A ring cycle: studies of heterometallic wheels†

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The synthesis of a series of heterometallic rings and chains is reported. The family is based on the octanuclear cages of general formula $[H_2NR_2][M_7M'F_8(O_2CR')_{16}]$, where M is a trivalent metal (Cr, Fe, V, Al, Ga or In), M′ is a divalent metal (Mn, Fe, Co, Ni, Mg, Zn, Cd), R is a linear alkyl chain and O_2CR' is one of around twenty carboxylates. Other members of the family with nonametallic and decametallic cores are described, and some new physics is outlined, including initial investigations of the proposed application of $\{Cr_7Ni\}$ rings as Qubits in quantum information processing.

Introduction

Around four years ago we had a conversation with a Swiss scientist named Florian Meier who was pursuing research with Prof. Daniel Loss in Basel. His research concerned theoretical predictions of quantum phenomena in anti-ferromagnetically coupled rings and included the prediction that if the anti-ferromagnetically (AF) coupled ring had a spin in its ground state the spin should "tunnel" from spin up to spin down. The prediction was published shortly afterwards.[1]

The idea was intriguing because no molecule existed which would allow this theory to be tested, and because although the mathematics underpinning the prediction was complicated the end result was straightforward. Finally, quantum tunneling is one of those curious phenomena that everyone has heard of but which is counter-intuitive. So we set out to make a molecule to test this theory. The result has been a large, and growing, family of molecules which are ideal for examining many ideas in the physics of magnetism.

Until 2002 the AF coupled rings in the chemical literature were somewhat restricted, and almost all were even-numbered and all were homometallic. The most famous is $[Fe(OMe)_2(O_2CCH_2Cl)]_{10}$, first reported by Taft and Lippard[2] and then studied in-depth with Gatteschi and co-workers.[3] This has an $S = 0$ ground state, because alternate iron(III) sites are spin up and spin down, and there are five Fe(III) centres in the "odd" sub-lattice (positions 1, 3, 5, 7, 9) and five in the "even" sub-lattice (positions 2, 4, 6, 8, 10). The other examples in the literature, made by the groups of Pecoraro[4] and Saalfrank,[5] and further compounds made by the group of Gatteschi[6] were also homometallic.

Another ring – slightly older than the Lippard's "ferric wheel" – was patented in the former USSR in 1985 as an oxidation catalyst.[7] This ring has the formula $[CrF(O_2C^tBu)_2]_8$ **1**. Ring **1** is made by reaction of hydrated chromium fluoride with excess pivalic acid in DMF at *ca.* 135 °C, and crystallised from acetone. The structure is an octagon of chromium(III) centres, each edge of the octagon bridged by a fluoride and two pivalates (Fig. 1). One of the pivalates on each edge is in the

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† In memory of Professor Nicolae V. Gerbeleu.

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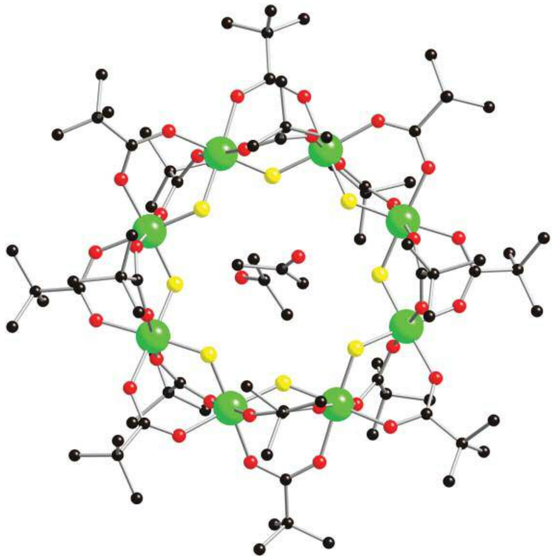

Fig. 1 The structure of $1{\cdot}2Me_2CO$ in the crystal. Colours: Cr, green; F, yellow; O, red; C, black. H-atoms omitted for clarity.

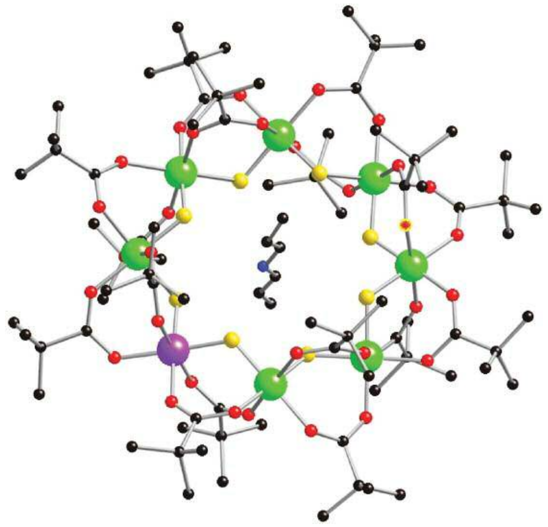

Fig. 2 The structure of **2** in the crystal. The heterometal site is disordered, the different colour is for aesthetic reason. Colours: Cr, green; F, yellow; O, red; C, black; Ni, purple.

plane of the octagon, and the other pivalate is alternately above and below the plane. Each Cr(III) ion has an octahedral coordination geometry. Two acetone molecules co-crystallise with the ring.

Ring **1** has an $S = 0$ ground state,[8] for precisely the same reason as the other AF rings. However the synthesis is very easily changed by addition of a source of a divalent metal and a amine to the reaction mixture. The overall reaction then becomes:

$$7\ CrF_3{\cdot}4H_2O + \text{“}MX_2\text{”} + HNR_2 + xs\ HO_2C^tBu \rightarrow [H_2NR_2][Cr_7MF_8(O_2C^tBu)_{16}]$$

The use of a divalent metal was to produce an octametallic ring that was a monoanion, which we could then separate from the neutral homometallic ring **1**.[9] The reaction gives high yields, and works for M = Ni(II), Co(II), Fe(II), Mn(II), Cd(II), Zn(II) and Mg(II); R = Me, Et, ^{n}Pr, ^{n}Bu, ^{n}Oct. The structure is identical to **1**, with the heterometal disordered over all eight sites of the ring. The amine added to the reaction is present within the compound as the secondary ammonium cation, and is found at the centre of the ring H-bonded to the bridging fluorides (Fig. 2).

The stability of the ring is very high and the heterometallic ring is best characterised by the electrospray mass spectroscopy (ES-MS), with the only significant peak being $[Cr_7MF_8(O_2C^tBu)_{16}]^-$ in the negative ion spectrum and $\{Na[H_2NR_2][Cr_7MF_8(O_2C^tBu)_{16}]\}^+$ the only peak in the positive ion. The ES-MS is so clean and informative it is possible to identify M and R from this alone. The most stable rings, and the one with the most immediately interesting physics, are the {Cr$_7$Ni} rings such as $[H_2N^nPr_2][Cr_7NiF_8(O_2C^tBu)_{16}]$ **2** (Fig. 2).

The synthesis has five possible variables: the trivalent metal ion, the divalent metal ion, the carboxylate, the fluoride and the amine. We have attempted to vary each of these in turn. The least successful has been the fluoride; while we can produce $[Cr(OH)(O_2C^tBu)_2]_8$,[10] which is the hydroxide version of **1** we cannot include hydroxide in place of fluoride in the heterometallic rings. A possible reason for this is the requirement for an ammonium cation at the centre of the heterometallic rings; if hydroxide is present as the bridging ligand the H-atom of the hydroxide points at the ring centre. The result is that a cation cannot be encapsulated and the heterometallic anionic-ring does not form.

More successful is varying the divalent metal. The seven divalent metals listed above will all adopt an octahedral geometry. We therefore examined two ions which have the same charge, but different geometries. The first is vanadyl, VO^{2+}, where one site is blocked by the terminal oxide. The reaction gives $[H_2NR_2][Cr_6(VO)_2F_8(O_2C^tBu)_{15}]$ (R = Me, Et **3**, ^{n}Pr) (Fig. 3).[11] The structure contains an octagon of metal sites, but because VO^{2+} can only bond to five ligands, one

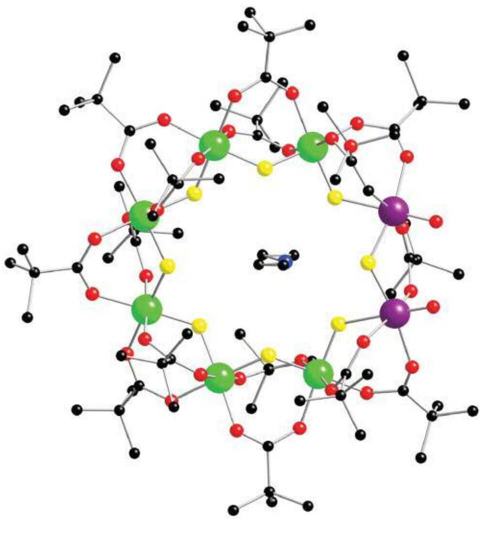

Fig. 3 The structure of **3** in the crystal. Colours as Fig. 1 plus V, purple.

edge-bridging pivalate is missing and two vanadyls are found in the structure, next to one another in the ring. The V···V edge is therefore bridged by one F and one O_2C^tBu.

If copper(II) is used $[R_2NH_2]_2[Cr_{10}Cu_2F_{14}(O_2CCMe_3)_{22}]$ **4** (R = Me or ^{i}Pr) forms (Fig. 4). This dodecanuclear complex has a shape akin to an hour-glass.[11,12] The Cu(II) sites are five-coordinate, with a square-pyramidal coordination geometry. A bridging fluoride is found in the axial position. As both Cu(II) sites make five bonds, two Cr···Cu edges are only bridged by a single fluoride and pivalate; therefore for the Cr(III) sites in those edges to achieve an octahedral geometry they need a terminal fluoride, which points towards the cavity of the ring. The charge balance within the dodecanuclear ring makes it a dianion, and therefore two ammonium cations are found. Unlike the previous heterometallic rings, with both vanadyl and copper(II) the positions of the heterometals are ordered.

A more extreme modification is to exclude the divalent metal entirely.[11] This gives a supramolecular double-horseshoe: $[(H_2NR_2)_3\{Cr_6F_{11}(O_2CCMe_3)_{10}\}(H_2O)]_2$ with R = Et, ^{n}Pr **5**, $^nC_5H_{11}$) and a different double horseshoe, $[[(H_2NR_2)_3\{Cr_7F_{12}(O_2CCMe_3)_{12}\}(H_2O)]_2$ **6** with R = ^{i}Pr (Fig. 5). In both cases the bridging motif found in **1** – one F and two pivalates – is found on each edge of the horseshoe, however formation of the complete ring is prevented by H-bonding of the ammonium cations to terminal fluorides. The reason for the different nuclearity of the horseshoes with the different R-groups in the cations is not obvious. Our feeling is that both length horseshoes are probably present in the reaction mixture, and that separation and crystallisation leads to one or other. It is noticeable that the yield of the heptanuclear horseshoe is much lower (*ca.* 10%) than the yields of other compounds discussed here.

As it was possible to change the divalent metal, it seemed worthwhile to attempt to replace chromium. Metal fluorides are readily available for vanadium(III), iron(III), aluminium(III), gallium(III) and indium(III); all work with nickel as the divalent metal.[13,14] Other divalent metals which, for example, gives us access to homometallic but heterovalent rings such as $[Fe^{III}{}_7Fe^{II}F_8(O_2C^tBu)_{16}]^-$ **7**.[13] Attempts to use 4f-fluorides have thus far been unsuccessful, and we are attempting to make 4d- and 5d-fluorides to access rings of elements such as Ru and Rh.

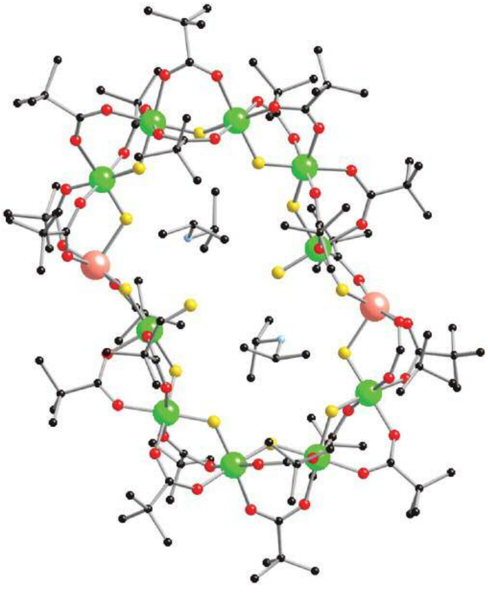

Fig. 4 The structure of **4** in the crystal. Colours as Fig. 1 plus Cu, brown.

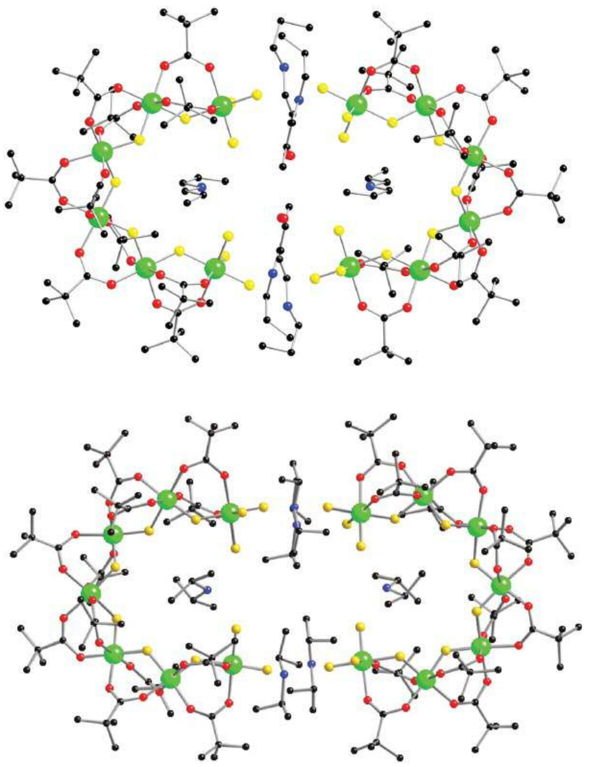

Fig. 5 (a) The structure of **5** in the crystal; (b) the structure of **6** in the crystal. Colours as Fig. 1.

The compounds which result are isostructural with the heterometallic chromium wheels. The yields, and the degree of crystallographic disorder, depend on the trivalent metal. For group 13 the yields are excellent for gallium (70–90%), moderate for indium (40–60%) and poor for aluminium ($\leqslant$10%).[14] This probably reflects the ionic radii of the cations; for Ga^{III} the match is good for the structure, whereas for In^{III} the radius is slightly too large and for Al^{III} it is too small. The crystallography for the aluminium version is difficult, with even the metal sites disordered over two positions in the structure.

The ability to vary both metals present allows us to vary the magnetic properties of the compounds, which in the long term is important in being able to understand the new magnetic phenomena we are seeing (see below). The spin ground state of the molecule depends on the difference of the spin of the divalent and trivalent ions present, so we can vary the ground state from $S = 0$ (*e.g.* $Fe^{III}{}_7Mn^{II}$) to $S = 5/2$ (*e.g.* $Fe^{III}{}_7Zn^{II}$), with all possible intermediate values (Table 1). We can also vary more subtle magnetic parameters, *e.g.* the anisotropy of the spin. Fe^{III}, with a d^5-configuration is very isotropic in the high spin state; Cr^{III} has some anisotropy, while V^{III}, with a d^2 ground state is very anisotropic. Similarly we can vary the anisotropy of the divalent ion from Mn^{II} to Co^{II}.

Table 1 Range of spin ground states available for $\{M_7M'\}$ rings

	M'					D^a of M
M	**Ni**	**Co**	**Zn**	**Fe**	**Mn**	
Cr	1/2	1	3/2	1/2	1	Medium
V	0	1/2	1	1	3/2	Large
Fe	3/2	2	5/2	1/2	0	Small
Ga	1	3/2	0	2	5/2	Zero

[a] *D* is the axial zero-field splitting.

One major issue in molecular magnetism, especially in the area of "single molecule magnets" is to understand how the anisotropy of a molecular cluster arises from the anisotropy of individual metal ions that comprise the cluster. The heterometallic rings will allow a very detailed analysis of this problem.

The fourth variable is the carboxylate. Originally the synthetic procedure required a carboxylate which was a liquid at *ca.* 160 °C; this is not a huge restriction and allowed us to crystallise rings with 2,2-dimethylbutyrate, *tert*-butylacetate, 2-methylbenzoate, 3-methylbenzoate, 1-methyl-1-cyclohexanecarboxylate, diethylacetate, 3,3-dimethylacrylate, *trans*-2,3-dimethylacrylate, chloroacetate, furan-2-carboxylate, hydroxypivalate, 2-thiophenecarboxylate, 3-thiophenecarboxylate, 2,3,4-trimethoxybenzoate.[13] More recently we have extended the family to include acetate, and by adding a small amount of DMSO to the reaction, 1-adamantane carboxylate (O_2CAd) which melts at 172 °C (Fig. 6).[15] While some of these carboxylates have very simple side-chains, others contain functional groups which creates the potential to perform chemistry on the rings once formed. We can also control the level of interaction between rings, which again could be important in controlling the physics of the system. Some of the combinations of metal oxidation states and carboxylate side-chains may prove incompatible, but certainly for the $\{Cr_7Ni\}$ core there seems to be no restriction on the carboxylate we can use.

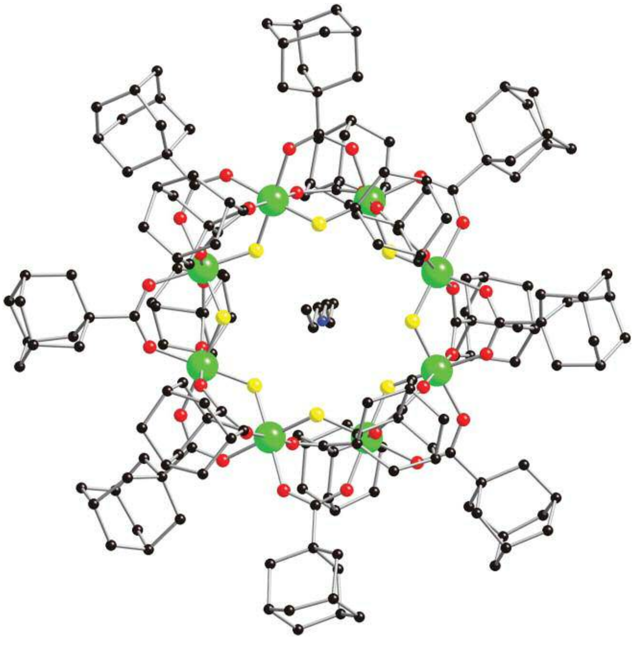

Fig. 6 The structure of $[H_2NPr_2][Cr_7NiF_8(O_2CAd)_{16}]$ in the crystal. Colours as Fig. 1. Ni site disordered around octagon.

The general formula for the compounds, at this stage, is therefore $[H_2NR_2][M_7M'F_8(O_2CR')_{16}]$; as long as R is a linear alkyl-chain we can vary the ammonium cation and retain the octagonal metal core. We can use seven different M′, six different M, at least ten different R and around twenty carboxylates; the family could extend to over four thousand members. This makes the family even larger than the family of oxo-centred carboxylate triangles.[16]

The most spectacular variation in the chemistry, at the moment, is achieved by varying the ammonium cation. The cation is always found at the centre of the ring, which suggests it could be used as a template for controlling the size and shape of the ring. Such ideas for controlling ring size have been proposed by Saalfrank *et al.*,[17] who showed that a hexanuclear or octanuclear Fe^{III} ring could be produced by adding Na^+ or Cs^+ respectively as a template. As the heterometallic AF rings involve an organic molecule as template the potential for variation is much greater.

The first change was to move from linear alkyl chains on the ammonium cation to branched chains: very simply move from *n*-propyl to isopropyl, or *n*-hexyl to cyclohexyl. The result is we can make, and crystallise $[H_2N^iPr_2][Cr_8MF_9(O_2C^tBu)_{18}]$ (M = Ni, Co, Cd).[18] The nonametallic ring which results is the first large odd-numbered ring; a nonanuclear iron(III) "ring" has been reported since our original paper.[19] The nonagon is no longer planar, because, while it is possible to arrange nine pivalates "in the plane" of the metal ring, it is not possible for the other nine to be arranged alternatively above-below the plane around an odd-numbered structure. This may contribute to the very diffuse diffraction shown by these nonanuclear rings.

If we move to a larger amine, HN^tBu^iPr, and used Cd(II) we can make $[H_2N^tBu^{is}Pr][Cr_8CdF_9(O_2CCMe_3)_{18}]$ **8**, where the structural characterisation is very good (Fig. 7), and where the puckering is very clear.[20] This amine also illustrates the interplay of size of metal and ammonium template; with Ni(II)

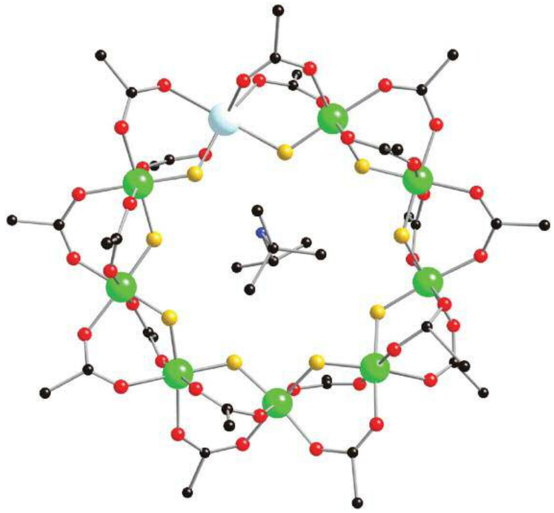

Fig. 7 The structure of **8** in the crystal. Colours as Fig. 1 plus Cd, pale blue. Me groups of pivalate excluded for clarity.

we can make the equivalent nonanuclear ring but also $[H_2N^tBu^IPr][Cr_9NiF_{10}(O_2CCMe_3)_{20}]$ **9** a decanuclear ring. In these rings the bridging on each edge is equivalent. Using a tertiary amine, $NMe(c\text{-}C_6H_{11})_2$, we make $[HNMe(c\text{-}C_6H_{11})_2][Cr_9NiF_{12}(O_2CCMe_3)_{18}]$ **10** and $[HNMe(c\text{-}C_6H_{11})_2]_2\text{-}[Cr_8Ni_2F_{12}(O_2CCMe_3)_{18}]$ **11** simultaneously. These compounds can be separated by chromatography. The additional cation in the crystals of **11** is found in channels between the heterometallic rings, but the anion in **10** and dianion in **11** appear identical by crystallography.[20] In each case it is oval rather than circular, and two edges have two fluorides and one pivalate bridging. We believe the Ni(II) sites are found in these edges.

Thus with saturated amines we can tune between eight-, nine- and ten-membered rings. We have not yet made each of these rings with all the trivalent metals and carboxylates that form octagonal wheels, but there seems little reason to assume this should be impossible. The general formula can then be extended to: $[H_{2-x}NR_{2+x}][M_nM'F_8(O_2CR')_{16+2n}]$ ($x = 0$ or 1, $n = 7$, 8 or 9).

Saturated amines can be replaced by some *N*-heterocycles; for example imidazole and *N*-alkylimidazoles work well as templates.[20] The major difference with imidazoles is that two imidazolium cations are always found at the centre of the ring, with a π stacking interaction between the imidazolium rings. This requires the heterometallic ring to be a dianion, which can be achieved in at least two different ways. For example, the reaction using imidazole gives an octametallic ring $[Himid]_2[Cr_6Ni_2F_8(O_2CCMe_3)_{16}]$ **12** (Fig. 8), which contains two divalent metal centres but where each edge of the ring is bridged by one F and two pivalates, and a nonametallic ring $[Himid]_2[Cr_8NiF_{11}(O_2CCMe_3)_{17}]$ **13** which contains only one divalent metal but where two terminal fluorides are found in place of one bridging pivalate. **12** and **13** can be separated by crystallisation from different solvents. The *N*-alkylimidazoles give decametallic rings $[HRimid]_2[Cr_8Ni_2F_{12}(O_2CCMe_3)_{18}]$ (R = Me or ^{n}Bu). These complexes, as with **10** and **11**, show oval rather than circular rings, with two edges bridged by two fluorides and one pivalate.[20]

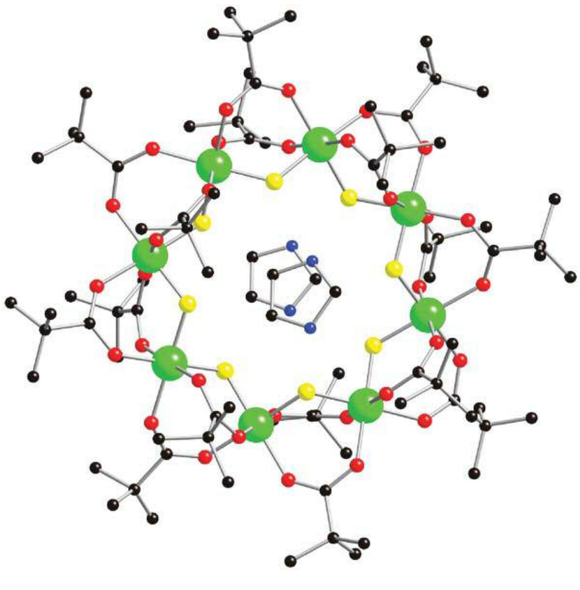

Fig. 8 Structure of **12** in the crystal. Colours as Fig. 1. Ni sites disordered around octagon.

Presumably other *N*-heterocycles should work, however the oddest template we have used yet is a metal complex.[21] If $[Ni(tacn)_2][O_2C^tBu]_2$ (tacn = 1,4,7-triazacyclononane) is added to the reaction a circular decametallic cage $[Ni(tacn)_2][Cr_8Ni_2F_{10}(O_2CCMe_3)_{20}]$ **14** forms (Fig. 9). The ring forms about the Ni-macrocyclic complexes. Magnetic measurements indicate that the dianion in **14** has an $S = 0$ ground state, which implies the two Ni centres are probably next to each other.

Going to a larger macrocycle, cyclen (1,4,7,10-tetrazacyclododecane) leads to our first "failure". The Ni complex does not act as a template, but rather binds to the end of the chain producing $[\{Ni(cyclen)\}_2Cr_{12}NiF_{18}(O_2CCMe_3)_{24}]$ **15** (Fig. 10).[21] **15** contains two $\{Cr_6\}$ chains that were previously seen in the "horseshoes", and a central Ni(II) site, which is bound to four fluorides and two oxygen donors from pivalates. The structure spells the letter "S" with fifteen paramagnetic metal centres, and perhaps proves the dictum that there's no success like failure.[22]

Many further templates could be tried. The difference from previous work, for example the beautiful work of Saalfrank,[5] is the fact that we can choose between many possible structures using a template, and not just between two structures. The use of an organic template rather than an alkali metal ion gives much more flexibility.

Some physics

When such control can be achieved with chemical synthesis it becomes necessary to find some use for the molecules you are making. This project started because of a desire to produce objects that could allow theories in quantum physics to be examined.

The original idea was to test a theory by Loss and Meier concerning quantum tunnelling of the spin of the AF-ring.[1]

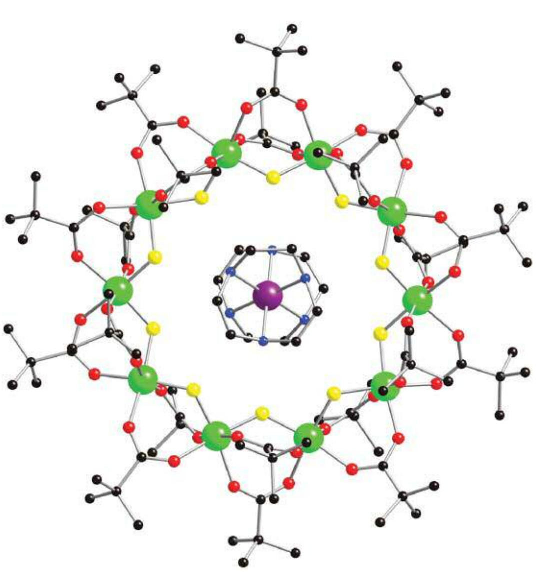

Fig. 9 The structure of **14** in the crystal. Colours as Fig. 1.

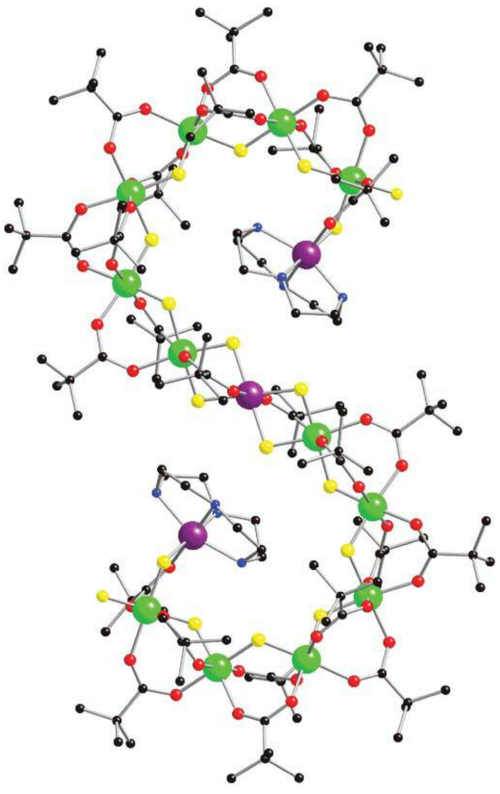

Fig. 10 The structure of **15** in the crystal. Colours as Fig. 1.

None of the experiments we have tried have been successful in demonstrating phenomena that can be assigned to such tunnelling, however others have claimed to see this "tunnelling of the Neel vector".[23]

Another theory which appeared around four years ago concerned quantum fluctuations of the total spin of a molecule at avoided crossings; a theory proposed by Carretta *et al*,[24] and which was demonstrated by experiments in collaboration with Waldmann and Thompson and co-workers.[25] The idea is not too difficult to understand by analogue with electronic spectroscopy.

If a Tanabe–Sugano diagram is derived for Ni(II) in an octahedral field the "weak-field" limit is given by a ^3F ground state, with a ^3P state being the only other state with the same spin degeneracy. When placed in a crystal field the ^3F splits into an $^3A_{1g}$, $^3T_{1g}$ and $^3T_{2g}$ and the ^3P becomes a $^3T_{1g}$. As the field increases the two $^3T_{1g}$ states should cross, but because they have belong to the same irreducible representation they mix, and therefore cannot cross. This produces an avoided crossing or anti-crossing.

By analogue if two spin states belong to the same irreducible representation they will mix and create an avoided crossing. Taking any of the $\{Cr_7Ni\}$ rings the ground state will be $S = 1/2$ in zero-field, and the two M_s states ($\pm 1/2$) are degenerate. When placed into a magnetic field these states will split and, using the $|S, M_s\rangle$ notation, the $|1/2, -1/2\rangle$ will fall in energy while the $|1/2, +1/2\rangle$ will rise: this is the Zeeman splitting. The first excited state is $S = 3/2$, and this splits in field with $|3/2, -3/2\rangle$, $|3/2, -1/2\rangle$ falling and $|3/2, +3/2\rangle$, $|3/2, +1/2\rangle$ rising. As the slope depends on M_s then $|3/2, -3/2\rangle$ will fall faster than $|1/2, -1/2\rangle$, and at some point they should cross (Fig. 11). However the symmetry causes mixing, and there is an avoided crossing rather than a crossing. At the crossing the spin ground state should fluctuate between S and $S + 1$, *i.e.* for $\{Cr_7Ni\}$ between $S = 1/2$ and $S = 3/2$.

The comparative simplicity of the structure, and the fact that making five grams of material is not difficult, allows very good characterisation of the parameters that describe the magnetism of these rings. A combination of susceptibility measurements,[9] heat capacity[26] and inelastic neutron scattering experiments[27] mean the spin Hamiltonian parameters of these rings are very well defined. Therefore these parameters can be included directly in the theory without adjusting them to "fit" experiments: we have a genuine prediction of behaviour.

The first experimental test comes from torque magnetometry which is particularly suitable to detect fluctuations of the magnetisation along the direction of the applied field.[28] If there is no mixing of spin states, at crossings the magnetic torque changes abruptly with a step; this has been seen for $\{Fe_{10}\}$[29] and for $\{Cr_8\}$[8] where the high molecular symmetry leads to spin states belonging to different irreducible representations. The prediction for $\{Cr_7M\}$ rings is that at avoided crossings there should be a peak in the torque because of the fluctuations in spin.[23] This is what is observed (Fig. 12). The mixing of states should depend on the angle between the magnetic field and the principle magnetic axis molecule – the mixing is zero when this angle is 0° or 90° and maximum at *ca.* 45°. This angular dependence is identical in the theory and experiment.

In previous experiments on molecular magnets, *e.g.* on single molecule magnets such as $[Mn_{12}O_{12}(OAc)_{15}(H_2O)_4]$, the quantum effects seen, such as tunnelling, have involved fluctuation of M_s between two values (*e.g.* resonant tunnelling through an energy barrier between $+M_s$ and $-M_s$).[30,31] Here the quantum fluctuations are between S-levels.

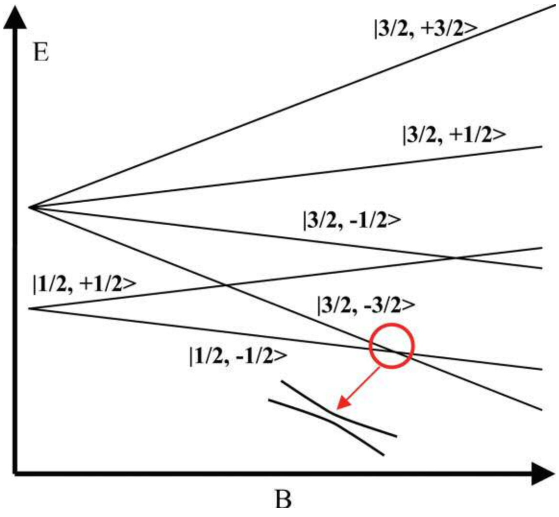

Fig. 11 Schematic representation of the Zeeman splitting of the lowest two spin states in **2**. The avoided crossing is circled in red.

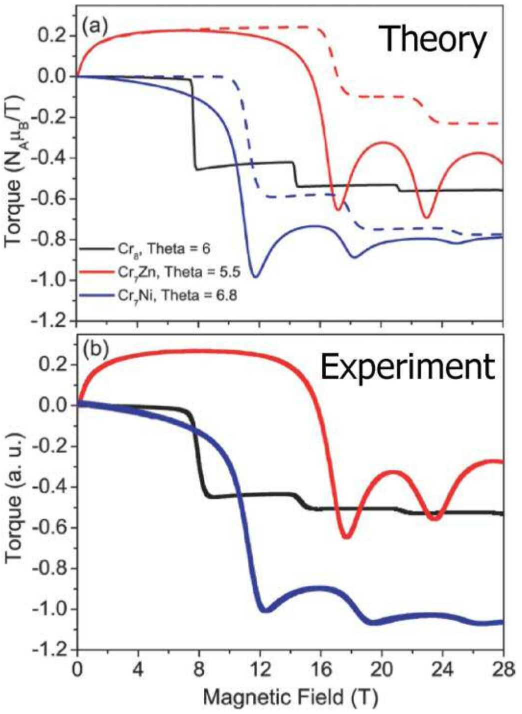

Fig. 12 Theoretical and experimental torque response of: **1** (black), **2** (blue) and {Cr_7Zn} (red). The dotted lines represent the calculated torque in the absence of *S*-mixing.

Quantum information processing (no really)

Theoretical physicists can be remarkably useful; shortly after we began making heterometallic rings to test one theory from the Loss group,[1] they published further theory suggesting that a pair of S = 1/2 clusters could be used in quantum information processing (QIP)[32,33] acting as a Qubit gate. Schematically a single Qubit is shown in Fig. 13. It has also been proposed by Troiani *et al.*[34] that Qubit gates could be designed using interactions between excited states of magnetic clusters.

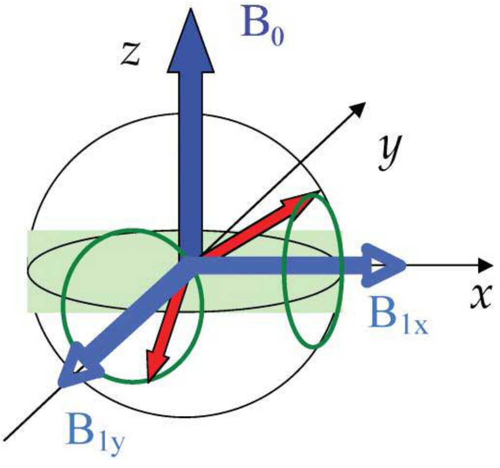

Fig. 13 A one-Qubit gate can be represented as a precession of spin S = 1/2 (red arrows) about a pulsed magnetic field in the *xy*-plane (B_{1x} or B_{1y}). A static magnetic field B_0 is applied along the *z*-direction in order to initialize the system.

The {Cr_7Ni} rings, which have an S = 1/2 ground state, have therefore been considered very carefully.[35,36] For future application in QIP the following has to be considered.

(a) The extent to which the ground state can be accurately described as a two-state system, *i.e.* is the ground state a "pure" S = 1/2 state. For {Cr_7Ni} the ground state very well described as an S = 1/2 doublet and there is very little mixing from higher S states at low fields.

(b) The energy gap to the first excited state (S = 3/2) is important. In {Cr_7Ni} this is around 13 K, and therefore at low temperature the only energy levels that concern us will be $|1/2, -1/2\rangle$ and $|1/2, +1/2\rangle$. These can therefore be regarded as equivalent to the 0 and 1 levels of a "bit" in computation.

(c) The $|1/2, -1/2\rangle$ and $|1/2, +1/2\rangle$ must separate in field, so that we can populate one in preference to the other without inducing significant leakage to the higher S states. This is called "initialisation" and can be imagined as creating a "bit" of information as either 0 or 1. At an external field of 2 T the Zeeman splitting is around 2.4 K, while the energy gap to the lowest level that arises from the S = 3/2 quartet is still 9.4 K.

(d) The rate at which information is lost to the rest of the system is called the "decoherence" rate. Measurements of decoherence times in spin clusters are rare, despite this being vital for applications in QIP. Pulsed EPR spectroscopy,[37] done by the group of Arzhang Ardavan and Steve Blundell (Clarendon Laboratory) on {Cr_7Ni} gives remarkable results. The decoherence time at 1.8 K is around 3 μs; this is a great deal longer than we had predicted and should allow coherent manipulations of the electron spins. The predominant decoherence path appears to be *via* coupling to nuclear spins[38] of H-atoms in the carboxylate ligands. This can be modified by deuteration of the samples – leading to these very long times.

The bottom line is that {Cr_7Ni} is a good candidate for a Qubit. Other S = 1/2 molecules might also be promising;[39] the key requirements are above. Most difficult is the decoherence time, which requires that the electron spin sees few if any nuclear spins. The choice of metal ions here is fortuitous – neither Cr nor Ni has an isotope of significant abundance which has a spin with a large nuclear magnetic moment. It is even more fortunate that the electron spin seems to have no measurable interaction with the nuclear spins of the bridging fluorides.

Linking {Cr_7Ni} rings can be done straightforwardly using diamines, *e.g.* use of 1,8-diaminooctane (1,8-dao) as the templating amine gives $[H_2\text{-1,8-dao}][Cr_7NiF_8(O_2C^tBu)_{16}]_2$ (Fig. 14) **15**.[40] A two-step route involves using $[EtNHCH_2py]$ as the template, producing $[EtNH_2CH_2py][Cr_7NiF_8(O_2C^tBu)_{16}]$, which can then be used as a ligand for other metal complexes. These other complexes can be mononuclear or dinuclear, *e.g.* $[M_2(O_2C^tBu)_4]$ dimers work very well (Fig. 15), for M = Cu **16**, Ni, Co, Mn, Fe.[40] This latter route looks more flexible, in that pyridine can be used generally to bind to any number of potential bridges.

Thus far measurements show little interaction between the rings and the bridging groups. However this is good – at least at an initial stage – as it represents the "off" state of the manipulation. The next stage is to produce a complex where the link can be manipulated to allow interaction between rings

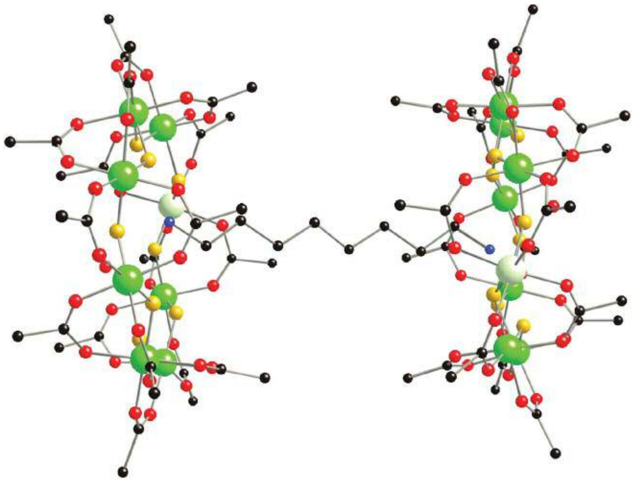

Fig. 14 The structure of **15** in the crystal. Colours as Fig. 1 with Ni, pale green. Me groups of pivalate excluded for clarity.

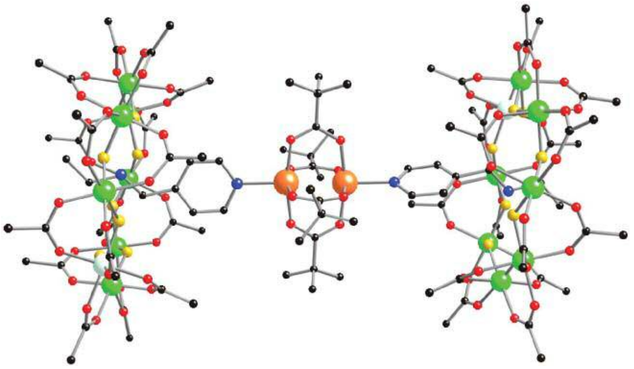

Fig. 15 The structure of **16** in the crystal. Colours as Fig. 4.

in an on-state, while maintaining the lack of interaction in an off-state. This could prove challenging.

Conclusions

The discovery in the early 1990s of molecules that showed slow relaxation of magnetisation – "single molecule magnets" – inspired a great deal of research to examine whether such molecules could be used in information storage.[41] More importantly, it provided a catalyst leading to better communication between chemists and physicists and a better understanding of quantum phenomena in molecular materials.[42] Chemists are remarkably good at making "quantum objects", we call them molecules. Molecular magnets are proving a wonderful playground for physicists to examine quantum theory in detail. Much is made of inter-disciplinary research between chemistry and biology, or chemistry and materials; work at the boundary between chemistry and physics will continue to prove equally productive.

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