23], manganese carboxylate clusters have to date proven to be the most fruitful source of SMM's. Examples include the archetypal $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ (Mn_{12}; R = various) family [2,24–49], Mn_2 [50], Mn_4 [4–9,51–53], Mn_6 [54,55], Mn_9 [56], Mn_{12} [57–59], Mn_{16} [55,60,61], Mn_{22} [62], Mn_{25} [63], Mn_{26} [64], Mn_{30} [65,66] and Mn_{84} [67] clusters. The R = Me (i.e., acetate) version of Mn_{12} ($Mn_{12}Ac$) was the first SMM discovered,

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and the most studied to date due to its large spin ($S = 10$) and high symmetry (S_4). The Mn_{12} family also possesses the largest blocking temperature ($T_B \sim 3$ K) against magnetization relaxation of any SMM. Only recently has a detailed understanding emerged concerning the symmetry breaking responsible for the QTM in $Mn_{12}Ac$ [68–70]. Hence, $Mn_{12}Ac$ and the Mn_{12} family remain an attractive and productive area for further research area.

One of our goals over the last several years has been to develop an arsenal of methods for modifying the Mn_{12} family of SMMs in a variety of controllable and useful ways. In these molecules, the central inorganic Mn/O core is contained within a shell of organic ligands, and one goal has therefore been the modification of this organic periphery (shell) via ligand substitution reactions. Among other things, this would allow us to tune the solubility, redox and magnetic properties of the molecules. Another objective has been to obtain Mn_{12} complexes in different oxidation states to investigate the influence of the electron count on various properties of the molecules. A further but more subtle way of modifying the molecules is to grow the crystals from various solvents, which can lead to variations in the space group and precise solvent content of the crystals, and this in turn leads to variations in the local site-symmetry and environment around the molecule. While the latter variation might be predicted to lead to insignificant changes to the properties of the molecule, in fact we have found these changes to lead to surprisingly large effects. All the above controlled modifications will be summarized in more detail in this paper, and these have greatly advanced our knowledge and understanding of the properties of these Mn_{12} SMMs.

In addition to modifying known types of SMMs, we have also continued to seek new synthetic methods to new structural types of high-nuclearity Mn clusters that might have interesting structural and/or magnetic properties, and that might be new SMMs. We shall also describe a number of new results along these lines. For example, the use of MeOH in some reactions has led to the synthesis of new clusters of nuclearities Mn_{12} [71], Mn_{16} [61], and Mn_{84} [67], and all of these have been discovered to be new SMMs. In addition, recent work with polydentate chelates containing alcohol groups has yielded a new Mn_{12} cluster with an interesting loop structure, which is also a new SMM. All these will be described in this report.

2. Modification of single-molecule magnets

2.1. Carboxylate substitution

Several procedures have been developed to replace the $MeCO_2^-$ ligands of $Mn_{12}Ac$ with almost any other type of carboxylate group, leading to increased solubility in organic solvents and greatly altered redox properties [41,72]. Methods have also been developed to obtain Mn_{12} complexes containing more than one type of peripheral bridging ligand (the four H_2O ligands are terminal). One such strategy involves the site-specific replacement of some of the bound carboxylates to give either: (i) mixed-carboxylate complexes of formula $[Mn_{12}O_{12}(O_2CR)_8(O_2CR')_8(H_2O)_4]$ [73] or (ii) mixed organic–inorganic ligation in the complex $[Mn_{12}O_{12}(O_2CR)_{12}(NO_3)_4(H_2O)_4]$, which contains bridging NO_3^- groups and is thus the first Mn_{12} complex to contain non-organic bridging ligands [34]. Subsequently, we showed that it is also possible to site-specifically substitute half the carboxylate groups with: (i) benzenesulfonate ($PhSO_3^-$) groups to give $[Mn_{12}O_{12}(O_2CMe)_8(O_3SPh)_8(H_2O)_4]$ [33] with the $PhSO_3^-$ groups occupying axial positions on the Mn_{12} cluster or (ii) with diphenylphosphinate ($Ph_2PO_2^-$) groups to give $[Mn_{12}O_{12}(O_2CMe)_8(O_2PPh_2)_8(H_2O)_4]$ with both axial and equatorial $Ph_2PO_2^-$ groups [30]. One such transformation is summarized as an example in Eq. (1), for the $PhSO_3H$ reaction.

$$[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4] + 8PhSO_3H \rightarrow [Mn_{12}O_{12}(O_2CMe)_8(O_3SPh)_8(H_2O)_4] + 8MeCO_2H \quad (1)$$

Considerable insight has been obtained from these chemical modifications on the Mn_{12} SMM, leading to much new magnetostructural knowledge and information on this important family of SMMs.

2.2. Reduced Mn_{12} complexes

The feasibility of chemically reducing a Mn_{12} SMM was initially established by the observation of quasi-reversible oxidation and reduction processes in the cyclic voltammograms. The oxidation processes are at rather high potentials, but the reduction processes are much more accessible, and it was therefore decided to initially seek isolation of one-electron reduced species. For this purpose, the reducing agent chosen was I^- because of its sufficient, yet mild reducing strength, its ready availability as a variety of salts of organic cations, and the high solubility of many of the latter in organic solvents. Indeed, chemical reduction of the $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$ complexes with C^+I^- (C^+ is NR_4^+, PPh_4^+, etc.) in MeCN or CH_2Cl_2 was found to provide a convenient route to the corresponding salts of the $[Mn_{12}]^-$ anions in good (>50%) yield. The C^+I^- reagent provides the required cation, and the only byproduct is elemental I_2, which is easy to remove (Eq. (2)).

$$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4] + I^- \rightarrow [Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]^- + \tfrac{1}{2}I_2 \quad (2)$$

It has been proven by X-ray crystallography that the added electron is localized on an outer (originally Mn^{III}) ion rather than an inner (cubane) Mn^{IV} ion, producing a trapped-valence $Mn^{II}Mn_7^{III}Mn_4^{IV}$ anion. These $[Mn_{12}]^-$ compounds have a half-integer ground state spin of $S = 19/2$ in almost all the cases studied [41–43], with $S = 21/2$ occasionally being reported [45]. In addition, they retain the SMM properties of the neutral Mn_{12} species, and are of particular interest for studying QTM in half-integer spin species; QTM is not allowed in such complexes in the absence of an applied field.

The carboxylate substitution reactions mentioned above have allowed the incorporation onto the Mn_{12} core of carboxylate groups containing strongly electron-withdrawing substituents (e.g., $CHCl_2CO_2^-$ groups), and these raise the reduction potentials to the point that the second reduction is also within the capability of our reductant of choice, iodide I^-. Thus, clean, two-electron reduction to $[Mn_{12}]^{2-}$ salts has consequently also been successfully accomplished (Eq. (3)) [46–49].

$$[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4] + 2I^- \rightarrow [Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]^{2-} + I_2 \quad (3)$$

As for the $[Mn_{12}]^-$ anion, the extra electrons in $[Mn_{12}]^-$ are localized on outer (originally Mn^{III}) ions rather than on inner (cubane) Mn^{IV} ions, producing a trapped-valence $Mn_2^{II}Mn_6^{III}Mn_4^{IV}$ anion. In contrast to the $[Mn_{12}]^-$ salts, the ground state spin is again an integer $S = 10$ for two-electron reduced species. In addition, they retain the SMM properties of the neutral Mn_{12} species and $[Mn_{12}]^-$ species. In fact, a detailed examination of the magnetic properties of the $[Mn_{12}]^z$ ($z = 0$, $1-$, $2-$) series has shown that although they are all SMMs, they show a decreasing effective barrier to magnetization relaxation (U_{eff}), which is primarily due to the decreasing magnitude of the axial anisotropy parameter $|D|$ as the Mn^{III} content of the clusters decreases; Jahn-Teller distorted Mn^{III} ions are the main source of anisotropy in the Mn_{12} molecules. All three Mn_{12} oxidation states display resonant QTM, and this work thus provides useful comparisons of QTM in half-integer versus integer spin systems, as well as of quantum phase interference.

2.3. High-symmetry Mn_{12} complexes

Among all Mn_{12} complexes to date, Mn_{12}Ac has become the most widely studied SMM, not only because it

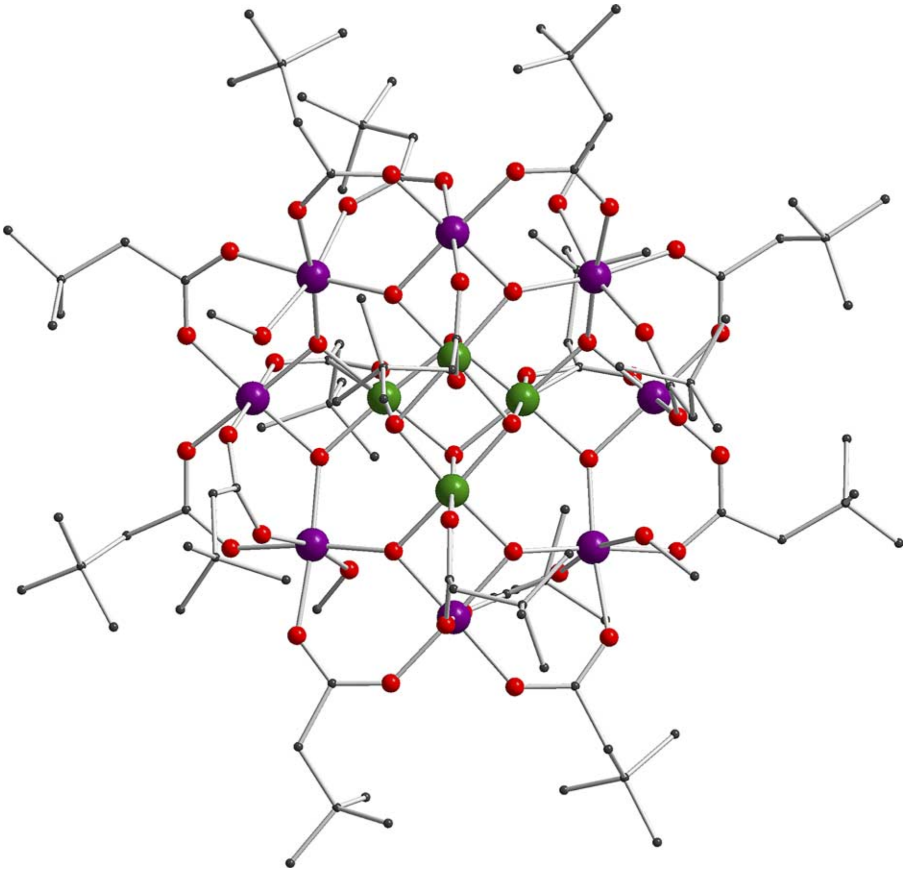

Fig. 1. The structure of $[Mn_{12}O_{12}(O_2CCH_2{}^tBu)_{16}(MeOH)_4]$, excluding hydrogen atoms. Color code: green, Mn^{IV}; purple, Mn^{III}; red, O; gray, C.

was the first to be recognized as an SMM but also because of its high spin of $S = 10$ and its high molecular symmetry (S_4). These factors contribute to the largest blocking temperature ($T_B \sim 3$ K) against magnetization relaxation of any known SMM. Recently, an improved understanding has emerged concerning the symmetry breaking responsible for the QTM in Mn_{12}Ac [68–70]. Disorder associated with the acetic acid solvent leads to discrete local environments, resulting in a significant fraction of the molecules (>50%) possessing twofold symmetry with a rhombic crystal-field parameter $E \sim 0.01$ cm^{-1} [69]. In effect, the Mn_{12}Ac complex is a mixture of species with different site symmetries, only some of which are truly axial, and it is clear that it is therefore *not* an ideal Mn_{12} for detailed study using models that assume axial symmetry in the spin Hamiltonians. We have thus been exploring the synthesis and study of other Mn_{12} complexes with true axial symmetry in order to finally obtain the real properties of axially symmetric Mn_{12} SMMs.

In 2001, the high symmetry (space group $I4_1/a$) $[Mn_{12}O_{12}(O_2CCH_2Br)_{16}(H_2O)_4] \cdot 4CH_2Cl_2$ (Mn_{12}BrAc) complex was reported by An et al. [26]. This was prepared using our ligand substitution reaction with bromoacetic acid. This complex is overall similar to Mn_{12}Ac in its structure and magnetic properties, except

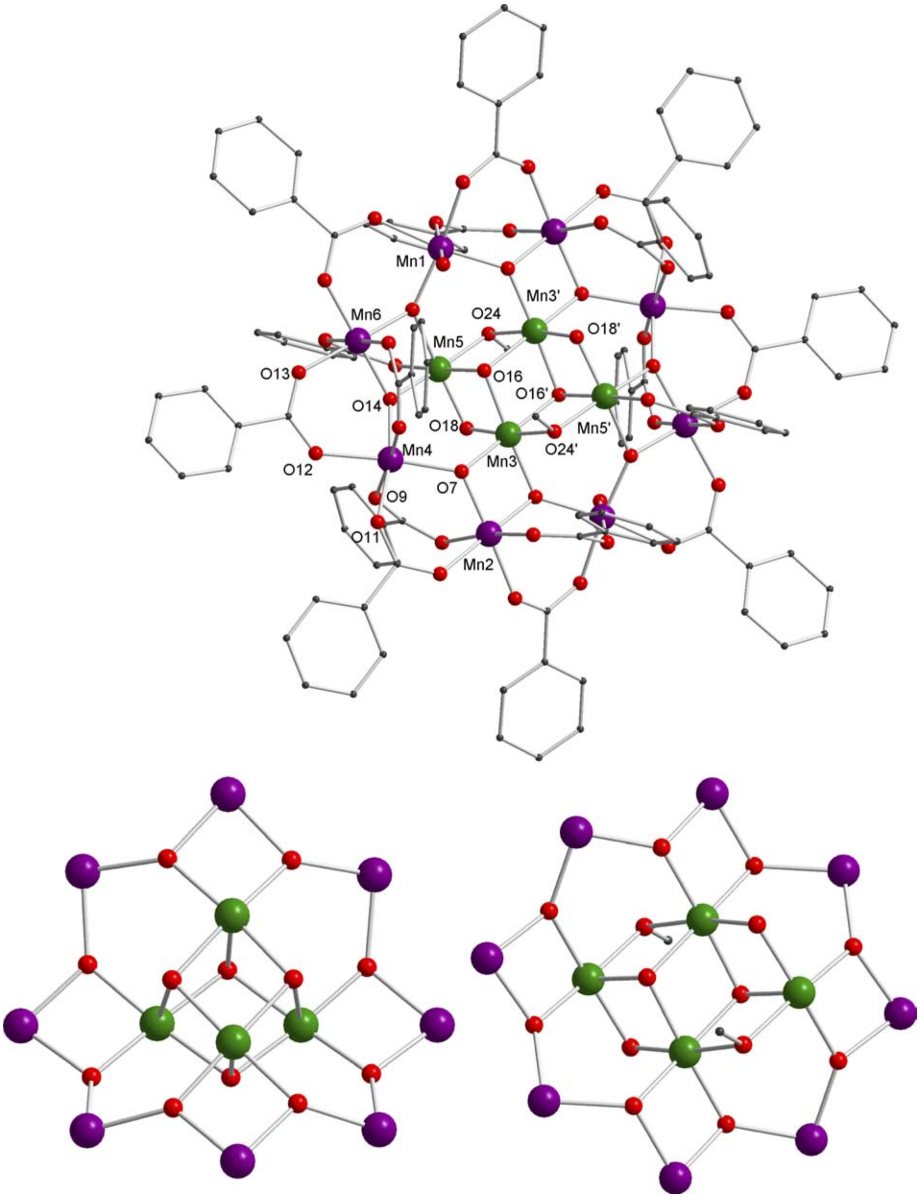

Fig. 2. The structure of the anion of $[Mn_{12}O_{12}(OMe)_2(O_2CPh)_{16}(H_2O)_2]$, excluding hydrogen atoms. Color code: green, Mn^{IV}; purple, Mn^{III}; red, O; gray, C. Bottom: Comparison of the cores of “normal” $[Mn_{12}]$ (left) and the anion of “flat” $[Mn_{12}]$ (bottom).

that it is much ‘cleaner,’ not being composed of a mixture of species with very different environments. We have recently investigated the properties of this complex in depth using micro-SQUID, high-frequency EPR and ^{55}Mn NMR techniques, in all cases using single crystals. All measurements reveal far superior quality data than for Mn_{12}Ac [74,75]. Given this improvement, we have also sought other high-symmetry Mn_{12} complexes, and have recently prepared $[Mn_{12}O_{12}(O_2CCH_2{}^tBu)_{16}(MeOH)_4] \cdot MeOH$, ($Mn_{12}{}^t$BuAc), (Fig. 1), which crystallizes in the high-symmetry space group *I*4(bar) [76]. In $Mn_{12}{}^t$BuAc, there is only one MeOH solvent molecule of crystallization, which sits on an S_4 symmetry axis and does not perturb the magnetic properties of this complex. Furthermore, the large bulky ^{t}BuAc groups more efficiently separate the clusters from their neighbors, minimizing inter-cluster interactions. Preliminary magnetic studies reveal the characteristic behavior of the Mn_{12} family. However, the data are remarkably clean and allow deeper insights into the fine details of the physical properties of Mn_{12} SMMs than has proven possible in the past.

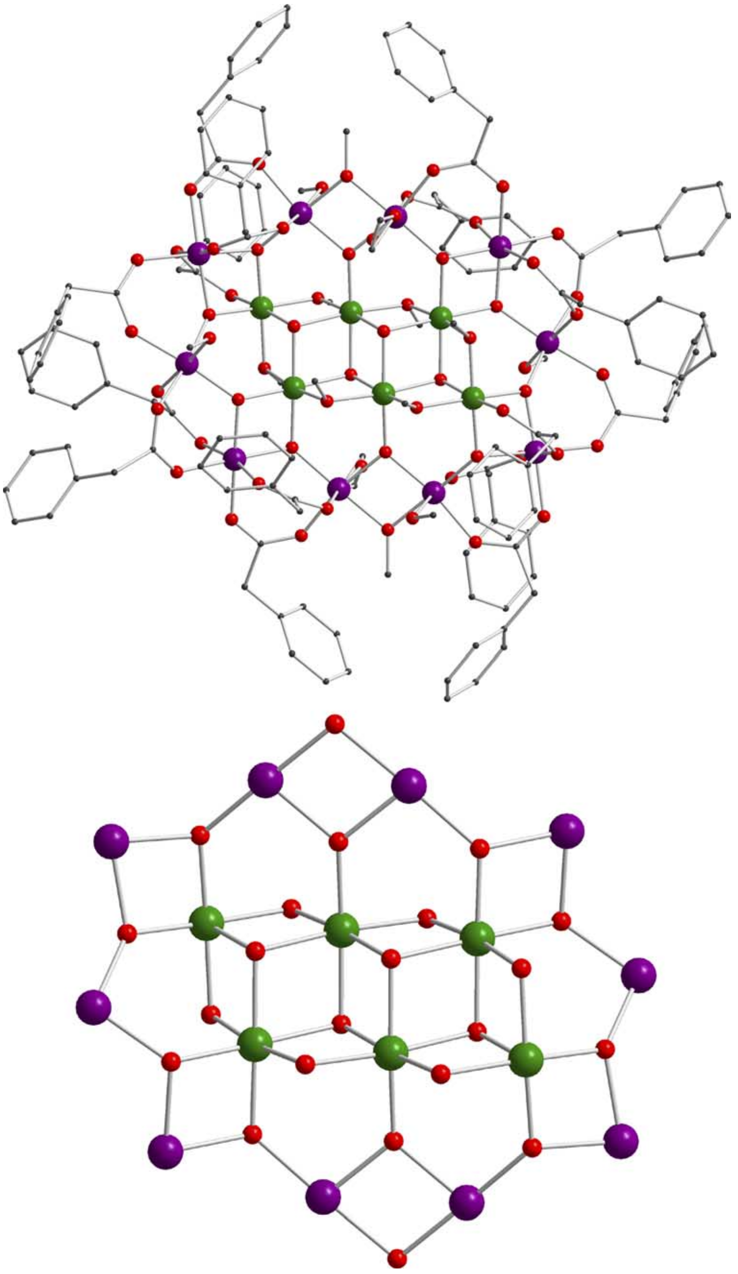

Fig. 3. The structure of $[Mn_{16}O_{16}(OMe)_6(O_2CCH_2Ph)_{16}(MeOH)_6]$ and its planar central core (bottom). Hydrogen atoms have been omitted for clarity. Color code: green, Mn^{IV}; purple, Mn^{III}; red, O; gray, C.

3. Some new procedures to SMMs

3.1. Reductive aggregation

The standard synthesis of Mn_{12}Ac consists of the comproportionation reaction between $Mn(O_2CMe)_2 \cdot 4H_2O$ and $KMnO_4$ in 60% aqueous acetic acid. This is a convenient procedure involving oxidation of Mn^{II} ions and concomitant reduction of Mn^{VII} ions, producing a product at the $8Mn^{III}$, $4Mn^{IV}$ oxidation level. The Mn^{II}:Mn^{VII} reaction ratio can readily be varied, as can other reaction conditions and the presence of other reagents such as chelates. Various complexes, including mixed-valent Mn^{IV}/Mn^{III} [4–9,24–49,51–53] and Mn^{III}/Mn^{II} [7,8] species, can thus be obtained. As part of our general search of new synthetic methods to Mn_x clusters, a new procedure was developed in which the Mn^{II} source was omitted and MeOH was used as both the reducing agent for Mn^{VII} and as a potential source of MeO^- bridging ligands, in the presence also of excess carboxylic acid to prevent formation of manganese oxides and/or hydroxides. The procedure, which we have termed 'reductive aggregation,' proved its worth with the synthesis of $(N^nBu_4)_2[Mn_{12}O_{12}(OMe)_2(O_2CPh)_{16}(H_2O)_2]$ (Fig. 2) when benzoic acid was employed [71]; this is a new cluster type and SMM not available, at least to date, by any other route. It has since been possible to isolate two different analogues of this new structural type of Mn_{12} complex, $[Mn_{12}O_{10}(OMe)_3(OH)^-(O_2CC_6H_3F_2)_{16}(MeOH)_2] \cdot 4MeOH$ and $[Mn_{12}O_{10}(OMe)_4(O_2C^tBu)_{16}(MeOH)_2]$. These complexes all have significant structural similarity with $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$, all comprising a non-planar Mn_8^{III} ring around a central Mn_4^{IV} unit, but the central core of the new type of Mn_{12} cluster now contains alkoxide bridges. In effect, the central $[Mn_4O_4]$ cubane

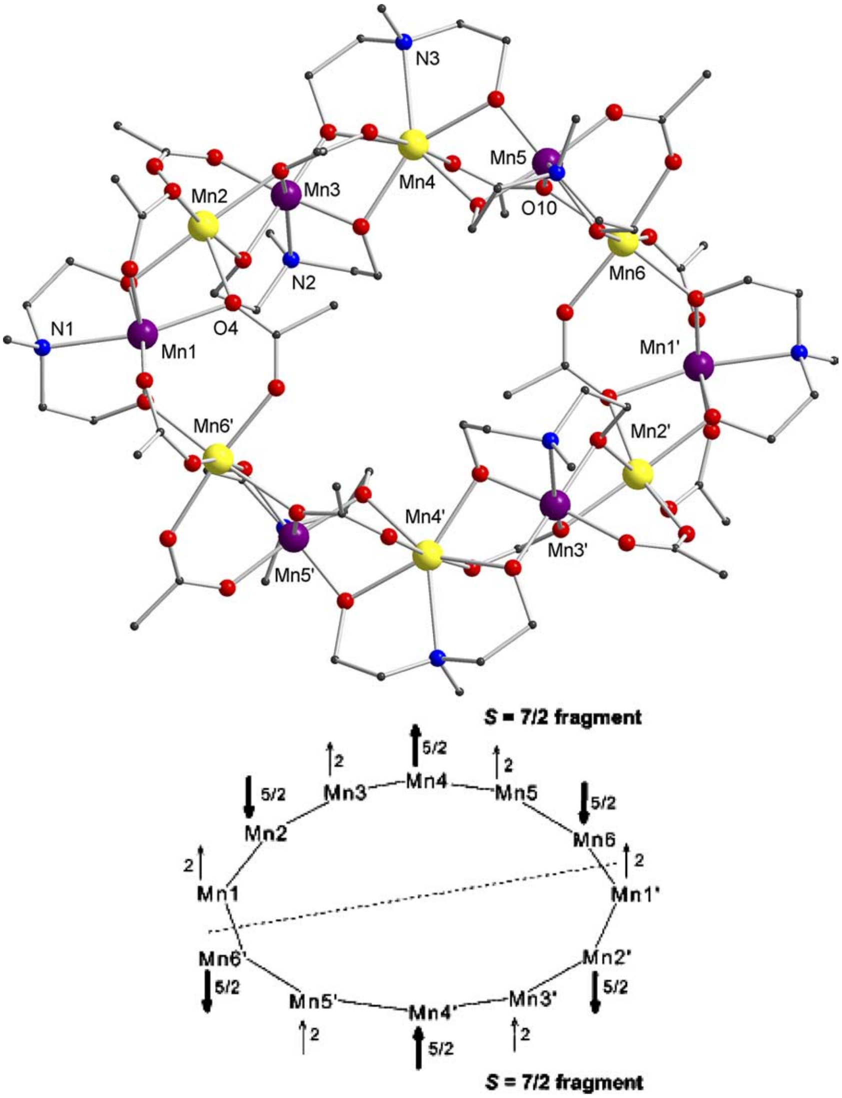

Fig. 4. The structure of $[Mn_{12}(O_2CMe)_{14}(mda)_8]$, excluding hydrogen atoms. Color code: yellow, Mn^{II}; purple, Mn^{III}; red, O; blue, N; gray, C. Bottom: Depiction of the spin alignments in the $S = 7$ ground state of the Mn_{12} loop as predicted by the DFT calculations.

of normal Mn_{12} complexes has been flattened, with the four central Mn^{IV} ions now forming a planar Mn_4 rhombus, i.e., the central core unit is a defect dicubane rather than a cubane (Fig. 2, bottom). In addition, the number of alkoxide bridges in the central core differs for all three of the new type of Mn_{12} clusters, ranging from two for the benzoate cluster, three for the difluorobenzoate cluster, and four for the pivalate cluster. Hence, these complexes represent the progressive replacement of oxide-bridges by alkoxide ones within the central core of $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$. In spite of their difference in the structure of the central core compared with normal Mn_{12} SMMs, the new types of Mn_{12} complexes still retain a significant barrier to magnetization relaxation, and they are thus SMMs, exhibiting hysteresis loops at low temperatures.

The new reductive aggregation procedure to Mn_x clusters has been subjected to further investigation by the use of various carboxylic acids. It was subsequently found that the reaction of phenylacetic acid, chloroacetic acid and bromoacetic acid with $N^nBu_4MnO_4$ in MeOH did not give further examples of the new Mn_{12} type of complex mentioned above, but instead a family of $[Mn_{16}O_{16}(OMe)_6(O_2CR)_{16}(MeOH)_6]$ complexes was obtained. These are similar but not identical to the Mn_{16} complex reported by Murray and co-workers [60]. The reductive aggregation reactions are clearly very complicated, and the reaction solutions likely contain a complicated mixture of several species in equilibrium, with factors such as relative solubility, lattice energies, crystallization kinetics and others determining the identity of the isolated product. One (or more) of these factors is undoubtedly the reason that changing the

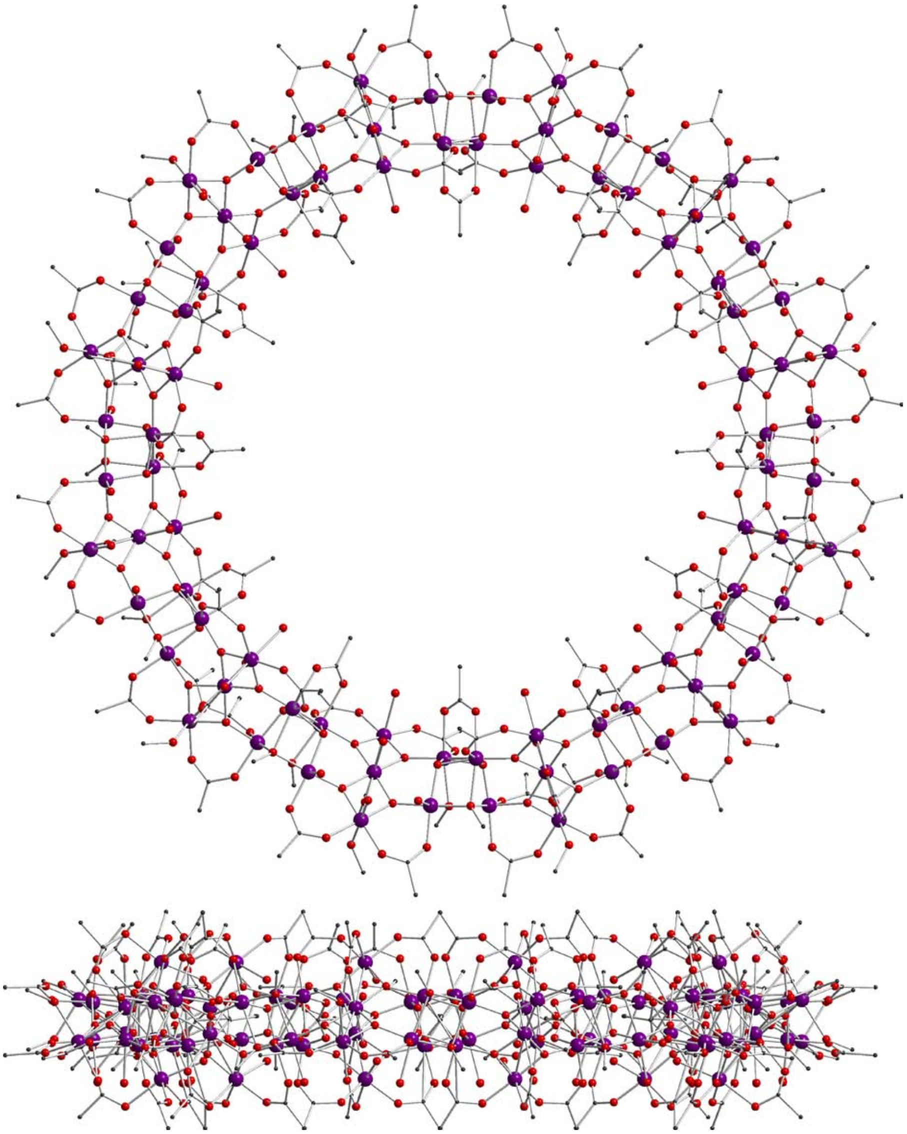

Fig. 5. The structure of the Mn_{84} torus, excluding hydrogen atoms. Bottom: Side-view of the molecule emphasizing its planarity.

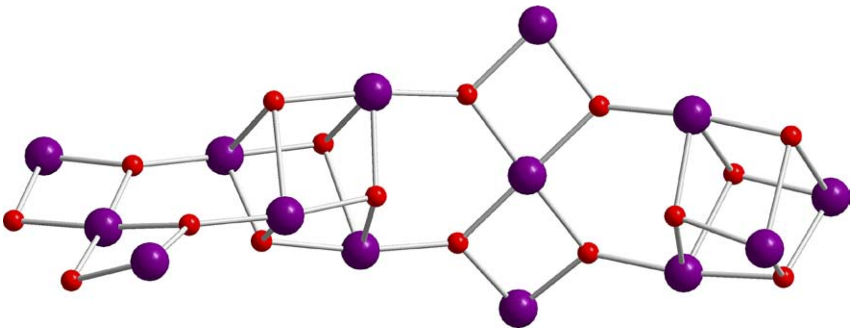

Fig. 6. The repeating [Mn_{14}] unit that represents the contents of the asymmetric unit; for clarity, carbon atoms and hydrogen atoms have been omitted.

carboxylic acid used from benzoic acid to the ones mentioned causes a major change in the isolated product from a Mn_{12} species to a Mn_{16} one. Furthermore, the three carboxylic acids employed are all derivatives of acetic acid, and it is thus interesting that when acetic acid itself was used, the product was the previously reported [$Mn_{84}O_{72}(O_2CMe)_{78}(OMe)_{24}(MeOH)_{12}(H_2O)_{42}(OH)_6$] [67]. This contrasts with the fact that it was the acetate cluster [$Mn_{16}O_{16}(OMe)_6(O_2CMe)_{16}(MeOH)_3(H_2O)_3$] that was obtained by Murray and co-workers [60] from the comproportionation reaction of $Mn(NO_3)_2$and $N^nBu_4MnO_4$ in excess MeOH; Murray's compound is essentially isostructural with the above Mn_{16} clusters, except for the terminal H_2O molecules replacing three of the MeOH molecules.

The phenylacetate Mn_{16} cluster (Fig. 3) has a roughly planar core comprising six Mn^{IV} and 10 Mn^{III} ions bridged by 14 μ_3-O^{2-}, two μ-O^{2-}, six μ-MeO^- and 16 μ-$PhCH_2CO_2^-$ groups (Fig. 3, bottom). The six Mn^{IV} ions are located within a central $[Mn_6^{IV}(\mu_3\text{-}O)_4(\mu\text{-}O)_2(\mu\text{-}MeO)_4]^{8+}$ core, with the six Mn^{IV} ions planar and the bridging O atoms above and below this plane, reminiscent of the planar CdI_2-type sheet structure. Encapsulating the central core is a non-planar ring of 10 Mn^{III} atoms to which it is connected by 10 μ_3-O^{2-} ions in the plane of the molecule and two μ-$PhCH_2CO_2^-$ groups one above and one below the plane. Thus, a useful description is as a small piece of a Mn oxide mineral held within a non-planar ring of Mn^{III} ions. The remaining 14 μ-$PhCH_2CO_2^-$ ligands, two μ-MeO^- groups (bridging Mn1 and Mn7a, and their symmetry equivalents) and six terminal MeOH molecules provide the peripheral ligation of the complete complex.

The Mn_{16} complexes have $S = 2$ ground states, and single-crystal magnetization versus DC field scans down to 0.04 K for the phenylacetate Mn_{16} cluster show hysteresis loops at <1 K, confirming SMM behaviour. No clear steps characteristic of QTM were observed in the hysteresis loops. Hence, although this compound has a small ground state, the near-parallel alignment of the Mn^{III} Jahn-Teller elongation axes provides sufficient molecular anisotropy to result in a small barrier to magnetization relaxation and hysteresis loops at very low temperatures.

3.2. Reactions with N-methyl-diethanolamine

Recently, we have been exploring the products from reactions employing alcohol-based ligands such as *N*-methyldiethanolamine ($mdaH_2$) to complement our previous work with the less flexible 2-hydroxymethylpyridine (hmpH) and pyridine-2,6-bis(dimethanol)

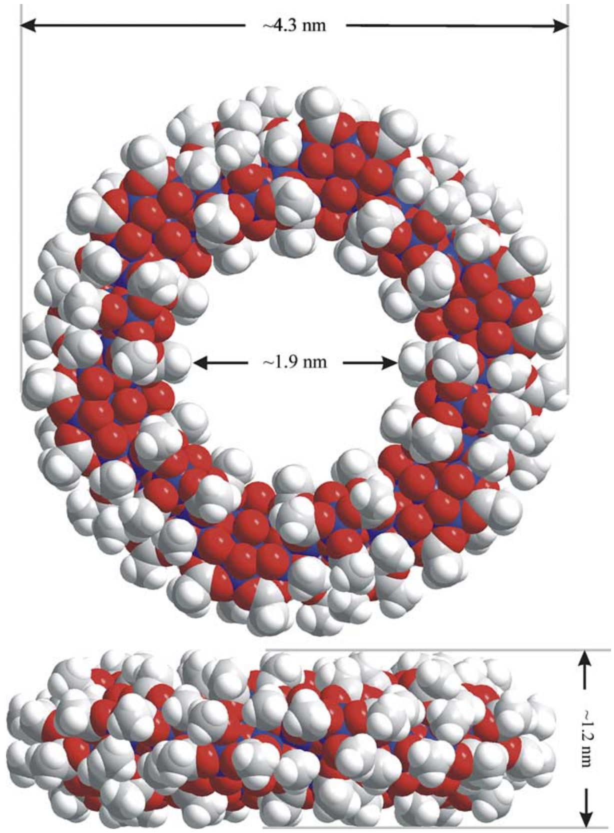

Fig. 7. Space-filling representations (including hydrogen atoms) from viewpoints perpendicular (top) and parallel (bottom) to the plane of the torus, showing the dimensions of the molecule and its central hole.

(pdmH_2). With this reagent, we have isolated mixed-valent $[Mn_{12}(O_2CMe)_{14}(mda)_8]$ ($Mn_6^{II}Mn_6^{III}$), whose structure consists of a centrosymmetric Mn_{12} loop with a chair conformation (Fig. 4). All the manganese centers are six-coordinate except Mn^{II} ions Mn4 and Mn4′, which have a very distorted pentagonal-bipyramidal coordination sphere. Six mda^{2-} ligands each chelate a Mn^{III} ion, and the two alkoxide O atoms bridge to the adjacent Mn^{II} ions. The other two mda^{2-} groups chelate Mn^{II} ions and bridge by their alkoxide O atoms to Mn^{III} ions. As a result, the mda^{2-} groups alternate between being axial and equatorial with respect to the plane of the Mn_{12} loop. Each Mn_2 pair is additionally bridged by an acetate group in its familiar η^1,η^1,μ(*syn*, *syn*) binding mode on the outside of the loop, whereas the final two acetate groups bridge in a rarer η^1,η^2,μ^3 mode on the inside of the loop. This Mn_{12} loop complex has also been reported by others [57]. The complex has a relatively large ground-state spin value of $S = 7$: this is unusually intermediate in magnitude for a single-stranded Mn_6^{II}, Mn_6^{III} loop complex: antiferromagnetic or ferromagnetic Mn^{II}/Mn^{III} exchange interactions would be expected to give $S = 3$ or 27 ground states, respectively, so it is clear that there must be both types of interaction within this low-symmetry complex. To probe this further, we have carried out DFT calculations [77–81], and found both ferro- and antiferromagnetic interactions to be present, with all the J values being very weak, in the range $4.0 > J > -4.6$ cm^{-1}. This range is fully consistent with values for $Mn^{II}Mn^{III}$ exchange parameters, which are always weak and either side of zero, depending on the bridges [82]. Within the uncertainty of the DFT calculation, the Mn1–Mn6′ and Mn1′–Mn6 interactions are calculated to be 0.0 cm^{-1}: in fact, they are almost certainly either very weakly positive or negative. Since the spin of each half of the molecule is calculated to be $S = 7/2$, positive Mn1–Mn6′ and Mn1′–Mn6 interactions would give a ground-state spin of $S = 0$ while negative Mn1–Mn6′ and Mn1′–Mn6 interactions give $S = 7$ for the complete molecule (Fig. 4, bottom). On the basis of the magnetization data that clearly rule out an $S = 0$ ground state, we conclude that the ground state is $S = 7$, resulting from the spin alignments in (Fig. 4, bottom), in complete agreement with the magnetization studies.

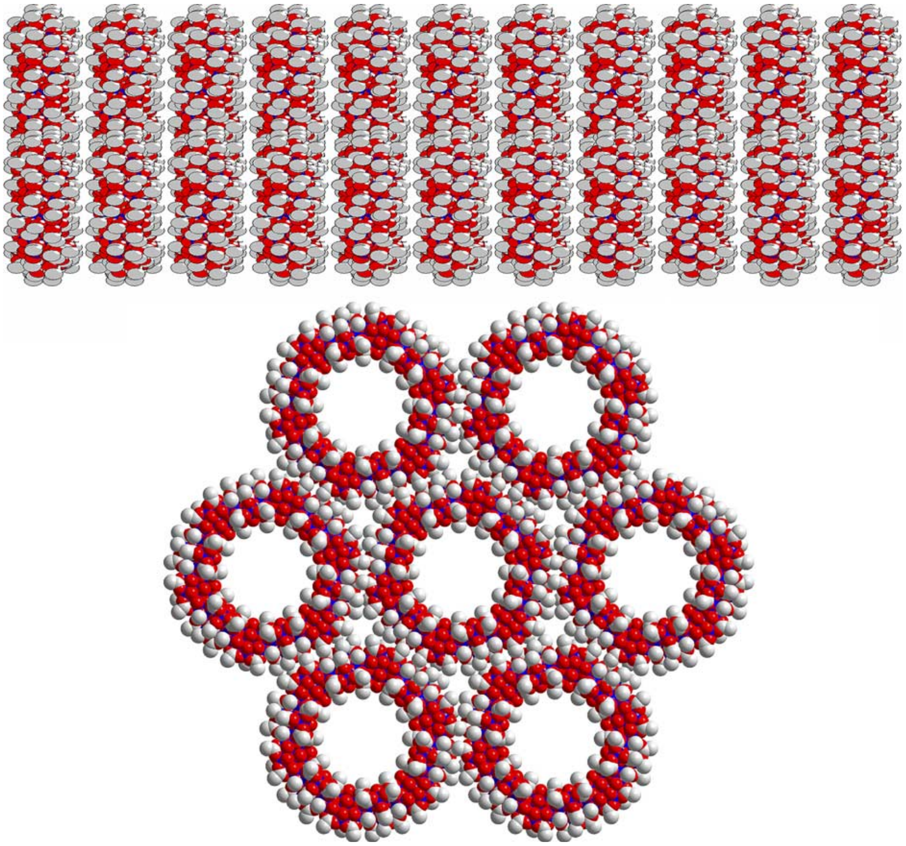

Fig. 8. Top: Ordered arrangement of Mn_{84} molecules (excluding hydrogen atoms) into two adjacent supramolecular nanotubes viewed perpendicular to the propagation axis; this view emphasizes the exact registry of molecules in adjacent tubes and thus the sheet-like structure formed. Bottom: A view along the propagation axes of seven tubes showing the hexagonal packing of neighbors within a single sheet of molecules (excluding hydrogen atoms).

3.3. Methanolysis routes to a Mn_{84} torus

We have long sought to synthesize SMMs of very large dimensions (by molecular standards) to probe whether products from the molecular (or bottom-up) approach to nanoscale magnetic materials can reach the size regime of the traditional (or top-down) approach. As part of these efforts, we have obtained $[Mn_{84}O_{72}(O_2CMe)_{78}(OMe)_{24}(MeOH)_{12}(H_2O)_{42}(OH)_6]$ (Mn_{84}) from the reaction of $Mn_{12}Ac$ with $N^nBu_4MnO_4$ in MeOH. The structure (Fig. 5) comprises a giant Mn_{84} torus with a >4 nm diameter composed of alternating near-linear $[Mn_3O_4]$ and cubic $[Mn_4]$ subunits (Fig. 6). All the Mn ions are Mn^{III}. The Mn_{84} complex exhibits hysteresis and QTM and is thus the largest SMM prepared to date. A better appreciation of the structure and the size of the molecule is provided by the space-filling plots of Fig. 7, which show that the torus has a diameter of about 4.3 nm and a thickness of about 1.2 nm, with a central hole of diameter 1.9 nm. The Mn_{84} molecules order within the crystal in an aesthetically pleasing manner, giving nanotubular stacks parallel to the crystal c axis and to their neighbors (Fig. 8). This yields a hexagonal close packing analogous to densely packed straws in a box. The crystalline structure of Mn_{84} thus displays extensive cylindrical channel formation along one dimension. Molecules in neighboring chains are exactly adjacent (Fig. 8), and thus the structure may be alternatively described as consisting of graphite-like Mn_{84} sheets lying on top of each other with perfect registry.

4. Conclusions

The field of single-molecule magnets, or molecular nanomagnets, continues to grow and branch out in several directions. We have tried in this short review to emphasize the importance of obtaining synthetic control over obtained species, so that they can be modified in desirable ways. This thus allows expansion of a particular structural type into a family of related species that are invaluable in probing the various factors that affect the observed magnetic properties. We have also tried to emphasize the variety of species that can be obtained in Mn chemistry, which continues to be the richest source of SMMs, as the number of synthetic methods continues to increase.

Acknowledgment

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