Magnetic coordination clusters and networks: synthesis and topological description

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With the discovery of the phenomenon of single-molecule magnetism, coordination chemists have turned their attention to synthesizing cluster aggregates of paramagnetic ions. This has led to a plethora of coordination clusters with various topologies and diverse magnetic properties. In this paper, we present ways of describing and understanding such compounds as well as outlining a new approach, which we have recently developed, to describing cluster topology. Our approach is based upon and pays tribute to the huge contribution made to coordination chemistry through the development of the Schläfli symbols for describing architectures. To illustrate the developments that are taking place in modern coordination chemistry, we start with some basic definitions. Then we describe approaches to discovering new magnetically interesting 3d/4f clusters, assigning their topological descriptions. Finally, we show how the concepts behind the construction of metal–organic frameworks can be extended to using clusters as nodes in the frameworks to give super metal–organic frameworks.

Keywords: metal–organic framework; nanoparticles; molecular magnetism

1. Introduction

With the discovery of the phenomenon of single-molecule magnetism (Sessoli et al. 1993), coordination chemists have turned their attention to synthesizing cluster aggregates of paramagnetic ions. This has led to a plethora of coordination clusters with various topologies and diverse magnetic properties. In this paper, we present ways of describing and understanding such compounds as well as outlining a new approach, which we have recently developed, to describing cluster topology. Our approach recognizes the huge contribution made to coordination chemistry through the development of the Schläfli symbols for describing architectures. To begin with, we give some basic definitions.

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One contribution of 13 to a Theme Issue ‘Metal clusters and nanoparticles’.
2. Definitions

(a) Cluster/co-ordination cluster

Recent years have witnessed an explosion of interest in clusters of metals, which may be either well-defined molecular species with structures that can be determined to atomic resolution and for which the number of metals remains constant from one entity to another, or else nanoparticles where the precise number of metals varies from one particle to another. In the latter case, well-defined species tend to be labelled as ‘monodisperse’, meaning that their dimensions are roughly constant within a set tolerance. In this paper we will confine our discussion to magnetic particles that are molecules. Furthermore, we will discuss molecular clusters where the metal centres are in positive oxidation states and linked together by various p-block bridging species, usually containing oxygen or nitrogen centres. Such magnetic clusters are contained within ligand shells that limit the growth of the metal ion structure to an infinite mineral and which we therefore term co-ordination clusters. Interesting magnetic behaviour in such molecular systems can be observed for collections of cooperatively coupled metal ions from three upwards. Additionally, the clusters can be isolated and labelled as zero-dimensional, in which case they can operate as single-molecule magnets (SMMs), or they can be linked in various ways. In fact, a very interesting subset of coordination compounds, where the clusters are used as ‘nodes’ and the ligands perform the function of linking these and possibly allowing for magnetic coupling pathways, are the so-called metal–organic frameworks (MOFs).

(b) Metal ions—electronic properties

The magnetic properties of cooperatively coupled clusters of metal ions will be strongly dependent on the nature of the individual ions. Probably the most useful way to embark on a study of any coordination cluster is to consider the electronic structure of the individual ions. This will result from the electronic configuration and the ligand field parameters. For example, in a coordination cluster containing Mn$^{II}$, Mn$^{III}$ and Mn$^{IV}$, all in octahedral coordination geometries, such as $[\text{Mn}^{II}_{6}\text{Mn}^{III}_{18}\text{Mn}^{IV}_{18}(\text{OH})_{12}(\text{pdm})_{6}(\text{Hpdm})_{6}](\text{Cl})_{2}\cdot 12\text{MeCN}$ (Hpdm=pyridine-2,6-dimethanol; Murugesu et al. 2004), there are five possible d configurations and ground terms for the individual ions, depending on whether they are low or high spin, namely, $^{2}T_{2g}$ low spin and $^{6}A_{1g}$ high spin for Mn$^{II}$, $^{3}T_{1g}$ low spin and $^{5}T_{2g}$ high spin for Mn$^{III}$, and $^{4}A_{2g}$ for Mn$^{IV}$. Furthermore, the size of $10D_{q}$ (or $\Delta_{O}$) will affect any zero-field splitting effects. This is clearly seen by comparing Mn$^{II}$ and Fe$^{III}$ high-spin d$^{5}$ configurations, where the latter has a significantly larger zero-field splitting as a result of the larger value of $10D_{q}$. Similarly, the Jahn–Teller distortion observed for Mn$^{III}$ high-spin systems, which are d$^{4}$, will be different from that seen for the high-spin d$^{4}$ Cr$^{II}$ ion. These factors will, in turn, affect the magnitude of the coupling between metal centres and the degree of anisotropy for the individual ions and also for the cluster as a whole. Since the magnetic properties in SMMs are governed by total spin, anisotropy and degree of coupling, these considerations play an important role in the quest for improved SMMs. Having said this, it is not our intention here to go into the fine details of ligand field theory in relation to magnetic coordination clusters (but see below...
within this section for further details on the intricacies of this). One reason is that
it is only beginning to be clear to researchers in this area what the important
factors to build in to a system really are. The other reason is that this paper is
specifically aimed at explaining the synthetic approaches that we have used to
obtain a wide variety of molecular magnetic systems. Before doing this, a few
more explanatory sections regarding magnetic properties will be useful.

(c) Cooperative effects—superexchange, double exchange, direct interaction,
coupling schemes, spin–orbit coupling, anisotropy

There are several possibilities for achieving cooperative magnetic coupling
in molecular systems. The most widely employed is superexchange, whereby a
diamagnetic bridging (linking) unit is used to pin spins on two paramagnetic
centres to be either antiparallel (antiferromagnetic) or parallel (ferromagnetic).
This is most famously seen in extended mineral structures such as NiO, which
crystallizes as a face-centred cubic (FCC) structure equivalent to NaCl and
where the oxides arrange the spins on the nickel ions to be antiparallel, with
antiferromagnetic coupling arising. Double exchange can be regarded as a special
case of superexchange, which occurs between paramagnetic centres with different
electronic configurations such as MnIII and MnIV. If electron movement from one
species to another does not involve a change of spin direction, then it is facilitated
as a result of Hund’s rule, and a ferromagnetic arrangement is preferred. A further
possibility is a direct interaction, whereby a triplet or singlet state results from the
close proximity of two paramagnetic centres. The most famous example of this is
the copper acetate dimer originally studied by Bleaney & Bowers (1952). Many
dinuclear carboxylates show similar behaviour, and in some cases have metal–
metal bonds, which can be regarded as arising from the very strong pairing of
the antiparallel electrons in favourable metal-based orbitals.

Further factors to consider are the relevant spin–orbit coupling schemes for
the paramagnetic ions in question and the degree of anisotropy within the
system. Some care needs to be taken with these since it is possible that what
might superficially appear to be antiferromagnetic coupling when viewing the
temperature dependence of the susceptibility in a cluster system can actually
originate in the high anisotropy of a system, for example, for clusters comprising
CoII ions (Klöwer et al. 2009).

(d) Homo- and heterometallic clusters

In terms of synthetic strategies, the routes to producing coordination clusters
with metal ions of one element are reasonably well investigated. Starting from
relatively simple metal precursors, such as simple salts or smaller coordination
clusters, can lead to a multitude of interesting coordination clusters via self-
assembly routes or by imposing specific binding regimes on the metal ions
in a more directed synthesis. In some cases, and relatively frequently for
manganese ions, these turn out to result in mixed-valent species. We can
term these as homometallic clusters, but bearing in mind that the metal ions
might not all be in the same oxidation (and thus spin) state. When it comes
to developing strategies for synthesizing mixed-metal coordination clusters, a
major hurdle to overcome initially was how to prevent the different metal
ions from forming homometallic clusters of the individual metal ions. Most
of what is discussed in the following explains approaches to overcoming this hurdle. The resulting compounds can be designated as heterometallic coordination clusters.

(e) Giant spin versus spin–orbit coupled systems

As the field of single-molecule magnetism has matured, it has become clear that the description of the electronic structure of a coordination cluster is not always straightforward. At the beginning of this research, several systems were studied where the ground spin state for the cluster could be rationalized in terms of a ‘giant spin’ model. This tends to work reasonably well for Heisenberg types of system where the anisotropy effects are relatively small or essentially non-existent (Ako et al. 2006; Waldmann et al. 2008). In favourable cases it is also possible to suggest the spin structure of the cluster in terms of the individual spins of the constituent metal ions. However, it soon became clear that the systems that show the strongest anisotropies are likely to produce the most useful SMMs, and these cannot adequately be described using a giant spin model. Such systems are often characterized by lack of saturation in their magnetization, which in turn does not allow a ground spin state to be assigned. This type of behaviour is seen frequently in homometallic clusters containing Mn$^{III}$ high-spin ions and is a consequence of the Ising nature of this configuration. It is also found that these sorts of clusters provide the SMMs with the most favourable parameters. This has led to the idea that it could be useful to mix metal ions and search for combinations that might optimize spin and anisotropy within one system. This has fuelled research into producing 3d–4f coordination clusters and screening their magnetic behaviour.

(f) Topological description of coordination clusters

Recently, we have developed a new approach for describing polynuclear clusters (Kostakis & Powell 2009). The approach is similar to the one that is used to describe MOFs, although in this case each metal centre of a cluster is a straightforward ‘node’ and the bridging heteroatoms then play the role of the ‘linker’. Thus, a vertex with connectivity given by \( N \) is connected to \( N \) neighbours, with \( M \) to \( M \) and so on. For example, a 2,3-connected cluster will have two sets of parameters, one for the 2-connected node (2-c.n.) and one for the 3-c.n., with these parameters giving information about the rings containing each node in the form of a total or cluster symbol corresponding to: (vertex symbol for 2-c.n.)$^{\text{subscript denoting number of occurrences}}$(vertex symbol for 3-c.n.)$^{\text{subscript denoting number of occurrences}}$. In this case, the 2-c.n. participate in only a three-membered ring, with the symbol being (3), and the two 3-c.n. participate in two three-membered rings and one four-membered ring, with the arithmetic representation being (3$^2$.4). The number that arises after counting all subscripts gives the total number of nodes in the cluster. In the cases where some nodes are repeated, then this can be simplified. For example, in the latter example there are four nodes, two for each 2-c.n. and 3-c.n., and therefore the total vertex symbol (v.s.) can be assigned as (3$^2$(3$^2$.4)$^2$.

Although the full symbols resulting from using this descriptive method can become rather long, they do allow for a complete description of the topology in the same way as the extensively used Schlafli notation for networks does. In future, we will develop analytical software to facilitate the description of coordination
clusters using approaches already developed for similar software for analysing three-dimensional networks. For the present, we have retained the use of the long symbols in this paper to assist the reader in a tutorial fashion.

3. Synthetic methods and resulting systems

(a) Hydro- and solvolytic synthesis and hydro- and solvothermal synthesis

Reactions carried out in protic solvents or where protic solvent molecules are available in the system result in compounds where metal centres are held together with a variety of oxygen bridges deriving from the solvent molecules present. These syntheses can be carried out at normal pressures and with only gentle conditions of heating, in which case we think of them simply as solvolysis reactions. Alternatively, the syntheses can be performed in sealed Teflon-lined autoclaves heated to temperatures above the boiling point of the solvent. During this process, an autogenous pressure will be developed and the reaction is described as hydro- or solvothermal. As a result of the higher pressure and elevated temperature, the reaction may be expected to proceed differently from the ambient reaction, not least because redox potentials and solvent properties are temperature- and pressure-dependent. Overall, the synthetic strategy is to halt the formation of the thermodynamic product of, for example, hydrolysis, which would be a metal oxide, and to trap portions of recognizable mineral lattices by using capping ligands to block sites of oxides or hydroxides. The resulting compounds can be zero-dimensional, in which case they are coordination clusters, or they can be networks of higher dimensionalities. We reviewed these approaches some years back in describing iron-based systems and their interesting magnetic properties, and the interested reader is directed to this review (Price et al. 1999).

(b) Routes to mixed 3d/4f

From a synthetic point of view, ways must be found to combine 3d and 4f ions within a coordination compound. Experience has shown that simply mixing the components does not lead to the self-assembly of the desired mixed compounds, but mostly to pure 3d compounds. This is probably the result of the ligand field stabilization for 3d compounds being a driving force. In order to circumvent this, two fruitful approaches have been developed. One is to design ligands that provide coordination pockets capable of both coordinating and connecting the different types of metal ion centres. In the other, an assisted self-assembly approach is used, where lanthanide ions combine with 3d transition metal ions deriving from polynuclear species in the presence of further coligands, which can also provide suitably stabilizing counterions/ligands to drive the reaction. Costes and co-workers have extensively employed the combination of 3d metals with Ln exhibiting a high anisotropy (Tb, Dy, Ho) as a prerequisite to designing SMMs (Costes et al. 2008 and references therein). Also, 3d–3d′–4f complexes have been reported. These were obtained through a stepwise synthetic procedure in which the metalloligand \([M(CN)6]^-\) is treated with preorganized trinuclear \([Co_2Ln(L)_2]^{3+}\) complexes to afford trimetallic magnets. For example, the compound \([Co_2Gd(L)_2(H_2O)_4][Cr(CN)_6]2H_2O\) \((H_2L=2,6-di(acetoacetyl)pyridine)\) is a three-dimensional network exhibiting

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three-dimensional ferromagnetic ordering with \( T_c = 15.4 \text{ K} \) (Shiga et al. 2006). More recently, a ‘site-targeted’ strategy has been proposed and developed. This allows mixed 3d/4f molecules to be investigated, where either the 4f or 3d sites can be swapped for different respective ions in order to gauge the influence that both can have on the magnetic properties of the resulting system.

(c) Schiff-base ligands and other ligand functionalizations to divide space

There are several examples of mixed metal systems that contain two or more ligands; however, there are few guarantees that this approach will lead to the two metal types cocrystallizing. Designing ligands with sites that favour two different types of metals is a more targeted approach. There is a growing number of systems that have different coordination environments either side of a phenolic group. By using salicyl aldehyde derivatives, it is straightforward to condense this with a useful amine, thus providing an imino nitrogen plus the additional coordination groups connected to the amine, which are, for example, favoured by CuII, FeII and MnIII ions. Introducing a further coordination site at the remaining ortho-position to the phenol, such as in \( o \)-vanillin, which has a methoxy group, results in a bidentate monomethyl catechol ether (guaiacol) type site, and is one way to capture metals that favour oxygen donors such as lanthanide ions. One such example is provided by a \{Cu5Gd2\} complex (1), where the aldehyde \( o \)-vanillin is condensed with the alcohol-rich amine tris(hydroxymethyl)aminomethane (Wu et al. 2007). Here, the CuII ions are each coordinated by the imine groups of the ligand, whereas the lanthanide ions are coordinated by the guaiacol group, and the numerous alcohol groups of the ligand, bromide counterions, phenol and oxo groups assist in linking the two types of metal together to give the discrete \{Cu5Gd2\} cluster (figure 1). Here ferromagnetic interactions are observed, giving rise to an \( S = 17/2 \) ground state. Simplifying the structure, Cu(1) is converted to a 6-c.n. with a v.s. (3.3.3.4.4), Cu(2) and Cu(3) are 2-c.n. with a v.s. (3) and finally Gd(1) is a 3-c.n. with a v.s. (3.3.4). The heptanuclear cluster can thus be considered as three-nodal (2,3,6) with total symbol (3)4(32.4)2(34.42).

In creating dinuclear \{CuLn\} complexes, the acyclic ligand formed by the condensation of two equivalents of \( o \)-vanillin to a diamine such as ethylenediamine has been studied (e.g. Costes et al. 1998). Here the CuII ions are again coordinated by the imine groups and the lanthanide is bridged through the phenol and coordinated to the methoxy groups. Recently, a similar unit was reported using hydroxymethyl groups in place of the methoxy groups, giving a similar dinuclear unit (Novitchi et al. 2009). However, it could then be shown that it is possible to link these dinuclear units together through the LnIII ions using benzene-1,3,5-tricarboxylic acid (H3btc), resulting in a propeller-type \{Cu5Tb3\} complex (2). These then form dimeric units containing both optical enantiomers linked through hydrogen bonding and the \( \pi–\pi \) stacking of the central btc3− ligand (figure 2). This assembly results in the observation of an enhanced single-molecule magnetic behaviour.

Of the many metal-based protein sites to have been modelled using standard coordination chemistry, the site within the photosystem II (PSII) protein is perhaps the most elusive. As the protein itself is photoactive, reliable X-ray-based structures are difficult to obtain and hence there is a need to try and replicate the Mn-based oxygen evolving centre (OEC) in the laboratory. The core has been
studied in some detail and is believed to contain a \{Mn_4Ca\} cluster. The most favoured topology has three Mn ions and a Ca in a tetrahedral arrangement, which with O sites forms a \{Mn_3CaO_4\} cubane with one of these Mn ions being oxo-linked to the fourth Mn ion. By using \(\phi\)-vanillin-based Schiff-base complexes, it has been possible to synthesize \{Mn_4Ca\} and \{Mn_4Na\} complexes (3) using a number of amino alcohols (Hewitt et al. 2006). One of these complexes is shown in figure 3. Here, three Mn\(\text{III}\) ions are coordinated by imine groups of the ligand,
Figure 2. (a) Scheme of the ligand used; (b) the assembled \{Cu₃Tb₃\} complex (2); which (c) cocrystallizes in enantiomeric pairs.
resulting in an oxo-centred triangle that forms the base of the tetrahedral plane. The phenol groups each bridge to a Ca or Na ion that is also coordinated by the methoxy groups from the o-vanillin aldehyde, while the amino alcohol with which the aldehyde has been condensed links the fourth Mn ion via the oxo site. Given the rarity of Mn–Ca complexes that exhibit direct relevance to the OEC in PSII, this approach looks particularly attractive. Simplifying the core of 3, a trigonal bipyramidal polyhedron is formed. Na(1) and Mn(4) are at the apices of the polyhedron, while Mn(1), Mn(2) and Mn(3) form the equatorial plane. Na(1) and Mn(4) are connected to Mn(1), Mn(2) and Mn(3), forming two 3-c.n. and three three-membered rings, while Mn(1), Mn(2) and Mn(3) can be considered as 4-c.n. with v.s. (3.3.3.3.3.42). In this way, a binodal (3,4) cluster is formed with total symbol (33)2(35.4)3.

Salicylhydroxamic acid is related to salicyl aldehyde, having an oxime attached to the carbonyl group. Depending on the orientation around the carbonyl group, the phenol can coordinate in conjunction with the N atom of the oxime or the O atom of the carbonyl. In the {Mn\textsuperscript{III}Dy\textsuperscript{III}} complex (4) reported by Zaleski \textit{et al.} (2004), the N atoms of the oxime groups all coordinate to the Mn\textsuperscript{III} ions present, and the O atoms of the carbonyl and oxime coordinate to the Dy\textsuperscript{III} atoms.
in a bidentate mode. In the simplified version of the compound, all Mn atoms are terminal points; therefore, a six-membered ring is formed through the six Dy atoms in a ‘chair’ conformation. Dy(1) and Dy(2) are 2-c.n., while Dy(3) is 5-c.n., but the v.s. of the three-nodal cluster is (6) (figure 4).

(d) Assisted self-assembly reactions

It has been found that preformed 3d metal carboxylato aggregates can be combined with simple metal salts in the presence of N-substituted diethanolamine ligands, possibly with further coligands, to produce larger
aggregates. This type of approach has been successfully applied by a number of groups to produce larger 3d clusters (Christou 1989, 2005), and it was recently shown to be a useful method for combining 3d and 4f metals within one aggregate (Murugesu et al. 2006; Milios et al. 2007).

For example, the isostructural cluster anions of general formula $[\text{Fe}^{\text{III}}\text{Ln}^{\text{III}}_{12}(\text{piv})_{12}(\text{NO}_3)_4(\text{OAc})_4]^- \ (5)$ for Ln = Pr, Nd and Gd and where piv$^-$ = CM$_3$CO$_2^-$ were synthesized by reaction of nBu-deaH$_2$ (dea = diethanolaminato) with $[\text{Fe}_3\text{O}(\text{piv})_6(\text{H}_2\text{O})_3](\text{piv})$ and Ln(NO$_3$)$_3\cdot x\text{H}_2\text{O}$ in the presence of NaOAc·3H$_2$O (Ako et al. 2007).

With reference to the structure for the Gd$^{\text{III}}$-containing compound, the $[\text{Fe}^{\text{III}}\text{Ln}^{\text{III}}_{12}]^{39+}$ core is held together by 12 $\mu_3$-OH$^-$ ions (figure 5). Peripheral ligation is provided by four chelating/bridging ($\mu_3$:$\eta^1$:$\eta^2$) dea$^2^-$, 12 bridging ($\mu$:$\eta^1$:$\eta^1$) piv$^-$, four bridging ($\mu$:$\eta^2$:$\eta^1$) MeCO$_2$ and four chelating and bridging ($\mu$:$\eta^1$:$\eta^1$) NO$_3^-$ ligands. The core of the centrosymmetric tridecanuclear cluster can be viewed as consisting of two distorted heterometallic $[\text{FeGd}_3(\mu_3\text{-OH}^\cdot)_4]^{8+}$ cubane units sharing Fe(1) as a common vertex. These are flanked by four edge-sharing heterometallic $[\text{FeGd}_2(\text{OH})_4]^{5+}$ units. Six of the eight Gd$^{\text{III}}$ ions are arranged in a planar hexagonal ring capped above and below the plane by the other two Gd(1) and Gd(1$'$). All five Fe$^{\text{III}}$ are close to coplanar, with four Fe$^{\text{III}}$ atoms located at the vertices of a rectangle and the fifth at the centre. In this way, the trinuclear iron starting material provides pivalate coordination to the lanthanide ions, and the acetates introduced from the sodium acetate link the ring Gd ions in a $\mu_2$:$\eta^2$:$\eta^1$ fashion, while the nitrates chelate exclusively to the out-of-plane Gd ions. Overall, each of the four peripheral Fe$^{\text{III}}$ ions is bridged to two Ln centres by two $\mu$:$\eta^1$:$\eta^1$ pivalate ligands, one $\mu_3$-OH$^-$ ion, and two $\mu$-oxygens from a nBu-dea$^2^-$ ligand, while the central Fe$^{\text{III}}$ ion is bridged to six Ln ions through six $\mu_3$-OH$^-$ groups. All the Fe atoms are 6-coordinate, exhibiting a distorted octahedral coordination geometry through six $\mu_3$-OH$^-$ ligands for the central Fe(1) atom, and an NO$_5$ chromophore consisting of an O$_2$N donor set from a dea$^2^-$ ligand moiety, one $\mu_3$-OH$^-$ group, and two bridging pivalate oxygens, for the peripheral Fe atoms. In contrast, the Ln atoms show three different types of coordination geometries: types I and II, 9-coordinate, and type III, 8-coordinate, all varying in their coordination environment. This underlines that the assisted self-assembly approach involves providing sufficient ligating and bridging species to satisfy the Ln coordination sphere. It can also be noted that the hydrolysis of water to provide the hydroxide bridges is an important feature of this chemistry. Simplifying the tridecanuclear metal–oxygen core, Fe(1) is a 6-c.n. with a v.s. (3.3.3.3.3.4.5.5.5.5.5.5.5), while both Fe(2) and Fe(3) are 2-c.n. with a v.s. (3). Gd(1) is a 3-c.n. with a v.s. (3.3.3), Gd(2) and Gd(3) are 5-c.n. with a v.s. (3.3.3.3.4.5.5.5.6.6) and finally Gd(4) is a 4-c.n. with v.s. (3.3.4.6.5.5). The cluster can be considered as five-nodal (2,3,4,5,6) and the total symbol is $(3^2.4.5^2.6)_2(3^3)_{2}(3^4.4.5^3.6^2)_4(3^6.4^2.5^6.6)(3)_{4}$. Magnetic measurements show that the compounds are weakly coupled, with the Gd compound displaying ferromagnetic coupling. None of the compounds showed slow relaxation of the magnetization and so do not possess single-molecule magnetic properties.

Using a similar strategy, the preformed hexanuclear Mn complex $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}\text{O}_2(\text{piv})_{10}(4\text{-Me-py})_{2.5}(\text{pivH})_{1.5}]$ was used as a source of Mn$^{\text{II/III}}$. The reaction of this with Gd(NO$_3$)$_3\cdot 6\text{H}_2\text{O}$ in the presence of 2-furan-carboxylic acid (fcaH)
Figure 5. (a) The structure of (5); (b) the core; and (c) its simplified version. Hydrogen atoms, apart from those in the core, have been omitted for clarity.
in CH$_3$CN results in the formation of the high-nuclearity complex [Mn$^{II}_9$ Mn$^{II}_2$Gd$_2$(O)$_8$(OH)$_2$(piv)$_{10.6}$(fca)$_{6.4}$(NO$_3$)$_2$(H$_2$O)]·13CH$_3$CN·H$_2$O (6) (Mereacre et al. 2007). The structure of 6 is shown in figure 6. The oxidation states of the manganese ions were assigned through a consideration of the coordination geometries and bond valence sum (BVS) calculations. Thus, Mn(1)–Mn(9) were
assigned as Mn\textsuperscript{III}, and Mn(10) and Mn(11) as Mn\textsuperscript{II}. The assignments of O(10) as \( \mu_3\text{-O}^2^- \) and of O(2) and O(3) as \( \mu_3\text{-OH}^- \) were also confirmed by BVS calculations, and the H atoms on O(2) and O(3) could be located and refined. The core can be described as bell-shaped. The Mn\textsuperscript{III} and Mn\textsuperscript{II} centres form the shell of the bell, with Mn(9) at the apex, Mn(5), Mn(8), Mn(10) and Mn(11) at the shoulder of the bell, and the remaining six Mn\textsuperscript{III} centres forming the rim of the bell. The two Gd centres can be thought of as forming the bell’s clapper, and, since the Gd···Gd vector is inclined with respect to the axis of the bell, this gives the impression that the bell is ringing. Gd(1) is 10-coordinate, and is connected to each of the 11 Mn atoms through the six \( \mu_4\text{-O} \), one \( \mu_3\text{-O} \) and two \( \mu_3\text{-OH} \) bridges. Its coordination polyhedron may best be described as a bicapped square antiprism. The second Gd is 9-coordinate and hangs below the rim of the bell. It is connected to the other Gd and four of the Mn\textsuperscript{III} atoms through one \( \mu_4\text{-O} \) and the two \( \mu_3\text{-OH} \) bridges, and two oxygen atoms from two \( \mu_3\text{-carboxylate} \) bridges. Its coordination sphere is completed by two chelating nitrate ions. The Mn centres all have octahedral coordination geometries, except for Mn(6), which is square pyramidal, with the Mn\textsuperscript{III} all showing the expected Jahn–Teller distortions. Of the 17 carboxylate ligands (10 pivalate, six furoate and one that is a disordered superposition), the unusual \( \mu_4\text{-bridging} \) \( \mu_3\text{-bridging} \) mode is seen for one furoate and one pivalate ligand. In addition to these \( \mu_4\text{-bridging} \) carboxylates, four of the furoates adopt a \( \mu_3\text{-bridging} \) \( \mu_3\text{-bridging} \) triply bridging mode, while the sixth furoate and all the remaining pivalates form simple bridges between two metal centres. In other words, five of the six furoates bridge between three or four metal centres, whereas all but one of the pivalates adopt a simple \( \mu\text{-bridging} \) mode. The Mn\textsuperscript{III} Jahn–Teller axes have an irregular arrangement within the aggregate core. Simplifying the core, Mn(1), Mn(2), Mn(5), Mn(8), Mn(10) and Mn(11) are 5-c.n. with v.s. (3.3.3.3.3.3.4.4.2.4.2), while Mn(3) and Mn(4) are 6-c.n. with v.s. (3.3.3.3.3.3.3.4.4.4.4.2.4.2) and Mn(6) and Mn(7) are 4-c.n. with v.s. (3.3.3.3.4.3.4). Finally, Mn(9) is 5-c.n. with v.s. (3.3.3.3.3.3.4.4.4.4.4). Gd(1) is a 12-c.n. with the short v.s. being \( (3^2.4^{31}.5^1) \), while Gd(2) is a simple 5-c.n. with v.s. (3.3.3.3.3.3.4.4.2.4.2). Therefore, the cluster can be considered as five-nodal with 4-, 5-, 6- and 12-c.n. and total symbol \( (3^2.4^{31}.5^1)(3^1.4^2)(3^{3}.4^3)(3^{7}.4^3) \).

The DC magnetic susceptibility was measured at 1000 Oe in the 1.8–300 K temperature range, and showed a room-temperature \( \chi T \) value per complex of 46.9 cm\textsuperscript{3} K mol\textsuperscript{-1}. On lowering the temperature, \( \chi T \) first continuously decreases, reaching 35.2 cm\textsuperscript{3} K mol\textsuperscript{-1} at 37 K, and then increases to a maximum value at 1.81 K of 74.5 cm\textsuperscript{3} K mol\textsuperscript{-1}. The fact that the \( \chi T \) product starts to saturate at 1.81 K suggests that, below this temperature, a well-defined high-spin ground state is almost exclusively thermally populated. The fit of the experimental data to a Curie–Weiss law above 30 K leads to a Curie constant of 50.8 cm\textsuperscript{3} K mol\textsuperscript{-1} and a Weiss constant of \(-28.1\) K, indicating dominant antiferromagnetic interactions between spin carriers. The Curie constant is close to the expected value for nine Mn\textsuperscript{III} \( (S = 2) \), two Mn\textsuperscript{II} \( (S = 5/2) \) and two Gd\textsuperscript{III} \( (S = 7/2) \) non-interacting ions \( (51.5 \text{ cm}^3 \text{ K mol}^{-1}) \).

The AC susceptibility measurements taken over the frequency range 1–1500 Hz and at temperatures 1.8–3 K display frequency-dependent out-of-phase signals indicative of slow relaxation of its magnetization and single-molecule magnetic behaviour. This was further investigated using micro-SQUID (superconducting quantum interference device) measurements at temperatures down to 40 mK.
Hysteresis loops collected at varying temperatures and sweep rates (figure 7) show a superparamagnetic-like increasing coercivity with decreasing temperature, confirming the compound to be an SMM. No steps due to quantum tunnelling of magnetization (QTM) were observed, probably as a result of ligand and lattice solvent disorder, as there are no obvious pathways for intermolecular interactions. DC magnetization decay data were collected in the 0.04–1.0 K range: at each temperature, the magnetization was saturated with a DC field, the temperature lowered to a chosen value, the field switched off and the decay monitored with time. The data were scaled to give a single master curve in order to construct the Arrhenius plot, and the fit of the thermally activated region above approximately 0.5 K gave $\tau_0 = 2 \times 10^{-12}$ s and an effective barrier $\Delta E/k_B = 18.4$ K, which was the highest value reported at this time for 3d–4f SMMs. Given the lack of obvious intermolecular interactions, the relatively low value of $\tau_0$ compared with other 3d–4f SMMs might be the result of the presence of a higher spin state. Below approximately 0.16 K, the relaxation time becomes essentially temperature-independent, consistent with the purely quantum regime, where QTM is only via the lowest energy $\pm m_s$ levels. It is possible that the Jahn–Teller distortions of the Mn$^{\text{III}}$ centres provide the major contribution to the anisotropy, with the Mn$^{\text{II}}$ and Gd$^{\text{III}}$ centres contributing to the spin.

**Site-targeted reactions**

Selective replacement of components of 3d–4f clusters has been identified as a promising way of studying how the different electronic structures and properties of the 3d and 4f ions can contribute to single-molecule magnetic behaviour. Compounds containing lanthanide ions often have the useful property that they form isostructures for given groups of 4f ions. We have found that it is possible to produce 3d/4f systems using assisted self-assembly reactions, where we can then choose to vary the 3d or 4f site, for example, by replacing

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isotropic Fe$^{III}$ with anisotropic Mn$^{III}$ and studying the effect on magnetic behaviour with a variety of 4f ions. It should also be noted that it is often the case that the larger lanthanide ions to the left of the series form one structural type, whereas those to the right form a different structure. For example, we found that it was possible to produce the Mn$^{III}$ analogues of the $[\text{Fe}^{III}_5\text{Ln}_8(\mu_3-\text{OH})_{12}(\text{piv})_{12}(\text{NO}_3)_4(\text{OAc})_4]^{-}$ (5) described above, but using $^1\text{Bu}-\text{N}$-diethanolamine in place of $^3\text{Bu}-\text{N}$-diethanolamine to give $[\text{Mn}^{III}_5\text{Ln}_8(\mu_3-\text{OH})_{12}(\text{piv})_{12}(\text{NO}_3)_4(\text{OAc})_4]^{-}$ (7) (Ako et al. 2009). Indeed, for the Mn$^{III}$ series it proves possible to crystallize examples further to the right in the lanthanide series up to the (often magnetically more interesting) Tb$^{III}$ analogue. We found that the Pr$^{III}$ and Nd$^{III}$ compounds have dominant antiferromagnetic interactions, the Sm$^{III}$ compound is paramagnetic, and the Gd$^{III}$ and Tb$^{III}$ compounds are ferromagnetically coupled with large spin ground states. However, although the Tb analogue also shows a significant anisotropy, we could not observe any slow relaxation of the magnetization, at least above 1.8 K.

This general approach did, however, lead to a series of SMMs when the diethanolamine ligand was changed to $N$-methylldiethanolamine (Mereacre et al. 2008) Here, we can illustrate how selective replacement of the lanthanide ions in a $[\text{Mn}_5\text{Ln}_4]$ single-molecule magnetic system forming with the smaller-radius Ln$^{III}$ ions can be used to establish the influences of the individual components on single-molecule magnetic behaviour. The assisted self-assembly reaction of $[\text{Mn}_6\text{O}_2(\text{piv})_{10}(4-\text{Me-py})_{2.5}(\text{pivH})_{1.5}]$ with $N$-methylldiethanolamine (mdeaH$_2$) and Ln(NO$_3$_3)$_3$·6H$_2$O leads to the formation of isostructural crystals of $[\text{Mn}_5\text{Ln}_4(\text{O})_6(\text{mdea})_2(\text{mdeaH})_2(\text{piv})_{6}(\text{NO}_3)_4(\text{H}_2\text{O})_2]$:2MeCN (8). By using Ln$^{3+}$ = Tb, Dy, Ho and Y it was possible to vary the contribution of Ln to the overall electronic structure of the system in a targeted fashion. We note here that the rare earth ion Y$^{3+}$ has an ionic radius of similar size to that of Ho$^{3+}$, but is, of course, diamagnetic. In this way, it was possible to compare the magnetic behaviour for an isostructural series of compounds, where the contribution from the Ln could be completely switched off.

The molecular structure of 8 (figure 8a) consists of a centrosymmetric $\{\text{Mn}_5\text{Ln}_4\}^{28+}$ core, held together by four $\mu_3$-$\text{O}^{2-}$ and two $\mu_4$-$\text{O}^{2-}$ ligands, and the oxygen atoms of two mono-deprotonated $\eta^2:\eta^2:\eta^1:\mu^2$- and two doubly deprotonated $\eta^3:\eta^2:\eta^1:\mu^4$-diethanolamine ligands. The structure is further described for the Dy analogue. Peripheral ligation is provided by six $\mu$-pivolate anions, four nitrate anions (one chelating each Ln ion) and a water molecule on each of Dy(2) and Dy(2a). The metal oxidation states (Mn$^{III}$, Mn$^{IV}$, Dy$^{III}$) and the deprotonation levels of $\text{O}^{2-}$, mdea$^{2-}$ and mdea$^{H-}$ ions were established by charge considerations, BVS calculations, inspection of metric parameters and the observation of Jahn–Teller elongation axes of Mn$^{III}$. All five Mn atoms are 6-coordinate. Dy(1) is 9-coordinate with a coordination polyhedron that may best be described as a triaugmented triangular prism, while Dy(2) is 8-coordinate and the coordination polyhedron could be described as between a distorted bicapped trigonal prism and a square anti-prism. Inspection of the central core reveals two distorted $\{\text{Mn}^{IV}\text{Mn}^{III}\text{Dy}_2\text{O}_4\}$ cubanes sharing a Mn$^{IV}$ vertex, Mn(1). One oxo ligand in each cubane, O(1), bridges to a further Mn$^{III}$ centre, Mn(3), which is further linked to Mn(2) and two Dy centres in the dicubane core by diethanolamine oxygen atoms. The mono-deprotonated mdea$^{H-}$ groups act as tridentate chelates on each of the outer Mn (Mn(3),
Figure 8. (a) Structure of 8; and (b) its simplified version.

Mn(3a)) atoms, while the two doubly deprotonated mdea\(^{2-}\) anions each chelate Dy(2). The Mn\(^{III}\) ions have the expected octahedral geometries with Jahn–Teller elongations along one axis, while Mn\(^{IV}\) has a rather symmetric octahedral
Scheme 1. Spin topology of the intra-complex magnetic interactions for the [Mn₅Y₄] derivative.

geometry. Simplifying the structure (figure 8b), Mn(1) is converted to an 8-c.n. with a v.s. (3.3.3.3.3.3.3.4.4.4.4.4.4.4.4.4.4.4.2.5₂₂.5₂.5₂.5₂.5₄.5₁), while the remaining nodes are 4-c.n. and possess different v.s., with (3.3.3.4.3.4) for Mn(2) and Mn(3) and (3.3.3.3.4₂) for Dy(1) and Dy(2). The cluster can thus be considered as three-nodal (4,8) with total symbol (3₁₂.₄¹₀.₅₆)(3₄.₄²)(3₅.₄).

The magnetic properties of all the complexes were studied. In the Y₃ compound, the rare earth ions are diamagnetic, which allows the contribution of the Mn₃ MnIV unit to be assessed. When the temperature is lowered at a field of 0.1T, the \( cT \) product of 8 decreases to a minimum value of 1.8 cm³ K mol⁻¹ at 1.8 K. Based on the structure of the compound, the \( cT \) product was simulated taking into account only three isotropic intra-complex magnetic interactions as shown in scheme 1 and neglecting the low-temperature data (below 20 K) to avoid additional effects coming from the magnetic anisotropy and/or weak inter-complex interactions. The following spin Heisenberg Hamiltonian was thus considered:

\[
H = -J_1 S_5 \cdot (S_1 + S_3) - J_2 S_5 \cdot (S_2 + S_4) - J_3 (S_1 \cdot S_2 + S_3 \cdot S_4)
\]

(3.1)

where \( J_1, J_2 \) and \( J_3 \) are the exchange interactions between MnIII and MnIV sites through double O bridges between MnIII and MnIV ions, through single O bridges, and between MnIII ions through single alkoxo bridges, respectively, and \( S_i \) are the spin vectors for each of the metal ions (\( S_i = 2 \) for MnIII with \( i = 1–4 \) and \( S_5 = 3/2 \) for MnIV). The simulation of the experimental data above 10 K gave \( J_1/k_B = -90(4) \) K, \( J_2/k_B = +12(1) \) K, \( J_3/k_B = -18(1) \) K and \( g = 2.1(1) \). Therefore, even if ferromagnetic interactions are present between MnIII and MnIV, the antiferromagnetic interactions dominate and lead to a global decrease of the \( cT \) product at high temperature as was, indeed, observed experimentally for all the compounds. This set of magnetic interactions induces an \( S_T = 3/2 \) ground state with the spin topology given in scheme 1. At 1.85 K, \( M \) versus \( H \) measurements revealed a lack of true saturation even at 7 T at which \( M \) reaches 2.7 \( \mu_B \), in good agreement with an \( S_T = 3/2 \) ground state. The slow saturation of the magnetization confirms also the presence of a significant anisotropy as expected in the presence of MnIII metal ions.

By studying the dynamics of the relaxation of the magnetization for all compounds, it was possible to estimate barrier heights for each. Thus, the [Mn₅Y₄] compound was found to have an energy gap of 20.2 K, while the ‘best’ of the SMMs was found to be [Mn₅Dy₄] with an almost doubled gap of 38.6 K. This compound shows a nice hysteresis behaviour, which is already visible at 1.8 K.
Figure 9. Field dependence of the magnetization measured in the easy direction of a single crystal of [Mn$_5$Dy$_4$]. (a) The temperature dependence at a fixed scan rate of 2 mT s$^{-1}$. (b) The scan rate dependence at a fixed temperature of 1 K.

This was the highest barrier recorded for 3d–4f systems and suggests promising ways forward in introducing rare earth anisotropy into single-molecule magnetic systems.

(f) Metal–organic frameworks and super metal–organic frameworks

The chemistry of coordination networks or MOFs is a subject that increasingly captures researchers' interest owing to the variety of compositions and topologies of the compounds produced. A series of two- or three-dimensional magnetic system coordination polymers or MOFs, behaving as ferromagnetic, antiferromagnetic or metamagnetic materials and possessing novel or very rare topologies, have been synthesized in our group.

In 2003, the synthesis of the three-dimensional MOF formulated as Cu$_3$(dcp)$_2$(H$_2$O)$_4$ (9), where dcpH$_3$ = 3,5-pyrazoledicarboxylic acid, was reported (King et al. 2003). In compound 9, trinuclear Cu$_3$(dcp)$_2$(H$_2$O)$_4$ repeating units in which two dcp$^{3-}$ ligands chelate the three Cu$^{II}$ ions with the central Cu$^{II}$

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ion, Cu(1) (on an inversion centre), link to form infinite two-dimensional sheets via syn–anti equatorial–equatorial carboxylate bridges between Cu(2) atoms in adjacent trimers. These layers are further linked by syn–anti axial–equatorial carboxylate bridging between Cu(1) atoms in adjacent sheets, resulting in the formation of a crystallographic three-dimensional network. Topologically, Cu(1) can be assigned as node A and the geometric centroid of the ligand can be assigned as node B. The Cu(2) metal centre is not a part of this network. In this way, the neutral three-dimensional network is formulated as AB2. Node A is connected through four short pillars to four B nodes possessing a square geometry, whereas node B is bridged to two A and two B nodes through two short and two elongated pillars adopting a tetrahedral configuration. The decorated compound that is formed is a four-connected binodal network, possessing a bbf topological structure (figure 10). The Schlafli symbol for a bbf network is \((6^4.8^2)(6^6)_2\), while the extended symbol for each node is \((6.6.6.6.6.6.6.6)_2\) for nodes A and B, respectively. The structure is related to the moganite (\(\text{mog}\)) structure (Kostakis et al. 2009a). To our knowledge (O’Keeffe et al. 2008), compound 9 represents the second example in the literature having a bbf topology (Zasurskaya et al. 2001). Magnetic studies on 9 reveal that the dcp\(^3\)− ligand acts to link Cu\(^{II}\) centres in three different ways, with coupling constants orders of magnitude apart in value. Above 50 K, the dominant interaction is strongly antiferromagnetic \((J/k_B = -32 K)\) within the trimer units mediated by the pyrazolate bridges. Below 20 K, the trimer motif can be modelled as an \(S = 1/2\) unit. These units are coupled to their neighbours by a ferromagnetic interaction mediated by the syn–anti equatorial–equatorial carboxylate bridge. This interaction has been estimated at \(J_{2D}/k_B = +2.8 K\) on the basis of a two-dimensional square lattice Heisenberg model. Finally, below 3.2 K a weak antiferromagnetic coupling \((J_{3D}/k_B = -0.1 K)\), which is mediated by the syn–anti axial–equatorial carboxylate bridges between the two-dimensional layers, becomes relevant to describe the magnetic \((T, H)\) phase diagram of this material.

Extending our systematic study on Cu\(^{II}\) multidimensional compounds, we recently reported the synthesis of an infinite two-dimensional network \([\text{Cu(N}_3)(p-\text{CPA})]_n\) (11), where \(p-\text{CPAH} = p\)-cyanophenoxyacetic acid (figure 11; Kostakis et al. 2009b). Cu(1) has a square pyramidal coordination environment \((\text{CuO}_2\text{N}_3)\). The equatorial plane is completed by two mutually trans carboxylato oxygen atoms, O(1) and O(2′), and two azide nitrogen atoms, N(2) and N(2′), with the four equatorial Cu–N/O distances in the range 1.9535(11)–1.9806(14) Å, while the apical position is occupied by the nitrile nitrogen atom of a CPA− ligand from an adjacent chain, Cu(1)–N(1′) = 2.5557(17) Å. Each pair of adjacent Cu centres in the chain are thus bridged by an end-on \((\mu_2,\eta^1-N_3)\) ligand and a syn–syn carboxylate bridge; the end-on azide bridge makes a Cu–N–Cu angle of 107.03(7)° and the intra-chain Cu⋯Cu separation is 3.1757(3) Å. Topologically, each Cu\(^{II}\) and the \(p\)-CPA ligand act as 5-c.n. and 3-c.n., to generate a new \((3,5)\) two-dimensional network (figure 11b). The total symbol for 11 is \((3.4.5)(3^2.4.5.6^2.7^4)\) and the network has been deposited in the TOPOS database as gek1. The Cu\(^{II}\) centres are one-dimensionally linked by end-on azide and syn–syn carboxylate bridges mediating strong ferromagnetic coupling along the infinite one-dimensional chain. The two-dimensional magnetic network exhibits spin orientation behaviour at low temperature, which has been confirmed from heat-capacity measurements.
Recently, four three-dimensional MOFs, \([\text{Mn}_3(3\text{-Me-sal})_4(\text{py})_4]_n\) \((12)\), \([\text{Mn}_3(4\text{-Me-sal})_4(\text{py})_4(\text{MeOH})]_n\cdot n(\text{H}_2\text{O})\) \((13)\), \([\text{Mn}_3(5\text{-Me-sal})_4(\text{py})_4(\text{H}_2\text{O})_2]_n\cdot n(\text{MeOH})\) \((14)\) and \([\text{Mn}_3(3\text{-Me-sal})_4(4\text{-Me-py})_4]_n\) \((15)\), and the one-dimensional coordination polymer \(\{[\text{Mn}_2(4\text{-Me-sal})_2(4\text{-Me-py})_2(\text{H}_2\text{O})_2(\text{MeOH})_2][\text{Mn}(4\text{-Me-sal})_2(4\text{-Me-py})_2]\}_n\) \((16)\) have been reported \((\text{Mukherjee et al. 2009})\). The topology of compounds \(12–15\) can be described as diamondoid networks \((\text{figure 12})\). Magnetic
Figure 11. (a) Structure of 11 in the crystal showing intra- and inter-chain linkages. Symmetry codes: (') 1/2 – x, y – 1/2, 1/2 – z; (") – x, 1 – y, 1 – z. (b) Topological representation of the \textit{gek1} two-dimensional net with total Schläfli symbol (3.4.5)(3^2.4.5.6^2.7^4).

studies (figure 13) show that weak Mn\textsuperscript{II}–Mn\textsuperscript{III} antiferromagnetic interactions (in the range of approx. $-0.55$ to $-0.22$ K) mediated by syn–anti carboxylate bridges are present in all compounds. While 16 remains paramagnetic down to 1.8 K, the three-dimensional networks exhibit long-range ferrimagnetic ordering below 7.4 K (12), 4.6 K (13), 3.0 K (14) and 7.7 K (15). The decrease of the critical temperature reflects the increase of the coordination sphere number around the Mn\textsuperscript{II} site from four in 12, five in 13 and six in 14, which lowers the bond strength and also the magnetic interactions. This result also reinforces the hypothesis that the structures of 12 and 15 are similar, as also suggested by the X-ray analysis.

Bearing in mind the magnetic anisotropy presented in Co\textsuperscript{II} centres, we carried out a systematic study on the system CoCl\textsubscript{2}/trans-3-pyridylacrylic acid (3-pycaH)/Et\textsubscript{3}N (Mondal \textit{et al.} 2009), which resulted in the formation of a new three-dimensional MOF (figure 14a) formulated as $\{[\text{Co}_4(\mu_2-H_2O)_2(3-pyca)_{8}]_{0.94}\{\text{Co}_5(\mu_3-OH)_2(3-pyca)_{8}\}_{0.06}\}$ (17). By varying the reaction conditions, different products can be obtained. Topologically, compound 17 can be considered

\cite{Mondal2009, Mondal2010, Mondal2011, Mondal2012, Mondal2013}
as a rare 5-connected noz (only seven examples were found in the literature) or a 6-connected pcu network. The magnetic measurements (figure 14b) show that the complex exhibits a combination of spin-canting and metamagnetic phenomena.
below the critical temperature of 9.5 K. In addition, the system shows a hysteresis loop characteristic of a magnet with a coercive field of 500 G and a remanent magnetization of 0.075 N\(\beta\).

In coordination polymer chemistry, the synthesis of multidimensional compounds using polynuclear clusters as nodes represents a great challenge. Along these lines, we published a compound that can be viewed as a hierarchical assembly of Fe
\(_{13}\) oxygen-bridged clusters linked into a close-packed superstructure.

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Figure 13. (a) Temperature dependence of the \(\chi T\) product of 12 at 1000 Oe (with \(\chi = M / H\)) and (inset) temperature dependence of the susceptibility below 20 K at 1000 Oe. (b) Field dependence of the magnetization from 1.8 to 8 K hysteresis loop at 2 K and (inset).
Figure 14. (a) The Co$_4$ unit found in 17. (b) Plots of $\chi M T$ versus $T$ at the indicated applied magnetic fields below 50 K.

$\left\{\text{Fe}_{13}(\mu_3\text{-OH})_6(\mu_3\text{-O})_6(\text{Hntp})_8(H_2O)_6}\right\} \left\{\text{Fe}_{13}(\mu_3\text{-OH})_6(\mu_3\text{-O})_6(\text{Hntp})_8\right\}_2(\text{NO}_3)_{15\cdot 55}H_2O$ (18) (Hntp = HN(CH$_2$CH$_2$COO)$_3$; Murugesu et al. 2005). Two different kinds of Fe$_{13}$ clusters can be found in 18, $\left\{\text{Fe}_{13}(\mu_3\text{-OH})_6(\mu_3\text{-O})_6(\text{Hntp})_8(H_2O)_6\right\}^{15+}$ (cluster A, figure 15a) and $\left\{\text{Fe}_{13}(\mu_3\text{-OH})_6(\mu_3\text{-O})_6(\text{Hntp})_8\right\}_2^{15+}$ (cluster B, figure 15b). Both clusters can be considered as 6-c.n., which are extended through carboxylate bridges, forming the three-dimensional super metal–organic framework (SMOF) KIT-100 (figure 15c), whose topology can be considered as a polytype of the NaCl structure. Magnetic measurements on this compound reveal a complex behaviour, reflecting the hierarchical nature of the structure. Slow relaxation of the magnetization, which becomes time- and temperature-independent, is observed, and the system can be described as comprising coordinatively and magnetically linked Fe$_{13}$ SMMs.

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Figure 15. The molecular structures of (a) cluster A and (b) cluster B found in 18 and (c) the topological representation of the SMOF KIT-100.

4. Summary and conclusions

In this paper, we have shown how molecular-based magnetism has driven coordination chemists to develop synthetic routes in order to create compounds with targeted topologies and dimensionalities. When the dimensionality is zero, we have coordination clusters that we have shown can be described using a topological approach similar to that developed for describing networks. Since this approach is completely new, it will be necessary first to establish a database of topologies and then to analyse this in order to discover magnetostructural relationships. With this in mind, we note that $[\text{Cu}(\text{L})(\text{N}_3)(\text{H}_2\text{O})_{0.5}]_n$ ($\text{L} = \text{nicotinate N-oxide}$) (He et al. 2006) can be topologically analysed and was found by us also to possess the gek1 topology described above for compound 11. It is noteworthy that $[\text{Cu}(\text{L})(\text{N}_3)(\text{H}_2\text{O})_{0.5}]_n$ exhibits similar spin-orientation magnetic
behaviour to that found for compound 11 described above. The successful application of topological analysis for networks in this way suggests that our new approach for describing cluster topology might significantly simplify the analysis of zero-dimensional systems.

References


