

Subproject C1.2

Synthesis and Characterization of Molecular Nanomagnets

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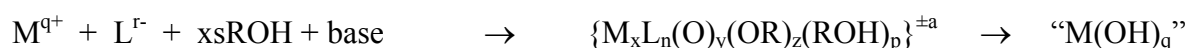
Synthesis and Characterization of Molecular Nanomagnets

Introduction and Summary

The major goal within this project was the synthesis, structural characterisation and investigation of the magnetic behaviour of polynuclear metal complexes, “coordination clusters”, in which the cooperative magnetic coupling of the spins on the individual paramagnetic centres results in unusual magnetic properties. Such compounds generally have a central “inorganic” core in which paramagnetic cations are bridged by a combination of oxo, hydroxo and alkoxo bridges, which mediate magnetic interactions between the metal centres. This core is then surrounded by organic ligands which prevent further nucleation, giving rise to molecular nanoscale particles. This “bottom-up” approach thus gives crystalline monodisperse materials, in which the molecules can be structurally characterized to high precision using X-ray crystallography, allowing correlation of magnetic properties with molecular structure. Initially, our work within the CFN was divided between two Subprojects, with C1.2 concentrating on the development of synthetic methods and structural characterisation, while detailed magnetic studies were undertaken in the context of C3.7. In 2008, Subproject C3.7 was subsumed into C1.2, and this report therefore includes work done during the period 2006-2008 within C3.7.

In the 1990s it was found[1] that some molecular aggregates of magnetically-coupled paramagnetic metal cations, the so-called Single-Molecule Magnets (SMMs), can show magnetic hysteresis, and in some cases also Quantum Tunneling of Magnetisation (QTM). These have obvious potential applications in high-density data storage and quantum computing. The conditions necessary for SMM behavior are now much better understood. The height of the energy barrier U to the reorientation of the ground state spin S is given by $U = -DS^2$ or $U = -D(S^2 - 1/4)$ for integer or half-integer spins, respectively. A large barrier therefore requires both a non-zero (and preferably large) spin S and a negative (*i.e.* uniaxial) anisotropy D . Significant rhombic anisotropy (given by the E term) will tend to quench SMM behavior. A significant separation between the spin ground state and excited states is also helpful if QTM behavior is to be observed. Combining high S and a significantly negative D in the same molecule has proved a great synthetic challenge, and recent opinion has shifted towards a strategy of optimizing D while accepting a more modest S [2]

Our general synthetic approach [3] can be summarized in the following scheme:



This involves the hydrolytic or solvolytic reaction of metal cations M^{q+} in a protic solvent (water or alcohols) in the presence of a chelating ligand L , which can arrest the hydrolysis towards the hydroxide or oxide mineral by coordinating to the outer metals of the growing particle, preventing further growth.

Previously we concentrated on metal cations from the $3d$ transition series, in particular Mn^{III} , Mn^{II} , Fe^{III} , Fe^{II} and Cu^{II} , with iminocarboxylates as organic ligands and carboxylates such as pivalate as co-ligands [4,5]. We have maintained our interest in aggregates of manganese and iron, since their cations can contribute both a significant number of unpaired electrons towards an overall spin S , and Mn^{III} can also provide uniaxial anisotropy. The magnetic interactions between these paramagnetic cations, which result in the overall magnetic behavior of the aggregate, can generally be modeled in a straightforward manner. Conversely, $3d$ cations such as Co^{II} and Ni^{II} have been much less studied, mainly because the significant spin-orbit coupling in these anisotropic cations

has largely precluded such modeling. Since we are now more interested in the overall magnetic properties of aggregates, rather than in modeling the individual interactions, we can put the anisotropy resulting from this spin-orbit coupling to good use in the search for aggregates with a large negative D . However, we have shown that, at least in some cases, the magnetic behaviour of polynuclear Co^{II} complexes can in fact be modeled, and the components of the g -factors calculated.[C1.2:38]

However, in comparison to anisotropic $3d$ cations, lanthanide cations have received far more interest in this area, since they can contribute up to seven unpaired $4f$ electrons to the overall spin, and many are also magnetically highly anisotropic. Initially, much interest was in mixed $3d/4f$ systems, but we are also studying aggregates containing only lanthanide cations. This has required further development of our synthetic method, in particular the use of di- and triethanolamine ligands in place of iminocarboxylates, since the former have been found to bridge very well between transition metal and lanthanide cations.[C1.2:13][C1.2:20] The use of co-ligands (carboxylates, azide, halides) has again been found both to give additional bridging between cations, leading to larger aggregates, and also to provide favorable ferromagnetic interactions.[C1.2:8] Organic oligoalcohol or mixed alcohol/phenol compounds can provide multiple alkoxo or phenoxo bridges between metal centres when deprotonated.[C1.2:3][C1.2:8][C1.2:21] We have also developed bifunctional Schiff-base ligands, in which one functionality has an affinity for a transition metal, while the second will preferentially bind lanthanides [C1.2:12].

Iron-based systems also have the advantage that we can probe their electronic and magnetic properties using our ^{57}Fe Mößbauer spectrometer, which was funded by the CFN. While magnetic susceptibility measurements are a bulk technique, Mößbauer spectroscopy probes individual Fe nuclei, and can provide information on local spin states, magnetic moments and spin-relaxation dynamics at the nuclei. More importantly, we can gain information about the anisotropy not only of the Fe centres, but also of other elements interacting with them, and about the relative orientation of the local axes of both types of elements. Such information is complementary to that available from magnetic susceptibility (SQUID) studies. We have recently shown how combined Mößbauer and susceptibility studies on mixed Fe-Ln systems can be applied [C1.2:37] [C1.2:43] [C1.2:45] [C1.2:61] and we are currently exploring ways of quantifying such anisotropic contributions to Mößbauer spectra.

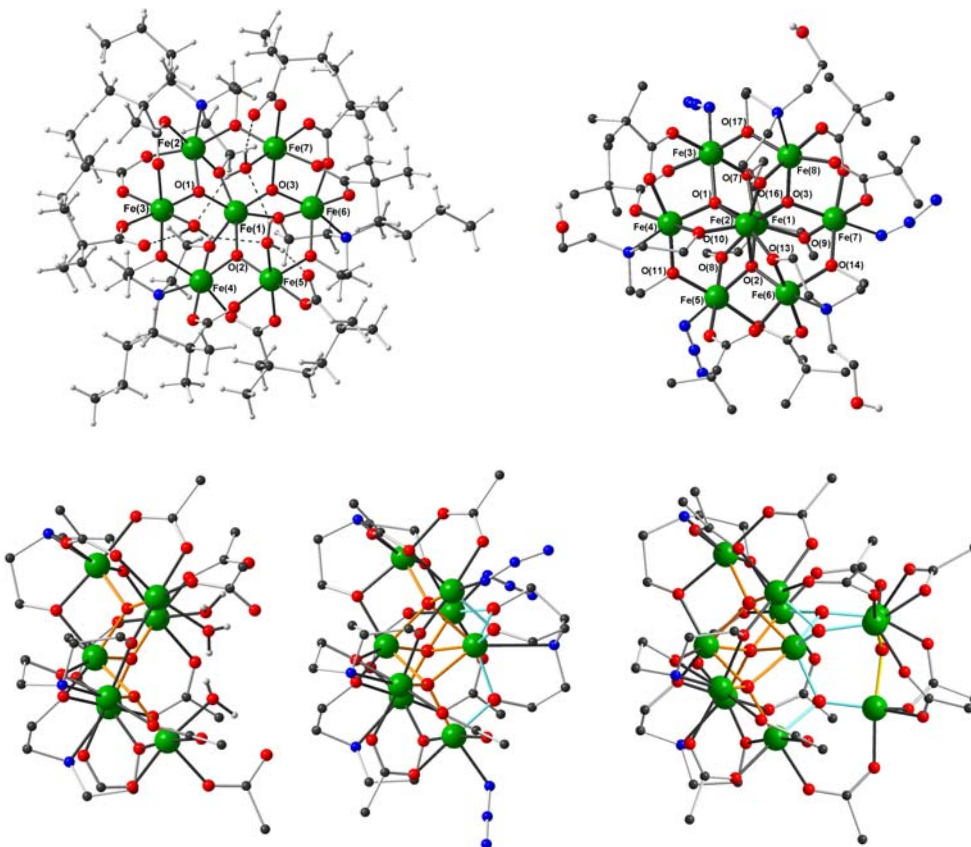
In the timeframe 2006-2010, subproject C1.2 (including C3.7) has published 74 peer-reviewed publications, including 5 articles in *Angew. Chem. Int. Ed.*, 1 in *J. Am. Chem. Soc.*, 16 in *Inorg. Chem.*, 6 in *Chem. Commun.*, 3 in *Phys. Rev. B.* and 10 in *Dalton Trans.*. 11 of these publications involve collaborative work with other CFN partners.

The work carried out within this subproject can be conveniently divided according to the nature of the metals used: transition metal ($3d$) aggregates, lanthanide ($4f$) aggregates, mixed $3d/4f$ systems, and two- or three-dimensional networks of aggregates, although some overlap between these areas is unavoidable.

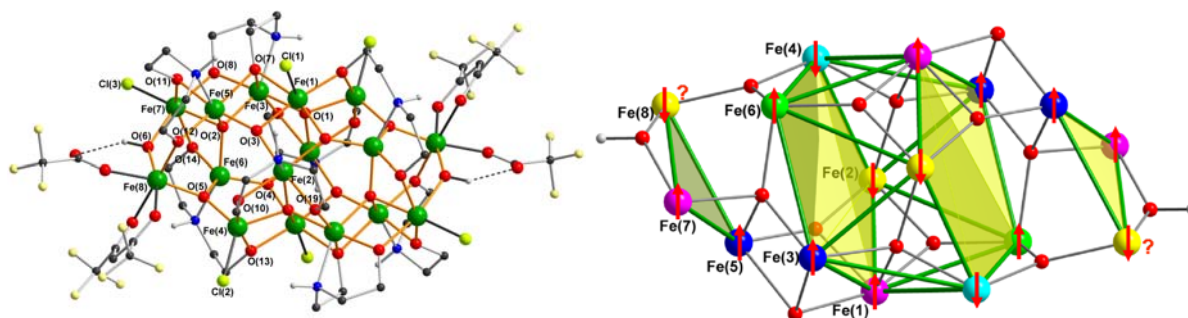
1. Aggregates of Transition-Metal ($3d^n$) Cations

Perhaps surprisingly, the large majority of higher-nuclearity polynuclear aggregates of Fe^{III} that have so far been reported contain an even number of Fe^{III} centres. Using a combination of di- or triethanolamine ligands H_2L and carboxylate co-ligands, we have synthesized a range of disk-like heptanuclear compounds $[\text{Fe}^{\text{III}}_7(\mu_3\text{-O})_3(\text{L})_3(\text{O}_2\text{CR})_9(\text{OH}_2)_3]$ in which a ring of six Fe^{III} centres is arranged around the seventh iron centre.[C1.2:10] This motif corresponds to the theoretical

“frustrated Heisenberg star” model. The compounds obtained have been the subject of a range of detailed magnetic, EPR and Mößbauer investigations which have allowed the relative orientations of the Fe^{III} spins to be mapped and the D and E anisotropy terms to be calculated [6]. The heptanuclear compounds can readily be converted to Fe^{III}_8 aggregates, in which the additional metal centre lies on the molecular threefold axis.[C1.2:10] We have also synthesized an $\text{Fe}^{\text{III}}_{11}$ aggregate, in which an additional trinuclear Fe_3 unit has been attached to the Fe^{III}_8 motif and this trigonally-symmetrical molecule shows interesting SMM behavior.[C1.2:55] The Fe_7 , Fe_8 and Fe_{11} structures are closely related:



Structures of $[\text{Fe}^{\text{III}}_7(\mu_3\text{-O})_3(\text{nbdea})_3(\text{O}_2\text{CBu}^t)_9(\text{OH}_2)_3]$ and $[\text{Fe}^{\text{III}}_8(\mu_3\text{-O})_3(\text{tea})(\text{Htea})_3(\text{O}_2\text{CBu}^t)_6(\text{N}_3)_3]$ (above) and the structural relationship between the Fe_7 and Fe_8 compounds and $[\text{Fe}^{\text{III}}_{11}(\mu_4\text{-O})_4(\mu_3\text{-O})_3(\text{dea})_3(\text{O}_2\text{CBu}^t)_{12}]\text{Cl}$



Structure of the $[\text{Fe}_{16}(\mu_4\text{-O})_4(\mu_3\text{-O})_6(\mu\text{-OH})_2(\text{dea})_8\text{Cl}_6(\text{hfac})_2(\text{O}_2\text{CCF}_3)_2]$ cluster (left), and its $\{\text{Fe}_{16}(\text{O})_{10}(\text{OH})_2\}$ core showing the proposed spin structure (right)

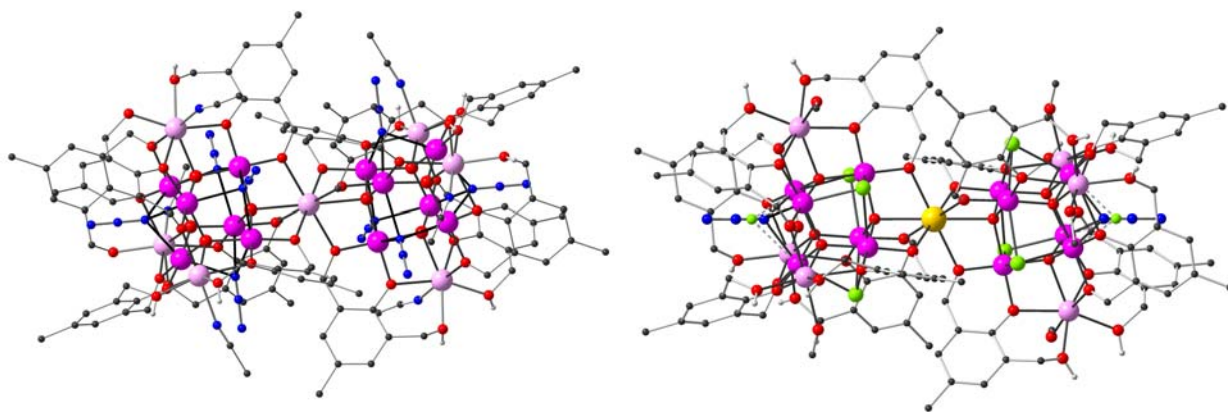
The high-nuclearity aggregate $[\text{Fe}_{16}(\mu_4\text{-O})_4(\mu_3\text{-O})_6(\mu\text{-OH})_2(\text{dea})_8\text{Cl}_6(\text{hfac})_2(\text{O}_2\text{CCF}_3)_2]$ has an unusual core based on a central pentagonal-antiprism Fe_{10} unit. It was possible to assign the doublets in the Mößbauer spectrum to the Fe centres, since these have a wide range of coordination

environments. On applying a magnetic field, the doublets become sextets, as expected, and the observed changes in local field at the Fe nuclei as the field is increased allowed a preliminary spin-map for the Fe^{III} centres to be drawn, which is in good agreement with the overall spin ground state of $S = 30/2$ obtained from susceptibility measurements.[7]

Larger aggregates of manganese cations are often mixed-valence, usually a combination of Mn^{II} and Mn^{III} centres, although Mn^{IV} is also not uncommonly found. This mixed-valency can be advantageous, as each Mn^{II} contributes the maximum of five unpaired 3d electrons while Mn^{III} brings a negative D ; furthermore, magnetic interactions between Mn^{II} and Mn^{III} are commonly ferromagnetic, encouraging high overall spins.

We have synthesized a large Mn₁₉ aggregate $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7(\mu_4\text{-O})_8(\mu_3\text{-}\eta^1\text{-N}_3)_8(\text{HL}^1)_{12}(\text{MeCN})_6]\text{Cl}_2 \cdot 10\text{MeOH} \cdot \text{MeCN}$ ($\text{H}_3\text{L}^1 = 2,6\text{-bis}(\text{hydroxymethyl})\text{-4-methylphenol}$), in which the metal core can be considered as two corner-sharing $\{\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_4(\text{O})_8\}$ supertetrahedra, in which the trivalent manganese ions form the central octahedron and the divalent cations are at the vertices. The face-bridging azides and the oxo-ligands were expected to mediate ferromagnetic interactions, and so it proved, in the ground spin state of the aggregate all the unpaired electrons are aligned parallel giving a record $S = 83/2$ ground state.[C1.2:8] The Mn₁₉ aggregate, however, did not show any SMM behavior. The Jahn-Teller axes of the twelve Mn^{III} centres are aligned such that their uniaxial anisotropies cancel almost exactly, and an EPR study showed that D was indeed very small and positive.[C1.2:16] We are currently investigating analogues of the Mn₁₉ complex with different *para*-substituents on the phenol ring of the ligand. This will enable us to determine if the magnetic behaviour is influenced by the electron density on the bridging phenolate oxygens, but more importantly we are developing ligand analogues in which the substituents carry organosilicate functionality appropriate for attaching the cluster to glass surfaces. Such surface attachment is expected to break the cluster symmetry and hopefully switch on SMM behavior.

In Mn₁₉, the central Mn^{II}, Mn(1), has a rather rare octa-coordinate environment, in which the Mn(1)-O bond distances, 2.344-2.509 Å, are rather long for Mn^{II}. Since such an environment is much more typical for trivalent lanthanide cations, we reasoned that it might be feasible to replace Mn(1) by lanthanide ions which can provide the magnetic anisotropy that was unfortunately not present in the Mn₁₉ complex. Indeed, simple addition of a lanthanide salt to the synthesis mixture resulting in the clean replacement of the central Mn^{II} by *e.g.* Dy^{III}, giving in this case $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_6\text{Dy}^{\text{III}}(\mu_4\text{-O})_8(\mu_3\text{-Cl})_{6.5}(\mu_3\text{-N}_3)_{1.5}(\text{HL}^1)_{12}(\text{MeOH})_6]\text{Cl}_3 \cdot 25\text{MeOH}$, which has an analogous structure to Mn₁₉. Such targeted selective replacement is almost unprecedented, and achieved the objective of introducing uniaxial anisotropy to high-spin compound; the Mn₁₈Dy compound shows SMM behavior.[C1.2:28]

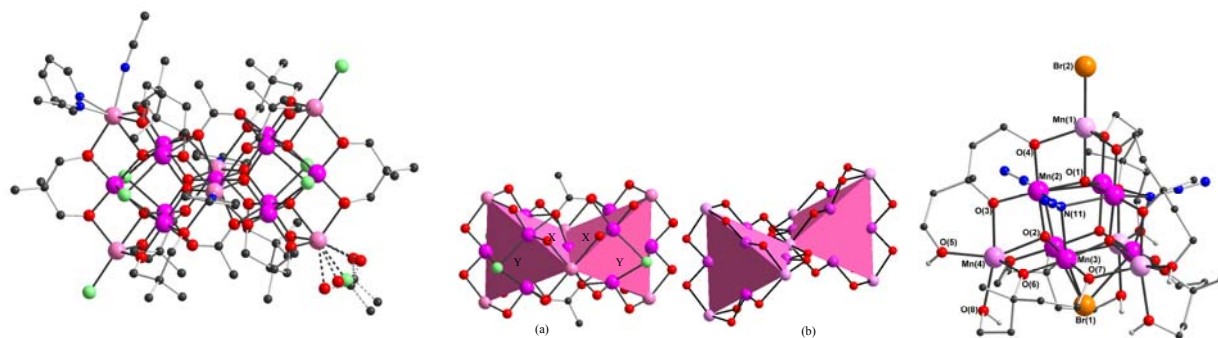


Structures of $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_7(\mu_4\text{-O})_8(\mu_3\text{-}\eta^1\text{-N}_3)_8(\text{HL}^1)_{12}(\text{MeCN})_6]^{2+}$ and $[\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_6\text{Dy}^{\text{III}}(\mu_4\text{-O})_8(\mu_3\text{-Cl})_{6.5}(\mu_3\text{-N}_3)_{1.5}(\text{HL}^1)_{12}(\text{MeOH})_6]^{3+}$ (Mn^{III} purple, Mn^{II} pink, Dy^{III} yellow)

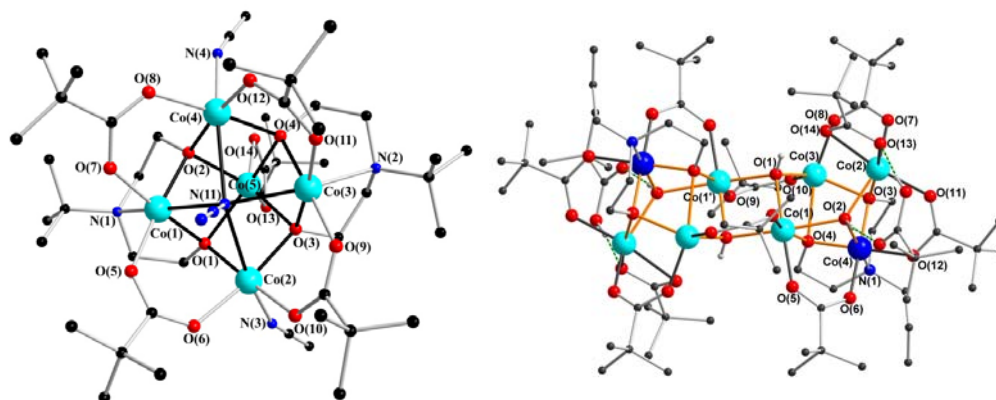
It has been possible to extend this methodology to produce a range of analogous compounds with almost all the trivalent lanthanides in the central position. We have also found that several diamagnetic cations (Sr^{2+} , Y^{3+} , Cd^{2+}) can also be introduced into the central position [8]. By dividing the Mn_{19} aggregate magnetically-speaking into two “halves” these compounds will assist in modeling the magnetic structure of the Mn_{19} . Ca^{2+} , by contrast, replaces almost all the Mn^{II} centres in Mn_{19} , leaving magnetically-isolated Mn^{III}_6 octahedra, and this compound has also been of use in interpreting the Mn_{19} system.[8] We have also synthesised a $\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_4$ supertetrahedral aggregate $[\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_4(\mu_4\text{-O})_4(\text{Hmpt})_6(\mu_3\text{-N}_3)_3(\mu_3\text{-Br})(\text{Br})]^+$ ($\text{H}_3\text{mpt} = 3\text{-methyl-pentane-1,3,5-triol}$) for which the symmetry is the same as for the individual “halves” of the Mn_{19} molecule.[9] INS studies of the Mn_{19} , Mn_{18}Sr and Mn_{10} systems have been carried out.[8,9]

Replacement of the bis-(hydroxymethyl)phenol ligand in the Mn_{19} system with dimethylpropane-1,3-diol (H_2dpd) gave instead a Mn_{17} aggregate. The core of this is related to that in the Mn_{19} , but now the two $\text{Mn}^{\text{III}}_6\text{Mn}^{\text{II}}_4$ supertetrahedra are edge-sharing rather than vertex-sharing. Replacement of some of the face-bridging ligands in Mn_{19} with $(\mu_2,\mu_3\text{-O}_2\text{CMe})$ ligands has now introduced some antiferromagnetic interactions.[C1.2:32]

The Mn_{19} , Mn_{17} and Mn_{10} molecules described above, with their high ground-state spins, have also been found to show a significant magnetocaloric effect, and thus have potential applications as magnetic cryogens.[C1.2:71]



Structure of $[\text{Mn}^{\text{III}}_{11}\text{Mn}^{\text{II}}_6(\mu_4\text{-O})_8(\mu_3\text{-Cl})_4(\mu_2,\mu_3\text{-O}_2\text{CMe})_2(\mu_2,\mu_2\text{-dpd})_{10}\text{Cl}_{2.34}(\text{O}_2\text{CMe})_{0.66}(\text{py})_3(\text{MeCN})_2]$ (left), the relationship between its edge-sharing Mn_{17} core and the corner-sharing Mn_{19} core (centre), and the structure of the $[\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_6(\mu_4\text{-O})_4(\mu_3\text{-N}_3)_3(\mu_3\text{-Br})(\text{Hmpt})_6\text{Br}]^+$ aggregate (right)



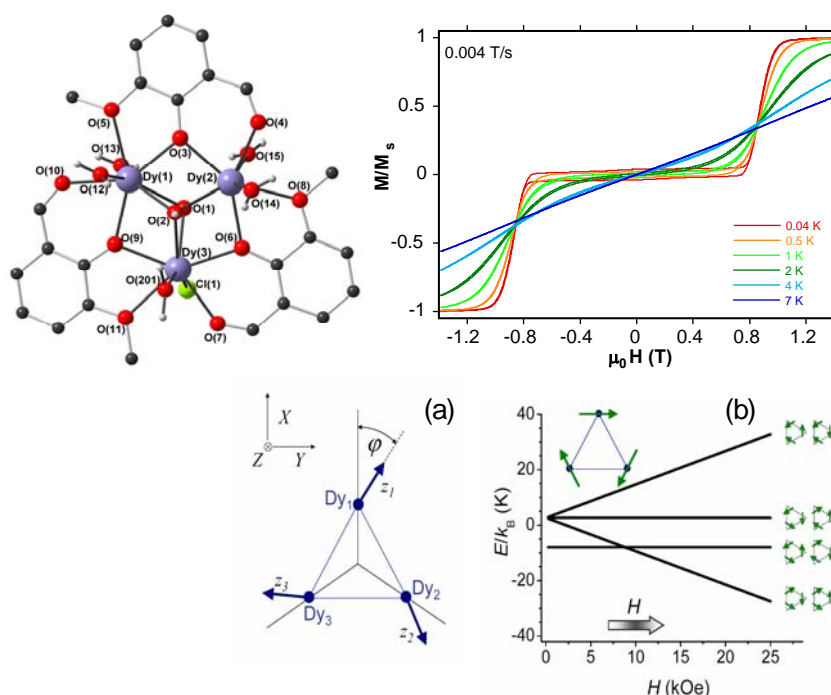
Structures of $[\text{Co}^{\text{II}}_5(\mu_4\text{-N}_3)(\text{tbdea})_2(\mu\text{-piv})_4(\text{piv})(\text{MeCN})_2]$ and $[\text{Co}^{\text{III}}_2\text{Co}^{\text{II}}_6(\mu_3\text{-OH})_4(\text{adea})_2(\text{piv})_{10}]$

A series of Co^{II}_5 complexes with very similar square-pyramidal cores has been synthesised, which differ in the μ_4 -bridging ligand over the square face (chloride or azide) and the ligand coordinating to the apical Co^{II} (chelating pivalate or terminal chloride). It was possible to model the magnetic behaviour of the complexes, showing how the single-ion anisotropies combined together, and so to explain why one of the compounds showed clear SMM behaviour while the others did not.[C1.2:38]

This approach is now being extended to other Co^{II} complexes.[10] A methodology for full *ab initio* calculations of such Co^{II} systems is being developed in collaboration with the Kloppe group (C3.3), following their successful calculations on a $\text{Mn}^{\text{III}}\text{Mn}^{\text{II}}\text{Ca}$ cluster.[C1.2:34]

2. Lanthanide Ln^{III} Aggregates

The trinuclear dysprosium complex $[\text{Dy}_3(\mu_3\text{-OH})_2(\text{L}^2)_3\text{Cl}(\text{H}_2\text{O})_5]\text{Cl}_3 \cdot 4\text{H}_2\text{O} \cdot 2\text{MeOH} \cdot 0.7\text{MeCN}$ ($\text{HL}^2 = o\text{-vanillin}$) has an equilateral triangular $\text{Dy}^{\text{III}}_3(\mu_3\text{-OH})_2$ core. Analogous complexes have been prepared using other lanthanides. The Dy_3 system is of particular interest from a magnetic point of view. The ground state is diamagnetic, in spite of the odd number of unpaired electrons, and can be described as the archetype of the non-collinear Ising triangular lattice model for a discrete molecular compound, with the three single-ion easy axes of magnetisation in the Dy_3 plane and lying at 120° to each other.[C1.2:2] [C1.2:22] Such an arrangement is common in extended lattices, but has not been seen before in a discrete molecule; it is in contrast to the (for molecular systems) more usual perpendicular arrangement of spins giving rise to spin frustration. Under an applied magnetic field, the Dy_3 molecule also shows relaxation of the magnetisation from a paramagnetic excited state, with sharp steps in the magnetic hysteresis curves resulting from resonant quantum tunneling at the crossings of the magnetic energy levels. Such SMM behavior from an excited state has not been seen before. Quantum-chemical CASPT2/RASSI-SO calculations showed that the single-ion anisotropies are indeed almost tangential to the Dy_3 triangle[11], in excellent agreement with the single-crystal magnetic studies.[C1.2:22] Muon spin relaxation measurements show the coexistence of static and dynamic internal magnetic fields; the latter has a fluctuation time of $0.55 \mu\text{s}$ below 4 K.[C1.2:73]

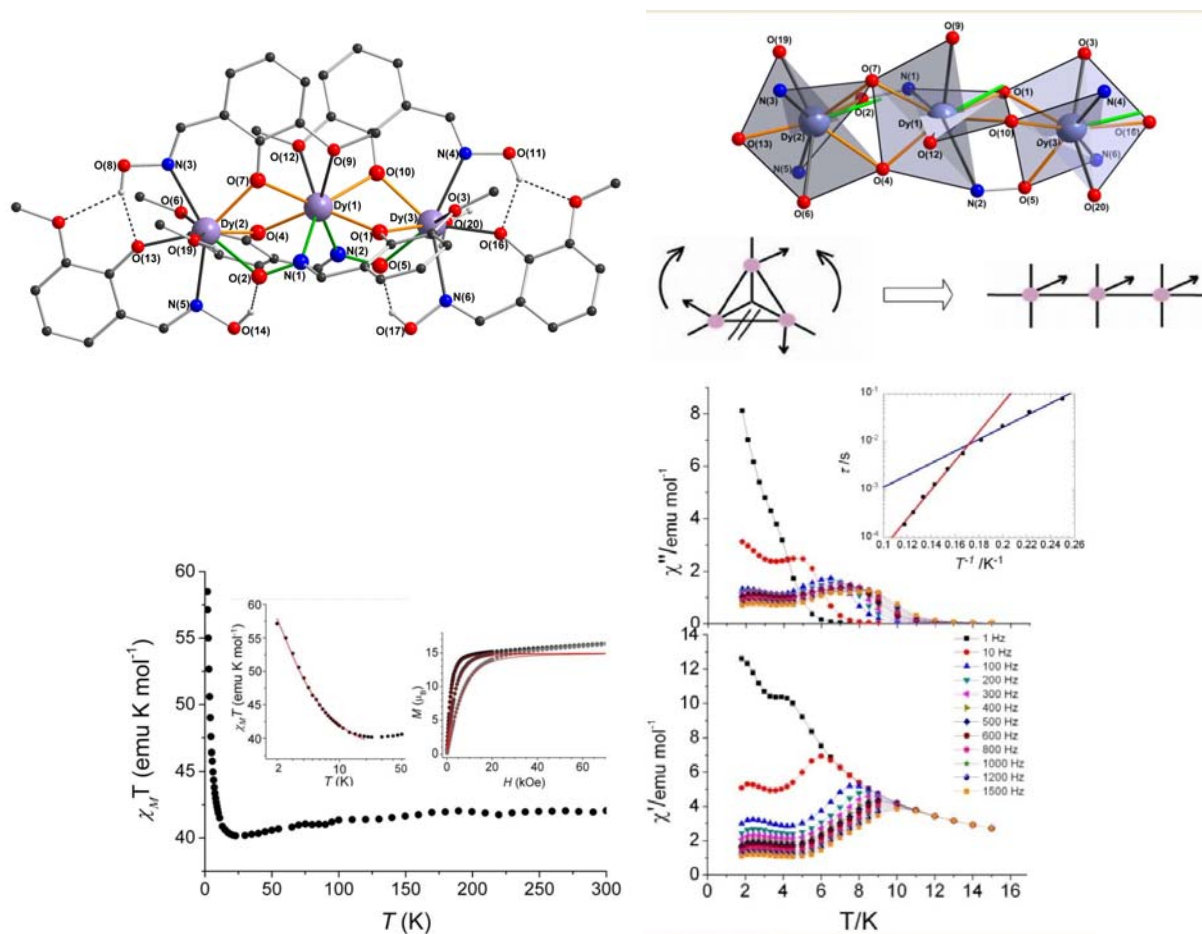


Structure of $[\text{Dy}_3(\mu_3\text{-OH})_2(\text{L}^2)_3\text{Cl}(\text{H}_2\text{O})_5]^{3+}$ (above left), the SMM behaviour with hysteresis originating from level-crossing to an excited state (above right), and the spin arrangement and calculated energy levels for Dy_3 (below)

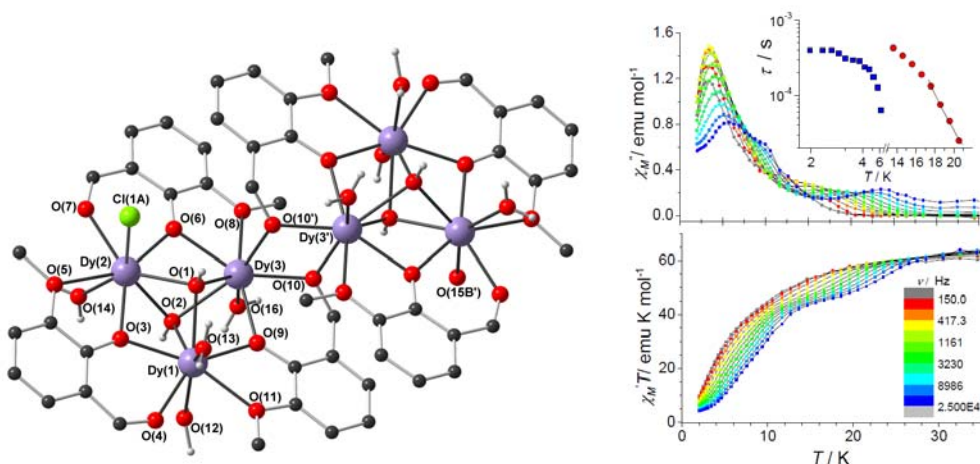
A similar synthesis, but using the oxime of *o*-vanillin (H_2vanox), also results in a trinuclear complex, but one in which the original triangle has been converted to a nearly linear structure. Since the Dy centres have rather similar coordination environments to those in the triangular complex, this “opening-out” of the triangle has resulted in the single-ion spins becoming close to parallel, as

C1.2 Powell

shown by CASSCF calculations. The dynamic magnetic susceptibility is now very complicated, and the slow relaxation of the magnetisation of the molecule shows two distinct processes.[C1.2:48]



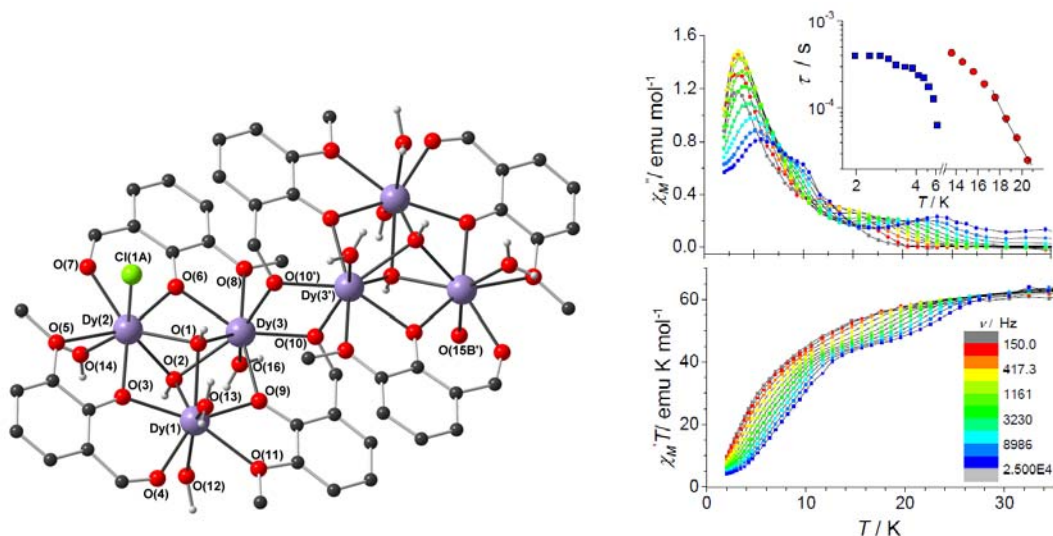
Structure of the $[\text{Dy}_3(\text{vanox})_2(\text{Hvanox})_4(\text{EtOH})_2]^+$ complex (above left) where the Dy_3 triangle has been opened to allow spin alignment and ferromagnetic coupling of the Dy ions (above right), with the static (below left) and dynamic (below right) susceptibility data.



Structure of the $[\text{Dy}_6(\mu_3\text{-OH})_4(\text{L}^2)_4(\text{L}^3)_2(\text{H}_2\text{O})_9\text{Cl}]^{5+}$ Aggregate, and its a.c. susceptibility data

Replacement of one-third of the *o*-vanillin in the synthesis of the Dy_3 compounds by 2-hydroxymethyl-6-methoxyphenol (H_2L^3) results in a hexanuclear complex, which can be regarded

as a dimer of the Dy₃ triangles in which the deprotonated alcohol groups have formed a pair of alkoxo bridges between the triangles. This has displaced the spin axis for Dy(3), which is involved in the linkage between the triangles, out of the plane of its triangle. The dynamic magnetic behaviour is again very rich, with (at least) two relaxation processes, and that operating in the 20-25 K regime corresponds to a very high barrier with $\Delta E = 200(10)$ K. Again, the orientation of the single-ion anisotropies could be determined, but these appear to be temperature dependent. The molecular ground state is non-magnetic, as for the Dy₃ triangle, but with a very low-lying excited state. At *ca.* 2 K the anisotropy of this state is mainly easy-plane in nature, but on increasing the temperature this state assumes an Ising (easy-axis) character, an unprecedented behaviour.[C1.2:62]



Structure of the $[\text{Dy}_6(\mu_3\text{-OH})_4(\text{L}^3)_4(\text{L}^4)_2(\text{H}_2\text{O})_9\text{Cl}]^{5+}$ Aggregate, and its a.c. susceptibility data

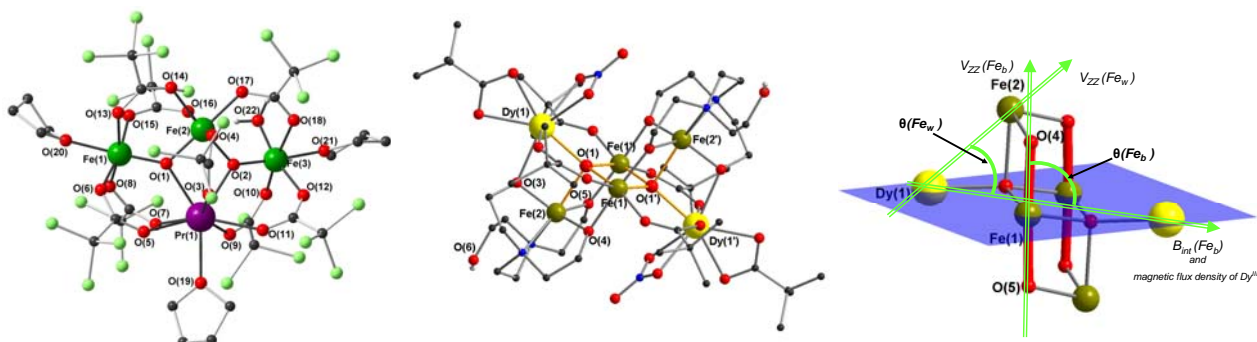
Using the diethanolamine/carboxylate system, we have characterised a range of tetranuclear Dy₄ compounds; some of these have a planar core, others a non-planar “butterfly” core. The planar Dy₄ systems show conventional SMM behaviour, while the non-planar shows two different relaxation mechanisms, with different energy barriers, depending on the temperature regime.[C1.2:24] [C1.2:68][12]

3. Mixed Transition-Metal Lanthanide Aggregates

Although a rapidly increasing number of aggregates containing both transition metal and lanthanide cations are appearing in the literature, the overall impression is that of a rather unsystematic approach. Understanding how the electronic properties of the lanthanide cations contribute to the overall magnetic properties of a molecule is at present in its early stages. We have therefore, whenever possible, aimed to synthesise isostructural aggregates (for which we proposed the term “lanthanologues”) in which only the lanthanide is changed. In this way we can track the geometrical changes resulting from the lanthanide contraction as we go along such a series, but more importantly we can compare the magnetic properties of the members of the series in order to investigate how the differing 4*f* electron configurations affect the overall molecular properties. Typically, we can compare compounds in which the lanthanide or rare earth cation is diamagnetic, (La^{III}, Y^{III}, or Lu^{III}) with the Gd^{III} lanthanologue (with its isotropic 4*f*⁷ configuration) and finally with the anisotropic lanthanides. In some cases, it is also possible to replace Mn^{III} with Fe^{III} or Cr^{III} (“switching off” the 3*d* anisotropy) or even Co^{III} (removing the 3*d* contribution altogether), while

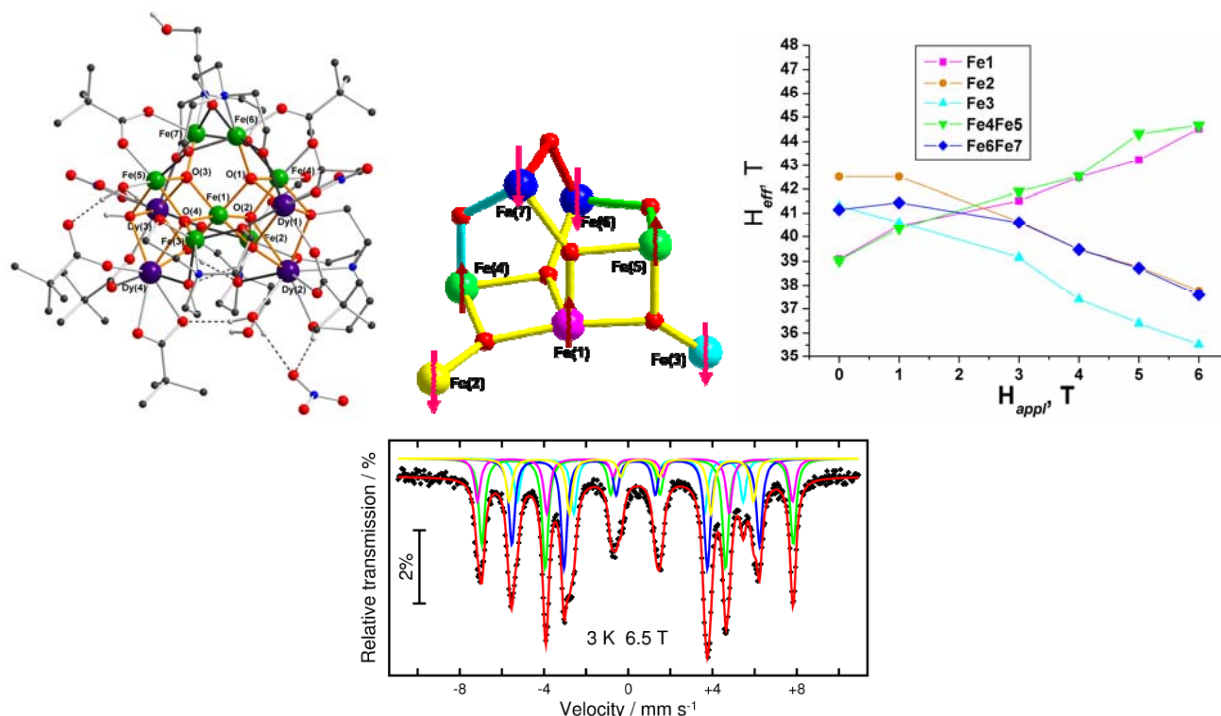
C1.2 Powell

keeping the lanthanide constant. In this way, we aim to investigate the relative contributions of the $3d$ and $4f$ cations to the overall properties, and find out how they are combined.



Structures of $[\text{Fe}_3\text{Pr}(\mu_3\text{-O})_2(\text{CCl}_3\text{COO})_8(\text{H}_2\text{O})(\text{THF})_3]$ (left) and $[\text{Fe}^{\text{III}}\text{Dy}_2(\mu_4\text{-O})_2(\text{NO}_3)_2(\text{piv})_6(\text{Hedte})_2]$ (centre), and the local anisotropy axes of the Fe and Dy atoms in the latter (right)

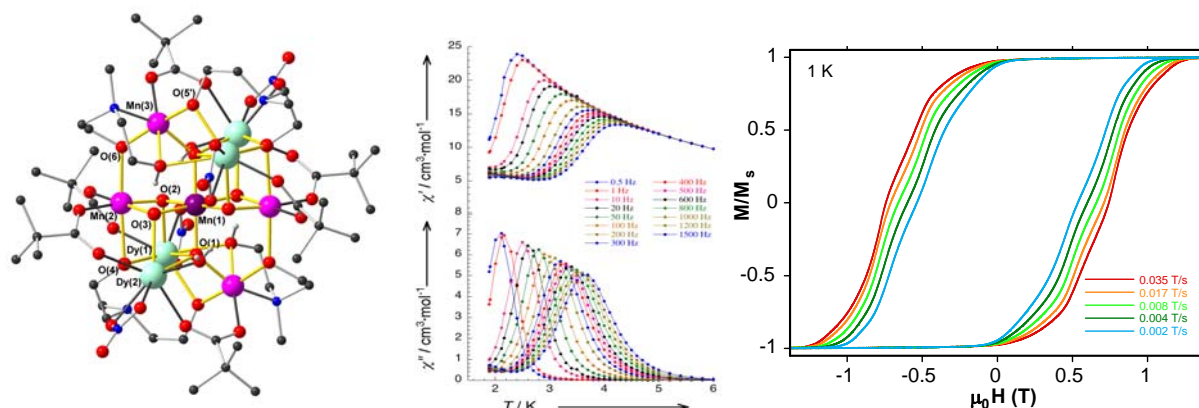
A series of $\text{Fe}^{\text{III}}\text{Ln}$ complexes $[\text{Fe}_3\text{Ln}(\mu_3\text{-O})_2(\text{CCl}_3\text{COO})_8(\text{H}_2\text{O})(\text{THF})_3]$ has been synthesised with all lanthanides except La and Pm (radioactive!); the Fe_3Y analogue was also prepared. This is the largest series of lanthanologues so far prepared. These compounds have been the subject of extensive magnetic and Mößbauer investigations, which have given useful insights into the nature of their magnetic relaxation phenomena.[C1.2:43] Two further series, of Fe_4Ln_2 and Fe_4Ln_4 aggregates are proving useful test systems for a combined magnetic, Mößbauer and theoretical study of the effects of the lanthanide anisotropy on the overall SMM properties of the aggregates [C1.2:37][C1.2:61] and we are exploring methods for extracting quantitative information on the lanthanide anisotropies from the spectral data.



Structure of $[\text{Fe}^{\text{III}}_7\text{Dy}^{\text{III}}_4\text{O}_4(\text{OH})_3(\text{tea})_2(\text{Htea})_3(\text{Piv})_7(\text{NO}_3)_2(\text{H}_2\text{O})_2]^+$, the Fe_7 core with the proposed spin structure, the field dependence of the local field at the nuclei, and the ^{57}Fe Mößbauer spectrum at 3 K under 6.5 T applied field. The colour code for the Fe centres is consistent that in the graph and the spectrum.

We have used Mößbauer spectroscopy to determine the relative orientations of the Fe^{III} spins in the undecanuclear complex $[\text{Fe}^{\text{III}}_7\text{Dy}^{\text{III}}_4\text{O}_4(\text{OH})_3(\text{tea})_2(\text{Htea})_3(\text{Piv})_7(\text{NO}_3)_2(\text{H}_2\text{O})_2]^+$. As for the Fe_{16} described earlier, the Mößbauer doublets could readily be assigned to the individual Fe centres. On

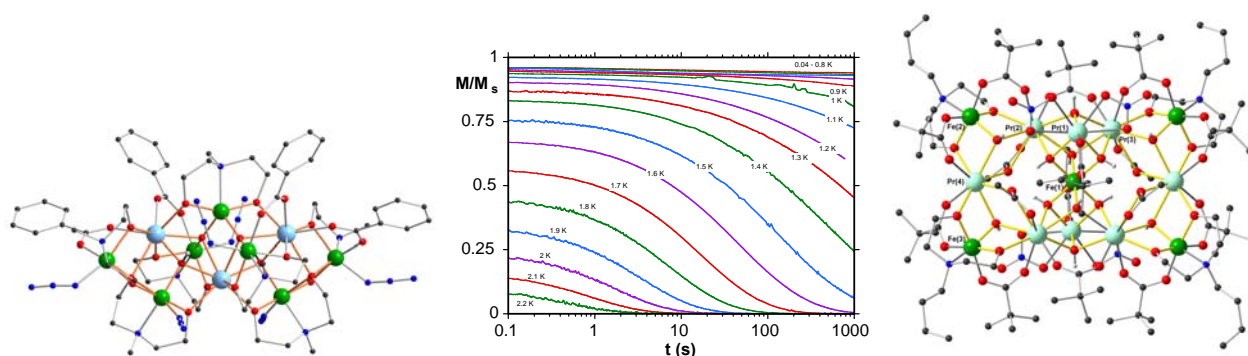
applying a magnetic field, the doublets become sextets, and the local field at each Fe nucleus can be determined. The changes in these local fields H_{eff} as the applied field H_{appl} is increased allowed the relative orientations of the spins around the nuclei (parallel or antiparallel) to be established. Such information cannot be obtained from SQUID measurements in heterometallic complexes such as this, as the temperature dependence of the susceptibility is dominated by the thermal depopulation of the Stark sub-levels of the lanthanide ions.[C1.2:72]



Structure of $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_4\text{Dy}_4(\mu_4\text{-O})_2(\text{Me-dea})_2(\text{Me-deaH})_2(\text{piv})_6(\text{NO}_3)_3]$, a.c. susceptibility data and magnetisation hysteresis loops measured at 1 K

The mixed-valence aggregates $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}_4\text{Ln}_4(\mu_4\text{-O})_2(\text{Me-dea})_2(\text{Me-deaH})_2(\text{piv})_6(\text{NO}_3)_3]$ show interesting modulation of SMM behaviour on changing Ln. With diamagnetic Y^{III} , the Mn_5 section of the core was found to be a very weak SMM. The Ho^{III} and Tb^{III} analogues show stronger SMM behaviour, while the Dy^{III} compound has the highest energy barrier to reversal of magnetisation yet reported for a mixed $3d/4f$ aggregate.[C1.2:20] For $[\text{Dy}_3\text{Fe}_7(\mu_4\text{-O})_2(\mu_3\text{-OH})_2(\text{mdea})_7(\mu\text{-benzoate})_4(\text{N}_3)_6]$ we were able to combine susceptibility and Mößbauer data in the study of an SMM with a high barrier to relaxation, $U_{\text{eff}} = 33.4$ K. [C1.2:45]

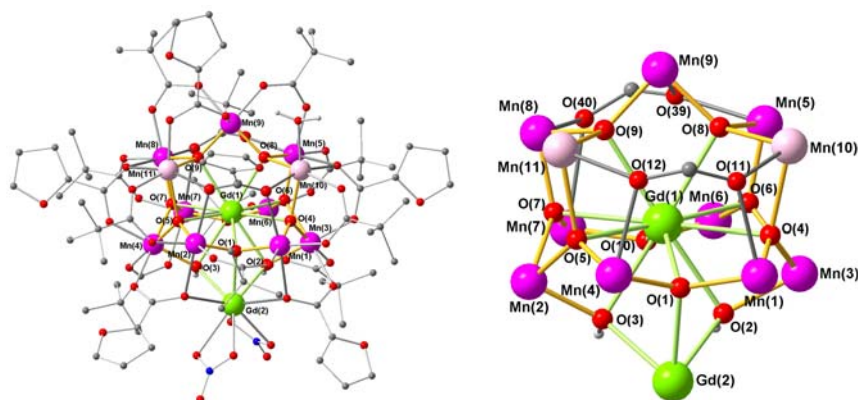
The larger aggregates $[\text{Fe}^{\text{III}}_5\text{Ln}_8(\text{OH})_{12}(\text{Bu-dea})_4(\text{piv})_{12}(\text{NO}_3)_4(\text{OAc})_4]$ and $[\text{Mn}^{\text{III}}_5\text{Ln}_8(\text{OH})_{12}(\text{Bu-dea})_4(\text{piv})_{12}(\text{NO}_3)_4(\text{OAc})_4]$ are isostructural. Unlike the Mn_5Ln_4 systems, they show no SMM behaviour, since the coupling between the metal ions is negligible, but this allowed us to establish the “zero-point” for Fe-O-Ln and Mn-O-Ln magnetostructural correlations.[C1.2:13][C1.2:39]



Structure of $[\text{Dy}_3\text{Fe}_7(\text{O})_2(\text{OH})_2(\text{mdea})_7(\text{benzoate})_4(\text{N}_3)_6]$ (left), its magnetisation decay at temperatures between 40 mK and 2.2 K (centre) and the structure of $[\text{Fe}^{\text{III}}_5\text{Ln}_8(\text{OH})_{12}(\text{Bu-dea})_4(\text{piv})_{12}(\text{NO}_3)_4(\text{OAc})_4]$ (right)

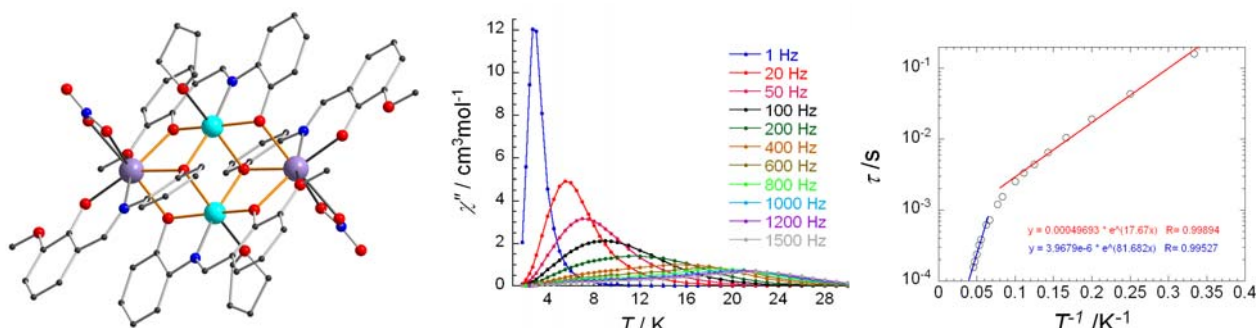
Even higher nuclearity systems have been characterised. The bell-shaped aggregate $[\text{Mn}^{\text{III}}_9\text{Mn}^{\text{II}}_2\text{Gd}_2(\text{O})_8(\text{OH})_2(\text{piv})_{10.6}(\text{fca})_{6.4}(\text{NO}_3)_2(\text{H}_2\text{O})]$ was the $3d/4f$ aggregate with the highest energy barrier for magnetisation [C1.2:11] until overtaken by the Mn_5Dy_4 compound described above. Replacement of the Gd^{III} ions with diamagnetic La^{III} showed that the anisotropy comes from

the $\text{Mn}^{\text{III}}_9\text{Mn}^{\text{II}}_2$ shell, but that this has a very low spin, and requires the additional $S = 14/2$ spin provided by the Gd_2 moiety for SMM behaviour to be “switched on”. [13]



Molecular structure and core of $[\text{Mn}^{\text{III}}_9\text{Mn}^{\text{II}}_2\text{Gd}_2(\text{O})_8(\text{OH})_2(\text{piv})_{10.6}(\text{fca})_{6.4}(\text{NO}_3)_2(\text{H}_2\text{O})]$

We have also found that the combination of lanthanides with later 3d metals can also yield SMMs with high relaxation barriers. The complex $[\text{Co}^{\text{II}}_2\text{Dy}_2(\text{L}^5)_4(\text{NO}_3)_2(\text{thf})_2]$ (H_2L^5 is the Schiff-base from the condensation of *o*-vanillin and 2-aminophenol) has a blocking temperature of over 20 K, with a barrier $U_{\text{eff}} = 81$ K. Presumably the Co^{II} and Dy^{III} single-ion anisotropies are well-aligned; calculations are being carried out to confirm this. The relaxation process is again temperature-dependent. A closely related $\text{Ni}^{\text{II}}_2\text{Dy}_2$ compound has a lower, but still respectable, barrier of 31 K. [14]



Structure of $[\text{Co}^{\text{II}}_2\text{Dy}_2(\text{L}^5)_4(\text{NO}_3)_2(\text{thf})_2]$, its out-of-phase a.c. susceptibility, and an Arrhenius plot showing the two relaxation processes in different temperature regimes.

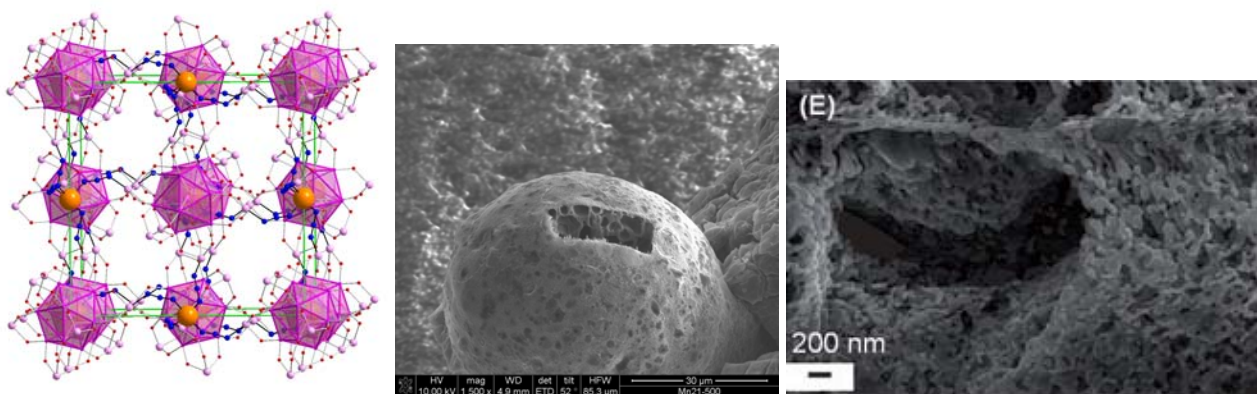
4. 2-D and 3-D Arrays of Aggregates

The aggregates described so far have all been molecular compounds, with at most only weak supramolecular interactions between them. We have previously reported porous networks in which single paramagnetic metal cations are built into three-dimensional networks [C1.2:4], but it is of more interest to build polynuclear aggregates into such networks. As well as investigating how the linkages might mediate inter-aggregate magnetic interactions, and so modulate the magnetic behavior, we are also interested in the porous properties of the networks themselves.

In the large majority of Metal-Organic Frameworks (MOFs), relatively small (generally up to tetranuclear) metal complex nodes are linked by long polyaromatic organic ligands, such that the internal surface available to guest molecules is dominated by the π -systems of the linking

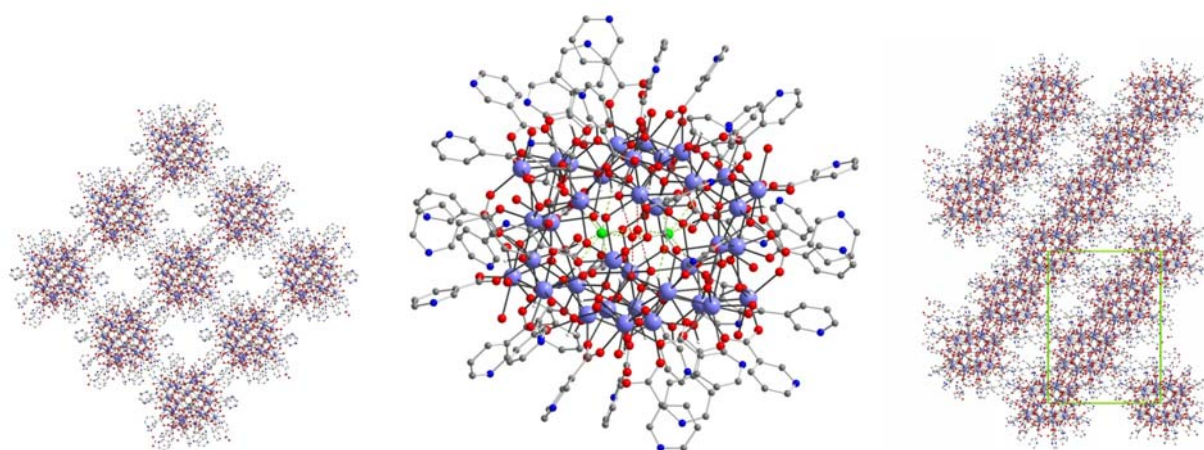
ligands.[15] We are now considering the converse approach, in which we look to build high-nuclearity aggregates into 3-D networks *via* rather small bridging ligands. Such networks, which we term Super Metal-Organic Frameworks or SMOFs, can still show a high level of porosity, but the cavities now have a significant contribution from the surface of the aggregates themselves, allowing a variety of functionalities to be available to a guest molecule. Network interpenetration is a common problem in MOF synthesis, but this cannot occur with SMOFs, which we also find to be robust materials.

Working under ambient conditions using glycerol as primary ligand, the network $[\{\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_9(\mu_4\text{-O})_8(\text{glycH})_{12}(\mu\text{-}1,1\text{-N}_3)_6(\text{OH}_2)_6(\text{N}_3)_{1/2}\}\{\text{Mn}^{\text{II}}(\mu\text{-}1,3\text{-N}_3)_{4/2}(\text{OH}_2)_{1/2}\}]\text{Cl}_4 \cdot \text{ca.}7\frac{1}{2}\text{H}_2\text{O}$ (where $(\text{glycH})^{2-}$ is the dianion of propan-1,2,3-triol) was obtained. Mixed-valence Mn_{21} aggregates are linked *via* (1,3-azide) ligands to mononuclear Mn^{II} centres, forming a cubic network that is isotypic with the FeS_2 structure [C1.2:21]. Pyrolysis of this network at 500 °C results in highly porous ($52 \text{ m}^2 \text{ g}^{-1}$) $\alpha\text{-Mn}_2\text{O}_3$. decomposition of the azide ligands to form N_2 gas has resulted in extrusion of a novel “foam-like” material from the decomposed crystals. This has been shown to be a highly-promising material for Li-ion battery anode, with a reversible charge/discharge capacity of 650 mA h g^{-1} . In addition, this multifunctional material is also an efficient heterogeneous catalyst for cyclohexene oxidation.[C1.2:60]



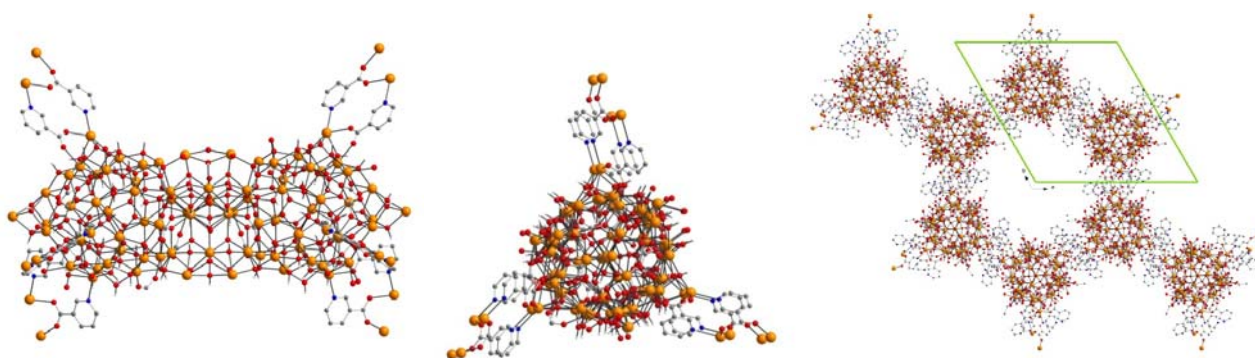
The cubic network of Mn_{21} aggregates and Mn^{II} cations in $[\{\text{Mn}^{\text{III}}_{12}\text{Mn}^{\text{II}}_9(\mu_4\text{-O})_8(\text{glycH})_{12}(\mu\text{-}1,1\text{-N}_3)_6(\text{OH}_2)_6(\text{N}_3)_{1/2}\}\{\text{Mn}^{\text{II}}(\mu\text{-}1,3\text{-N}_3)_{4/2}(\text{OH}_2)_{1/2}\}]\text{Cl}_4$ (left); SEM/FIB images of the extruded $\alpha\text{-Mn}_2\text{O}_3$ after pyrolysis (centre and right)

We have also linked lanthanide aggregates into arrays. Hydrothermal reaction of lanthanide salts with nicotinic acid (Hnic) gives high-nuclearity $[\{2\text{Cl}\cdot 2\text{H}_2\text{O}\}@\{\text{Ln}_{36}(\text{OH})_{56}(\text{CO}_3)_6(\text{nic})_{38}(\text{OH}_2)_n\}]$ aggregates, which depending on the reaction time are linked into either 2-D ($n = 18$) or 3-D ($n = 16$) networks. Some of the nicotinate ligands coordinate through both their pyridine nitrogens and carboxylate groups to two adjacent aggregates, linking each aggregate to four (2-D) or six (3-D) nearest neighbours. The rhombohedral 3-D network is porous, with the accessible solvent volume amounting to 33% of the unit cell, and containing *ca.* 80 waters per aggregate, and can be obtained using a range of different lanthanides, and also with yttrium. The Dy_{36} analogue shows SMM behaviour, and is the largest lanthanide-based cluster to do so; it also a heterogeneous catalyst for the cyanosilation of a range of aromatic aldehydes. It is therefore a true multi-functional material.[16]



Structure of the $\{\text{Dy}_{36}(\text{OH})_{56}(\text{CO}_3)_6(\text{nic})_{38}(\text{OH}_2)_{16}\}$ aggregate (centre), the 2-D array (left) and the 3-D network (right)

By changing the reaction conditions, we have also isolated networks of much larger Dy_{79} and Y_{79} aggregates, which can be considered to be built from two of the Ln_{36} units. The crystal structures of the Dy_{79} and Y_{79} systems were measured at the ANKA synchrotron source, and have a very open framework. Each $[\text{Ln}_{79}(\text{OH})_{140}(\mu_5\text{-CO}_3)_{12}(\text{nic})_{57}(\text{OH}_2)_{42}]$ unit, of dimensions $3.6 \times 1.7 \times 1.7$ nm, is linked to six others to give a very open hexagonal 3-D network, in which the accessible solvent volume amounts to *ca.* 63% of the unit cell. The calculated density of the empty Y_{79} network is therefore only *ca.* 1.2 g cm^{-3} , in spite of the very high nuclearity. The properties of these two network types are currently under investigation [17].



The core of the Dy_{79} aggregate, and the open hexagonal packing, in $[\text{Dy}_{79}(\text{OH})_{140}(\mu_5\text{-CO}_3)_{12}(\text{nic})_{57}(\text{OH}_2)_{42}](\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$

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